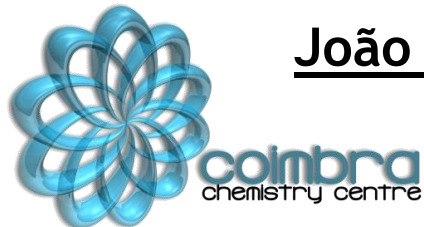




Harvesting and storage solar energy (Sunstorage)



João Pina, Ricardo Pereira, Ana Pontinha, Maria Pratas, Joana Sousa, Carlos Serpa,
Artur Valente, Marta Piñeiro, Hugh Burrows and J. Seixas de Melo

Paula Dias, João Azevedo and Adélio Mendes



Lisbon, 4 July 2018



Email: jpina@qui.uc.pt
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“UC725: Uma História de Luz”

CQC Research Groups



Theoretical and Computational Chemistry

- ♦ Environmental chemistry
 - ♦ Combustion
 - ♦ Astrochemistry
- ♦ Reactive intermediates

Organic Chemistry

- ♦ Synthetic and Mechanistic Heterocyclic Chemistry
 - ♦ Asymmetric Catalysis
 - ♦ Green Chemistry

Macromolecules, Colloids and Photochemistry

- ♦ Colloids and macromolecules
 - ♦ Multicomponent systems
 - ♦ Transport phenomena
 - ♦ Photochemistry

Structure, Energy, Reactivity

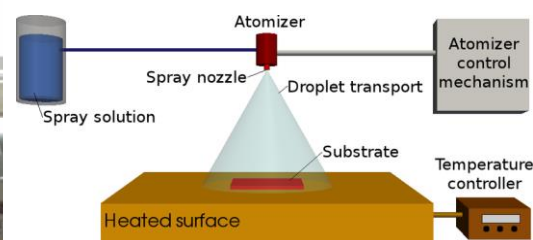
- ♦ Photonics and Reactivity
- ♦ Molecular Thermodynamics
- ♦ Catalysis and Fine Chemistry
 - ♦ Experimental Pathology
 - ♦ Molecular Cryo- and Biospectroscopy

Biological Chemistry

- ♦ Biomembranes: Structure and Function
- ♦ Protein Biophysics
- ♦ Molecular Systems Biology
- ♦ Molecular Imaging
- ♦ Inorganic Biochemistry

Materials Chemistry lab: *from molecular dimension to devices*

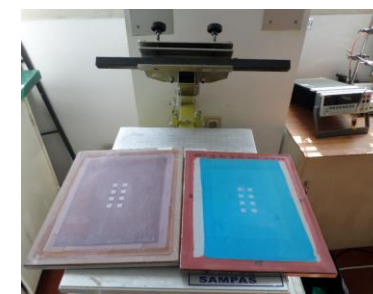
<https://www.uc.pt/en/uid/laserlab/>
<https://www.laserlab-europe.eu/>



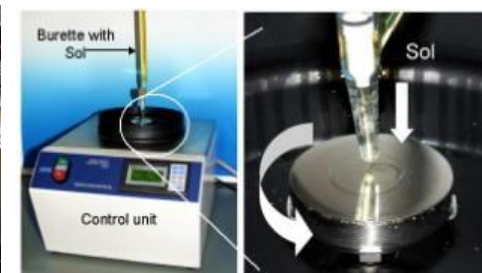
Spray-pyrolysis



Automatic film applicator



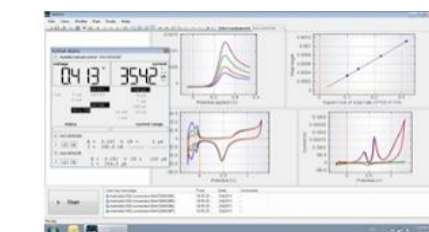
Screen-printing



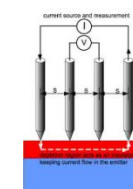
Spin-coating



IPCE, Solar simulator



Potentiostat, Galvanostat



Conductivity
measurements



Absorption of liquid and solid samples UV-Vis-NIR



Fluorescence Lab

Steady-state fluorescence



Horiba-JY
Fluorog 3-22 spectrometer
Detection range: 250-1400 nm

Horiba-JY Fluoromax4
Detection range: 250-850 nm

Quantaaurus-QY
Absolute PL quantum yield spectrometer
Detection range: 300-950 nm

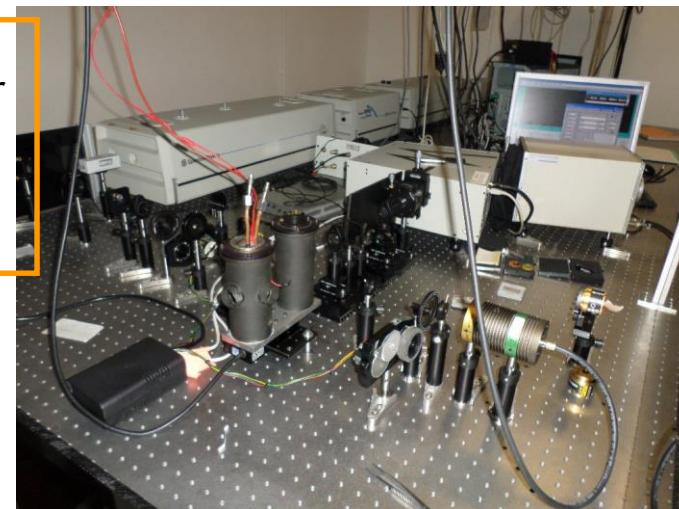
Time-resolved fluorescence

Excitation source:
Spectra Physics mode-lock Tsunami Laser
(Ti:Sapphire) and Picoquant picoLeds
Spectral windows available:
SHG: 360 nm - 470 nm
THG: 240 nm - 310 nm

