Synthesis and grafting of n and p type σ-π-σ systems on substrates for molecular electronic applications.

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ANR MEMO project

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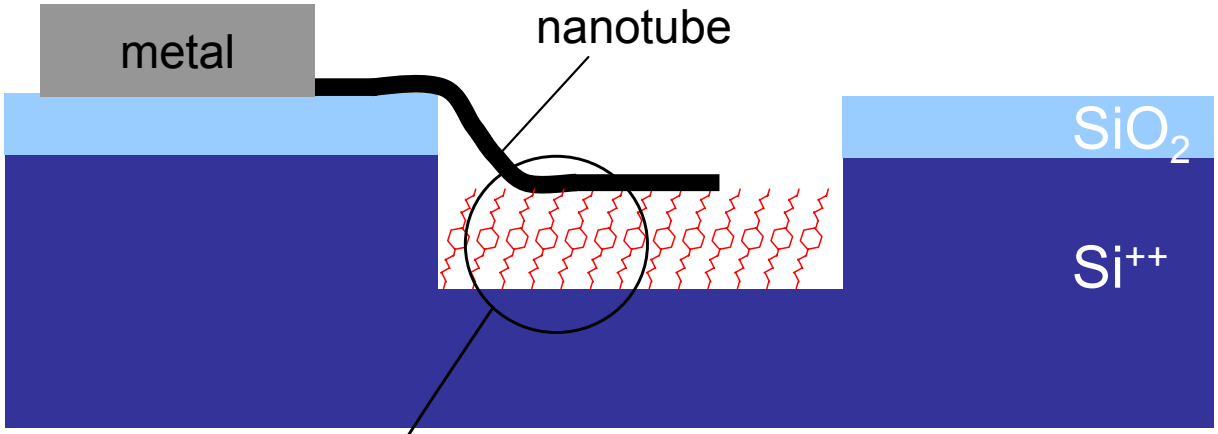
Coll. CEA-DAE

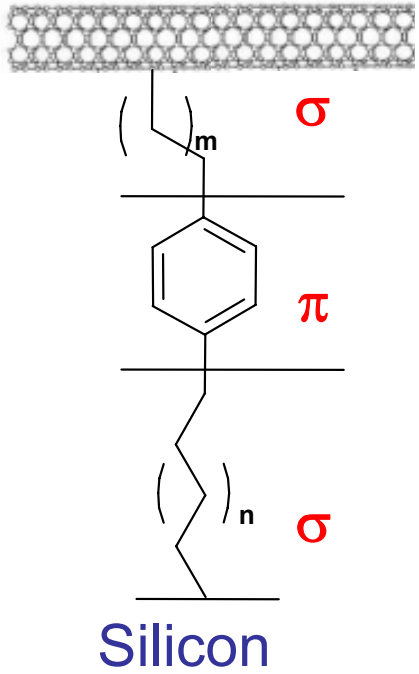
Structure of the molecular diode : Nanotube / Molecules / Silicon



(1) Connect few molecules

(2) Avoid metal evaporation to contact the molecules

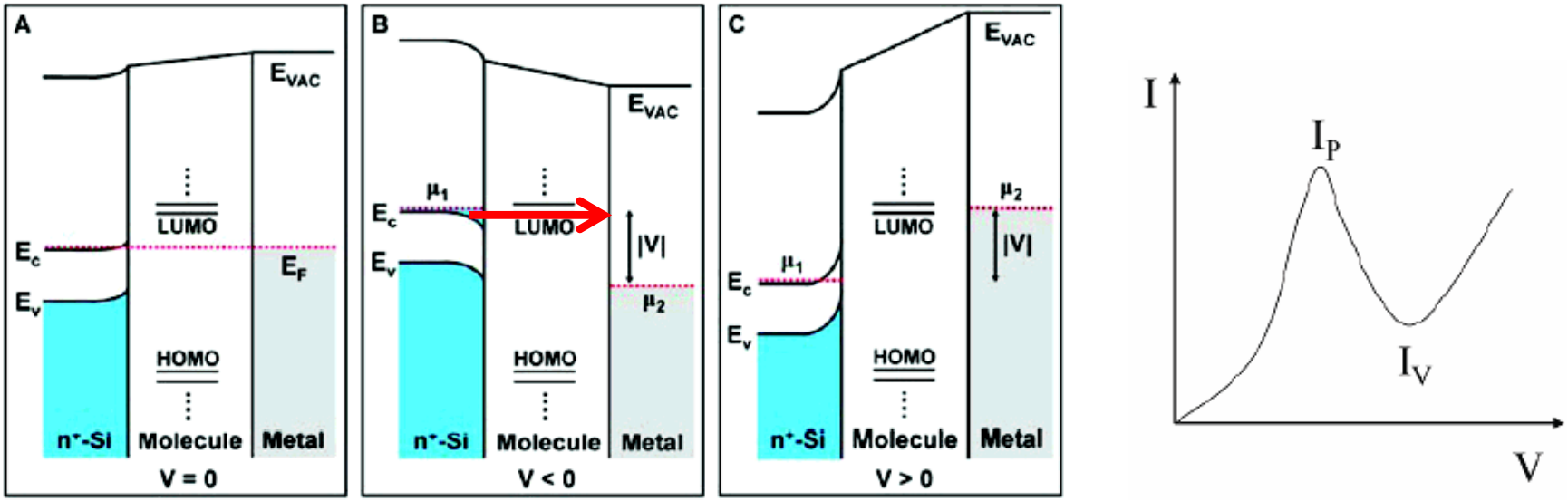
(3) Prove a negative differential resistance effect at room temperature



σ: alkyl-chains act as tunnel barriers

π: conjugated part acts as the potential well

negative differential resistance (NDR) effect

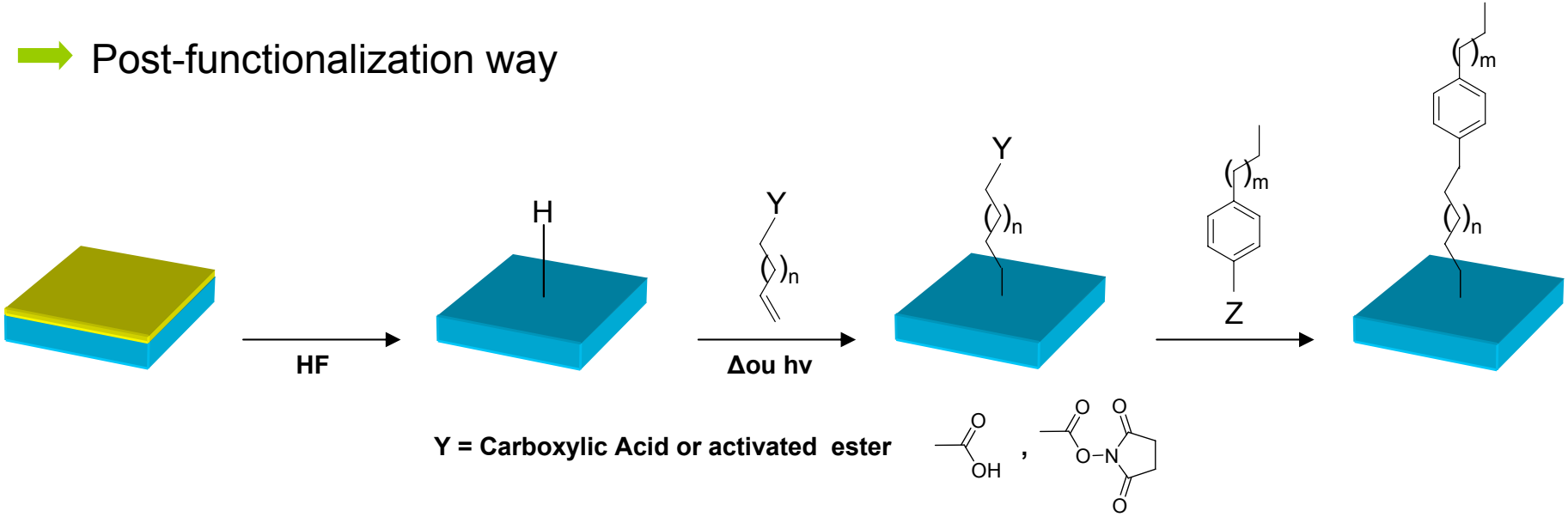


NDR peak should appear whenever an energy level of the molecule comes into resonance with the electrons of the conduction band of the silicon or holes in the valence band of the silicon.

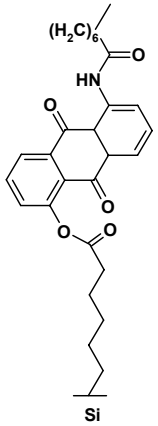
Nano Letters 4, 55 (2004)

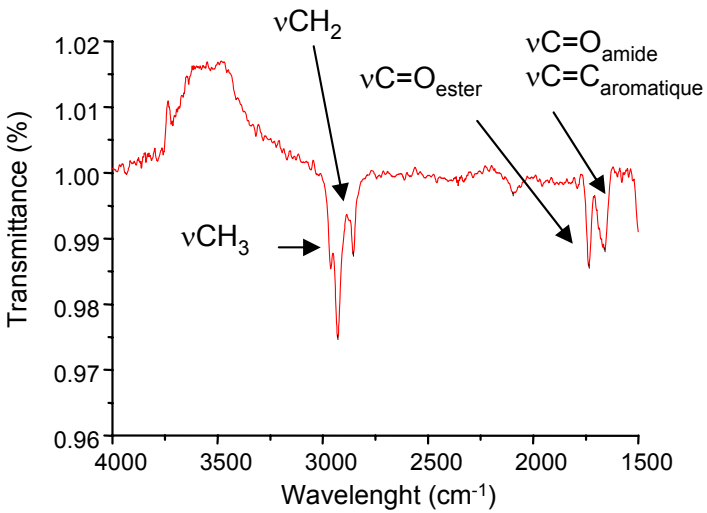
Sequential synthesis of a σ-π-σ monolayer on silicon (L. Baraton Ph. D Thesis)

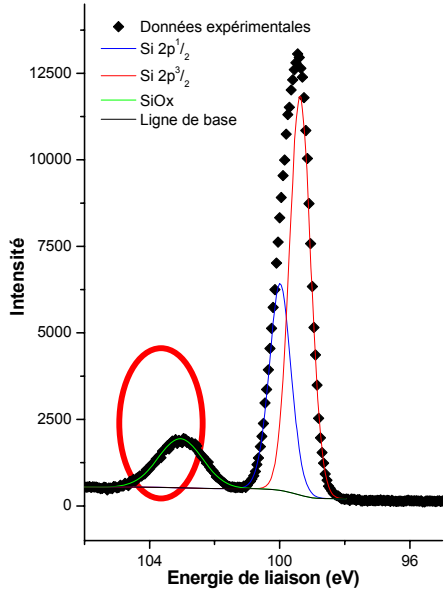
Post-functionalization way



Esterification reaction on a monolayer

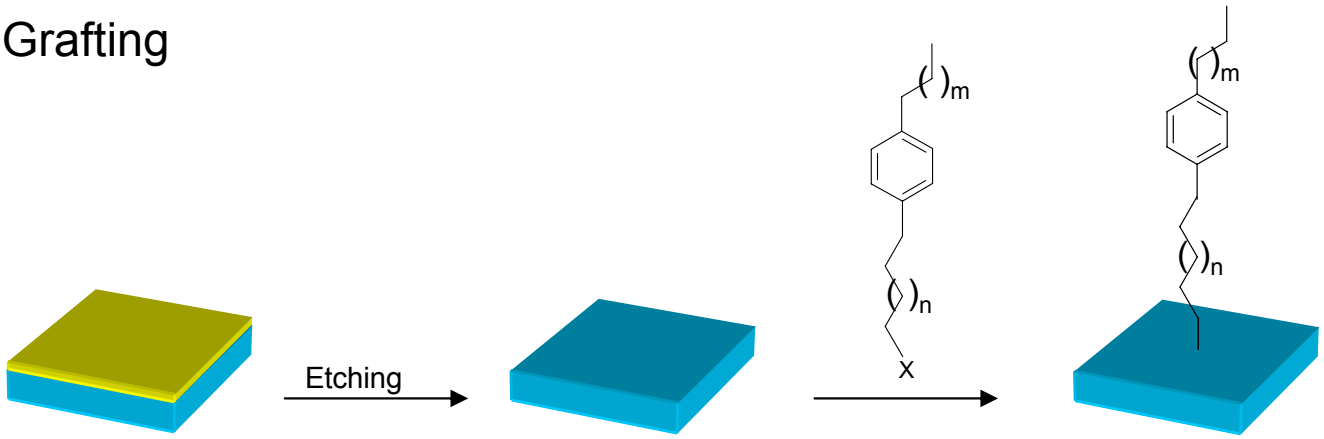






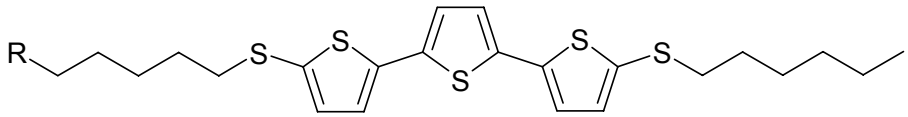
Approach used in the project

Direct Grafting



Chosen compounds

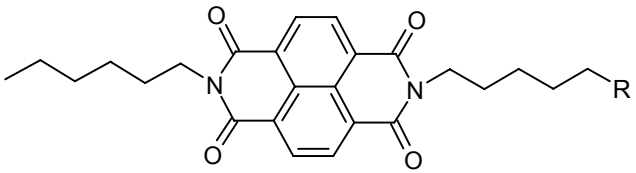
Terthiophene derivative



R= $CH=CH_2$, CH_2SH

Electron donor (p-type)

