POLYMERS UNDER ION BEAM IRRADIATIONS AT GANIL

Yvette NGONO

CIMAP

SUMMARY

- What for?
- Present research
- The future
- Conclusion

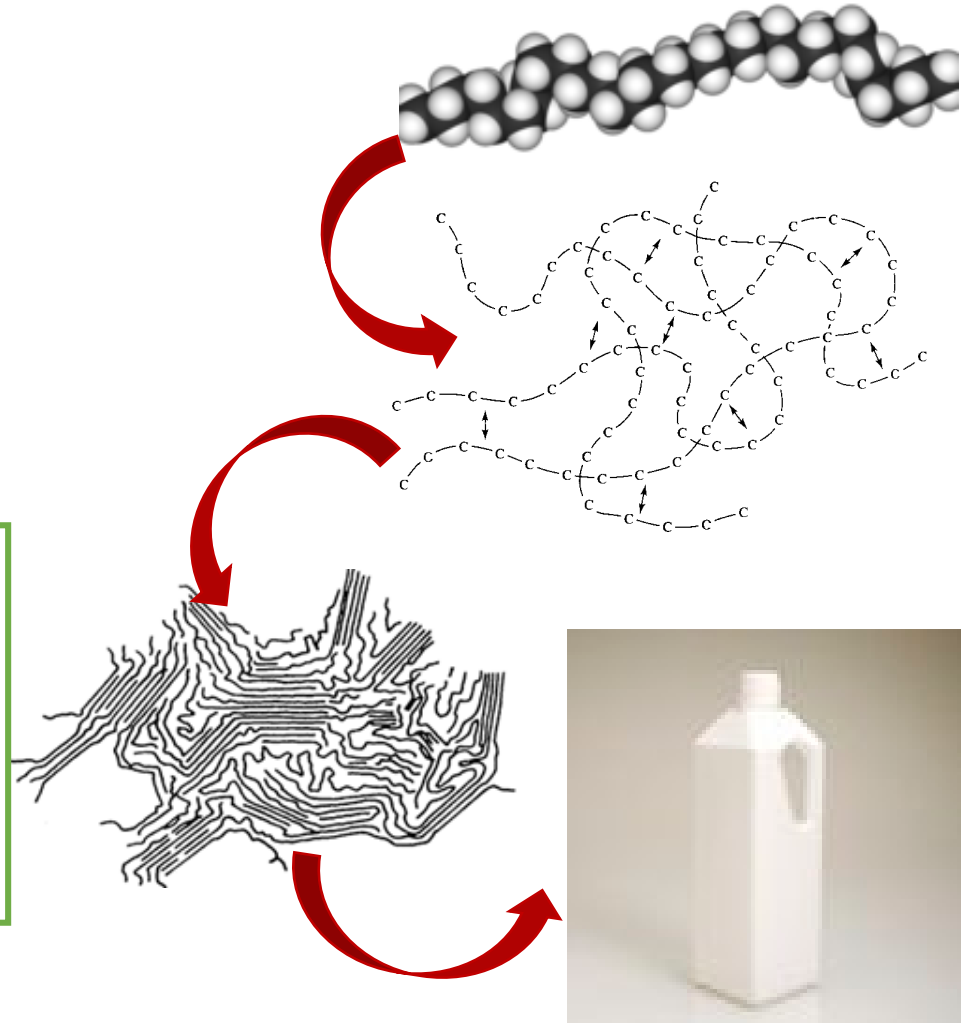
Polymers=complex structures

Polymers = Macromolecules

- Repeat unit
- Covalent bonds

Multiple organization levels

- Molecular
- Macromolecular
- Supra Macromolecular



Fate of primary species: defects creation

Energy deposition

↓

Ionization/excitation

↓

Covalent bonds = prone to radiolysis

Radicals

R° + H°

f(monomer chemical structure)

Macromolecular defects

Gas Emission

f(monomer chemical structure, microstructure, irradiation conditions)

Quantifying both defect types mandatory

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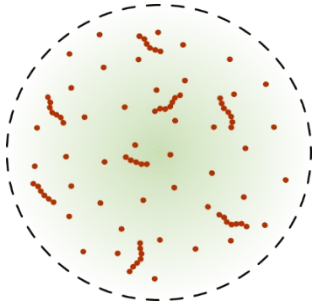
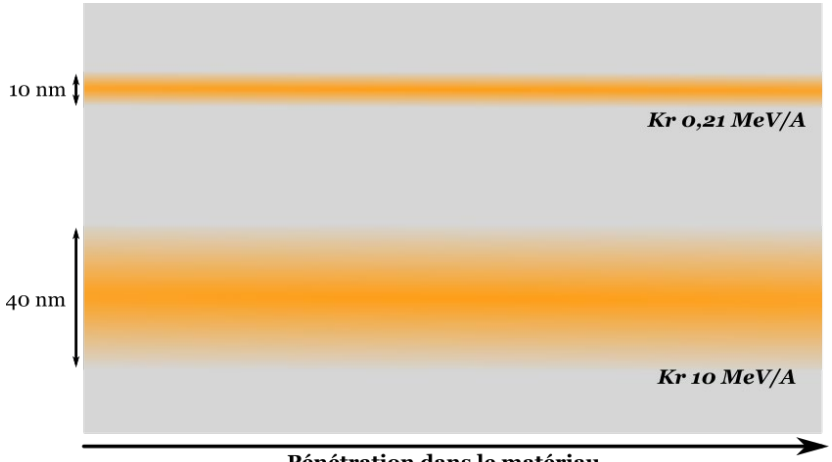
Influence of the radiation : energy deposition structure

X Rays, γ Rays, Electrons

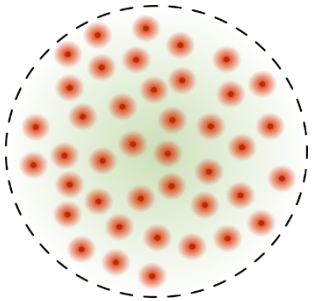


~Homogeneous

Swift Heavy Ions



Bouffard & Gervais 1994



Track formation

Heterogeneous at the nanometric level

- ✓ Radial dose distribution
- ✓ High local dose rate

SUMMARY

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- The future
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Basic research

- ✓ CIMAP : « Polymer » sub-group
- ✓ Kobe University : Pr. Yamauchi
- ✓ National Institute for Quantum Science and Technology / Radiation Measurement Research Group : Dr. Kusumoto
- ✓ PUCRS : Dr. Thomaz Raquel

Basic research

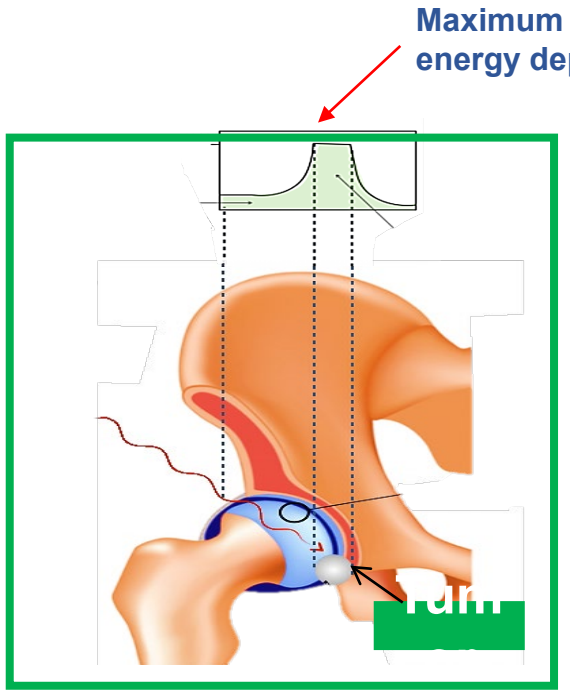
Modulation of the excitation and ionizing density

Defects creation

- Creation mechanism
  - Tailoring the energy deposition density
    - ✓ Formation kinetics
    - ✓ Characteristic creation time
  - Modulating the irradiation temperature

Polymers of biological interest: Application to hadrontherapy

- Radio & chemo-resistant cancers
  chondrosarcoma : a bone and joint cancer



➢ More precise dose deposition.
But:

What about healthy tissues on the ion path?

Cartilage extra-cellular matrix

Type II collagène under ionizing radiation ?