Excitation sources:
Horiba-JY nanoLEDs= 281,
311, 339, 373 and 460 nm

ps-TCSPC

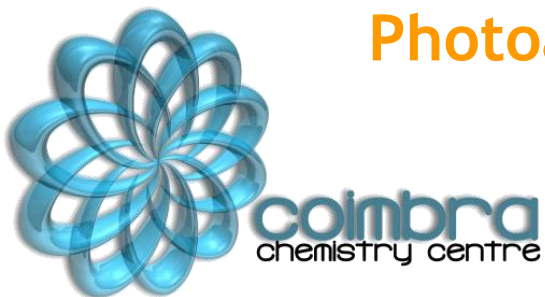
Time-resolution: 3 ps



ns-TCSPC

Time-resolution: 150 ps





Photoacoustics & Transient Absorption spectroscopy



Photoacoustic Calorimetry



ms, ns, ps transient kinetics and energetics



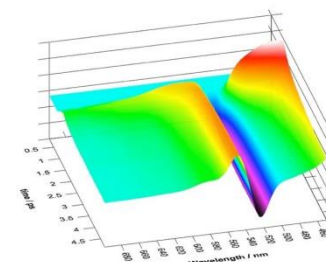
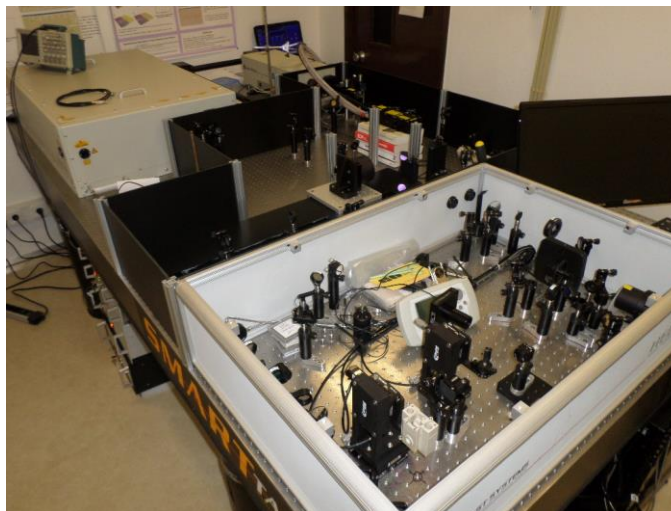
Temperature controlled PAC: listening to protein folding dynamics



Solid State PAC: towards critical measurements in Dye Sensitized Solar Cells

Flash photolysis: Applied Photophysics LKS.60 (includes the Nd-Yag/1.5J/8ns laser Spectra Physics Quanta-Ray model; second, third and fourth harmonic generator)

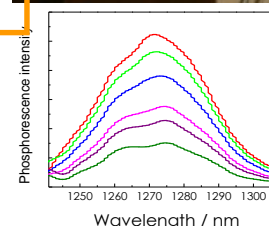
fs-ns TA spectrometer



Photophysics,
Photochemistry
Materials
Photovoltaics

Broad spectral coverage from UV to NIR (350-1600 nm) and a time window of up to 8 ns; 140 fs time resolution. Solstice Amplifier >3.5 mJ <100 fs and TOPAS Prime OPA.

