LE STUDIUM CONFERENCE, “WATER MICROPOLLUTANTS: FROM DETECTION TO REMOVAL”
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SURFACE MODIFICATION IN PROTIC IONIC LIQUID MEDIA: APPLICATION TO WATER MONITORING

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CAP-EL-CAHAP project (Région Centre-Val de Loire)

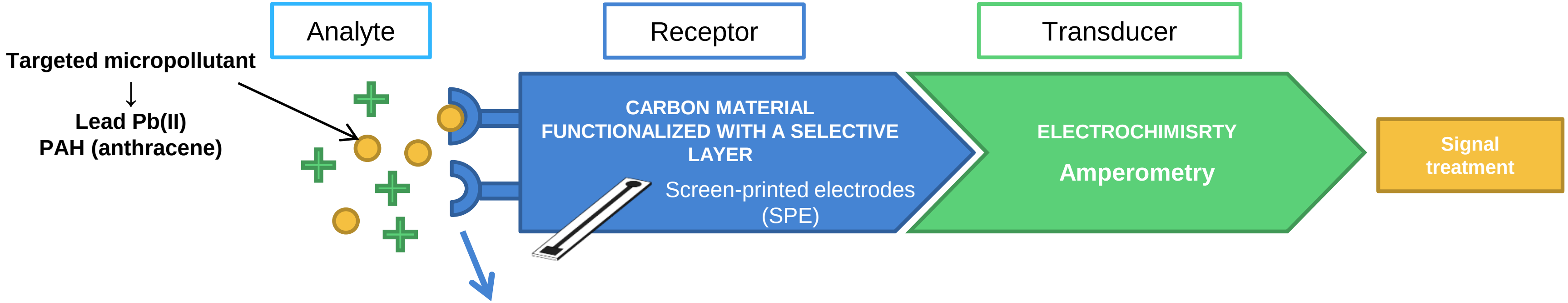
CONTEXT

- ➢ The European legislation on the water quality and micropollutants is in progress.
- ➢ Aqueous media = Complicated media with many chemical species at trace amounts level

Powerful analytical techniques already exist BUT not suitable for regular and *in situ* monitoring of aquatic media

→ Need to develop new devices, less expensive, and usable on site *in situ*

ELECTROCHEMICAL SENSORS



→ SELECTIVITY / SENSITIVITY

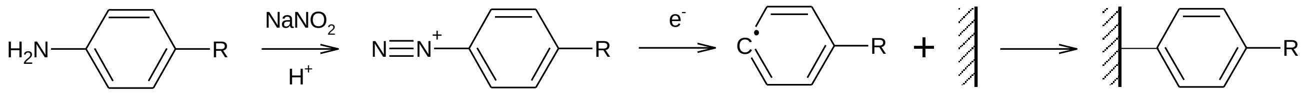
Functionalization by electrochemical reduction of diazonium salt

→ Need to control the grafting of the selective layer to ensure the reliability and repeatability of the sensors

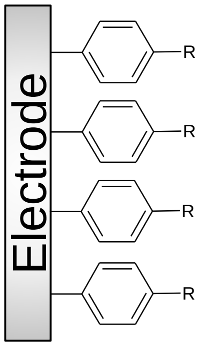
Electrochemical grafting by diazonium salts reduction

**Grafted layer allows the preconcentration of micropollutant on the sensor surface.
So, the control of the functional groups surface concentration at the electrode is a key parameter to increase the reliability of the analyzes.**

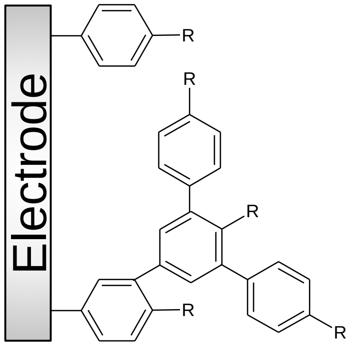
Grafting mechanism ⟹



Monolayers



Multilayers

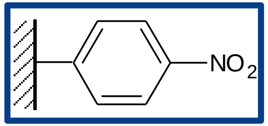


Monolayer control

- **Grafting hindered salts**
  (3,5-bis-tert-butyl benzene diazonium)
  Combellas et al., J. Am. Chem. Soc., 130(27) (2008) 8576-8577
- **Using radical scavengers**
  Menanteau et al., Electrochemistry Communications, 63 (2016) 70-73
- **Grafting in ionic liquid**
  Fontaine et al., Langmuir, 26(23) (2010) 18542-18549

Plan

- Ionic liquid choice



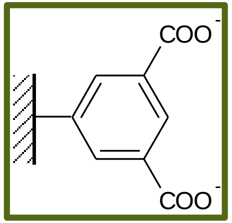
- 4-nitrobenzene diazonium salt grafting