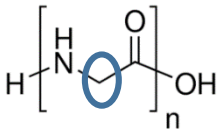
Hoda Al Assaad
Thesis - CIMAP

Methodology = simplify

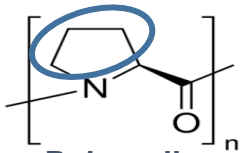
Homopolypeptides
Polyglycine
Poly-DL-alanine
Poly-L-proline

Collagen Model Peptides

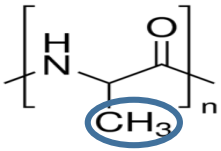
Type II collagen



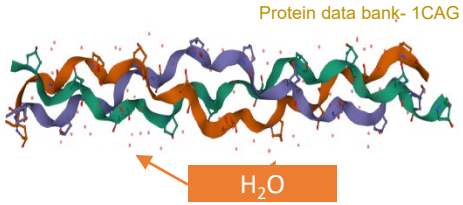
Polyglycine

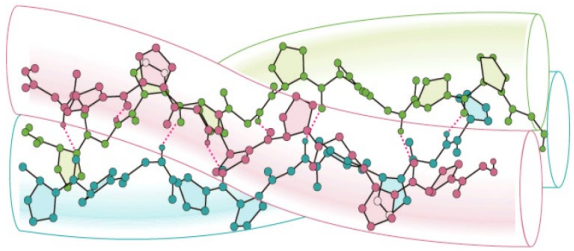


Polyproline



Polyalanine





- ✓ Same polypeptidic structure
- ✓ 1 type of amino acid
- ✓ No internal H_2O bonds
- ☒ No triple helix structure

- ✓ Triple helix structure
- ✓ Internal H_2O bonds
- ☺ Reduced number of the types of amino acids (n = 10)
- ☺ Reduced mass → Enhanced solubility

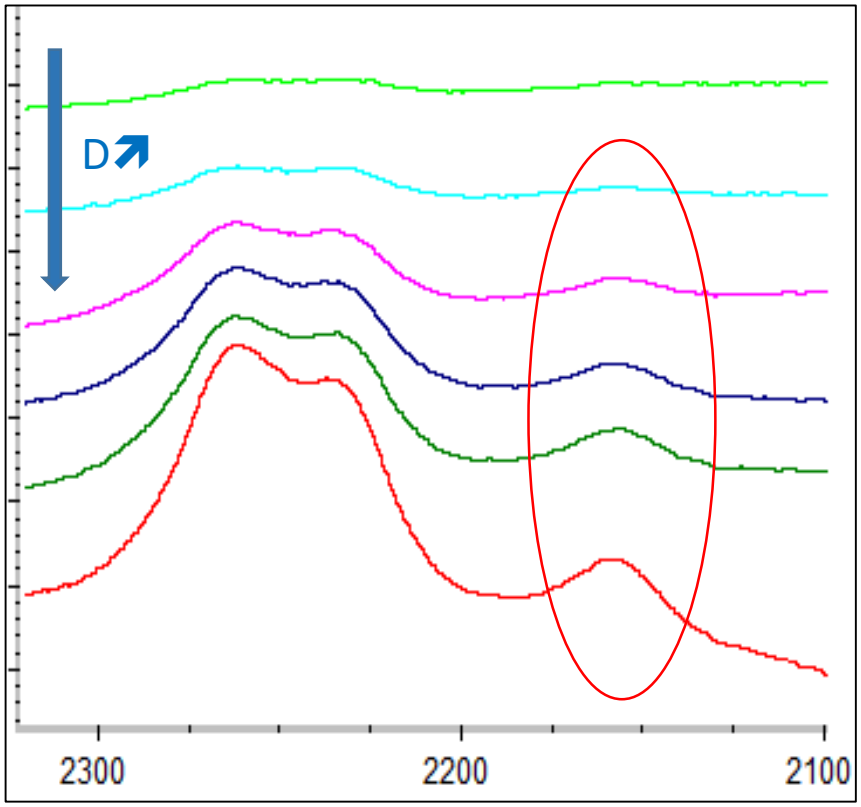
- ☹ Variety in amino acids
- ☹ Internal strongly bonded H_2O

Polymer of biological interest: LET effect

DRF/IRAMIS/LSI
DES/ISAS/DRMP/SPC/LC2R

$^{20}Ne^{9+}$
7,2 MeV/A

Polyglycine & Polyalanine



Macromolecular defects

- Highly insaturated defects
  - Concerted reactions ↗
  - Hydrophobic groups ↗

Reduced H_2O intake = potential lost in biomechanical properties

Polymer of biological interest: LET effect

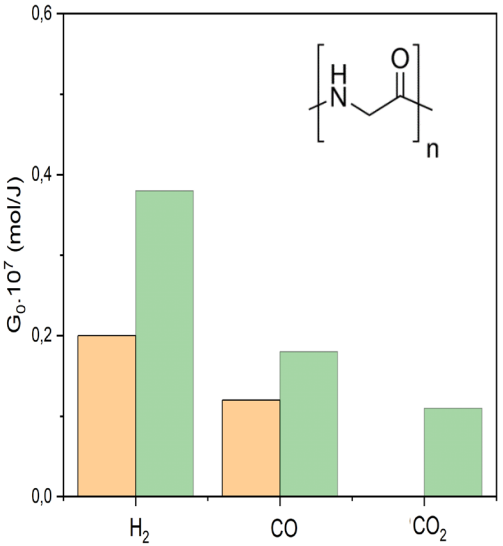
DRF/IRAMIS/LSI
DES/ISAS/DRMP/SPC/LC2R

Emitted gas :

- H_2, CO, CO_2
- Potentially hazardous for cells

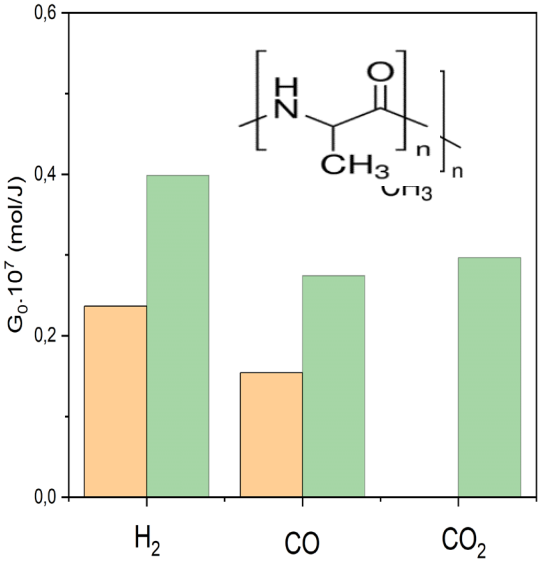
Ebeam: Reference beam

Polyglycine & Polyalanine



β : 1 MeV

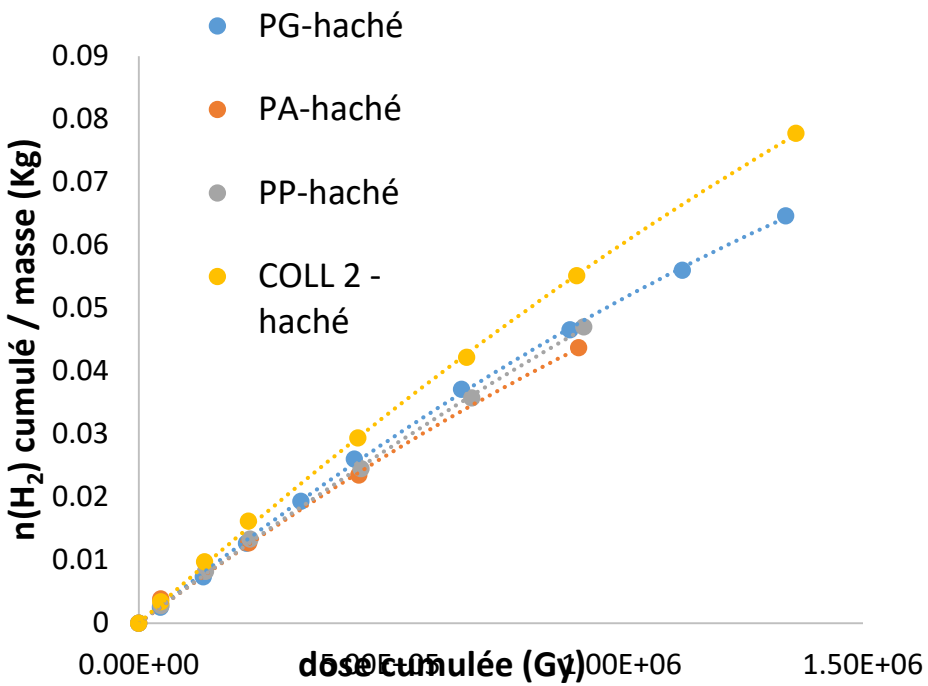
$^{20}Ne^{9+}$
7,2 MeV/A

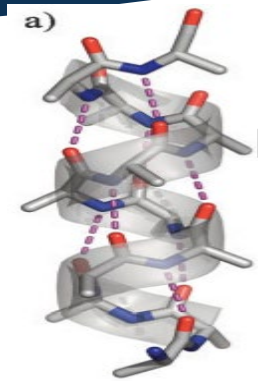


LET ↗ → G_0 (H_2) ↗ & G_0 (CO) ↗

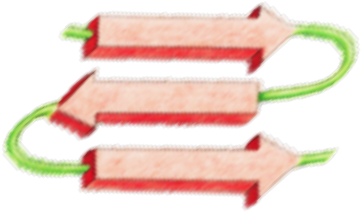
Polymers of biological interest: Application to hadrontherapy