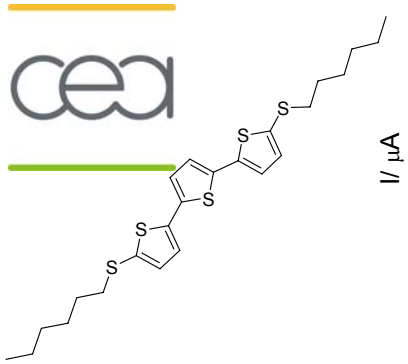
Naphthalene derivative

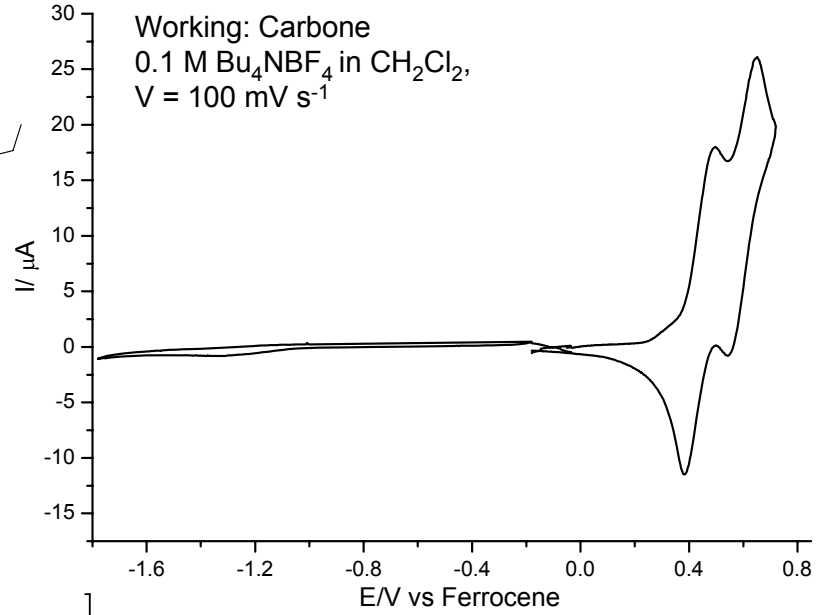


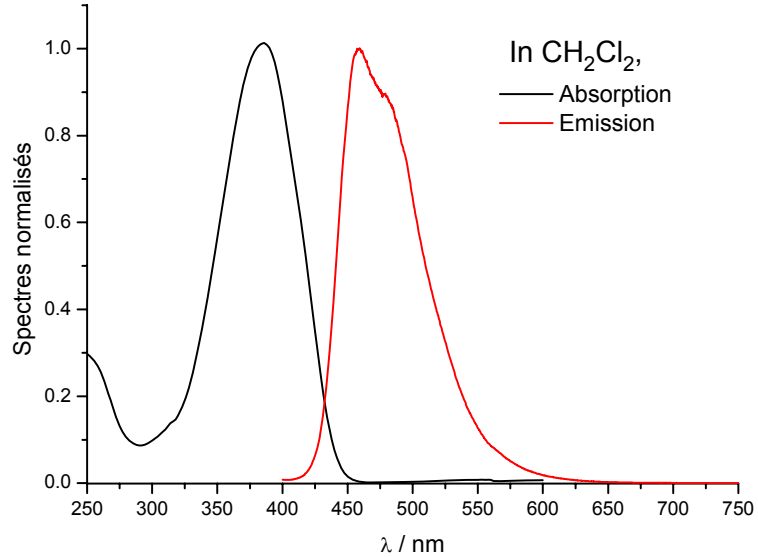
R= $CH=CH_2$, CH_2SH

Electron acceptor (n-type)

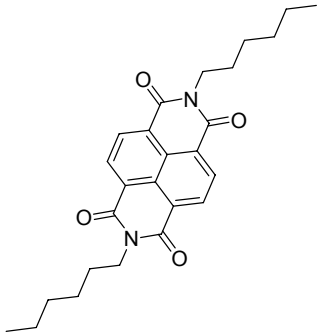
Optics and redox properties of the conjugated systems

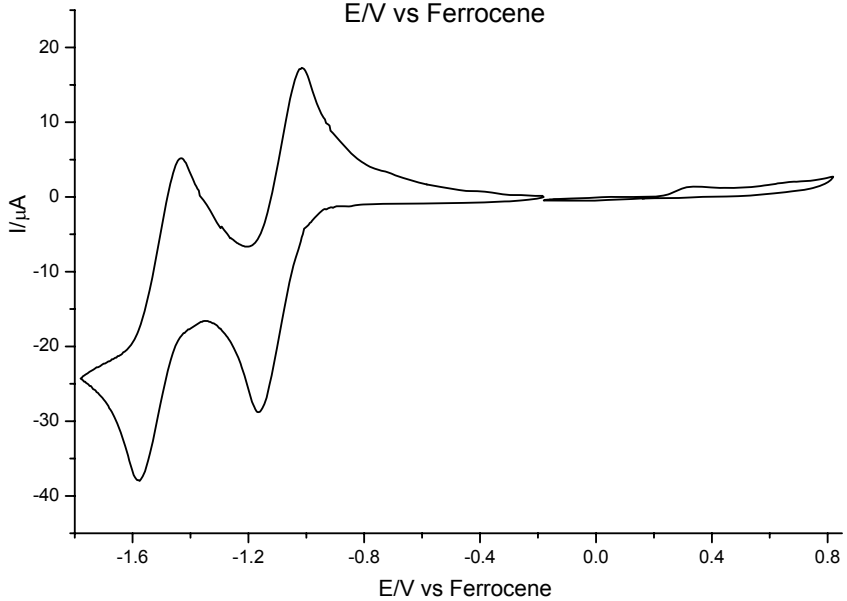


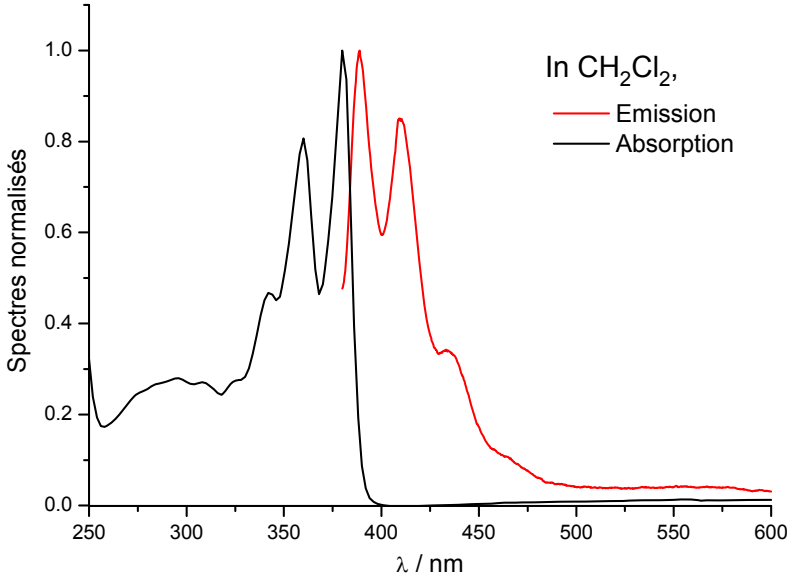




Optic Gap : 432 nm ⇒ 2.9 eV



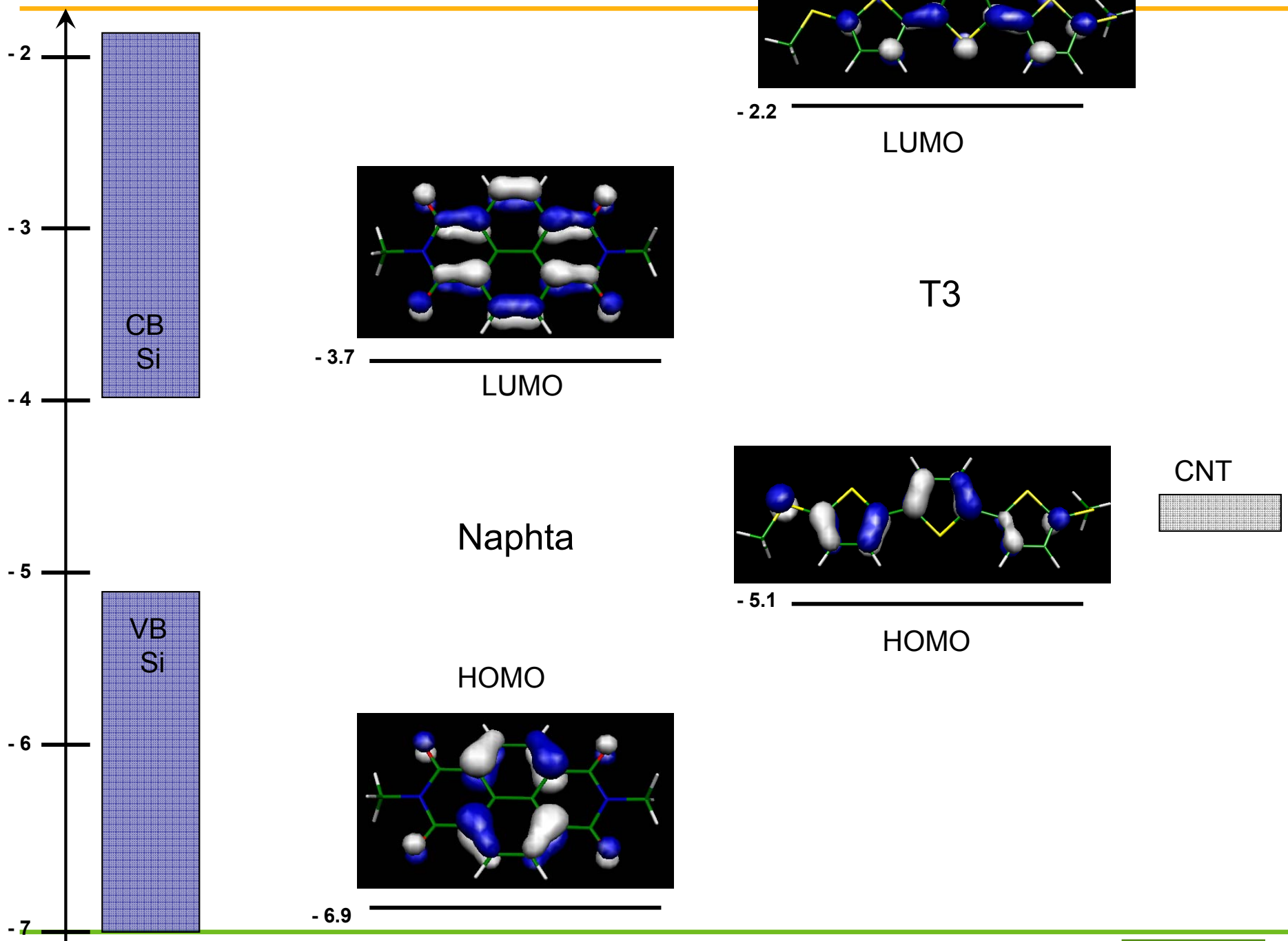




Optic gap : 384 nm ⇒ 3.2 eV

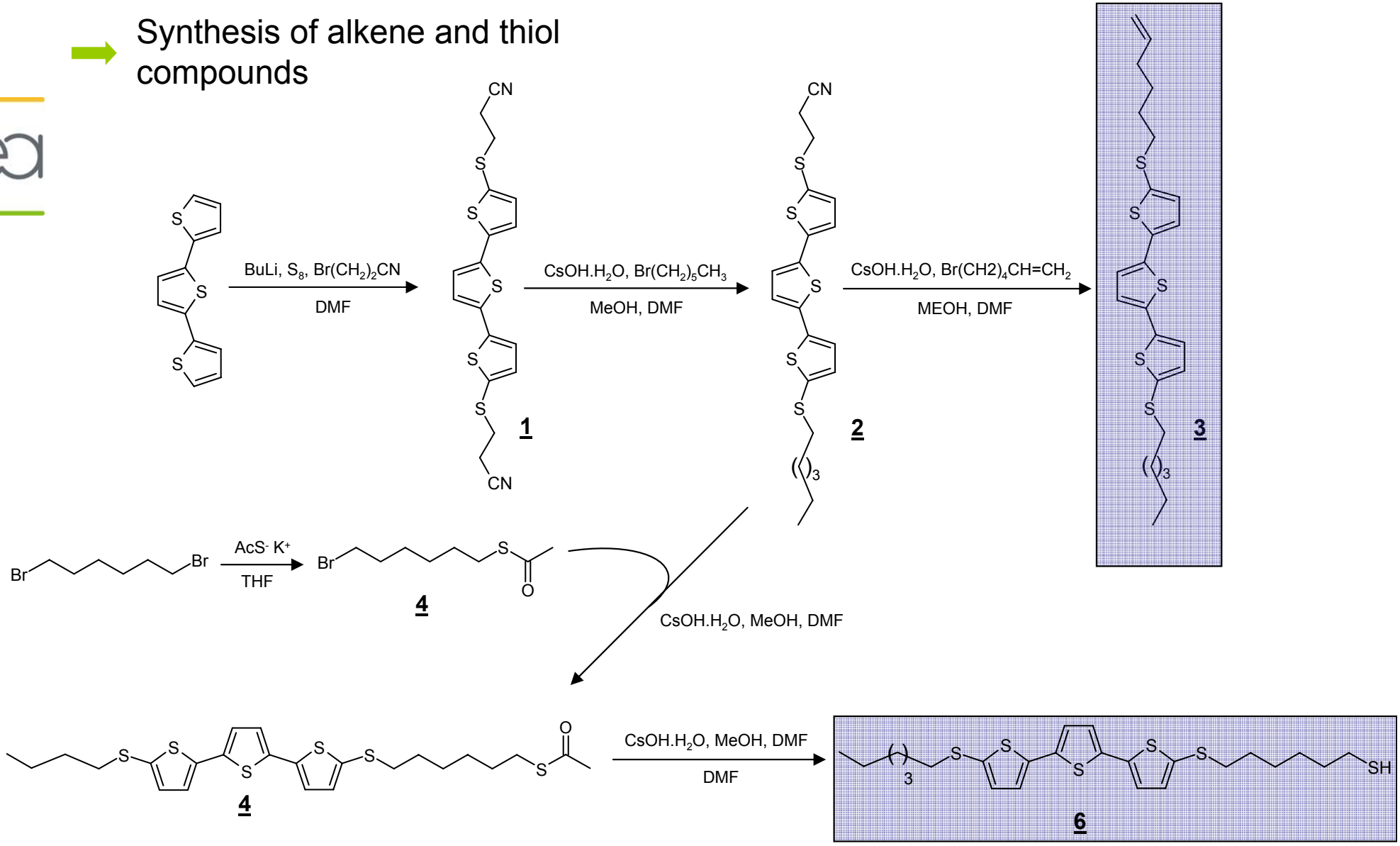
	$E_{ox/red1/2}^{1}$			$E_{ox/red1/2}^{2}$		
vs.	$Ag/AgNO_3$ (10 mM)	Fc^+/Fc	SCE	$Ag/AgNO_3$ (10 mM)	Fc^+/Fc	SCE
3T	0.520 V	0.430 V	0.820 V	0.663 V	0.573 V	0.960 V
Napht	- 0.990 V	- 1.080 V	- 0.690 V	-1.410 V	- 1.500 V	- 1.110 V