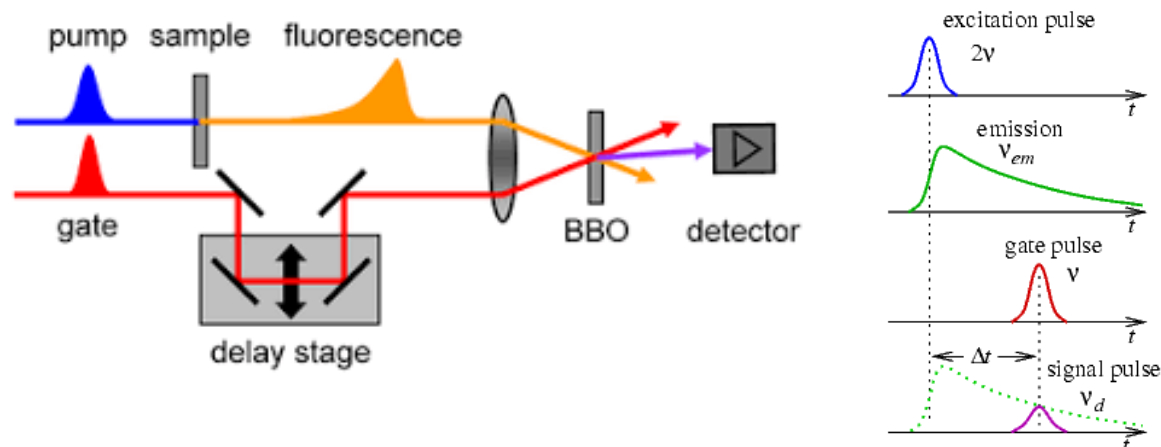
ns-ms TA spectrometer



Singlet oxygen emission lifetimes and spectral identification

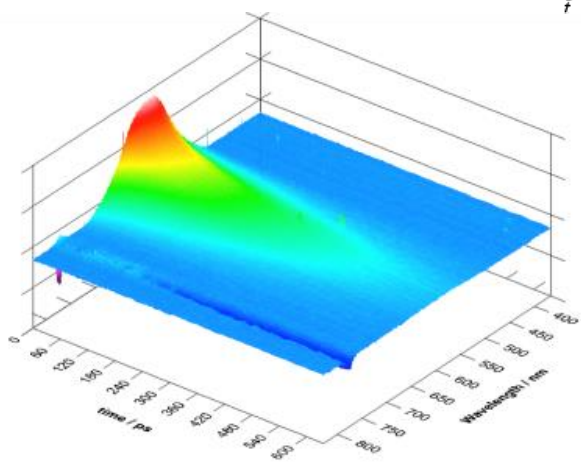
Detection: Photomultiplier Tube IR Hamamatsu R5509-42

Fluorescence up-conversion



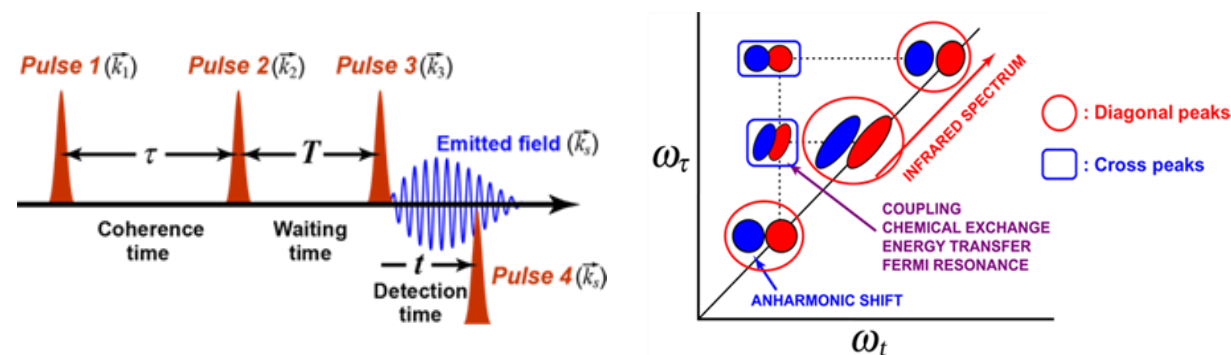
Applications

Photophysics
Photochemistry
Photobiology
Cell biology
Materials science
Nano-science

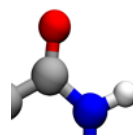


2D-IR spectroscopy

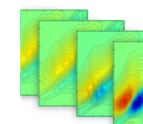
(the vibrational analogue of 2D NMR)



Applications



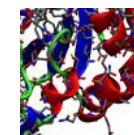
Molecular
Structure &
Dynamics



Real-time
Kinetics



Molecular
Interactions



Protein
Structure &
Dynamics



Materials
Science

Mechanisms of
energy relaxation, redistribution
and reaction pathways

SunStorage (Harvesting and Storage of Solar Energy)

Consortium

Sunstorage aims to convert sunlight into:

- (i) **electrochemical energy** in a redox flow battery (RFB)
- (ii) **chemical energy** by the solar electroreduction of CO_2 into CO and into methanol

in both cases using photoelectrochemical devices (PEC)