  Grafting pathway choice (*in situ* or isolated)

- 3,5-dicarboxyphenyl diazonium salt grafting

  Bouden et al., Electrochem. Com., 41 (2014) 68-71

  Lead Pb(II) detection



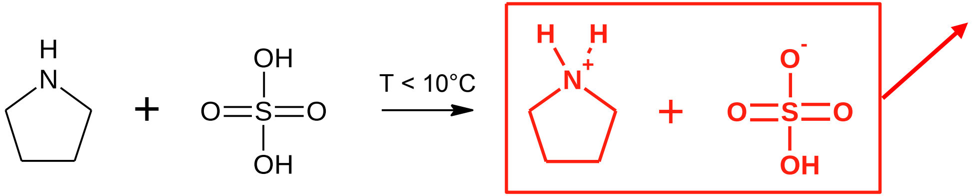
Ionic liquid choice

Ionic liquids = salts with a melting point below 100 ° C

Considered as "GREEN" SOLVENTS

High ionic conductivity and wide electrochemical window

→ GREAT INTEREST FOR ELECTROCHEMICAL SENSORS



Pyrrolidinium Hydrogenosulfate [Pyrr][HSO_4]

= Protic Ionic Liquid (PIL)

(synthesis done at PCM2E, Tours)

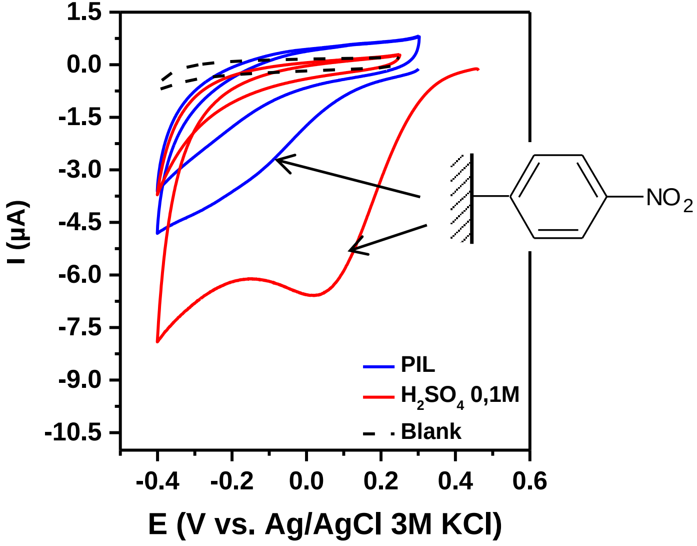
Viscosity at 25°C : 269-380 mPa.s

High viscosity compared to aqueous or organic media

→ Possible modulation of the viscosity by adding a co-solvent (water)

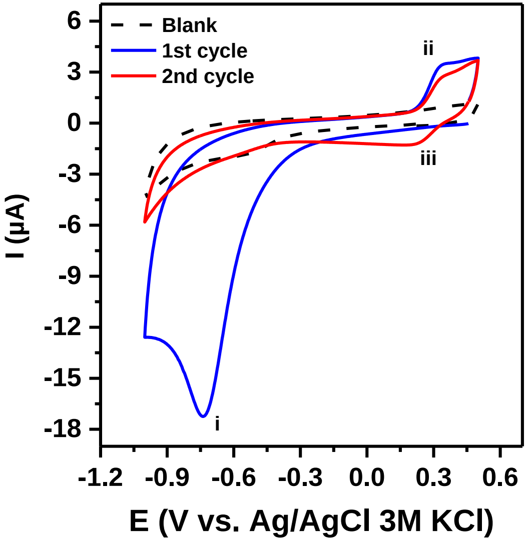
4-nitrobenzene diazonium (4-NBD) grafting in PIL or in H_2SO_4

1- Grafting



Grafting voltammograms of 4-NBD (10mM) in PIL or H_2SO_4 0.1M - Scan rate 100 mV/s

2- Characterization



Characterization in 0.1M H_2SO_4 medium of GCE grafted with 4-NBD (10mM) in H_2SO_4 - Scan rate 100 mV/s

Allows a routine electrochemical characterization of the grafted layer (electroactive NO_2)

Reduction peak :

$NO_2 + 6H^+ + 6e^- \rightarrow NH_2 + 2H_2O$

$NO_2 + 4H^+ + 4e^- \rightarrow NHOH + H_2O$

Oxidation peak :

$NHOH \leftrightarrow NO + 2H^+ + 2e^-$

→ Estimation of the surface concentration of NO_2 by means of charge quantities via the Faraday law