Energy level of the compounds targeted



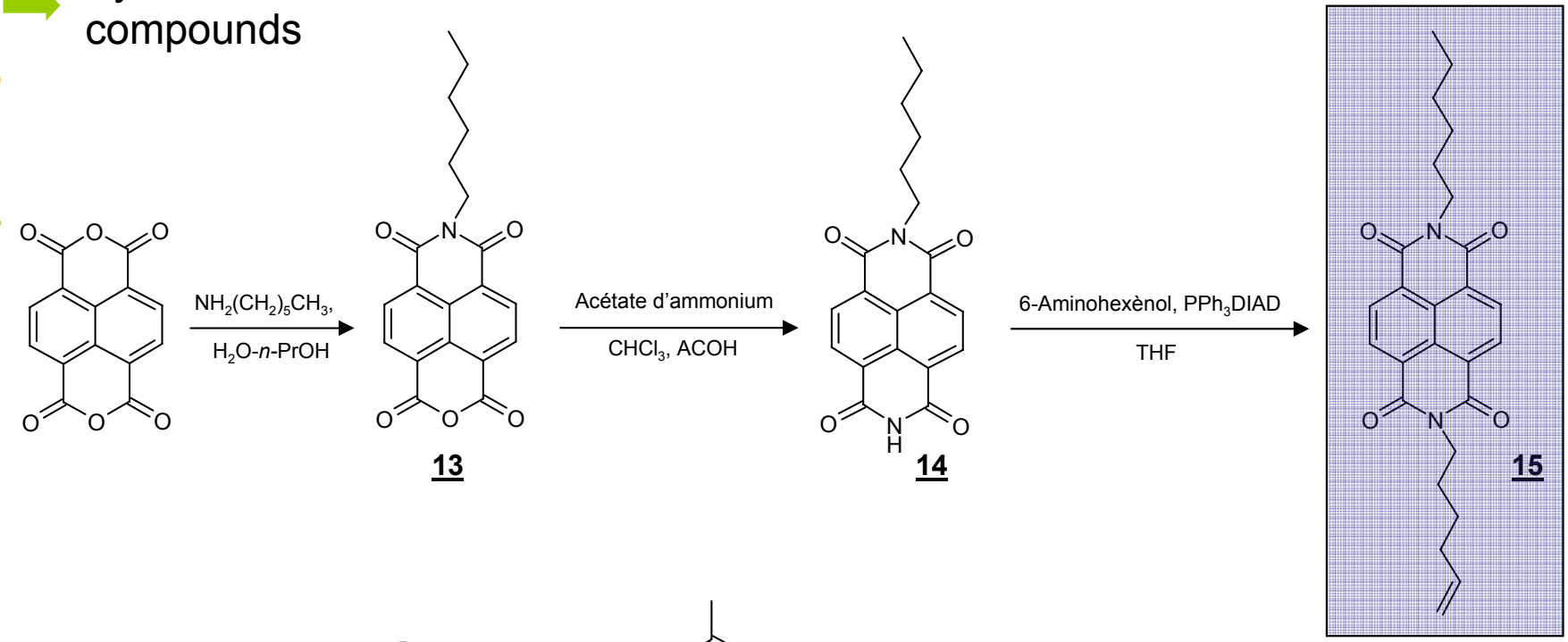
Synthesis of p-type compound : Terthiophene derivative (3T)

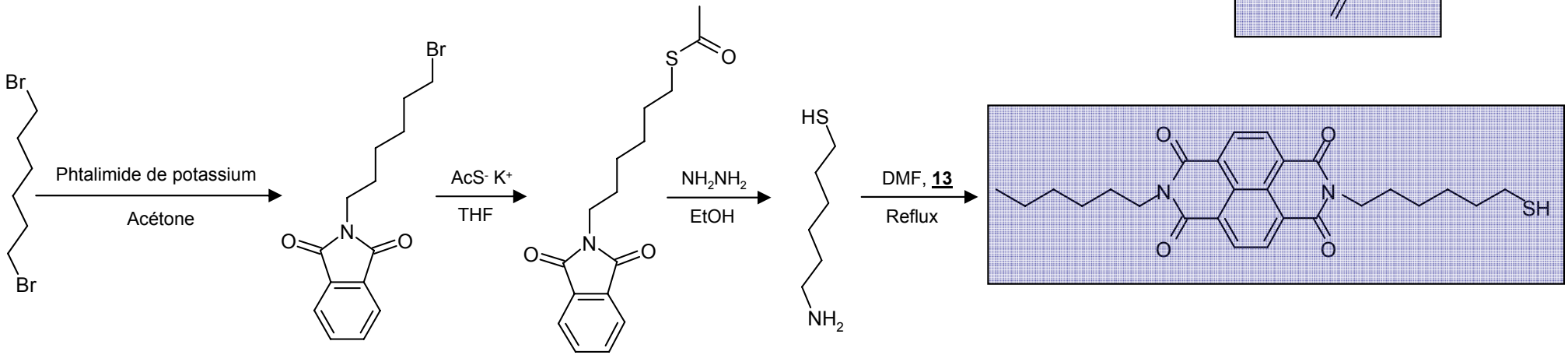
Synthesis of alkene and thiol compounds



Synthesis of n-type compound : Naphthalene tetracarboxiimide (Naph)

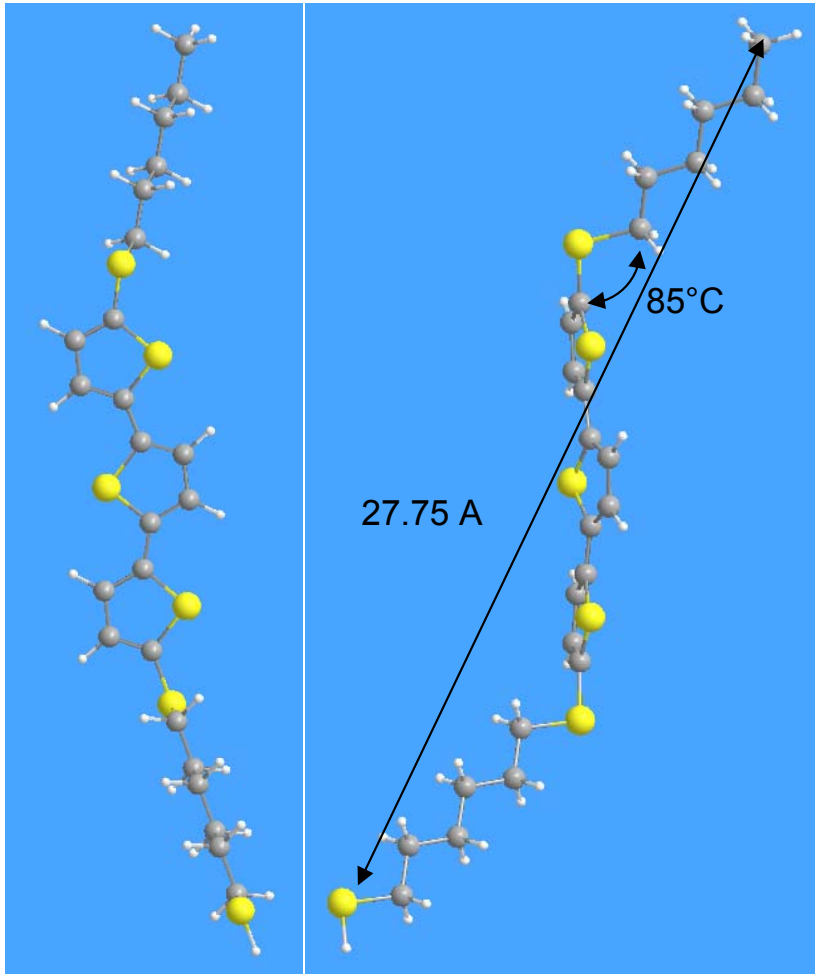
Synthesis of alkene and thiol compounds



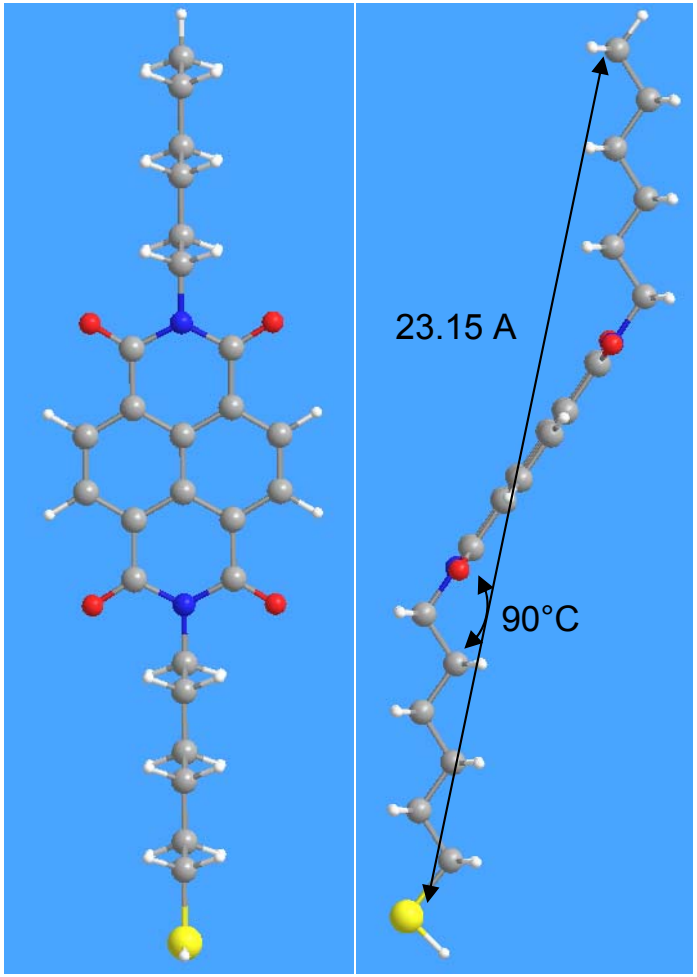


Geometries optimisation of 3T and Naph thiols derivatives

3TSH



NaphSH



Gaussian 98 DFT (Becke3lyp), Bases : 6-31G*.