Hydrogen Emission

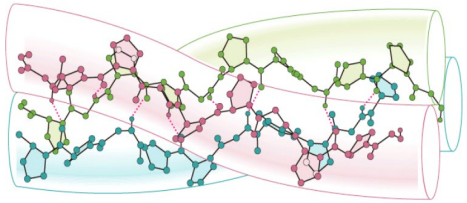




Polyalanine



Polyglycine



Coll II

Reduced influence of the secondary structure

Technological applications : nuclear waste

- ✓ CEA/DES: M. Ferry / S. Esnouf/ A. Dannoux-Papin
- ✓ CIMAP: Y. Ngono

Technological applications : nuclear waste ⇨SHI to simulate α particles

Storage (LL-ILW)

LONG TERM SIMULATIONS

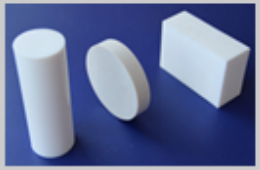
- Long-term fate of contaminated polymers under α irradiations
  - Gas emission ⇨ Nuclear safety
    - High doses : G(gas) = f(Dose)
  - Oxidized defects ⇨potential complexing agents for actinides
    - ✓ Hydrolysis of from radiation-induced oxidized polymers

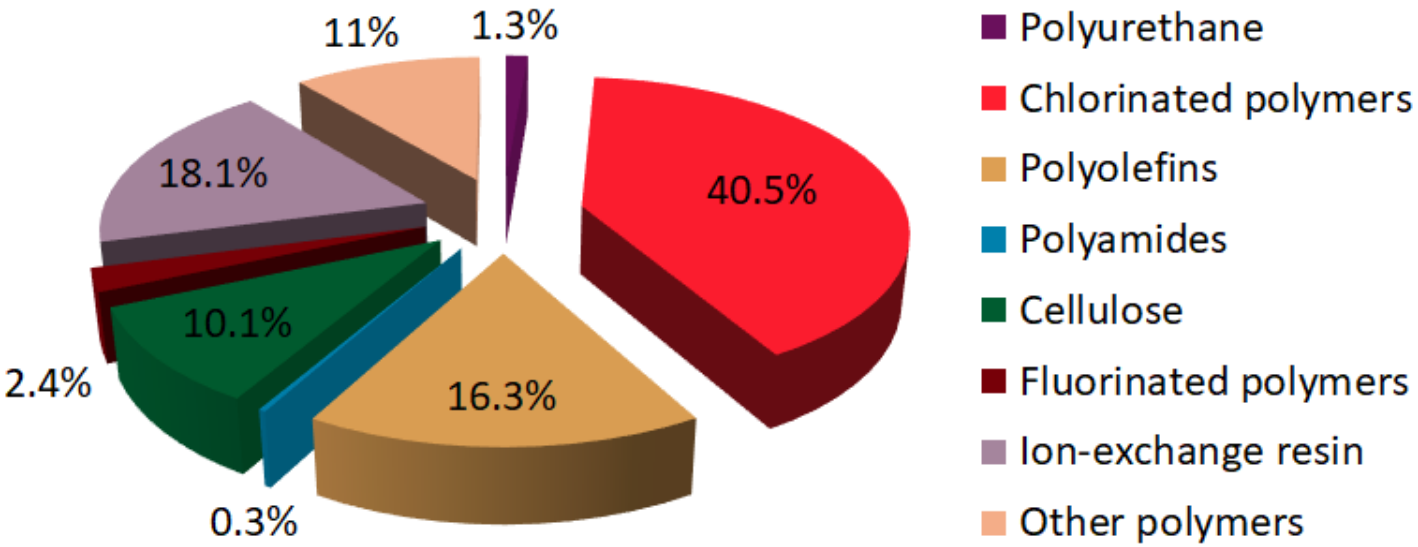
Transportation safety

- Thermolysis of radiation-induced defects
  - ✓ Gas emission evaluation from ILLW in accidental conditions during transportation

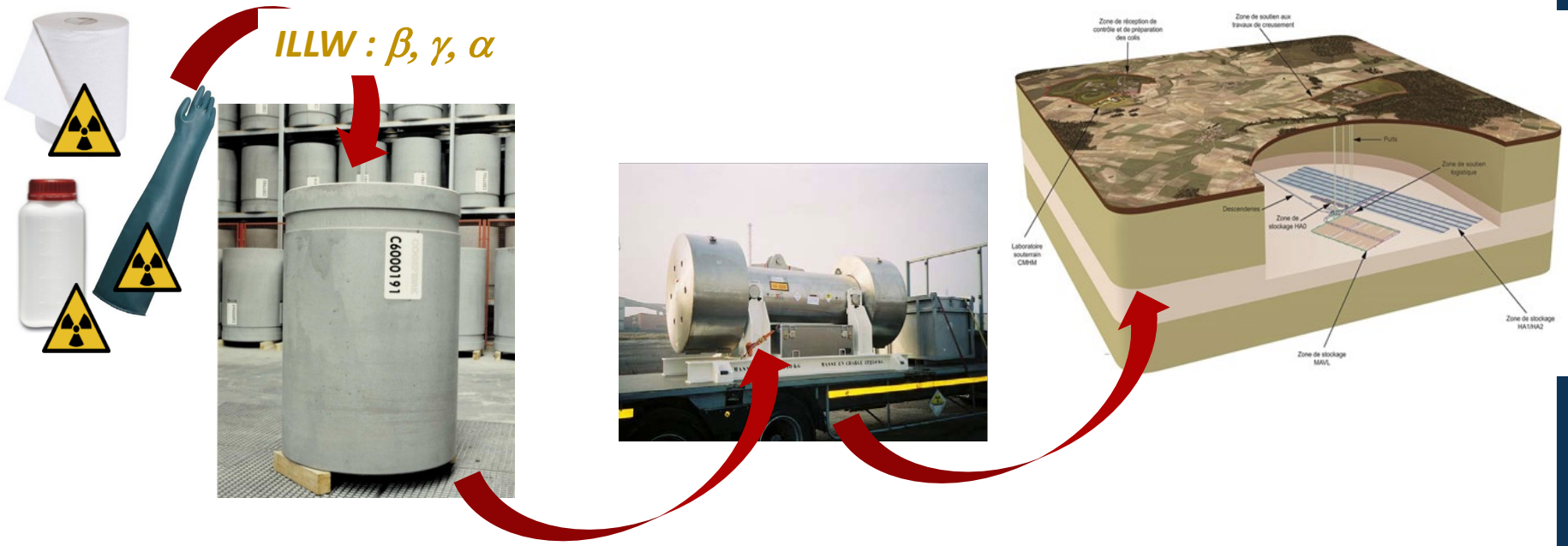
CIMAP

Polymers used in the nuclear power industry => LL-ILW

Nitrile rubber	Fluoro elastomer	Chlorinated polymer	EPDM	Epoxy	Polyurethane	Acrylic
						
Seals	Seals	Hot cell sleeve Protection sheet	Seals Insulation	Coating Paints	Gloves Cables sheath Insulation	Scotch



Technological applications : nuclear waste ⇨SHI to simulate α particles



Entreposage - Exploitation

- Emission gazeuse
  - RT Dose ++

Transport

- Emission gazeuse
- 150°C Doses +

Stockage (temps géologiques)

- Emission gazeuse ↘
- Lixiviation
- Complexation Rn = Mobilité ↗

Technological applications : nuclear waste ⇨SHI to simulate α particles

Storage (LL-ILW)

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Transportation safety

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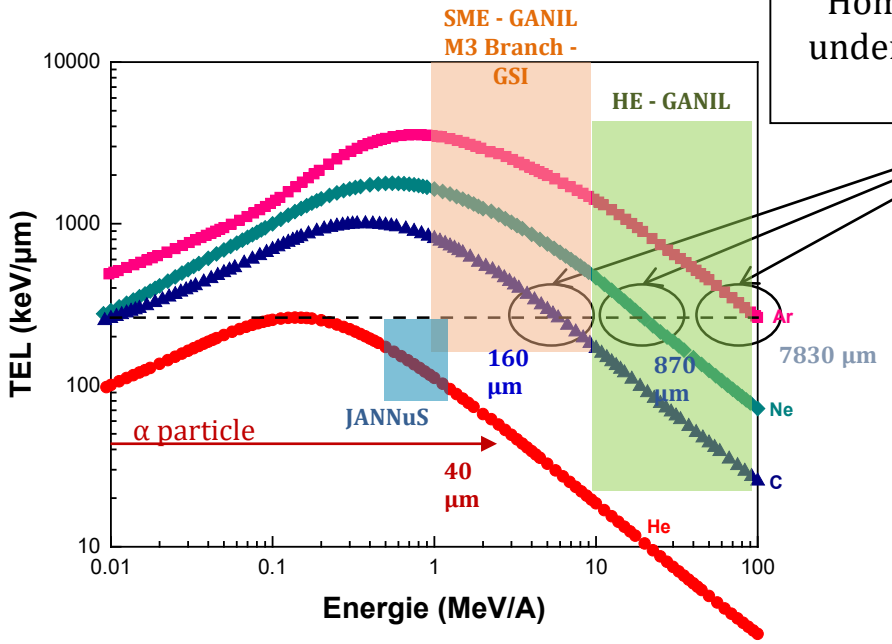
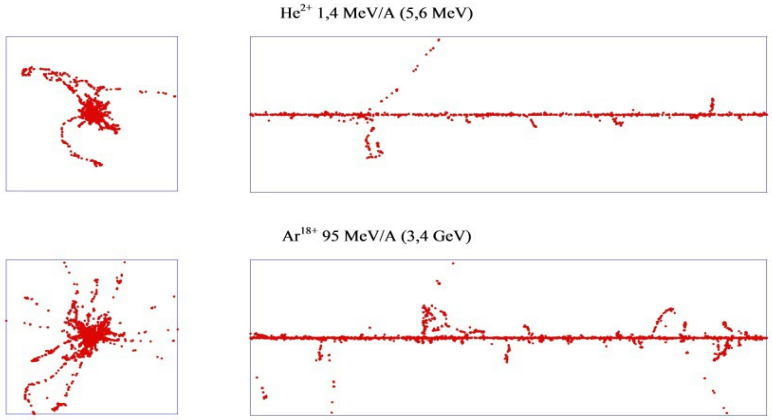
CIMAP