→ Grafting of diazonium salt in PIL medium is possible

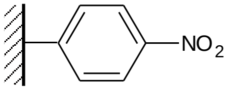
PIL = Protic Ionic Liquid

Grafting pathway choice (*in situ* or isolated)

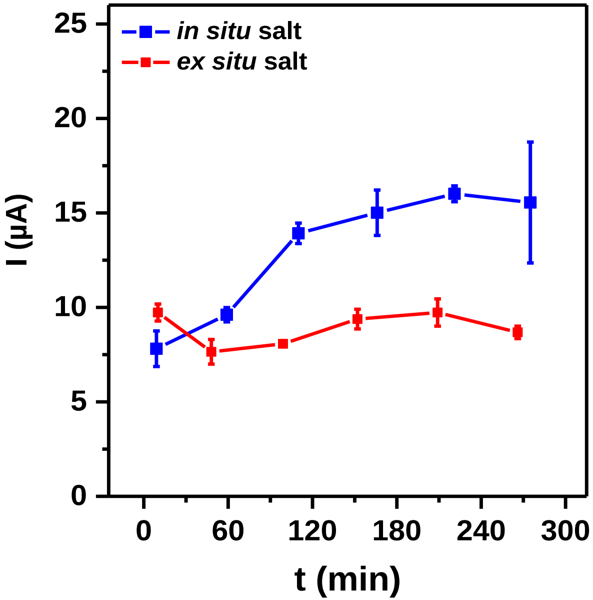
→ Evolution of the grafting medium

Grafting from:

- *in* situ salt
- *ex situ* salt → take more time



Shul et al., Electrochimica Acta 106 (2013) 378-385



Mean intensities of NO_2 reduction peaks versus time - after introduction of reagents

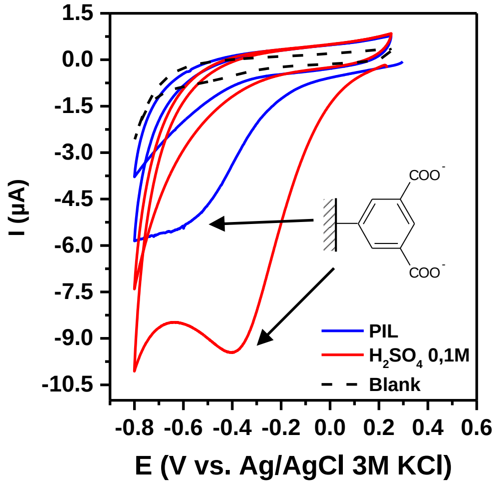
- **Signal evolution and highest dispersion of measurements with *in situ* salt**
- **Best repeatability for isolated salt**
- **Different behaviors between those observed for grafting in aqueous medium and organic solvents**

→ *ex situ* grafting will be selected.

3,5-dicarboxyphenyl diazonium (3,5-DCPD) grafting

Characterization of the grafted layer by detecting Pb (II)

FUNCTIONALIZATION

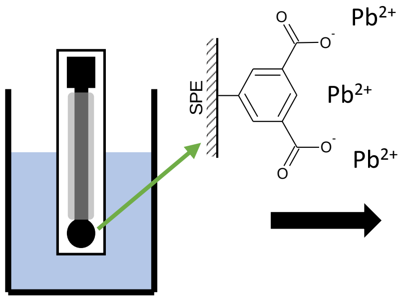


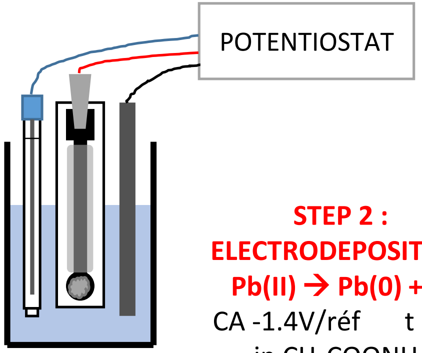
ANALYTICAL METHOD

STEP 1 : Pb(II) ADSORPTION

Preconcentration

5 min in CH_3COONH_4 + Pb(II)





STEP 2 : ELECTRODEPOSITION

$Pb(II) \rightarrow Pb(0) + e^-$

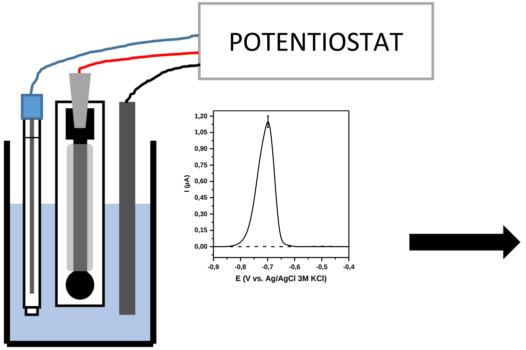
CA -1.4V/réf t = 5s

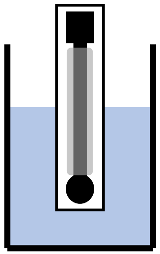
in CH_3COONH_4

STEP 3 : ELECTROCHEMICAL DETECTION

$Pb(0) + e^- \rightarrow Pb(II)$

SWV in CH_3COONH_4





STEP 4 : REGENERATION

Ultrasonication 1 min

in H_2SO_4 (pH 1)