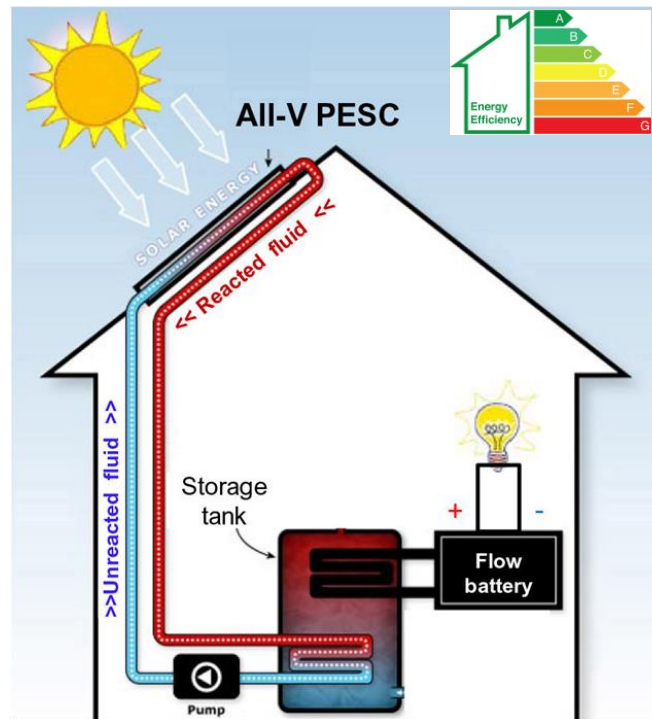
Lepabe

Laboratory for Process Engineering,
Environment, Biotechnology and Energy

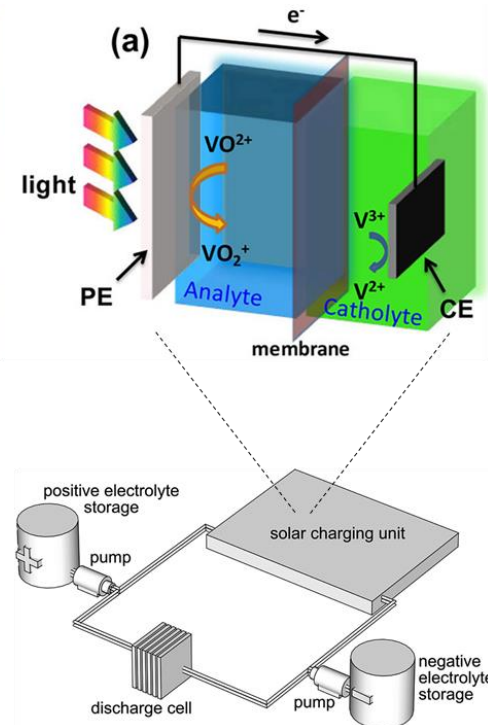


CQC

1. Photophysical characterization of the photoanodes, e.g., hematite, Cu_2O and WO_3 .
2. Synthesis and characterization of electrolytes.
3. Development of proton exchange membranes.
4. Synthesis, characterization and optimization of efficient photoelectroreduction catalysts for CO_2 .



Nearly zero-energy buildings



<http://sunstorage.pt/>

SUNSTORAGE



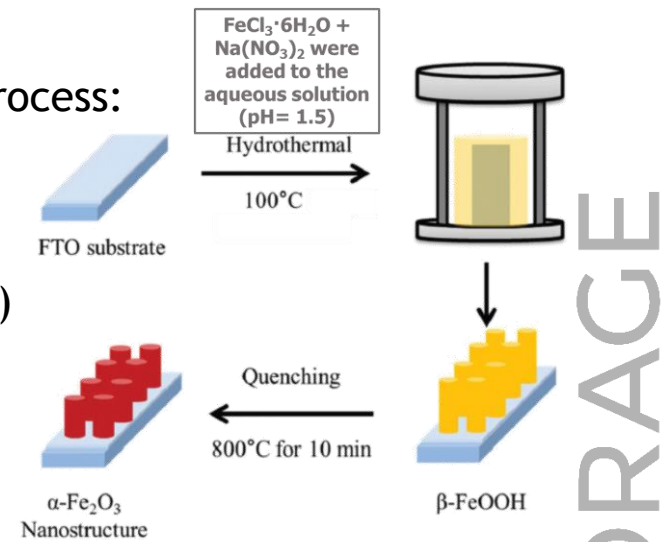
1. Ultrafast charge carrier dynamics in hematite thin films

Hematite samples prepared by spray-pyrolysis and hydrothermal process:

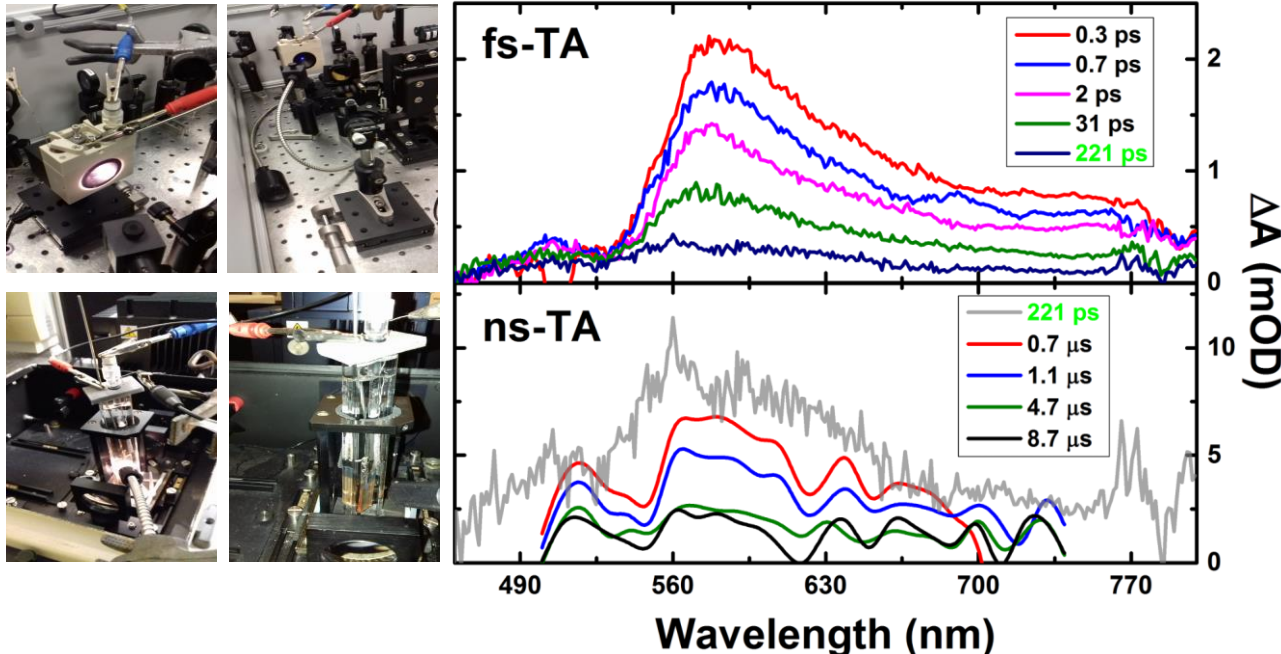
- spray-pyrolysis # thickness (13, 19, 20 and 24 nm)
- # morphology (annealing)
- # surface treatment (RuO_2 , $\text{RuO}_2/\text{IrO}_2$ and NiFeOx co-catalysts)
- # doping (Sn and Ti)