Why SHI to simulate α particles from actinides



Homogeneous irradiation under several microns (case of PE)



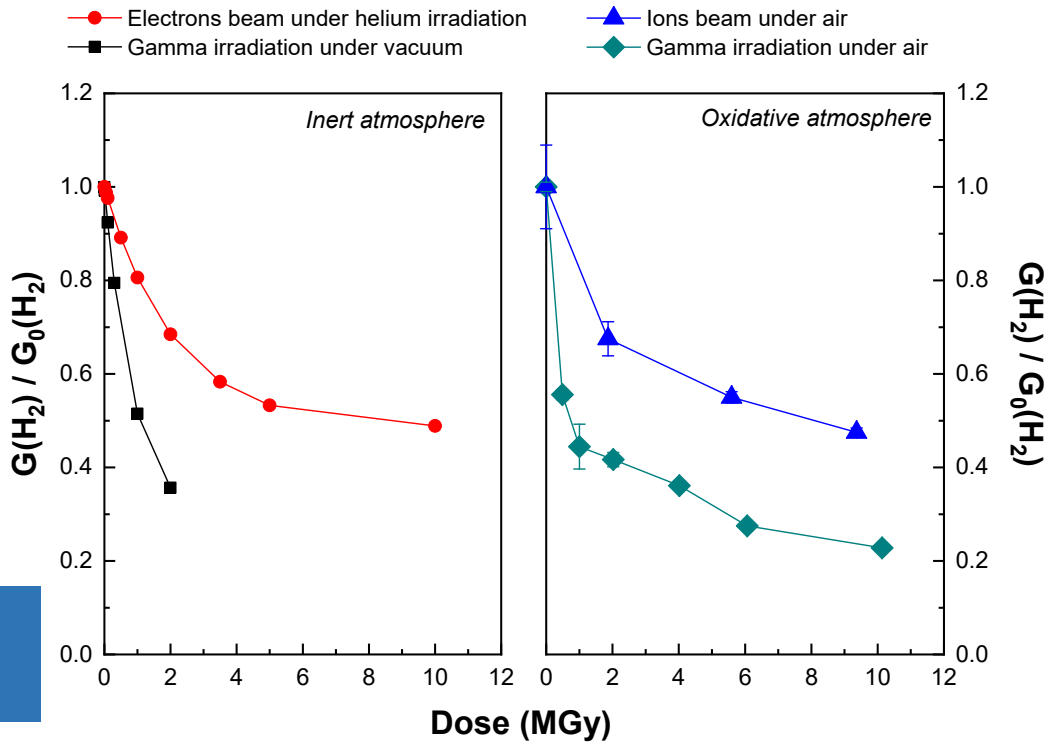
Gervais & Bouffard, *Nucl. Instrum. Methods Phys. Res., Sect. B* 88 (1994), 355-364

- Equivalent LET
- Equivalent Energy deposition structures
- Higher penetration range for SHI : homogeneous oxidation through the thickness

PRELOG integrated results examples

Dose, nature of irradiation and atmosphere effects

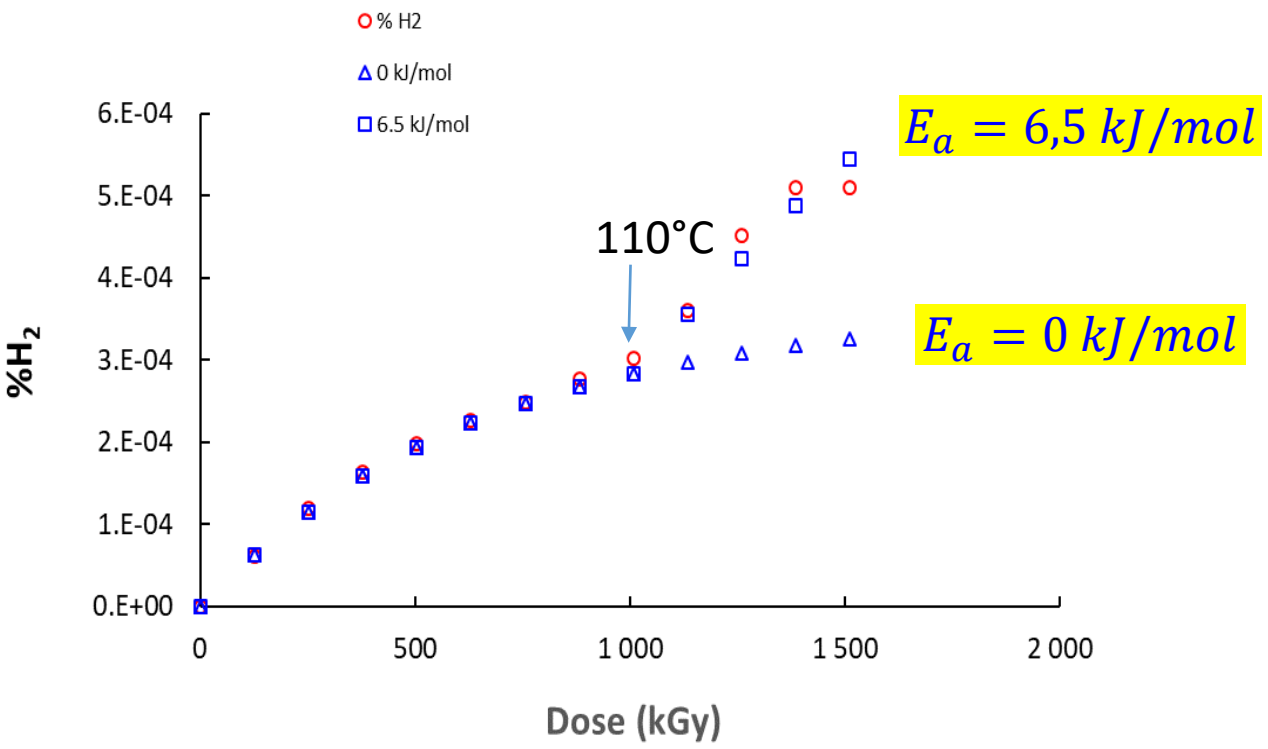
- $G(H_2)$ ↘ when D↗
- $G(H_2)$ decrease rate reduced under SHI



Use of $G(H_2)$ at 0 dose = worst case scenario

Ferry *et al.*, *Polymers in the nuclear power industry, In: Rudy Konings (editor-in-chief)*, Comprehensive Nuclear Materials 2nd Edition. Oxford: Elsevier (2020), volume 3, 545-580
Pellizzi *et al.*, *Gordon Research Seminar*, Proctor Academy, July 2014
Seguchi, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms* 185 (2001), 43-49
Seguchi, *Radiat. Phys. Chem.* 85 (2013), 124-129
Ventura, Thesis from Caen - Basse Normandie university, France (2013)

Polystyrene under helium atmosphere



$E_a = 6{,}5\ kJ/mol$

$E_a = 0\ kJ/mol$

Atactique Polystyrene $T_g = 100°C$

Ion Track Technology

Track-etched polymer membranes functionalization for developing real-time solutions