Grafting parameters studied →

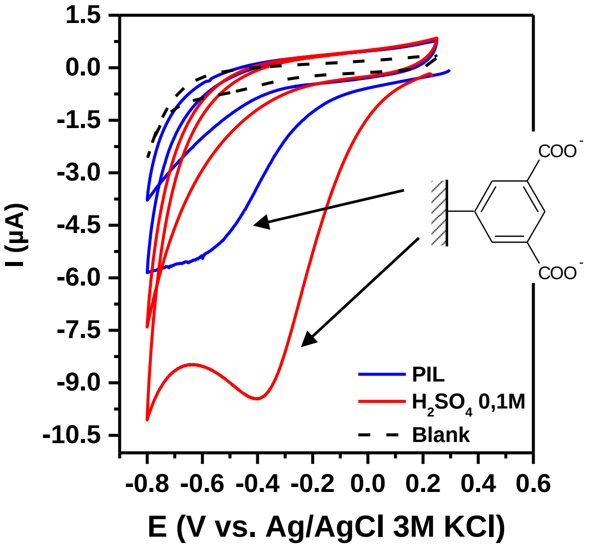
Concentration of diazonium salt

Electrochemical grafting method

Viscosity of the grafting medium

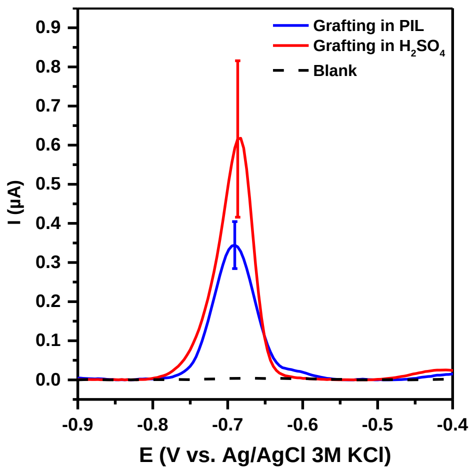
PIL = Protic Ionic Liquid

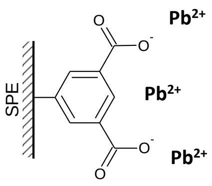
Comparison of Pb(II) detection on grafted electrodes in aqueous and LIP media



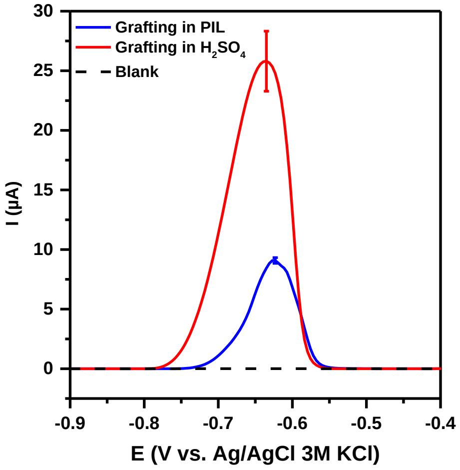
Grafting voltammograms of 4-NBD (10mM) in PIL or H_2SO_4 0.1M - Scan rate 100 mV/s

[Pb(II)] = 5.10^{-8} M





[Pb(II)] = 10^{-5} M



Lead detection at 5.10^{-8} M and 10^{-5} M in 50mM CH_3COONH_4 on grafted GCE with 3,5-DCPD in PIL or 0,1M H_2SO_4 - Scan rate 100mV/s

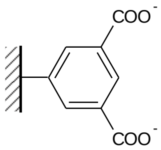
Lower peak intensities in PIL → Less thick layers than in aqueous media

→ Better reproducibility of the measurements in the case of grafting in PIL medium