Conditions

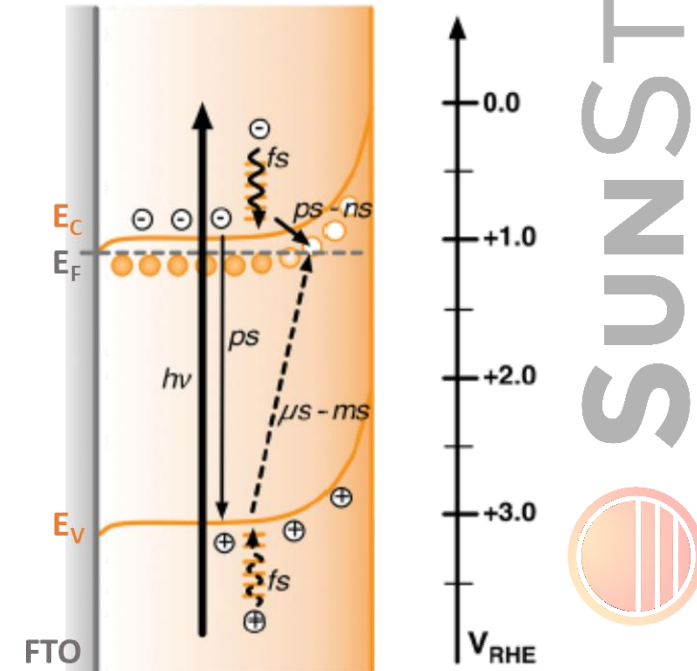
- ♦ Films only
- ♦ Films in 1M NaOH
- ♦ Three-electrode configuration in 1M NaOH with # potential applied (0.8, 1.4 and 1.6 V_{RHE})
- ♦ Three-electrode configuration with $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ redox-pair hole scavenger



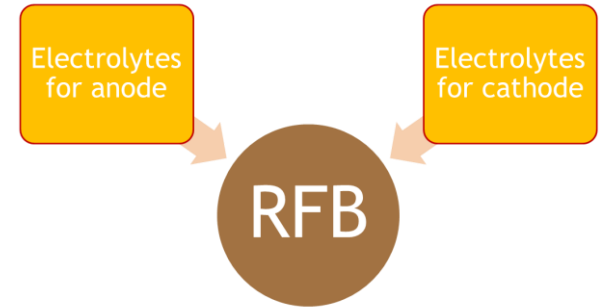
Hematite 19 nm film, showing *1000 h of stability*, in 3-electrode configuration 1.4 V_{RHE} in 1M NaOH + bias light



$$\begin{aligned}\tau_1 &= 660 \text{ fs} \\ \tau_2 &= 10 \text{ ps} \\ \tau_3 &= 197 \text{ ps} \\ \tau_4 &= 0.8 \text{ } \mu\text{s} \\ \tau_5 &= 11 \text{ } \mu\text{s}\end{aligned}$$