LSI : Dr. Clochard / Dr. Aubrit
ENS: Dr. Lepoitevin
Univ. Montpellier: Dr. Balme

Ion Track technology :Polymer nanostructuration for new materials development

Use of tracks formed under high LET ion beam irradiation

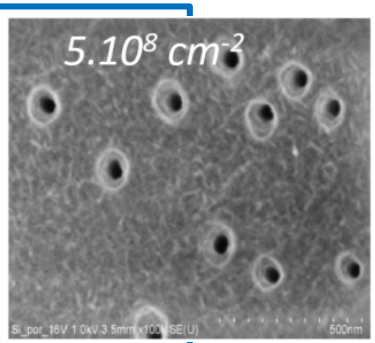
Latent Tracks

Use of the high specific surface of the track walls

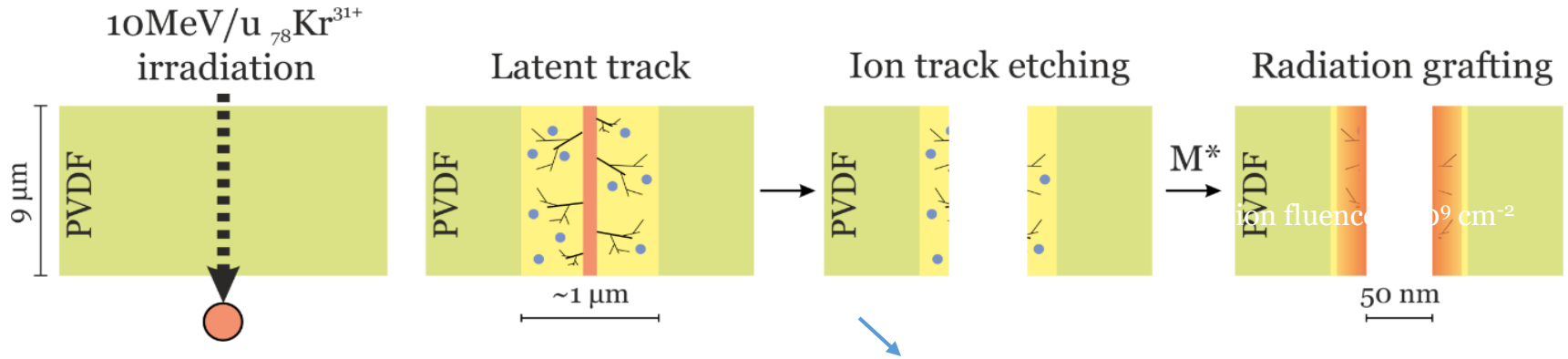
- Grafting on radiation induced radicals
  - Tailoring of the material properties as a function of the grafted component
  - New materials with specific chemical and physical-chemical properties

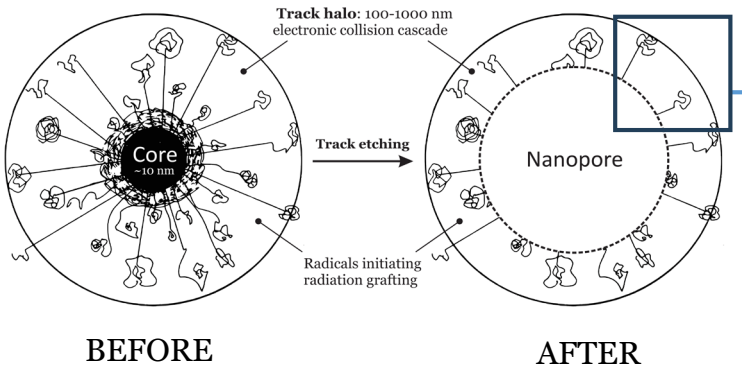
Etched Tracks

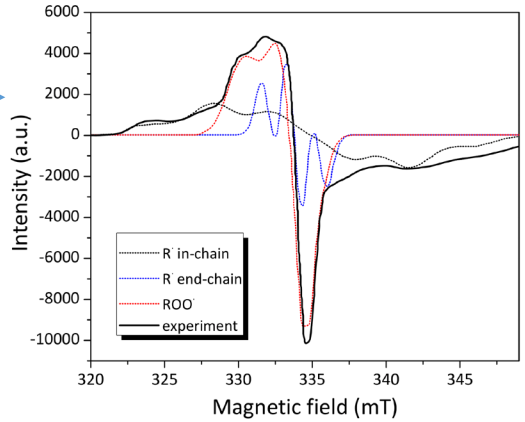
- Grafting on radiation induced radicals
- Non covalent insertion of organic or inorganic components
- Membranes for filtration and other applications



Track-etched membranes functionalization

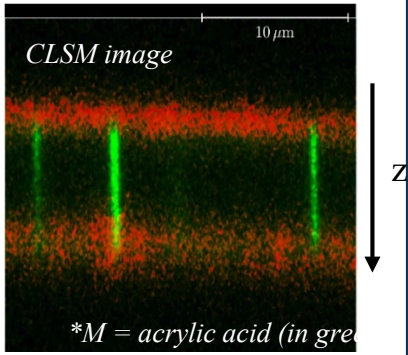






M*

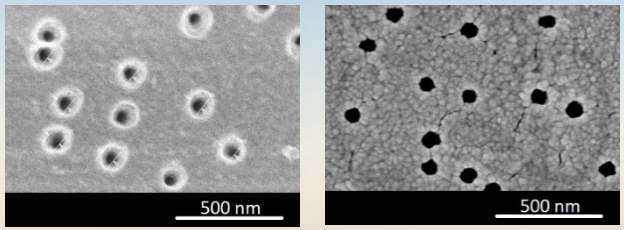
monomer



Application for Health & Environment

CapTÔT Technology

Converting radio-grafted membranes into electrodes



no gold with gold

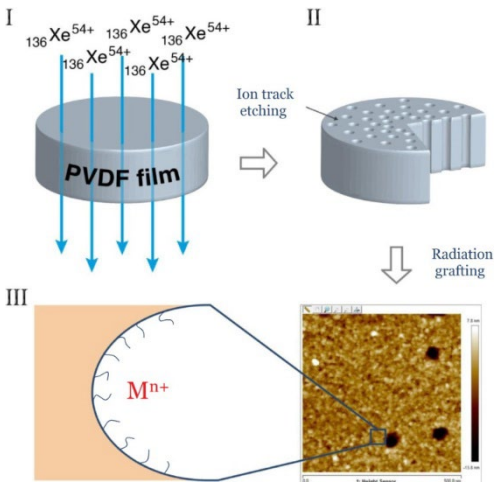
* ion fluence = 10^9 cm^{-2}

compatible with marine applications

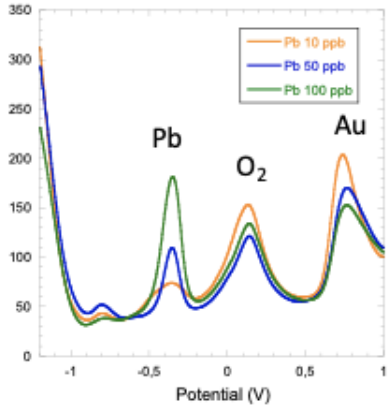
CAPTÔT

Protéger l'eau passe d'abord par la connaître

Metal ion trapping



Metal ion detection

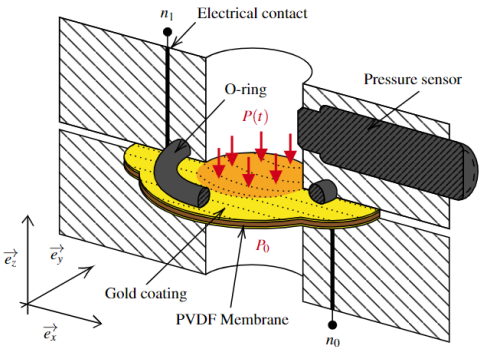


Prototype IIIrd generation

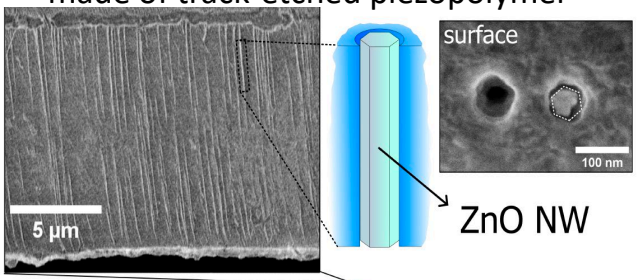
Packaged product

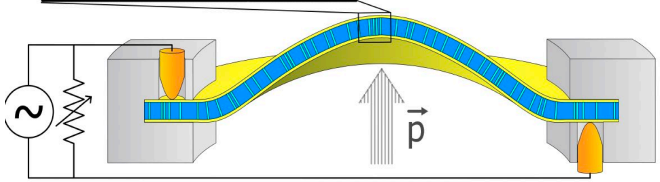
Flexible piezoelectric nanostructured generator

Experimental set-up

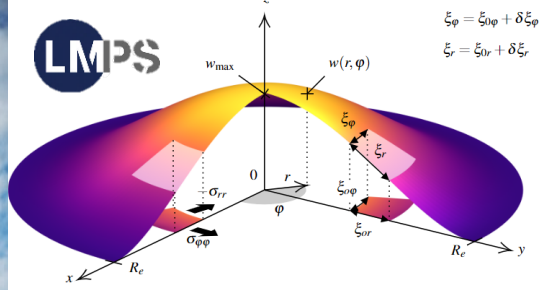


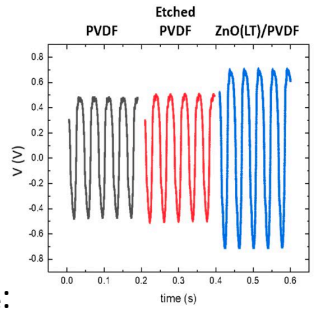
Composite material
made of track-etched piezopolymer

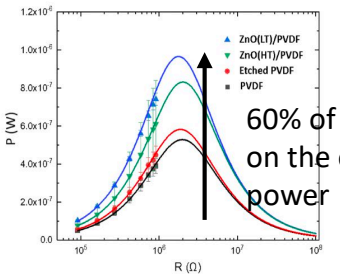




Model for large bending regime







60% of increase on the output power

Z components, surface average on A_e:

$$\overline{E_z^e}\left(\pm\frac{\ell}{2},t\right) = -\frac{A_p}{A_e}\frac{q_{31}}{\varepsilon_{33}^T}\left(3\frac{1-\nu}{7-\nu}\frac{P_{\omega_{in}}(t)}{E}\frac{R_e}{\ell}\right)^{\frac{2}{3}} + \frac{1}{\varepsilon_{33}^T}\overline{D_z^e}\left(\pm\frac{\ell}{2},t\right)$$

Sarrey et al. JAP (submitted)

What may the future hold?