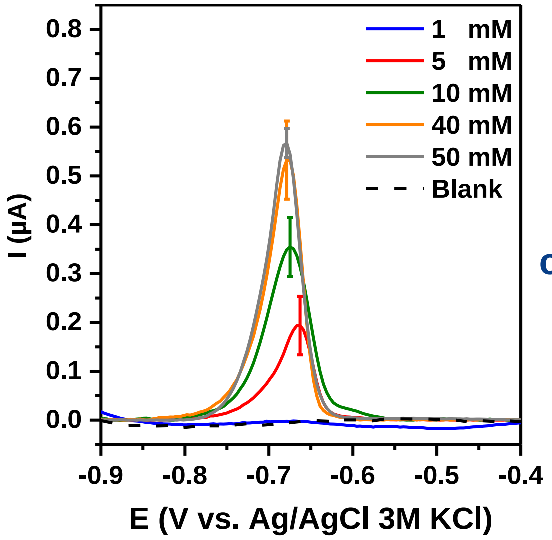
PIL = Protic Ionic Liquid

Influence of grafting parameters on the intensity of Pb(II) detection peaks

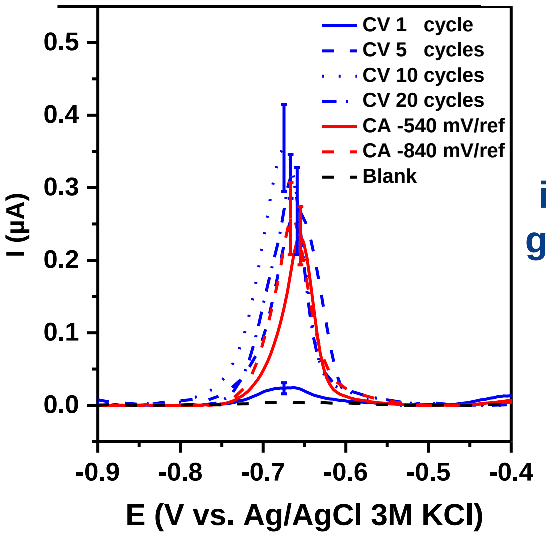
Salt concentration and electrochemical method



[Pb(II)] = 5.10^{-8} M



Sensibility improved by an high salt concentration

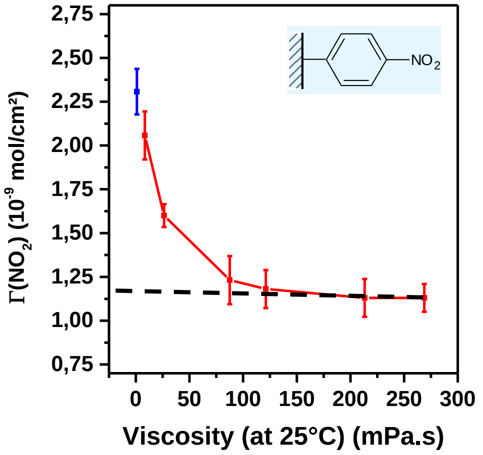


Sensibility improved for grafting by CV

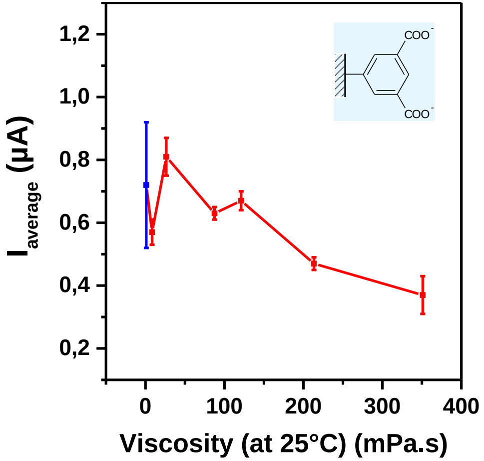
→ Tendencies more marked than for aqueous or organic media

PIL = Protic Ionic Liquid

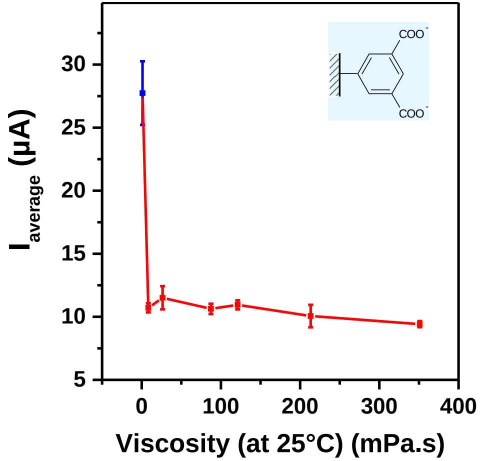
Influence of the grafting medium viscosity



[Pb(II)] = 5.10^{-8} M



[Pb(II)] = 10^{-5} M



- ➢ **Decrease of the surface concentration when the viscosity increases**
- ➢ **Surface concentration close to the monolayer at 75 mPa.s**

- ➢ **Decrease in peak detection intensity when the viscosity increases**
- ➢ **The viscosity increases with the repeatability**

→ The Modulation of the viscosity makes it possible to control the thickness of the layers