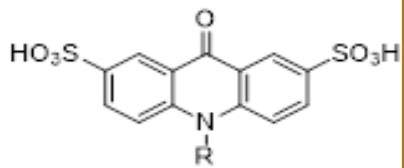


2. Synthesis and characterization (electrochemical and photophysical) of electrolytes

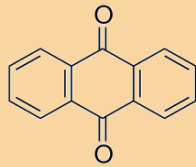


Electrolytes

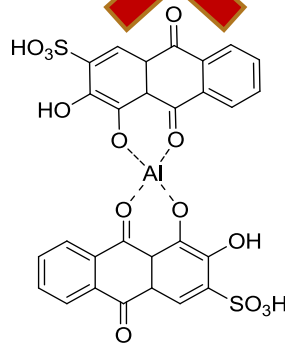
Acridones



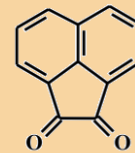
Anthraquinones



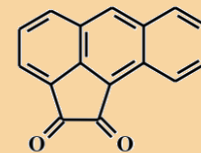
Lakes



Ortho-Diones

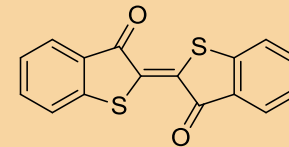


F12

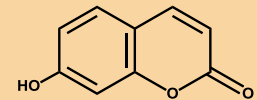


F11

Thioindigo



Coumarin

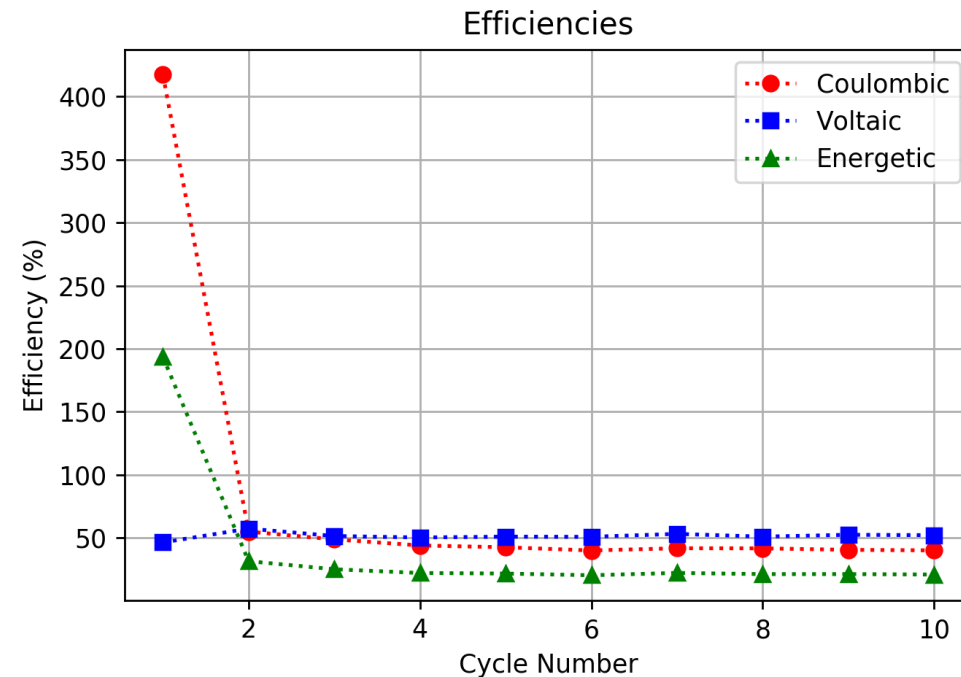
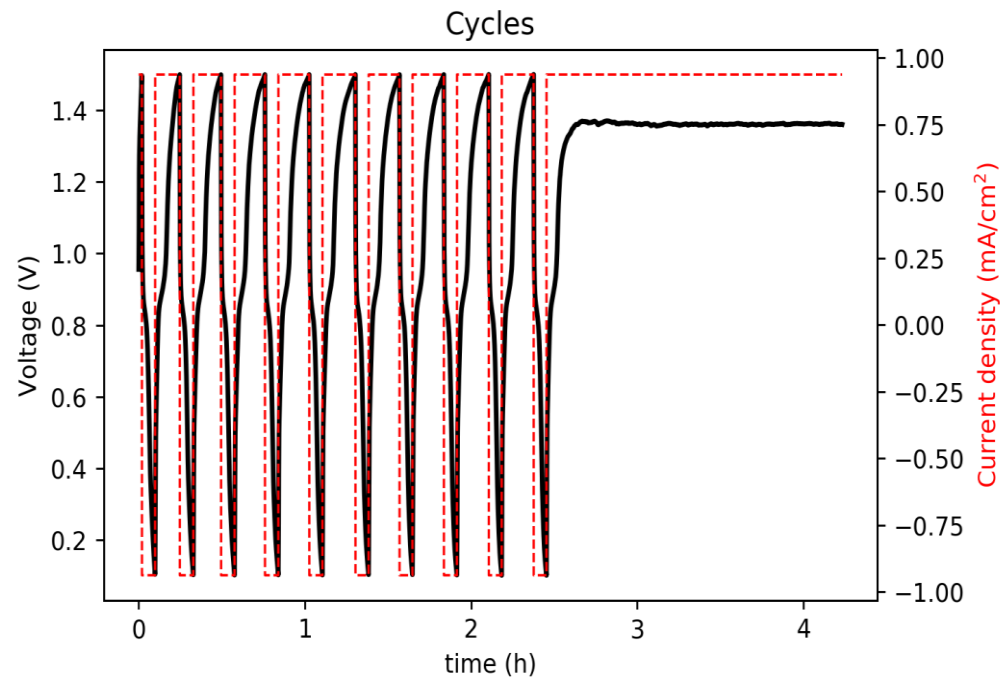
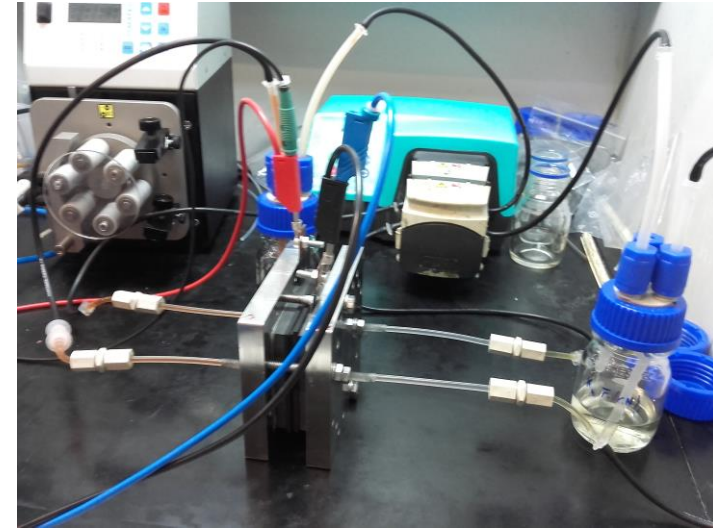
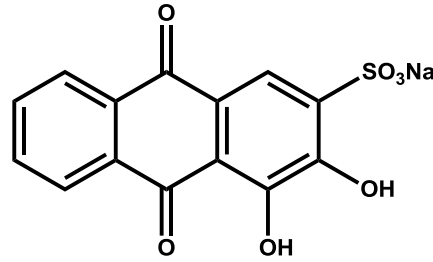