SAMs on gold

Conditions

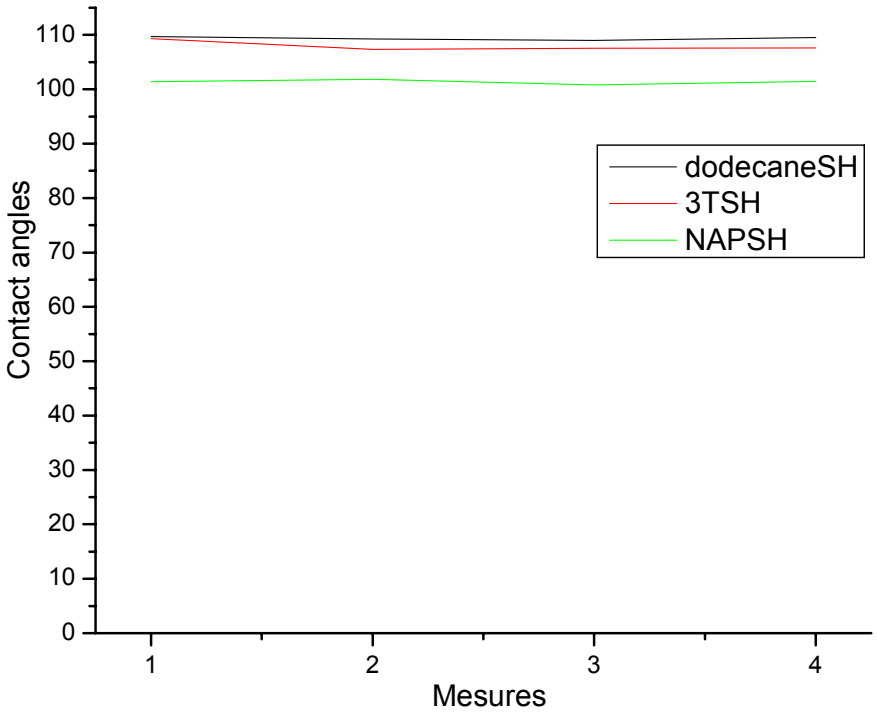
Thiol Concentration : 10^{-3}M

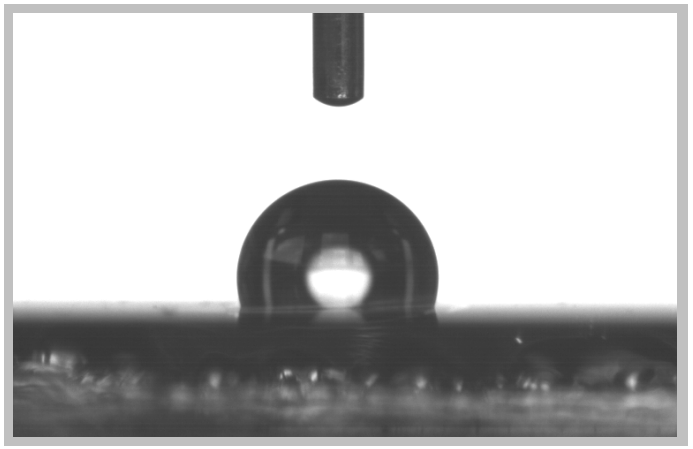
Solvent : Methylene Chloride/Ethanol

Reaction time : 24 hours

$\theta \approx 100 - 110°$

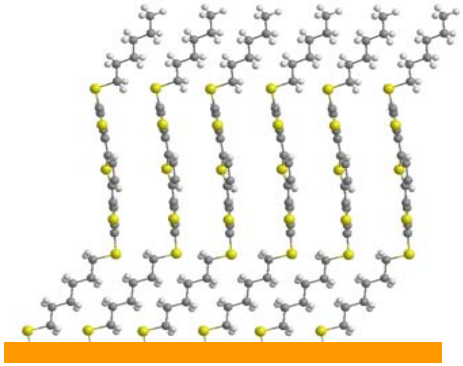
Contact angle measurements

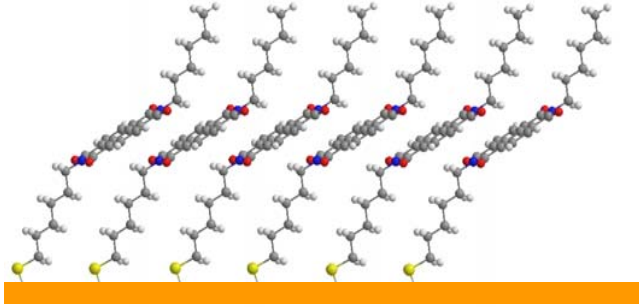




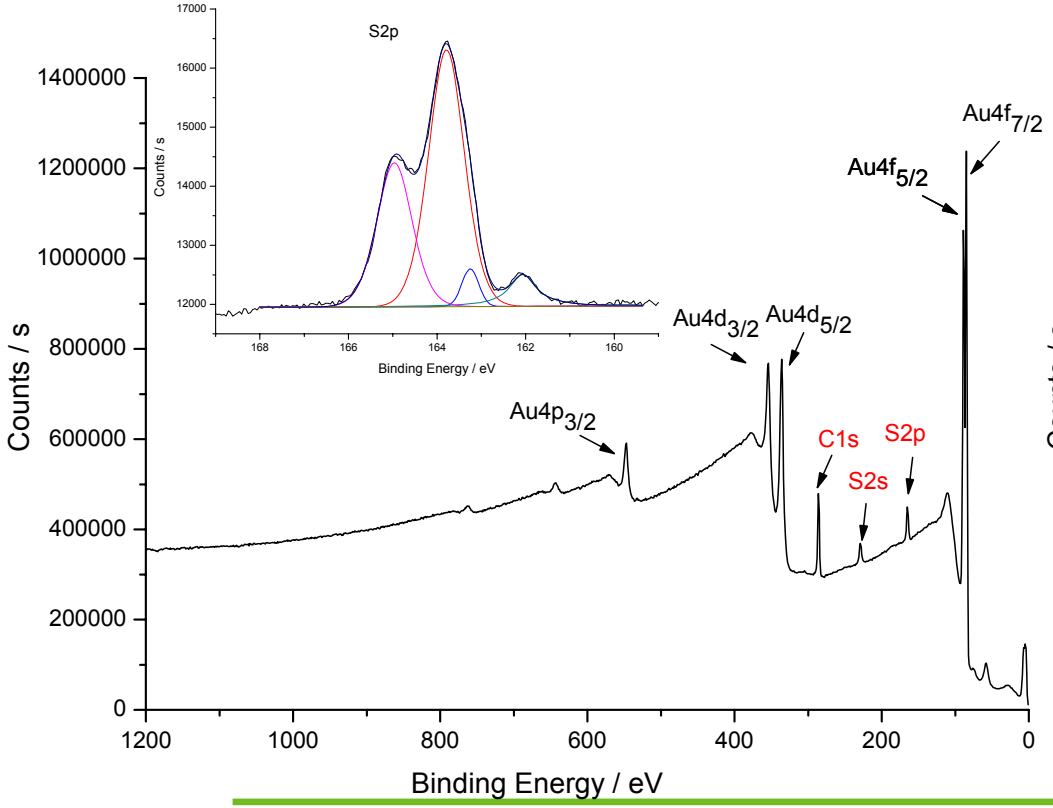
3T-SH

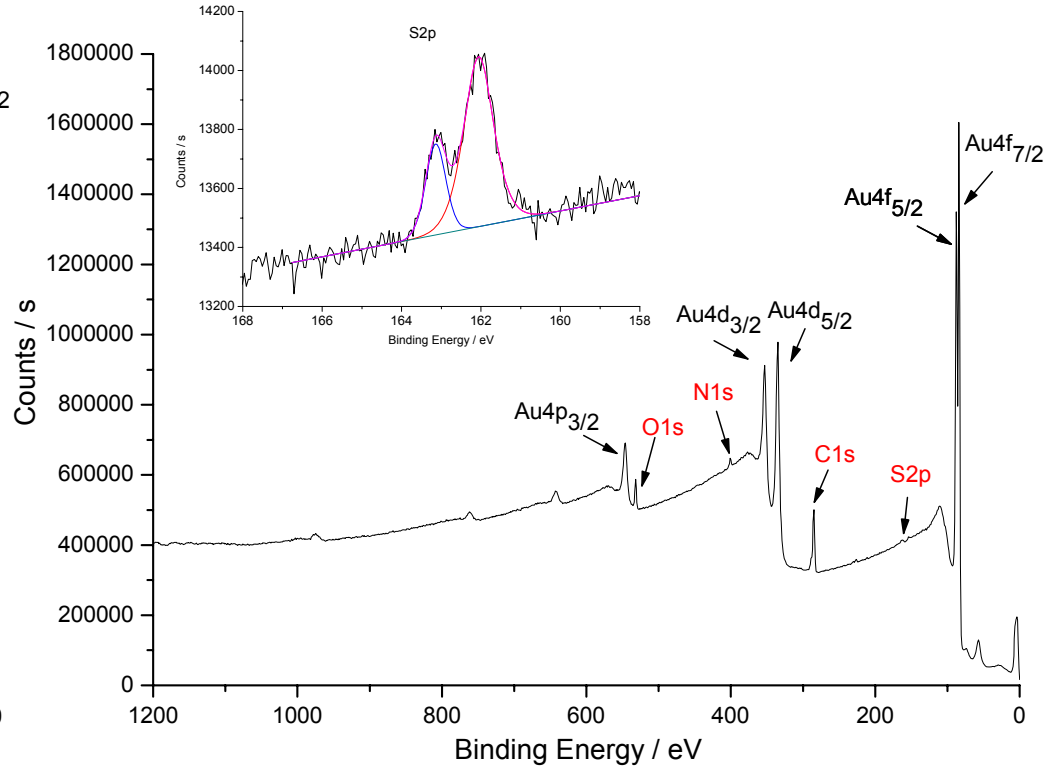
XPS analysis of SAMs on gold



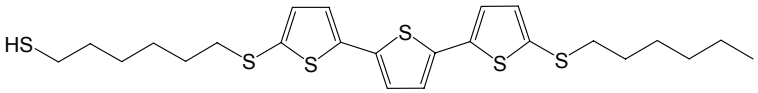


$$R-S-H+Au_n^0 \rightarrow R-S^-Au^+Au_n^0+1/2H_2$$

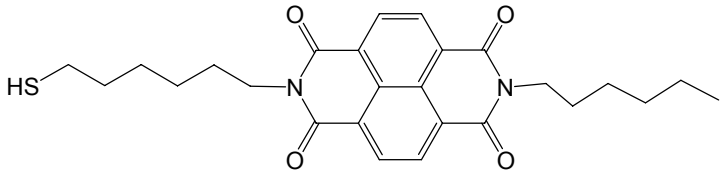




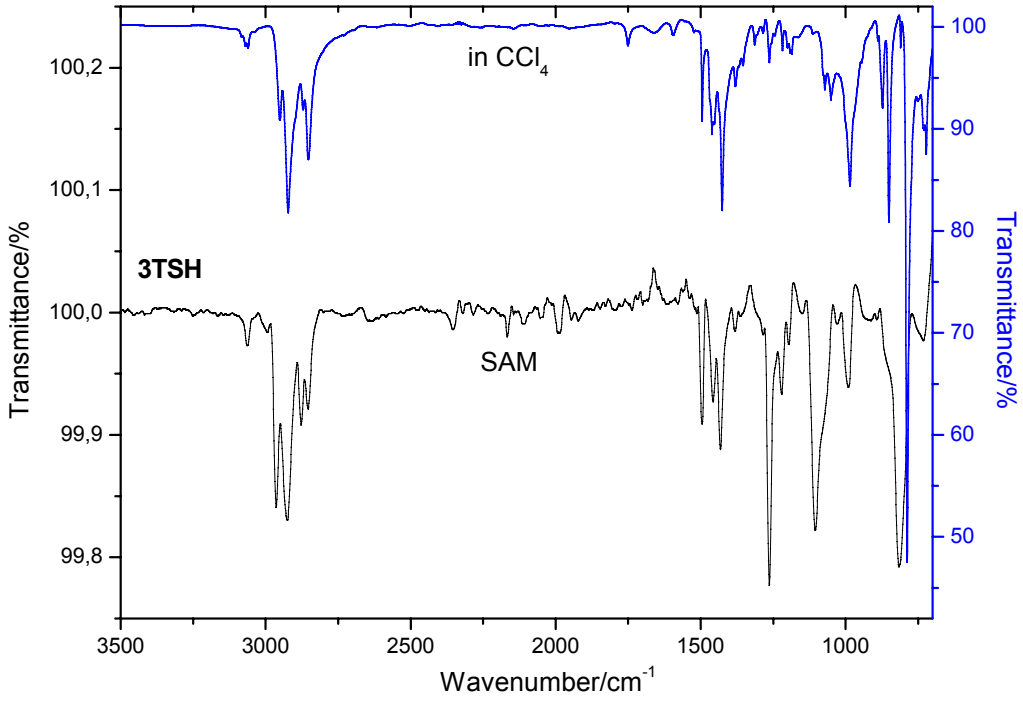
FT-IR analysis of SAMs on gold

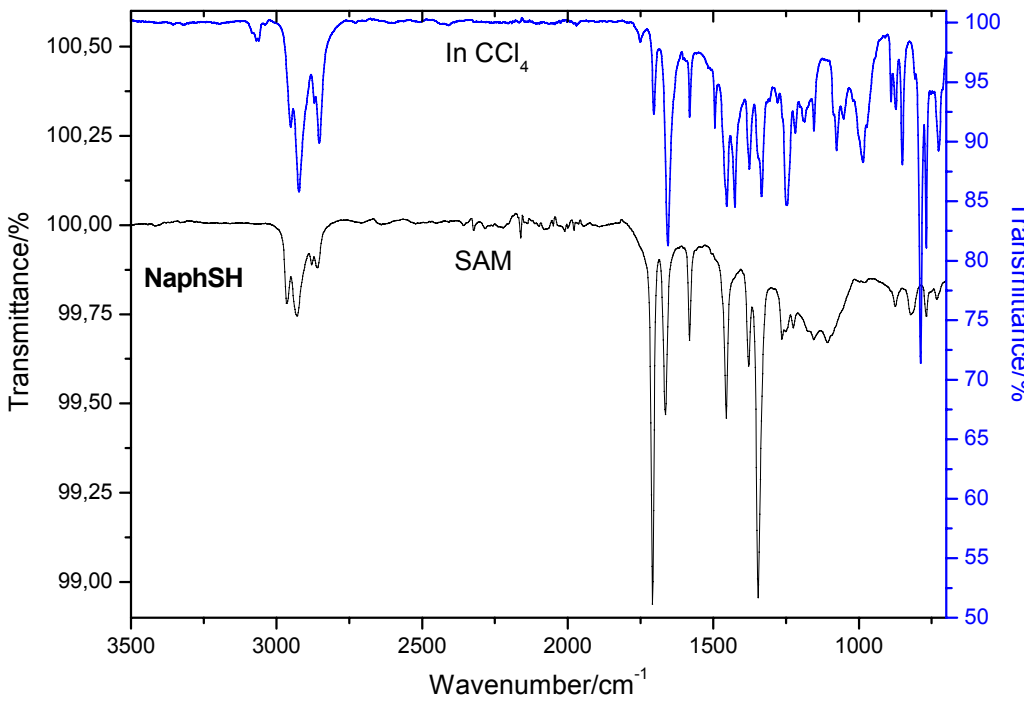


3TSH

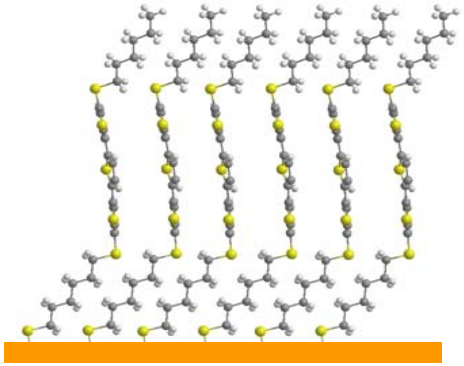


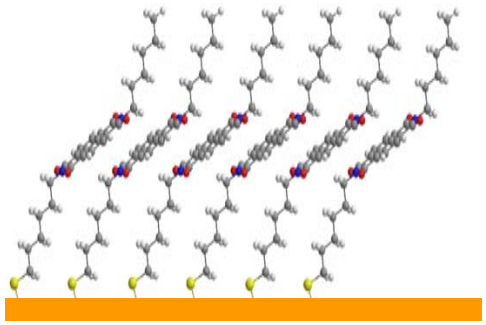
NaphSH

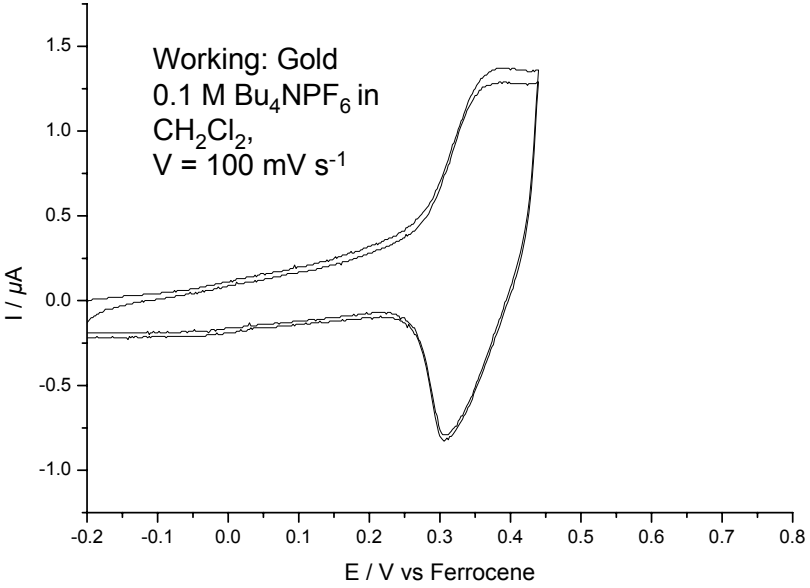


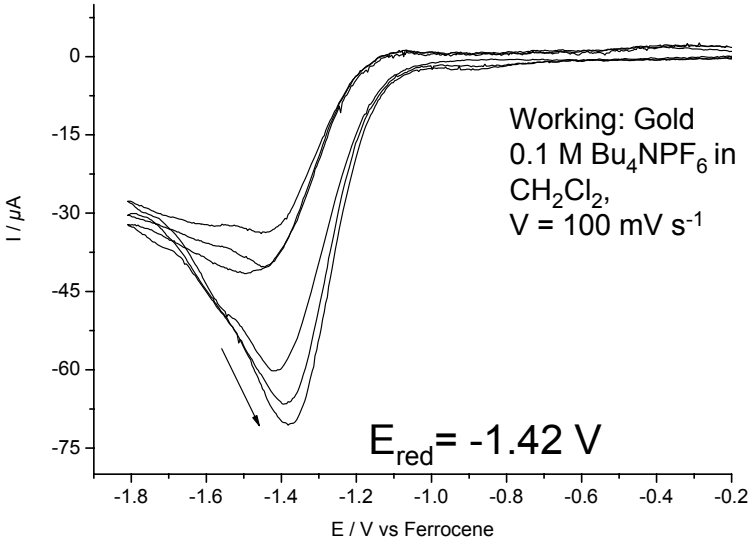


Cyclic voltamperometry of a SAM of 3TSH on gold









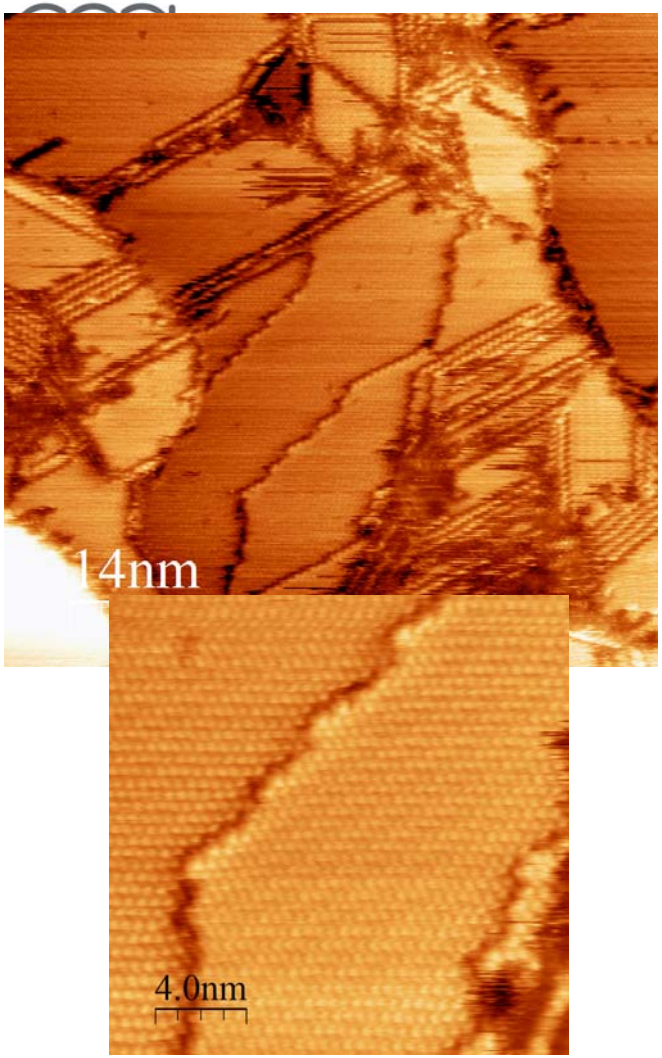
$E°_1$= 325 mV Versus ferrocene
≠ -110 mV / in solution