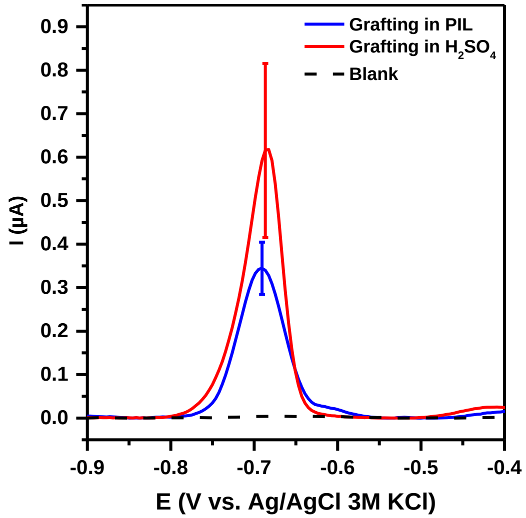
PIL = Protic Ionic Liquid

Performance of Grafted Layers for Pb (II) Detection

Comparison between grafting in PIL and H_2SO_4 0,1M

Grafting media	Grafting scan rate	LOD ($\mu g.L^{-1}$)	LOQ ($\mu g.L^{-1}$)	R^2	Sensitivity ($A.M^{-1}$)
0.1 M H_2SO_4	100 mV/s	0,70	2,34	0,995	10,97
PIL	100 mV/s	0,80	2,65	0,995	8,31
	5 mV/s	0,57	1,91	0,997	8,21
PIL/water 90/10	100 mV/s	0,30	1,01	0,999	7,49

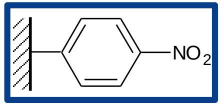
[Pb(II)] = 5.10^{-8} M



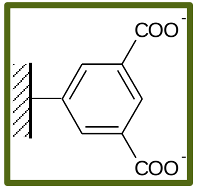
Lower LOD and LOQ obtained for grafting done in PIL/water 90/10 and higher reproducibility
→ **Grafting in PIL allows to improve sensors perfomances**

PIL = Protic Ionic Liquid

Conclusions



- Grafting by electrochemical reduction of two diazonium salts: 4-NBD and 3,5-DCPD



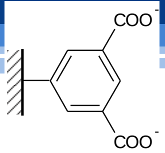
- Grafting pathway from the *ex situ* salt more appropriate - The stability of the grafting medium, and the quality of the layer are more favorable for a better reproducibility
- Highlights the influence of grafting parameters as the salt concentration or the grafting electrochemical methods on the density of the grafted layer
- Control of the grafted layer possible by modulation of the viscosity of the ionic liquid
- Grafting in PIL allows to improve electrodes performances

PIL = Protic Ionic Liquid

Thank you for your attention

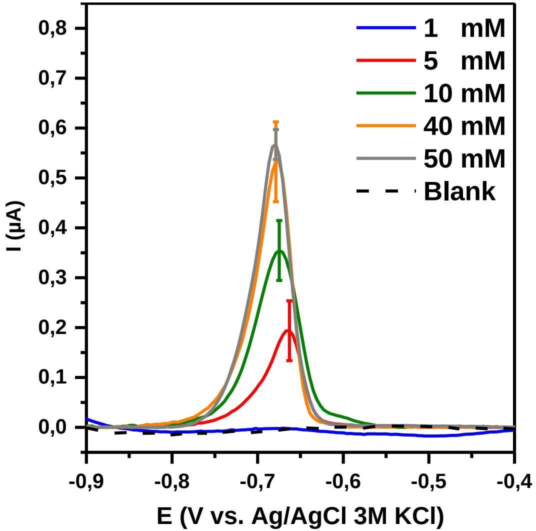
Questions ?