2. Synthesis and characterization (electrochemical and photophysical) of electrolytes

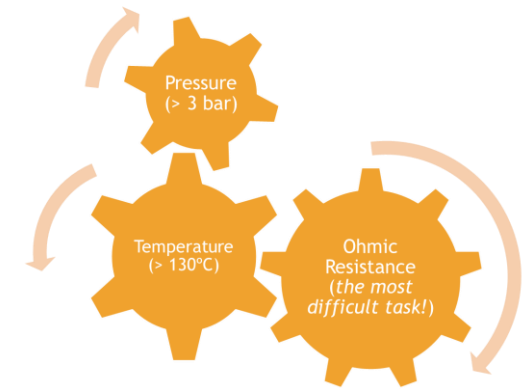
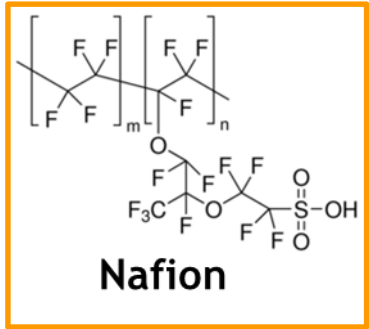
Cathode: 1.5 mM de AlizarinRed S

Anode: 3 mM de potassium ferrocyanide

1M NaOH

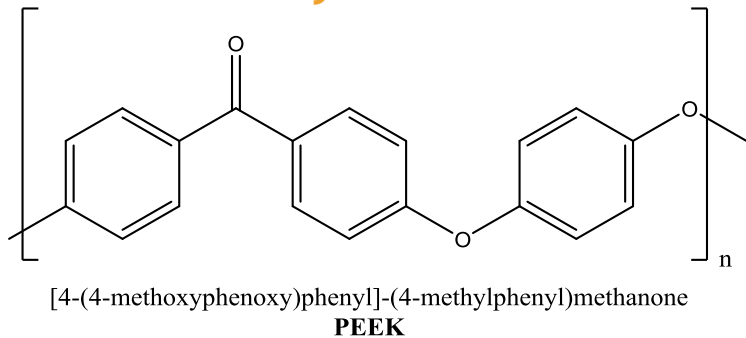


3. Development of proton exchange membranes (Decrease of ohmic resistance of the RFBs)

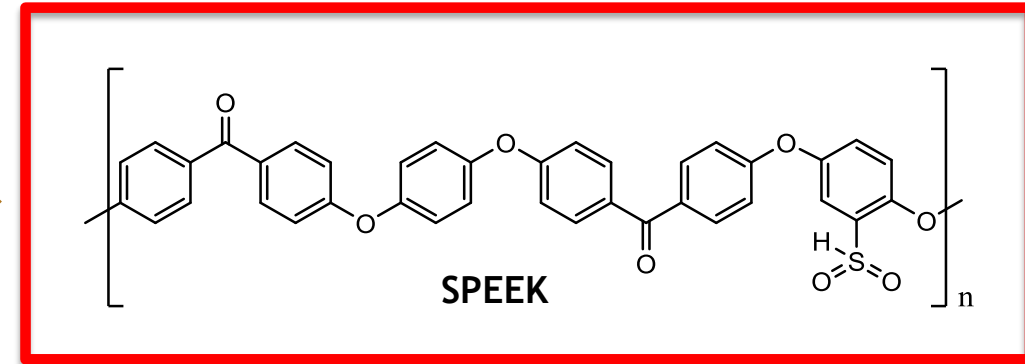


Polymer \longrightarrow Conducting Polymer \longrightarrow Composite membranes

Polymers



a) H_2SO_4
b) Fuming H_2SO_4



$\eta \approx 60\%$

Additives

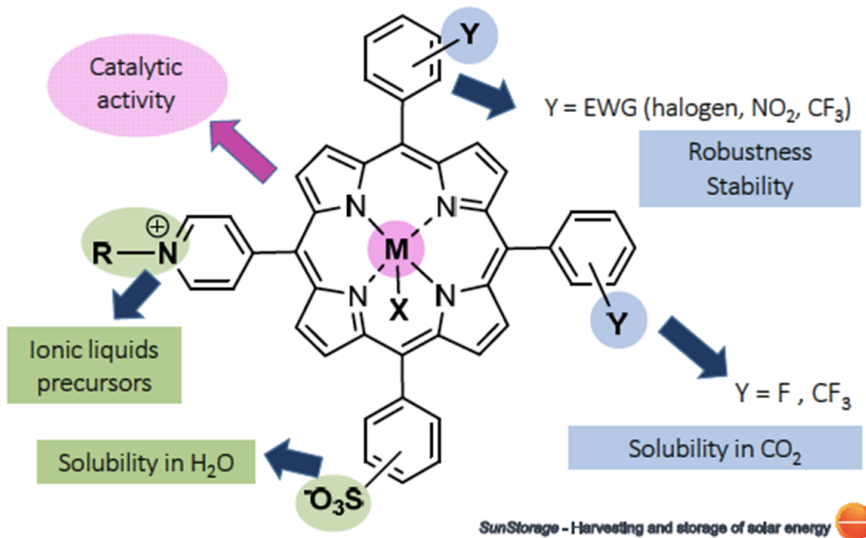
- Montmorillonite
 $(\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
- Silicon dioxide $(\text{SiO}_2)_n$

- ◆ SPEEK proton mobility still lower than that of Nafion
 - ◆ DMF-based membranes show improved thermal (252 °C) and mechanical properties.
 - ◆ Membranes further immersed/activated with H_2SO_4 show better thermal and mechanical properties.
 - ◆ The electrical and mechanical properties seems to be dependent on polymer density.

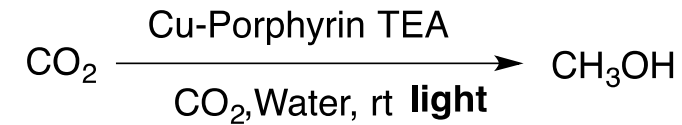
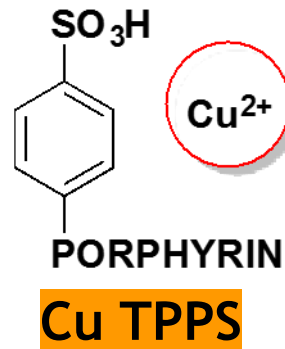