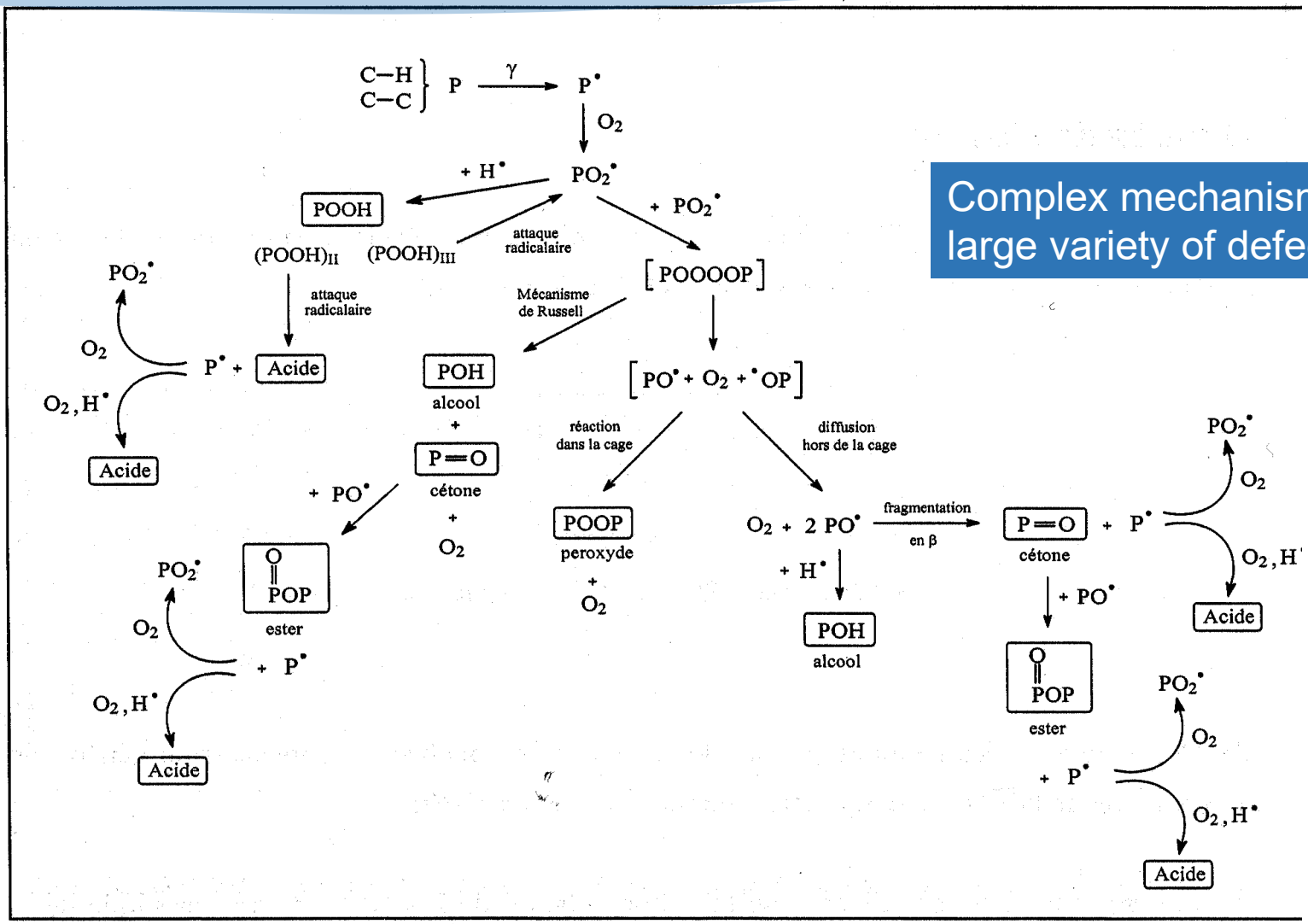
Basic Science and technological applications

Modulation of the excitation and ionizing density

Radiation-induced oxidation

- Modulating the chain reaction kinetics
- Simulation of the oxidation heterogeneity
- Kinetic constants determination

Radiation-induced oxidation



Complex mechanism and large variety of defects

Thèse Stéphanie Cambon (2001) Université Blaise Pascal Clermont-Ferrand

Tailoring the reactions with the LET

Tuning specific radical recombinations

- ✓ POO° + POO°
- ✓ P°+P°

Termination reactions modulation

- ➢ Relative evolution of oxidation routes
- ➢ Local dose rate increase

Defect type modulation
Oxidation level modulation

Basic Science and technological applications

Oxidation modelling and ageing tailoring for application in recycling

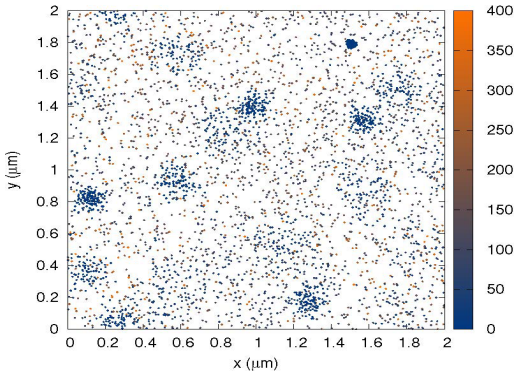
Kinetics consideration

Combining experiments and simulation

In-situ analysis of oxidized radicals reaction

few µsec to a few seconds

Development of an on-line EPR spectrometer



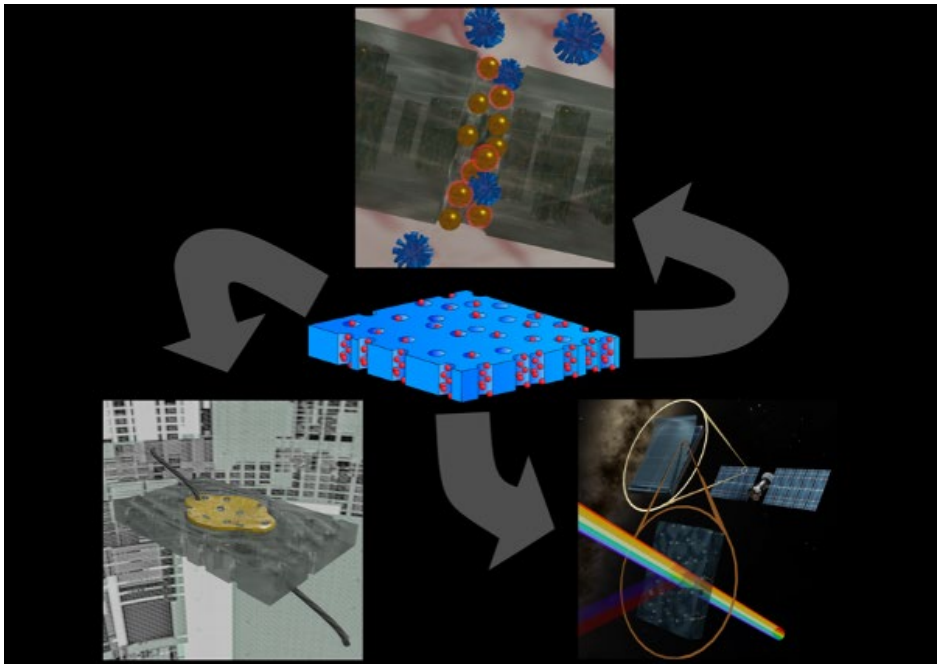
Kinetics Monte-Carlo

CiMap

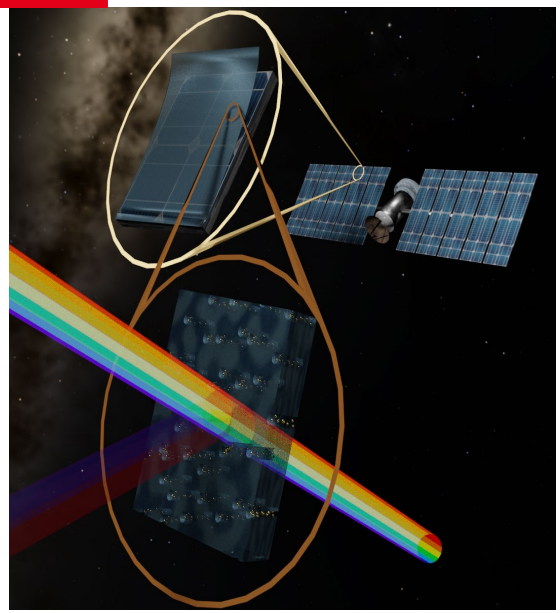
Ion Track technology

Track-etched polymer membranes functionalization for developing real-time solutions for :