Influence of the grafted salt concentration on intensity of Pb(II) detection



3,5-DCPD grafting at several diazonium concentrations, in LIP media

[Pb(II)] = 5.10^{-8} M

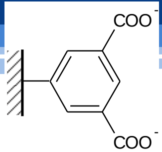


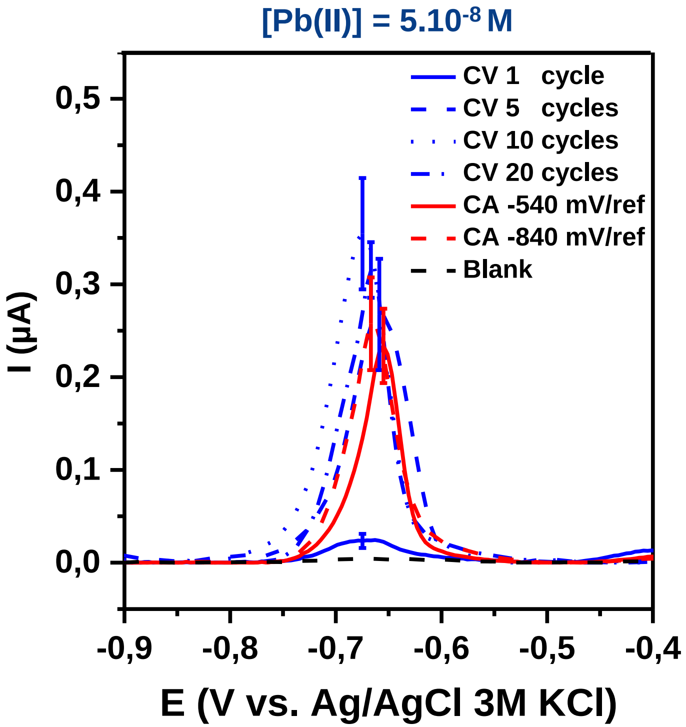
Pb(II) detection at 5.10^{-8}M in 50mM CH_3COONH_4 on grafted GCE with 3,5-DCPD in PIL with several salt concentrations – Scan rate 100mV/s

- **Detection peak intensity increases with the salt concentration**

→ Different behavior from what is observed in an aqueous medium or in organic solvents

Influence of the grafting electrochemical method, in PIL





Pb(II) detection at 5.10-8M in 50mM CH_3COONH_4 on grafted GCE with 3,5-DCPD in PIL with several electrochemical conditions

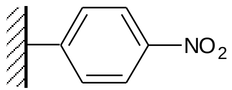
GCE grafted by
CYCLIC VOLTAMMETRY (CV)
or by **CHRONOAMPEROMETRY (CA)**

- **Higher electrode sensitivity when the surface is grafted by CV rather than CA**

→ Tendency more marked than in aqueous medium

Caractérisation des couches greffées

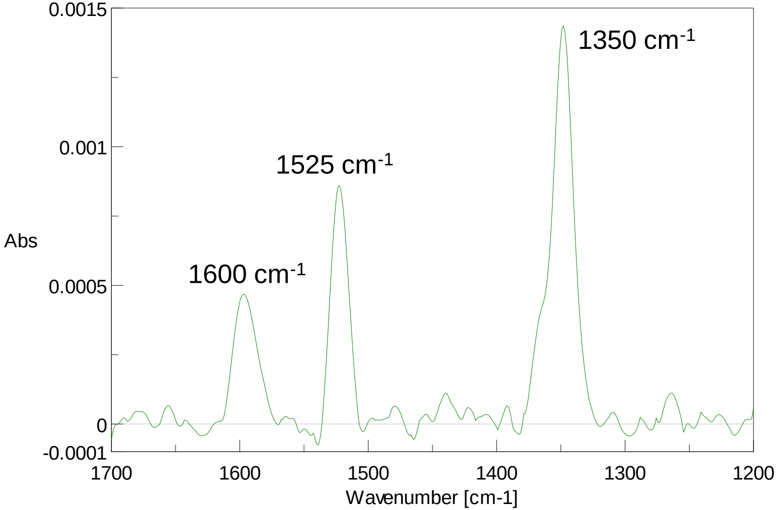
Spectroscopie infrarouge IRRAS



$$Abs = 0,0024 \,.\, e$$

$$Abs^{1350} = \varepsilon^{1350} \,.\, \Gamma(NO_2)$$

Abs : Absorbance (u.a.)
e : épaisseur (nm)
ε^{1350} : coefficient d'absorption molaire (cm²/mol)



Milieu de greffage	Conc. en sel de diazonium	Epaisseurs calculées (nm)	Conc. surfaciques calculées (mol/cm²)
Plaque nue		___	___
H_2SO_4 0,1M	10 mM	1,44	$1,38.10^{-9}$
LIP	10 mM	0,60	$0,58.10^{-9}$

Pour le sel de 4-NBD:
Epaisseur théorique de la monocouche : 0,4 nm
Concentration surfacique pour une monocouche compacte : $1,35.10^{-9}$ mol/cm²