➡ π - π interactions

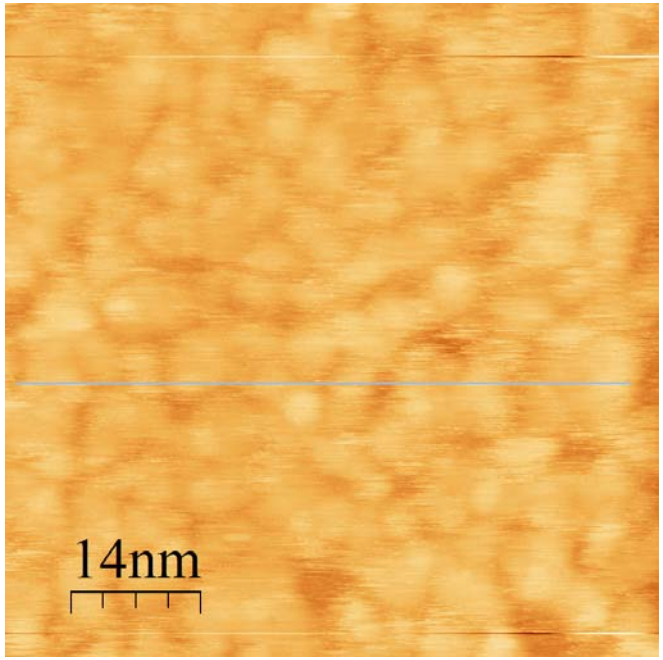
≠ -200 mV / in solution
Dimerization, Thiolale, Alkyl Chain

Morphology of the SAMs - STM

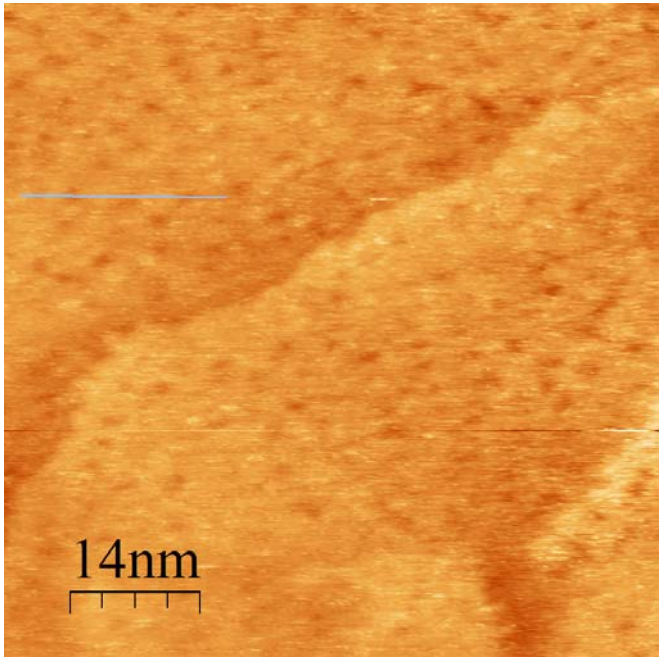
DodecaneSH



3TSH

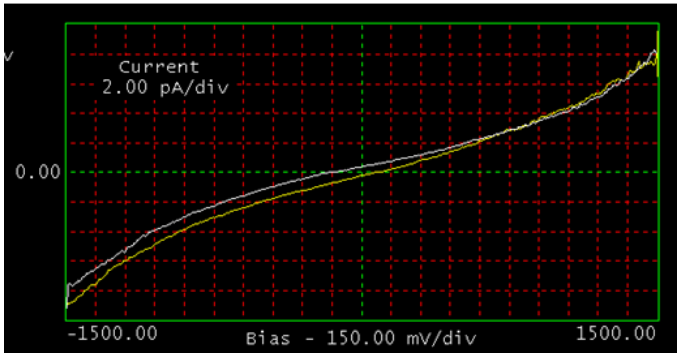


NaphthSH

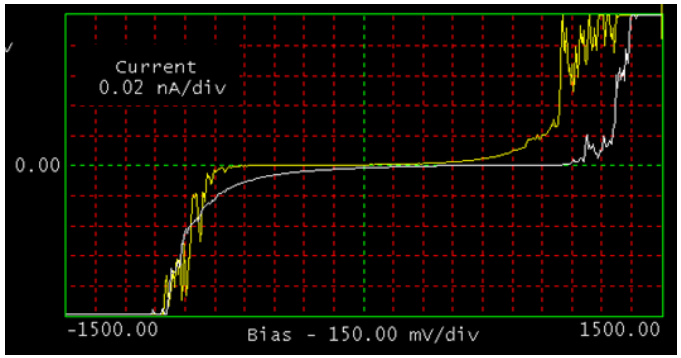


I/V measurements - STM

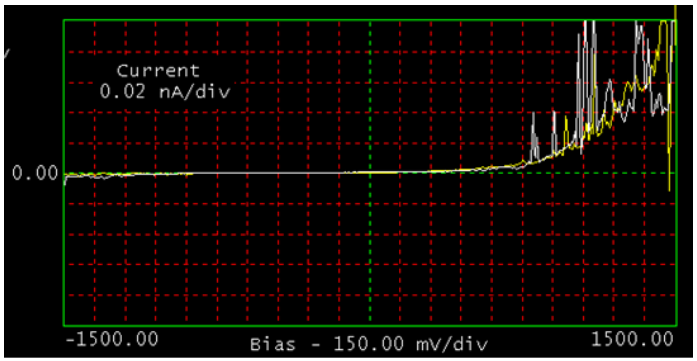
DodecaneSH

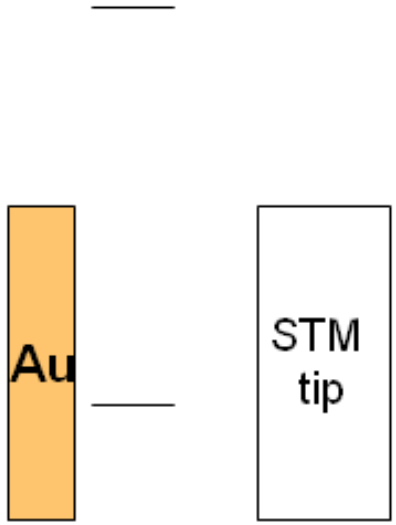


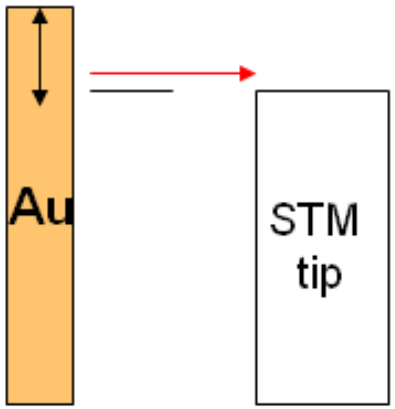
3TSH



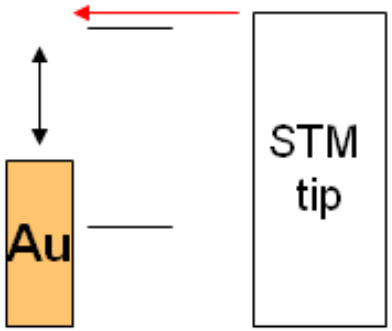
NaphthSH







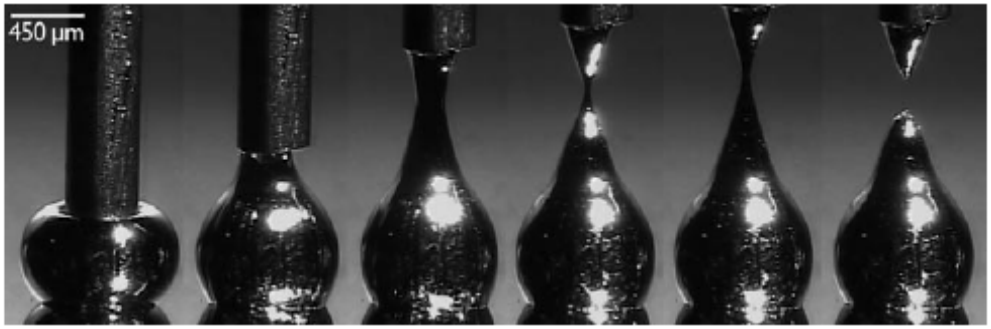
V < 0



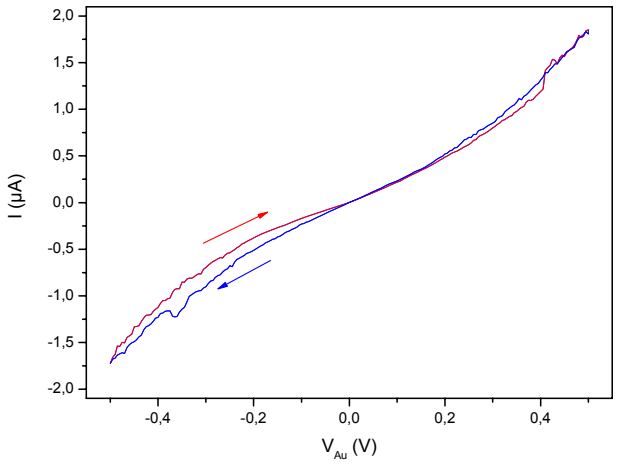
V > 0

Contact with InGa Eutectic and I/V measurements

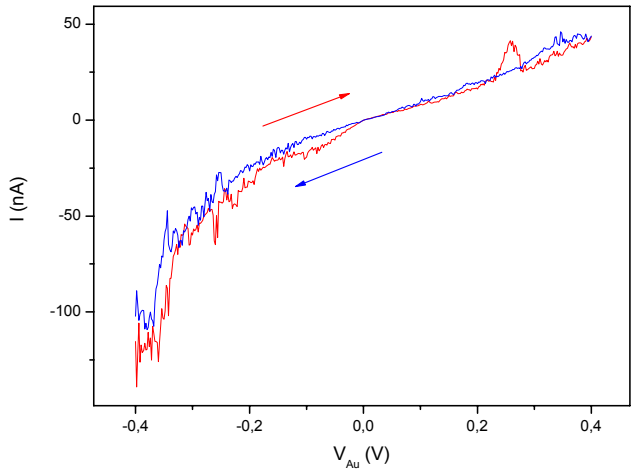
• Whitesides & al. , Angew.Chem.Int.Ed. **47**, *142* [2008]



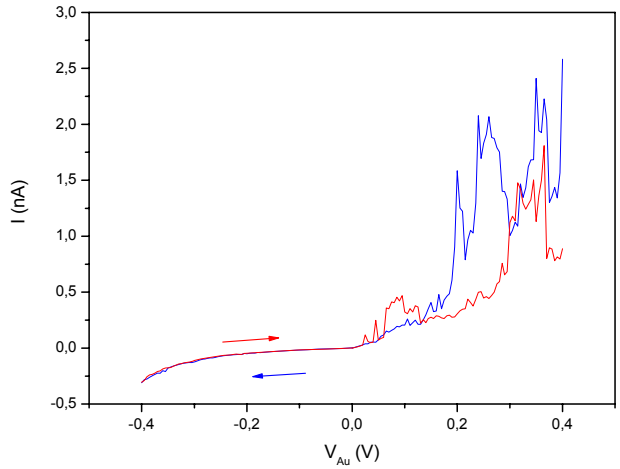
DodecaneSH



3TSH

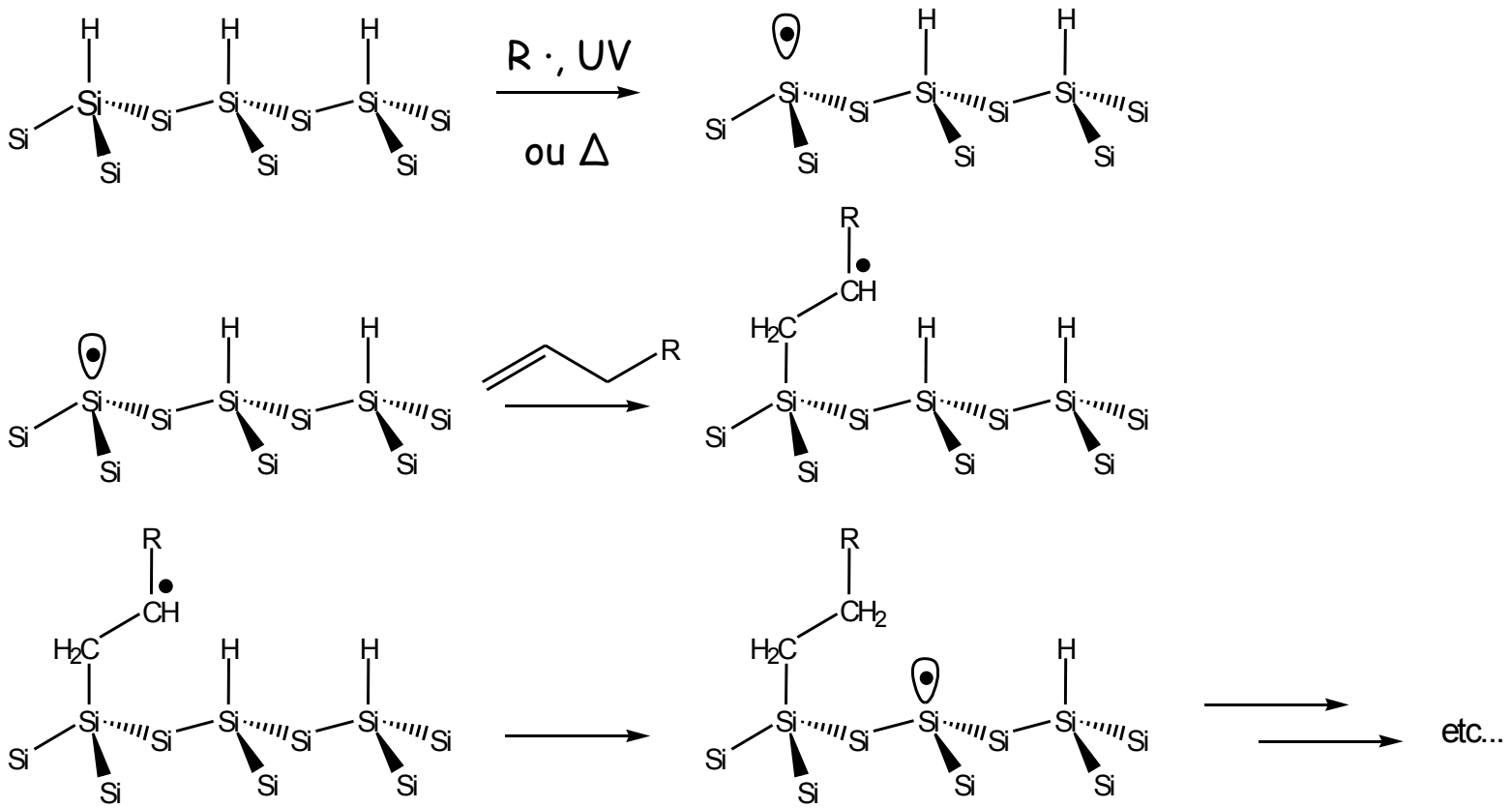


NaphthSH



Hydrosilation reaction mechanism on SIH

$$[RC(O)O]_2 \longrightarrow 2\,RC(O)\bullet \longrightarrow R\bullet + CO_2$$



Grafting of the alkenes compounds on silicon

Different ways were tested for the 3T derivative:

- *Sublimation* → sublimation impossible
- *Dilution* → re-oxidation of the silicon
- *Irradiation* → degradation

→ **Grafting Neat**

Different ways were tested for the Naphth derivative:

- *Sublimation* → sublimation impossible
- *Neat* → mp>200°
- *Dilution* → re-oxidation of the silicon

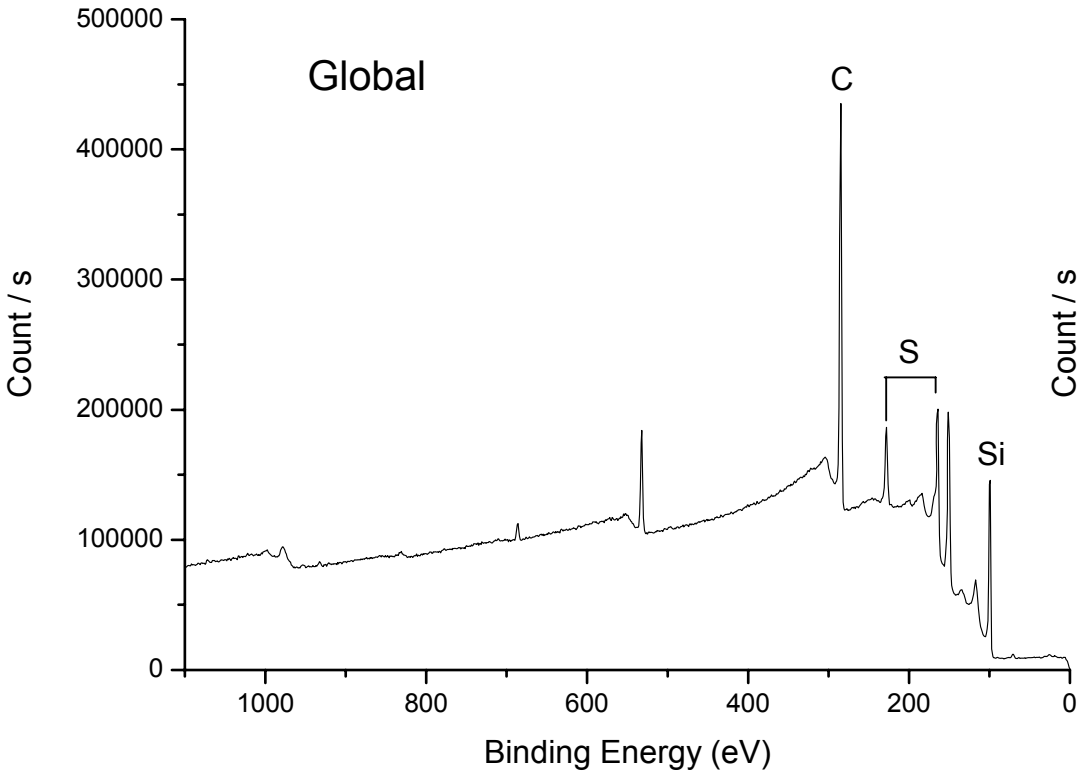
→ **Grafting Neat**

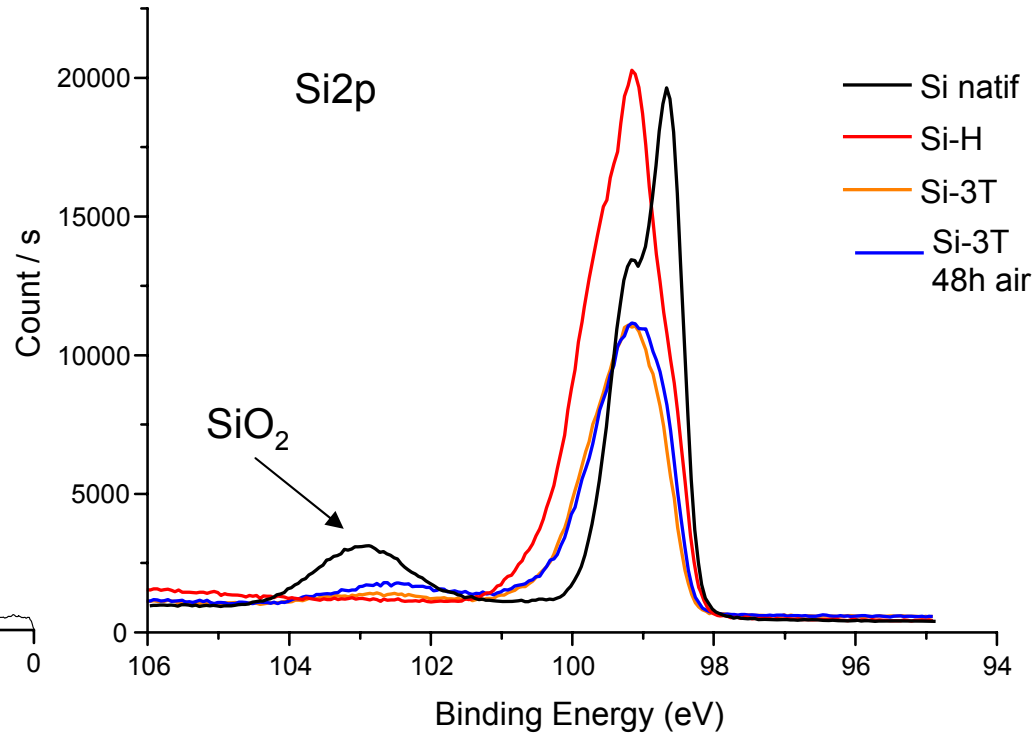
Grafting of the 3T on silicon p++ (100)

Conditions : Neat, 150°C, under vacuum, 12H

Contact angle of 105°

XPS :



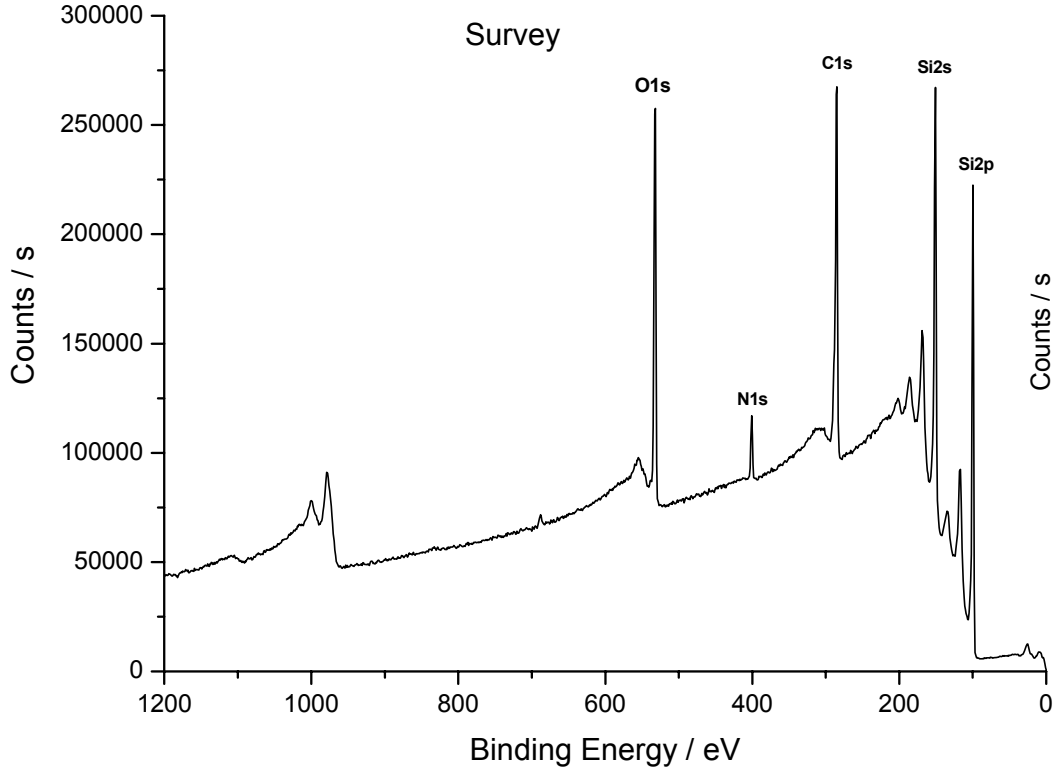


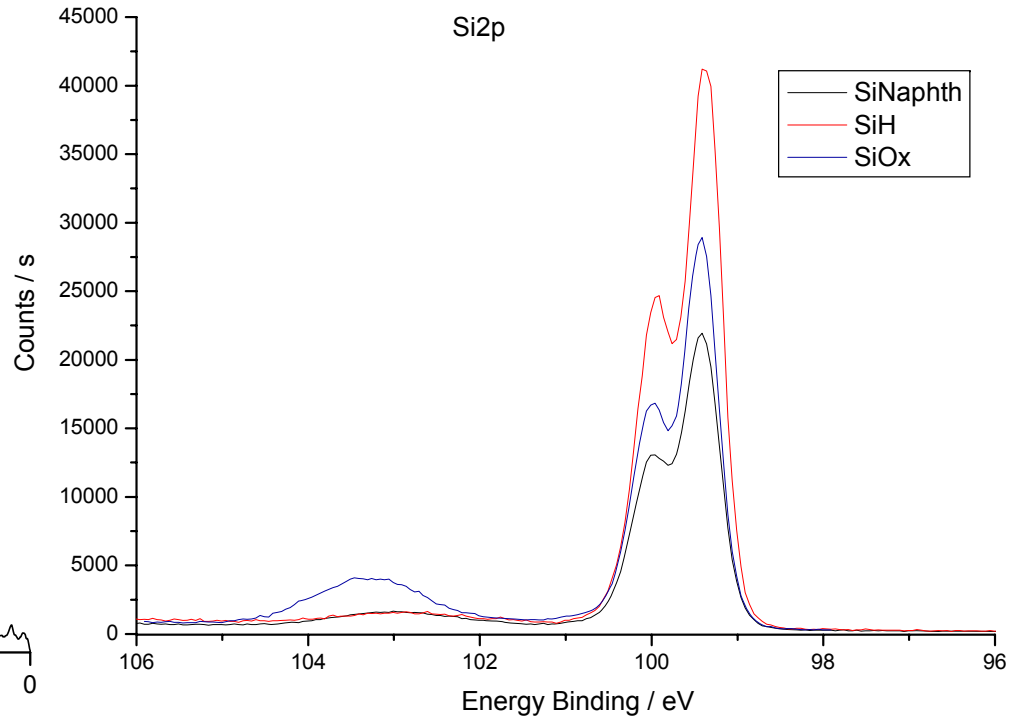
Grafting of the Naph on silicon n++ (111)

Conditions : Neat, 220°C, 2H, under vacuum (10^{-7} mbar)

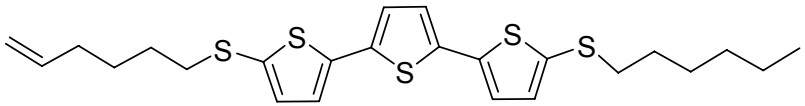
Contact angle of 100°

XPS analysis:

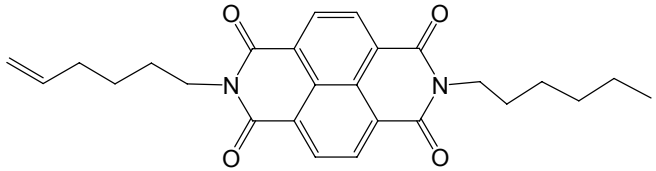




Cyclic Voltamperometry

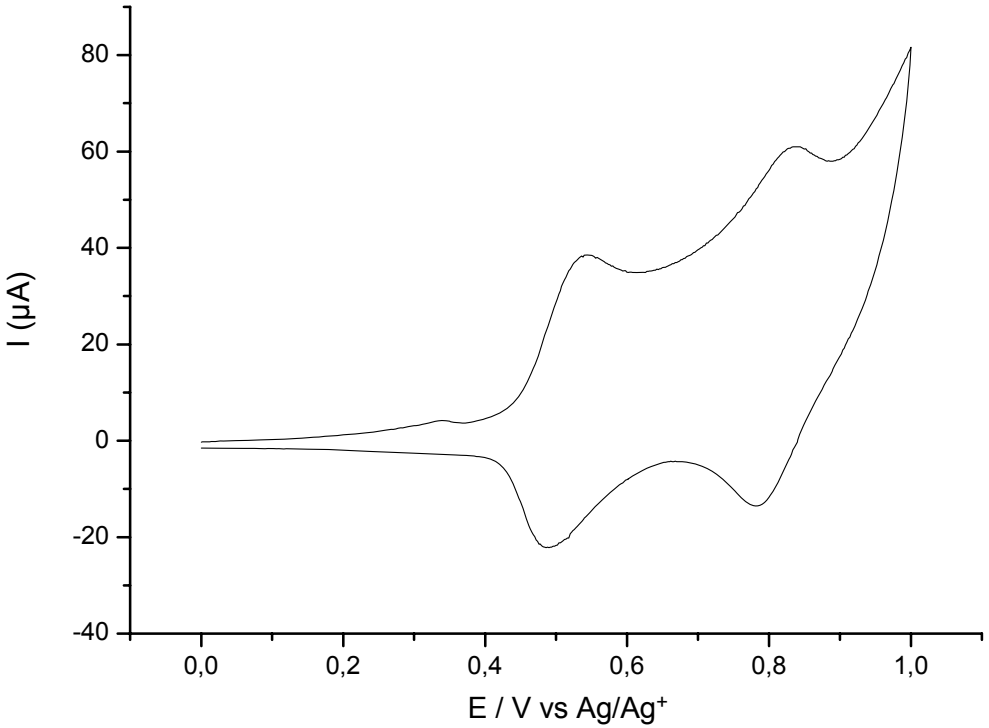


3TAL

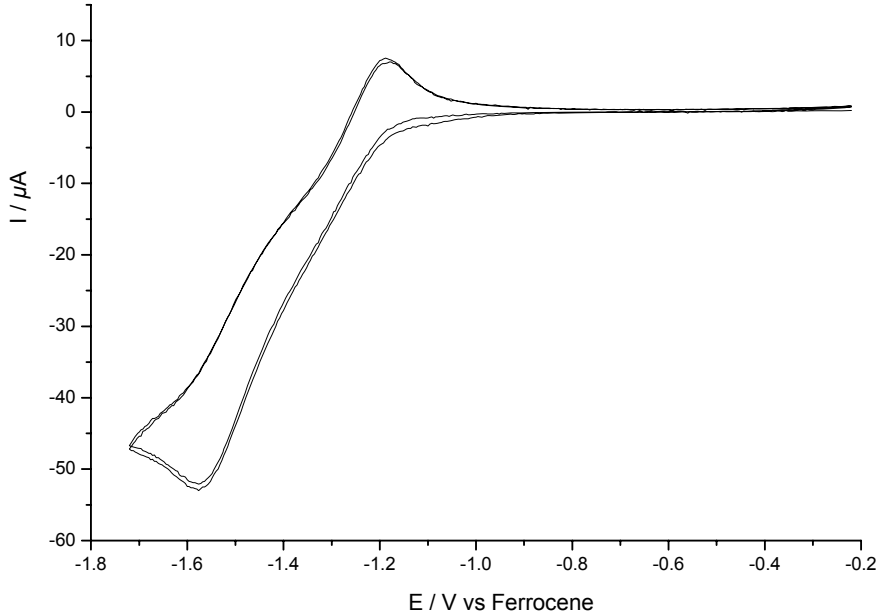


NaphAL

On Si(100)-P^{++} CH_2Cl_2,
TEAP (0.1M), 100 mV.s^{-1}



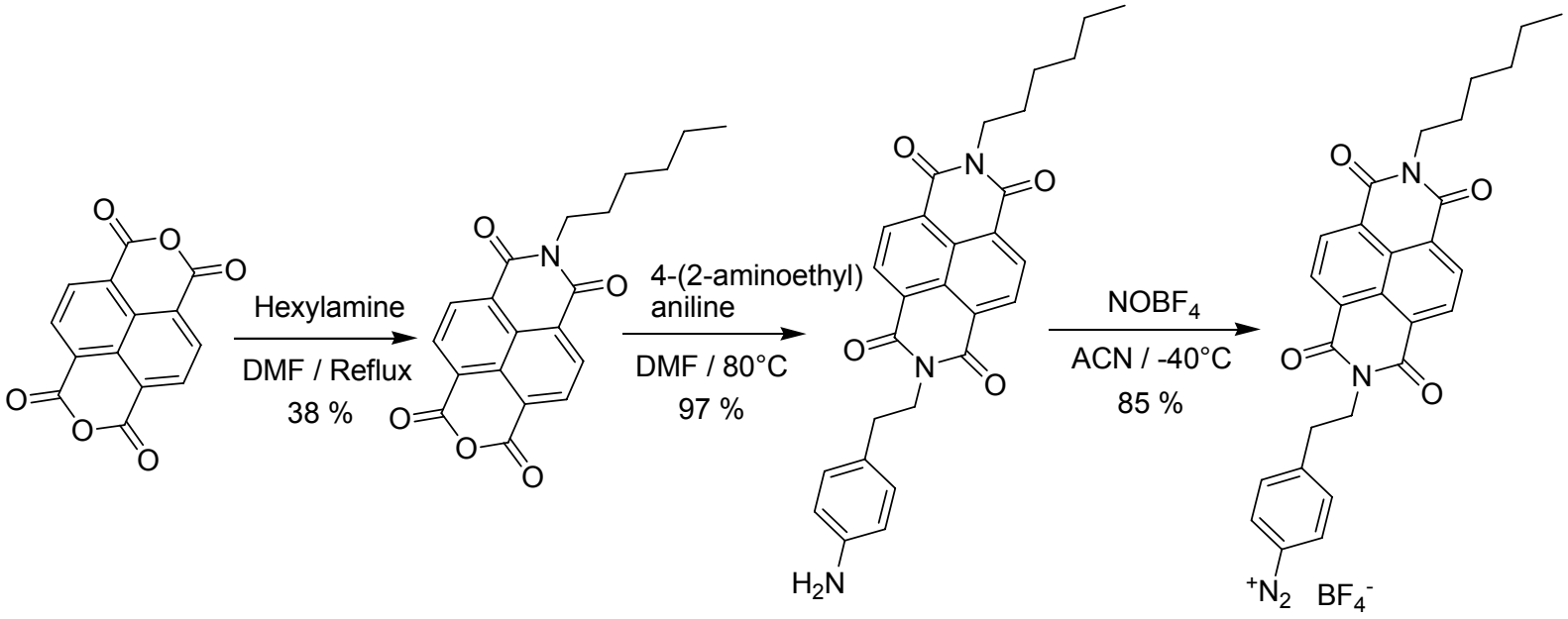
Working: Silicon 111 n++
0.1 M Bu_4NPF_6 in CH_2Cl_2,
V = 100 mV s^{-1}

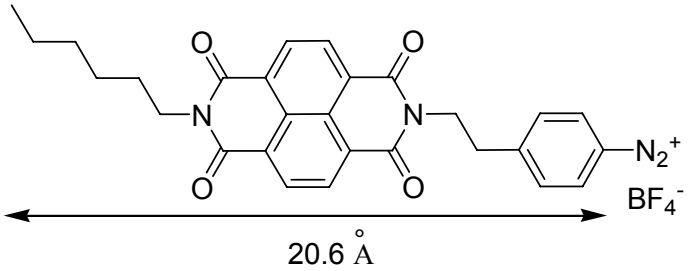


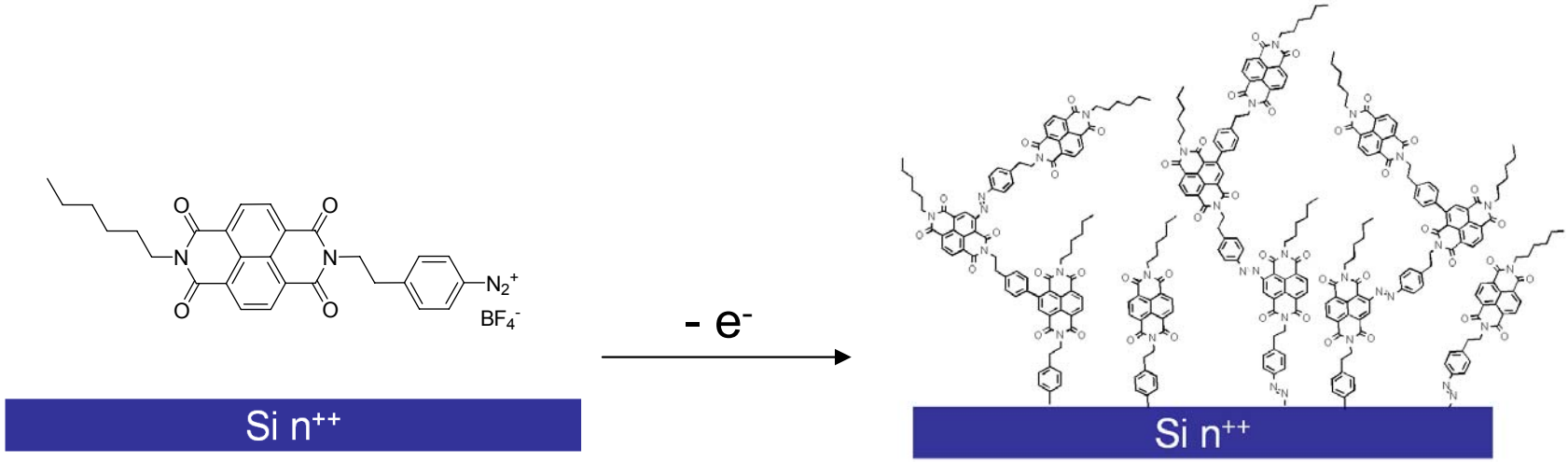
Conclusion of the first part

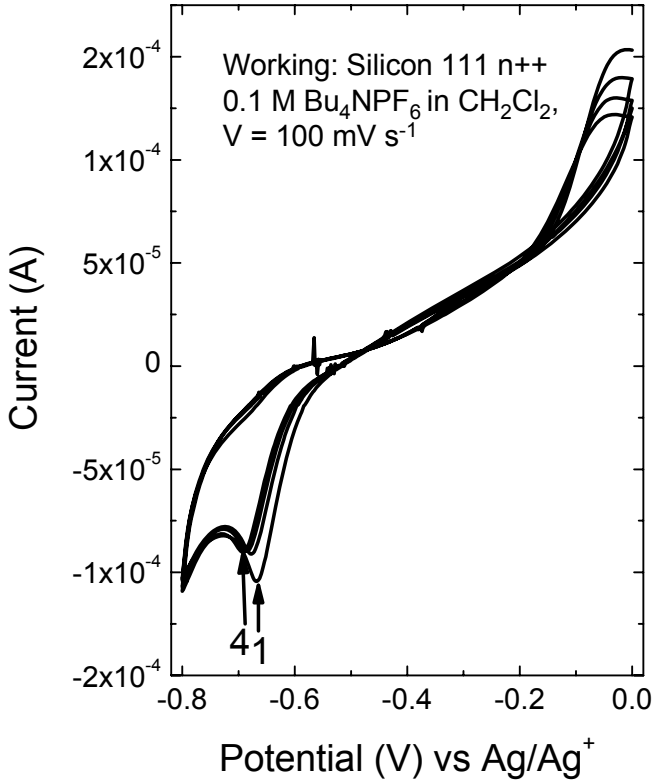
- Synthesis of two new σ-π-σ compounds with Thiol or alkene functions
- Monolayers on gold and on silicon (Contact angle, XPS, infrared spectroscopy, STM).
- NapthSH has a better packing than 3TSH on gold.
- I/V measurements on gold (STM and Eutectic InGa) next on silicon

Synthesis of
N-(2-(4-diazoniophenyl)ethyl)-*N*'-hexylnaphthalene-1,8:4,5-tetracarboxydiimide tetrafluoroborate





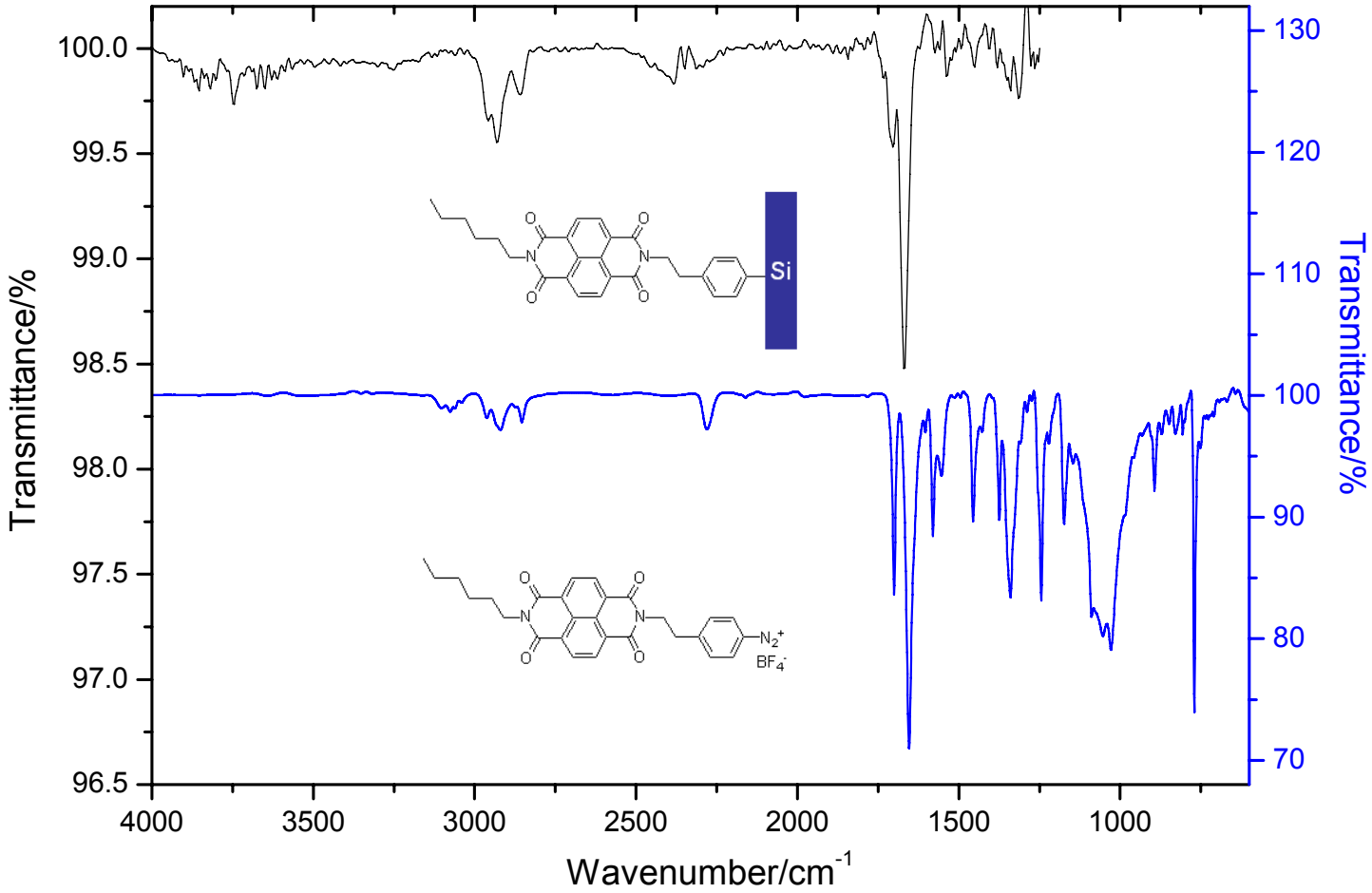


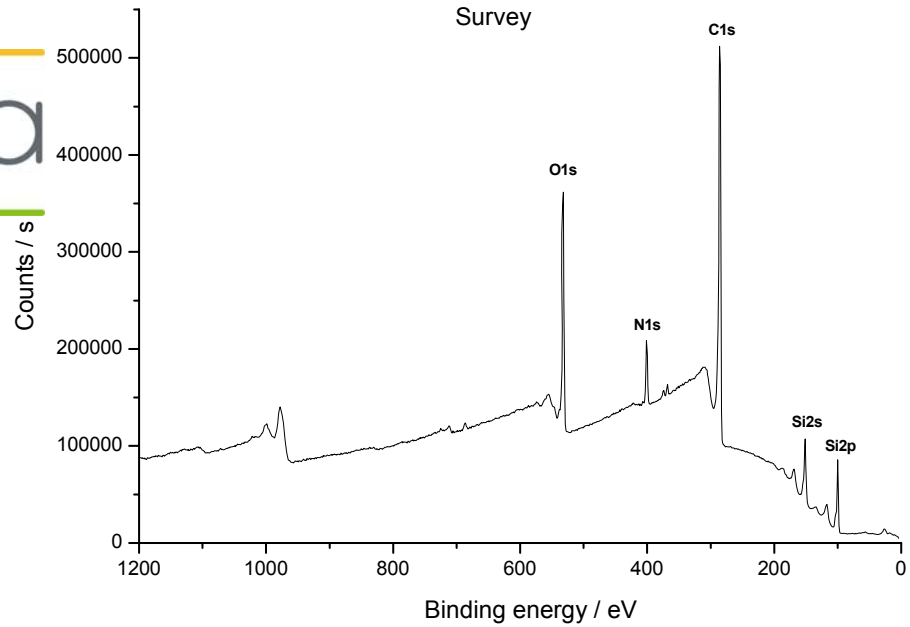


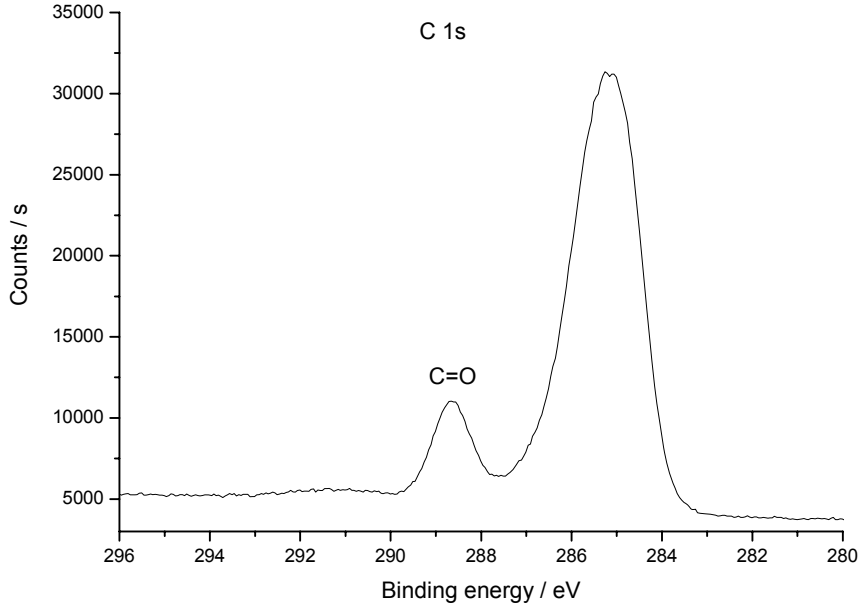
CV recorded using diazonium salt of σ–π–σ molecules using H-terminated Si (111) as working electrode. Note the shift in the irreversible peak to higher potentials with increasing number of scans.