- Renewable energies,
- The Environment protection
- Health

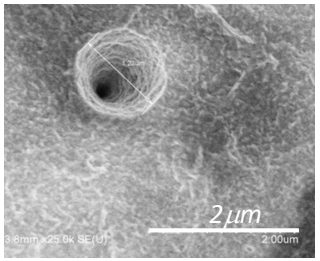


Antireflective coatings for PV cells in Space



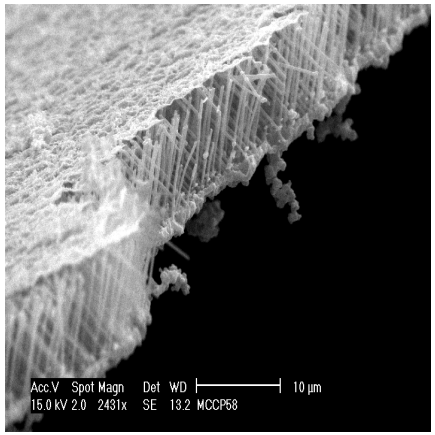
Project EU : JUMP INTO SPACE
EIC Pathfinder Challenges start next oct. 2024

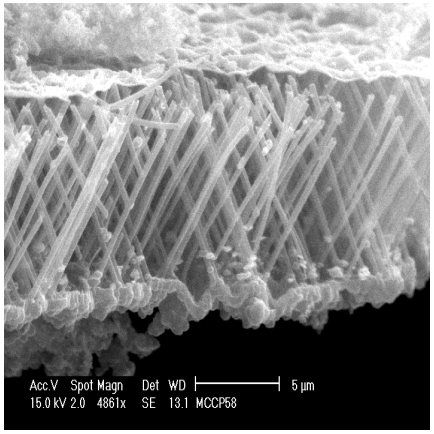
Alternative materials to glass: Refractive index decrease with increase conical nanopore density and orientations



Conical nanopores in a copolymer

Varying the irradiation angles



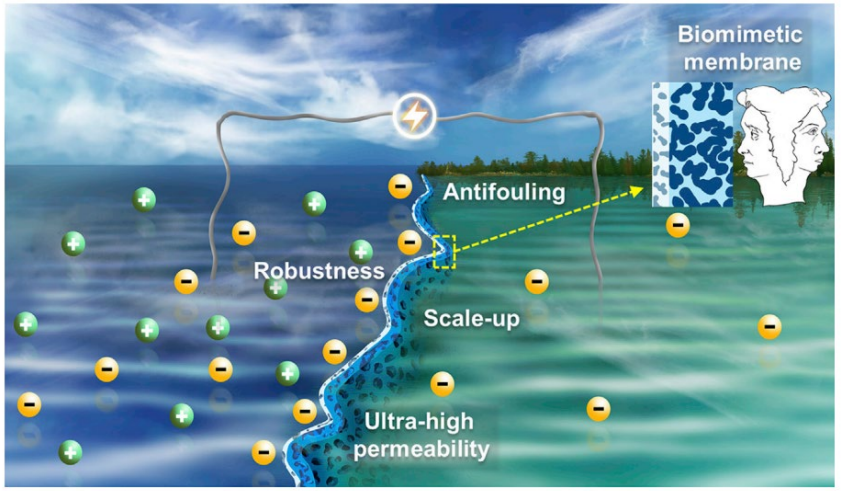


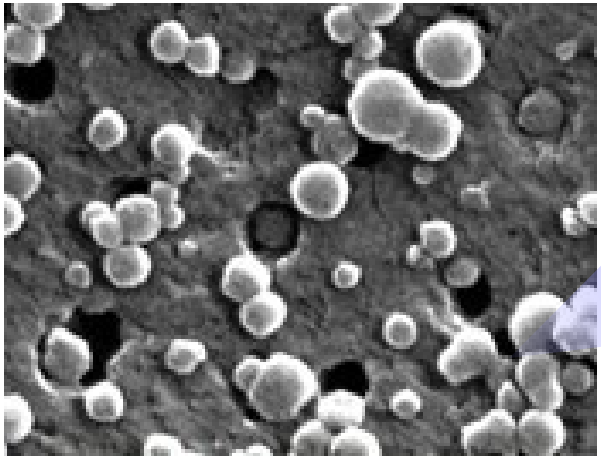
Conductive polymer grown by diaphragmatic method in a track-etched polymer membrane

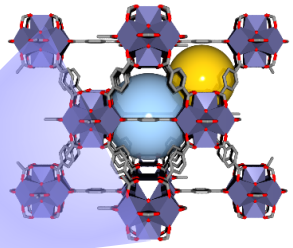
Nanoporous Membranes with MOFs for blue energy application

Blue Energy

Present a promising **energy source** coming from the difference concentration of salt between seawater and fresh water.
(fresh water / brine)

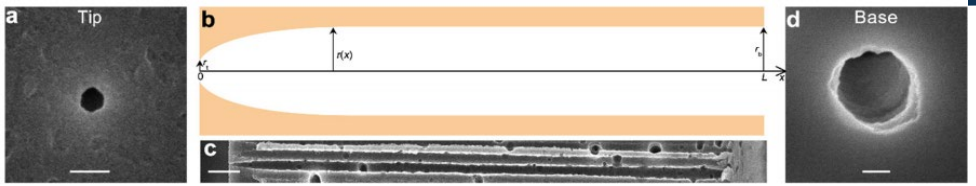


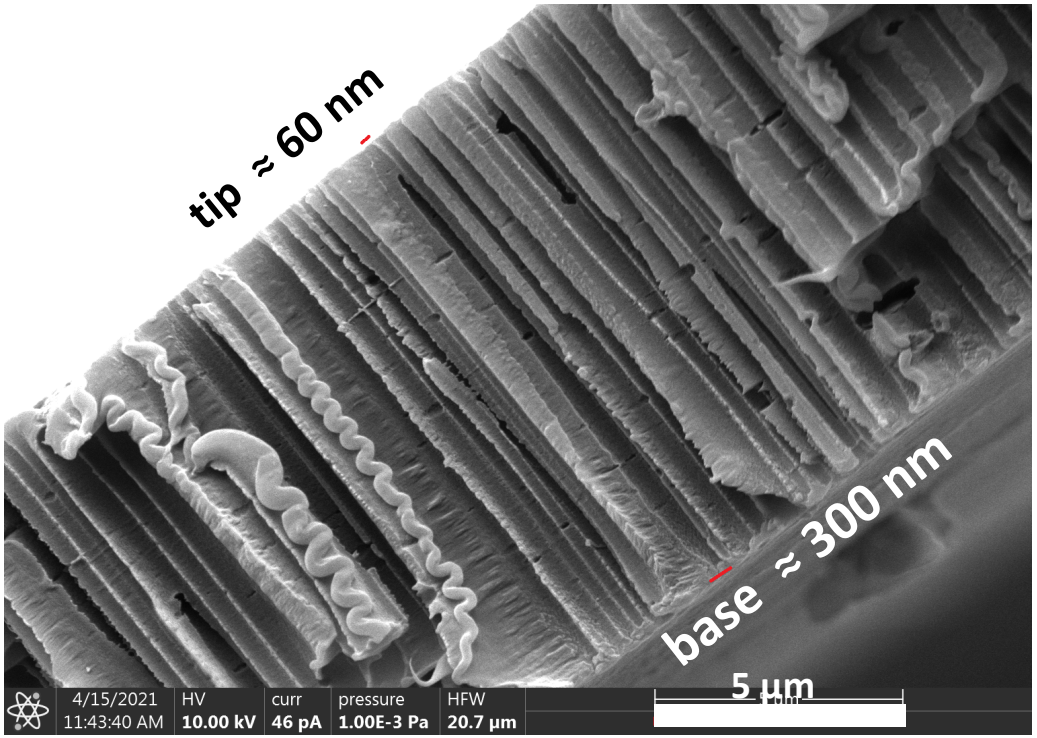


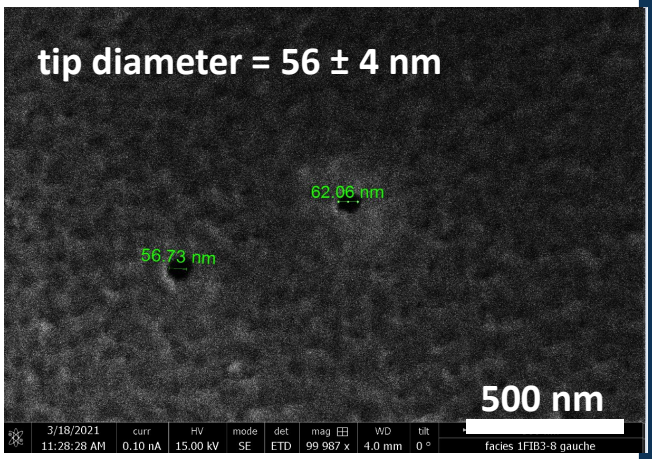


Ion-selective nanochannels promising in the field to add new physicochemical properties to the nanochannel.