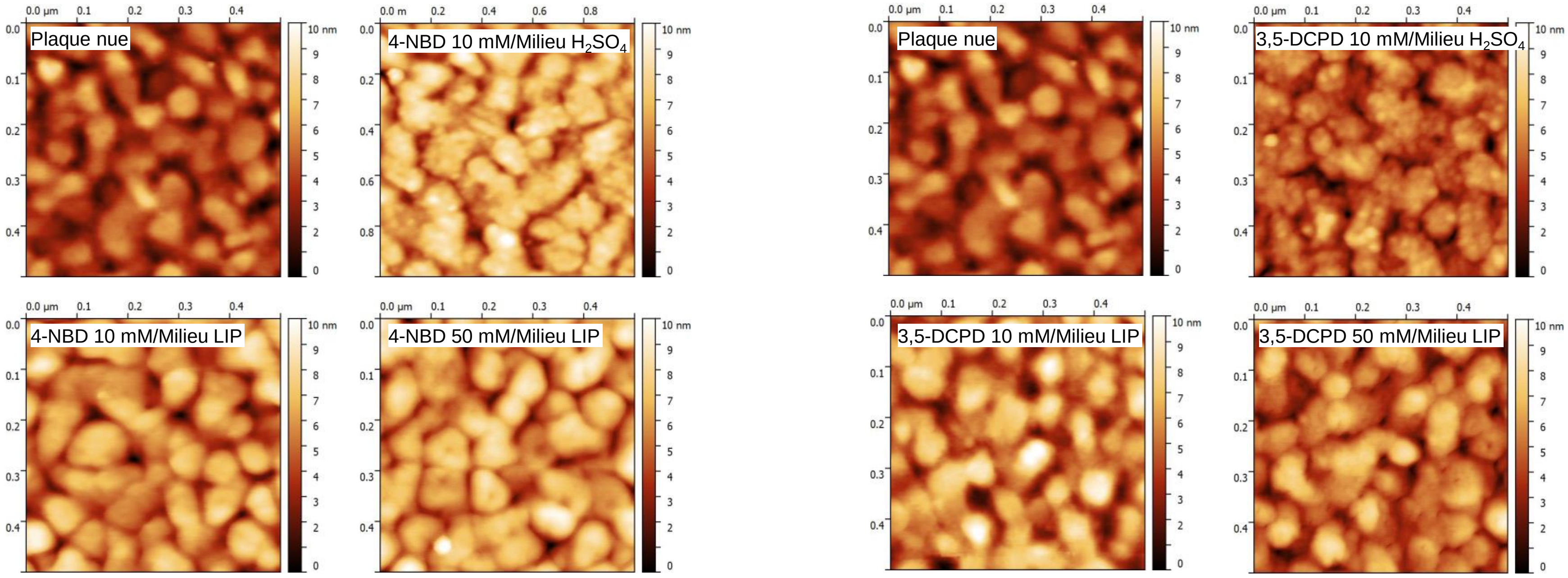
En milieu LIP : obtention de couches proches de la monocouche

Hetemi et al., Langmuir 31 (2015) 5406-5415

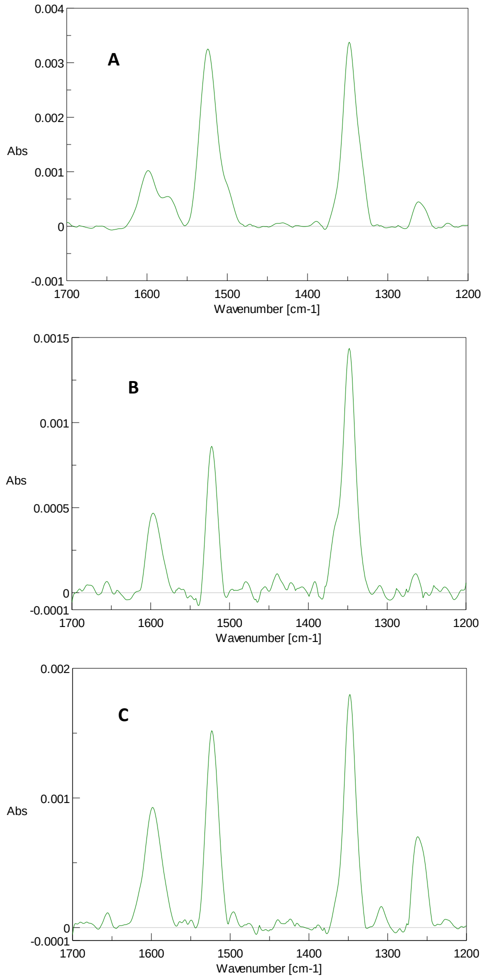
Caractérisation des couches greffées

Microscopie à force atomique

Images AFM de plaques d'or nues ou greffées en milieu H_2SO_4 0,1M ou LIP



Mise en évidence de la présence d'une couche greffée pour les deux milieux.
Couches greffées moins épaisses et plus homogènes pour le greffage en milieu LIP



Spectres IRRAS obtenus pour des plaques d'or greffées par voltammétrie cyclique (5 cycles à 100mV/s) avec le 4-NBD à 10 mM en milieu H_2SO_4 0,1M (A), à 10 mM en milieu LIP (B) et à 50 mM en milieu LIP (C)