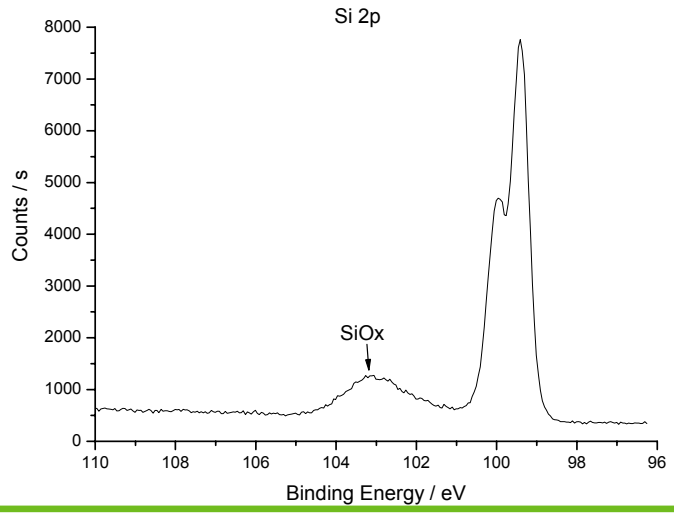
- Contact Angle : 70°

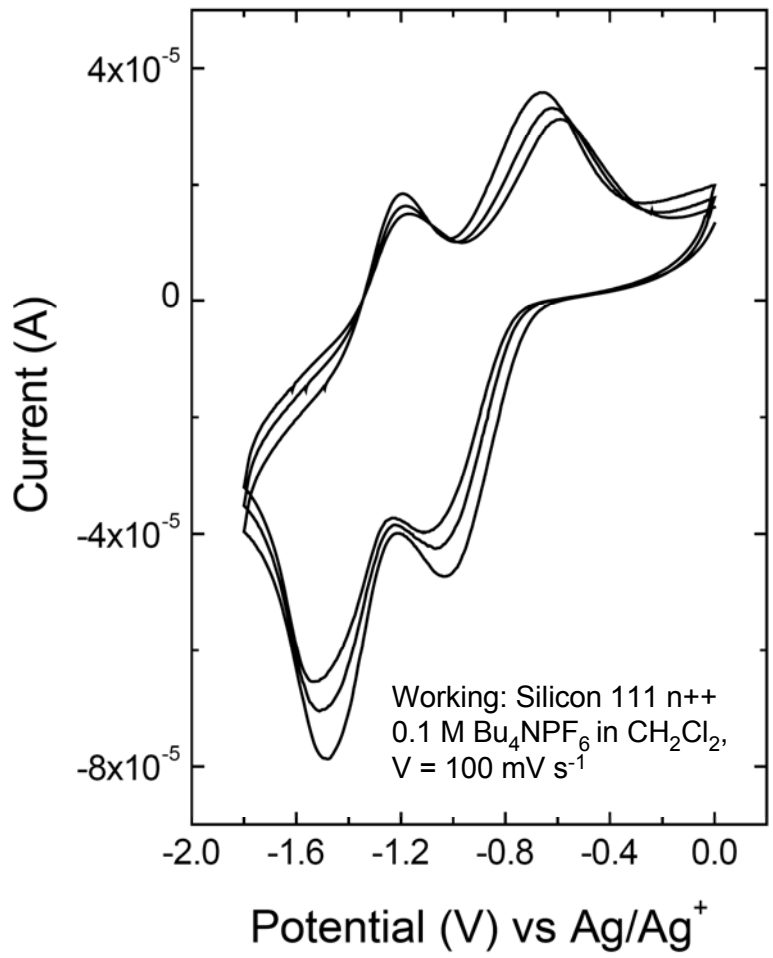
- Infrared spectrum



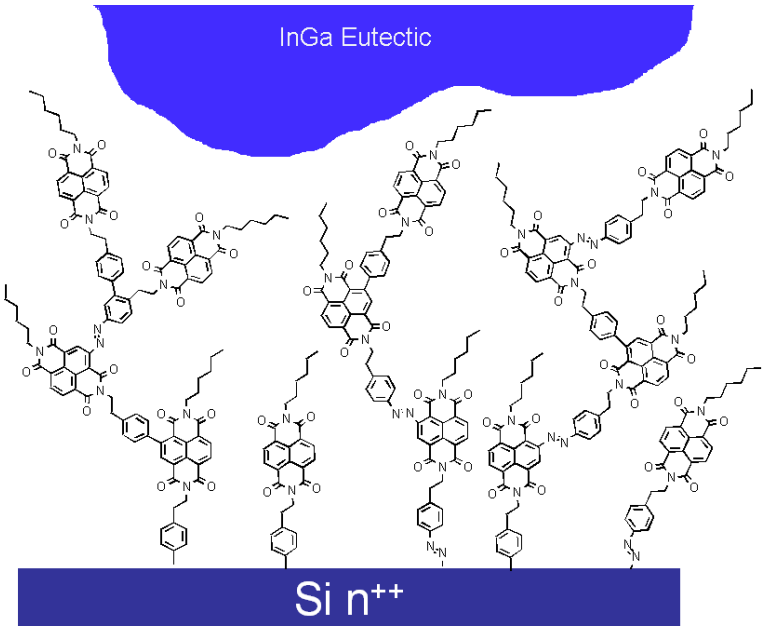

Survey
C1s
O1s
N1s
Si2s
Si2p
Counts / s
Binding energy / eV

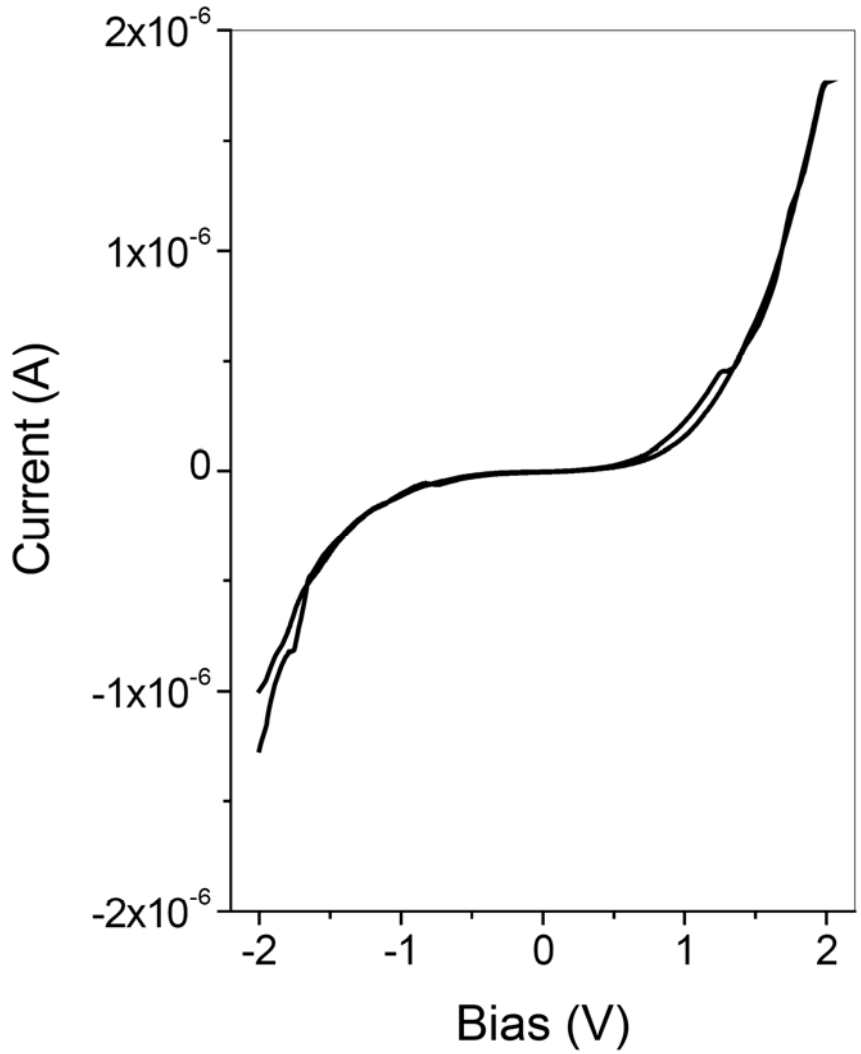

C 1s
C=O
Counts / s
Binding energy / eV


Si 2p
SiOx
Counts / s
Binding Energy / eV



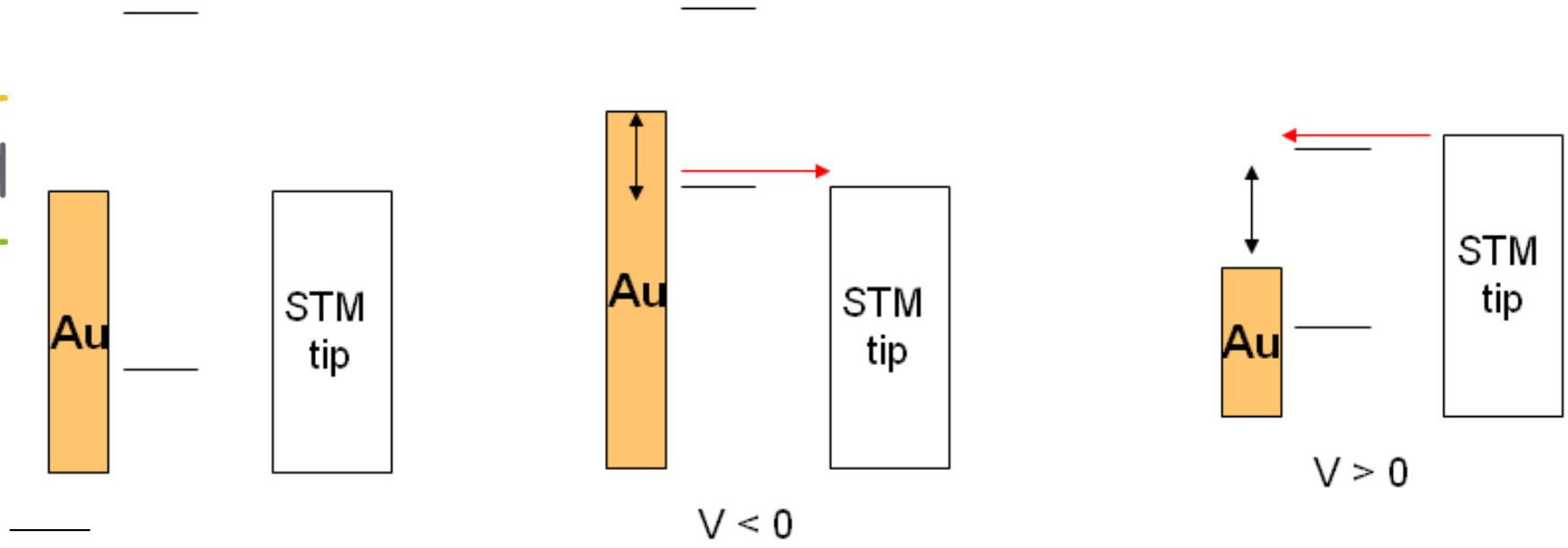
CV recorded for the electrografted organic layers on Si grafted using the reduction of diazonium salt.

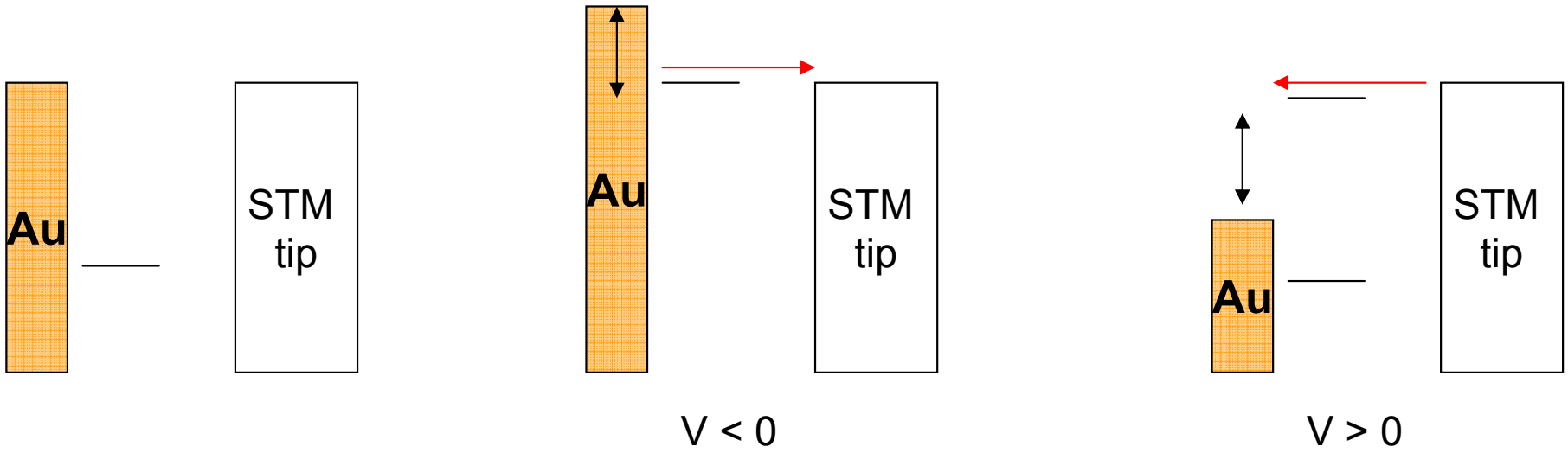




Current-voltage characteristic of the σ–π–σ layers (12 nm) grafted on Si using diazonium salt

the end


Au
STM
tip
Au
STM
tip
V < 0
Au
STM
tip
V > 0


Au
STM
tip
Au
STM
tip
V < 0
Au
STM
tip
V > 0