4 - Synthesis, characterization and optimization of efficient photocatalysts for electroreduction of CO₂ into CO and into methanol

- Synthesis and characterization of transition metal-organic catalysts, such as metalloporphyrins.
- Spectroscopic, photochemical and phenomenological characterization.

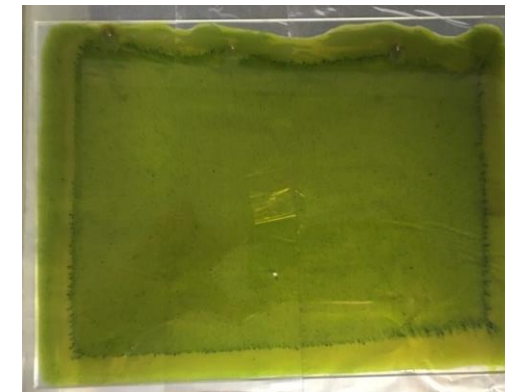
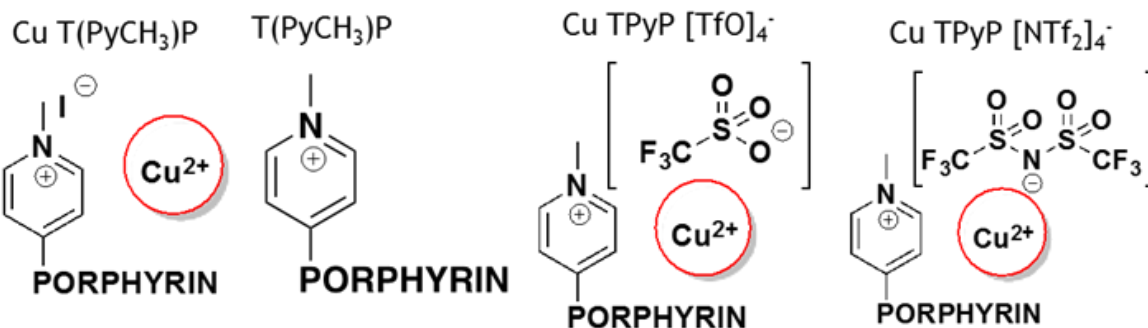
Synthesis and functionalization of metalloporphyrins



Homogeneous catalysts for CO₂ transformation into methanol



Evaluation as photocatalyst when immobilized in SPEEK membranes



Thank you for your Attention!

“This work was performed under the project **“SunStorage - Harvesting and storage of solar energy”**, with reference **POCI-01-0145-FEDER-016387**, funded by European Regional Development Fund (ERDF), through **COMPETE 2020 - Operational Programme for Competitiveness and Internationalization (OPCI)**, and by national funds, through **FCT - Fundação para a Ciência e a Tecnologia I.P.**”



UNIÃO EUROPEIA
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FCT
Fundação para a Ciência e a Tecnologia
MINISTÉRIO DA CIÊNCIA, TECNOLOGIA E ENSINO SUPERIOR