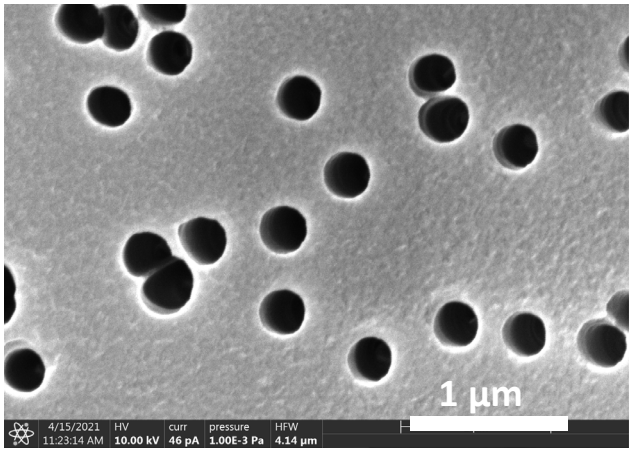
Bullet-shaped nanopores







base diameter = 301 ± 19 nm



The candidates to functionalize the nanopore: MOF

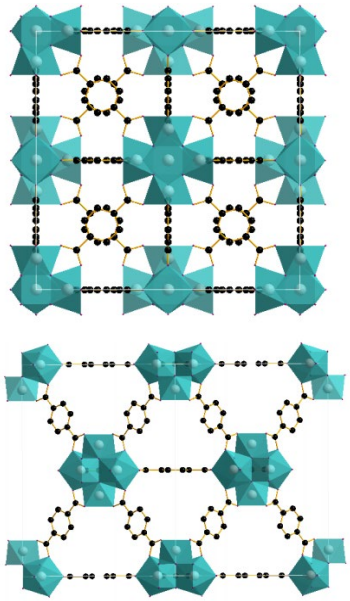
UiO-66

$Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(BDC)_6$

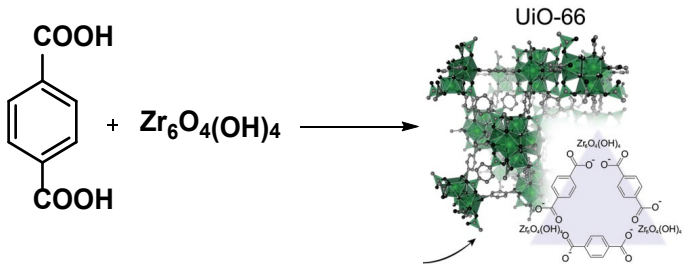
Pore size: 0.6 nm

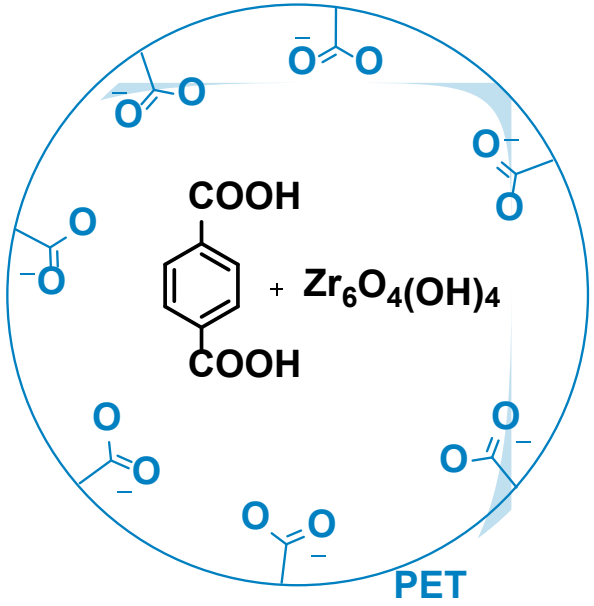
Cages: 5.9 & 10.2 Å

pH(I): 5.5



Y. S. Seo et al., *Chem. Eng. J.*, 2015, **270**, 22-27

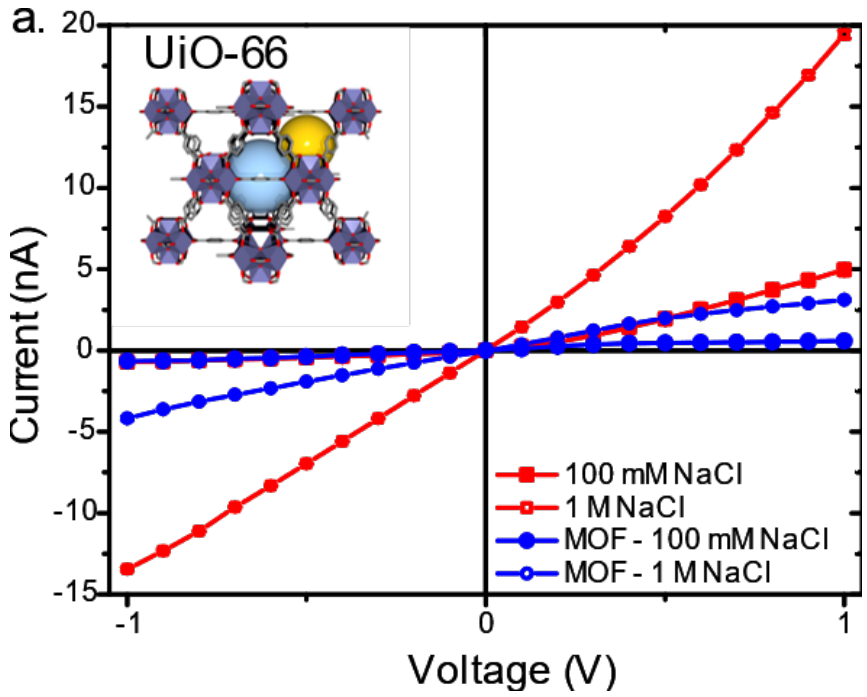


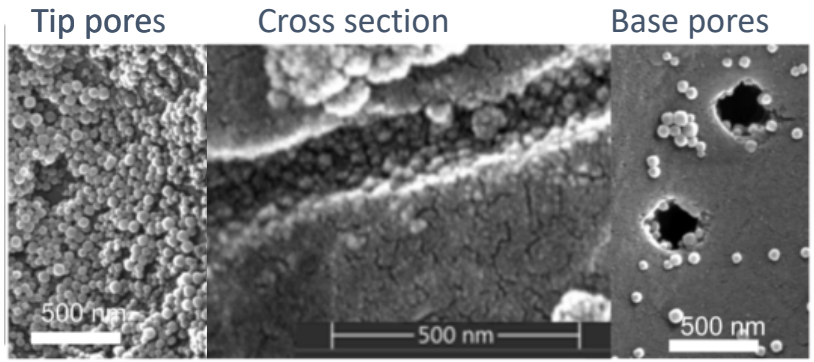


In-Situ MOF growth into a Single Nanopore

Nanopore

- Bullet-shaped
- 6 M NaOH 0.05% surfactant, 4 minutes at 60 °C
- Base pore diameter: 248 ± 19 nm
- Tip pore diameter: 41 ± 7 nm

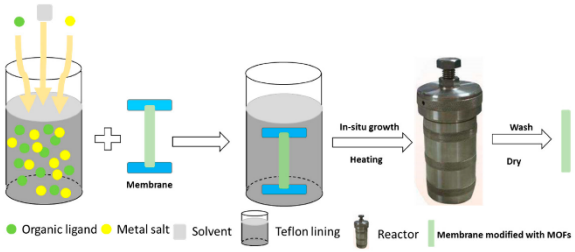




current rectification observed, surface modification of pore successful

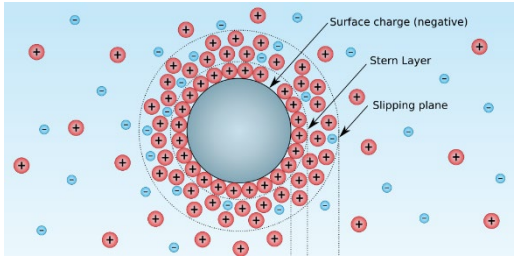
Conclusions and next steps

MOFs synthesis



- ✓ *Correct Set-Up*
- ✓ *Functionalization of linker*
- ✓ *Membranes SEM characterizations*
- *New MOFs synthesis*
- *Evaluation of MOFs*

Material characterizations



- ✓ *Characterizations of bulk materials (TGA, BET, XRD)*
- *Electrochemical properties of the membranes*
- ✓ *Chemist and Physics point of view of membrane' s properties*

Power density

- *Next characterizations*
- *New comparisons and studies*

Work in progress

What may the future hold?

Work in progress and new research topics

- Cyclotrons and IRSSUD Mandatory
- Development of new set-ups
- Multiple beam irradiations?

Thank you for your attention