# Advanced MOF-based materials towards dual carbon dioxide capture and conversion


## Simone C. Fernandes

up201603496@up.pt

Supervisor(s): Luís Cunha-Silva[1], Salete S. Balula[1]

1. LAQV/REQUIMTE, Faculdade de Ciências da Universidade do Porto, 4169-007, Porto, Portugal

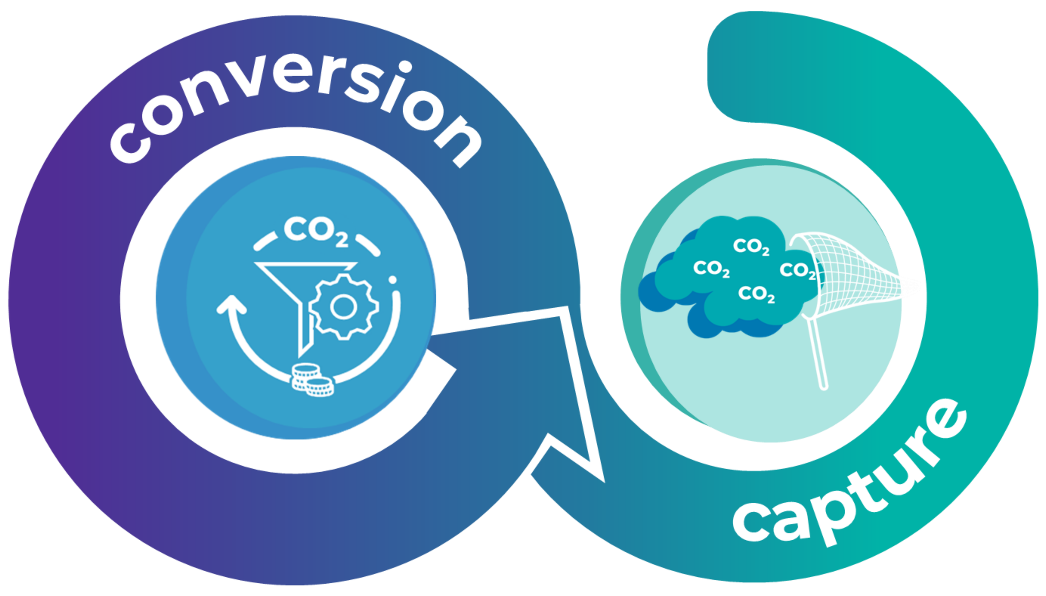

IDEAS TO IMPACT

MIT Portugal
2024 Annual Conference

## INTRODUCTION AND MOTIVATION

- Excessive release of $CO_2$, a greenhouse gas, to the atmosphere
- Catastrophic environmental consequences such as the increase in average global temperature
- Decarbonization and climate neutrality by 2050 are extremely important!
- Solutions for this worldwide problem has become a current subject of modern research

Since $CO_2$ is a cheap, abundant and renewable carbon source, the utilization of $CO_2$ is an ideal solution!



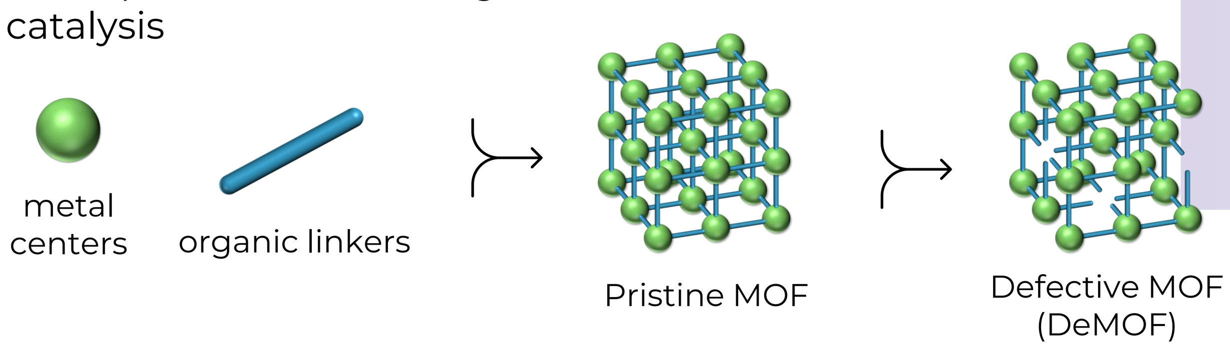

The $CO_2$ molecule is thermodynamically and kinetically relatively stable, which is the main obstacle to utilization.

The search for an active catalyst, with the ability to simultaneously capture and convert $CO_2$, is still a challenge.

### Metal-Organic Frameworks

MOF

- ✓ Highly porous and ordered networks
- ✓ Structural and chemical versatility
- ✓ Great mechanical and chemical stability
- ✓ Great potential in heterogenous catalysis




### Defect Engineering

creating strategic and deliberate defects in a "perfect" crystalline structure

defects can act as active sites

increase in catalytic performance

### $CO_2$ Capture

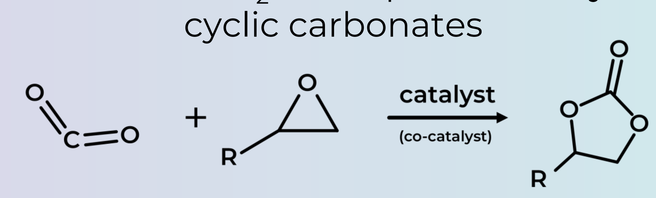
$CO_2$ capture and storage (CCS) in underground reservoirs is method employed currently.

However, this contributes to the waste of abundant feedstock for valuable products.

Capture of $CO_2$ is not efficient and sustainable enough as a standalone strategy.

### $CO_2$ Conversion

Cycloaddition of $CO_2$ with epoxides to synthesize cyclic carbonates




**Industrial Applications of Cyclic Carbonates**

- Electrolytes in Lithium-ion Batteries
- Synthesis of fine chemicals, pharmaceuticals, and other organic compounds

100% atom-economical reaction

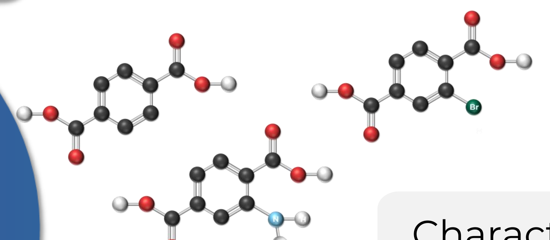
## GOAL OF THE PROJECT

Design of MOF-based materials with dual function: $CO_2$ capture and conversion into useful products, under ambient conditions (temperature and pressure)

## WORK PROGRESS: METHODOLOGY AND RESULTS

**Conceptualize DeMOFs-based catalysts with potential for both applications**

Different strategies such as the mixture of ligands that introduce $-NH_2$ or halogens groups, potentially improving catalytic performance and avoid addition of a co-catalyst.



**Preparation of DeMOFs-based catalysts**

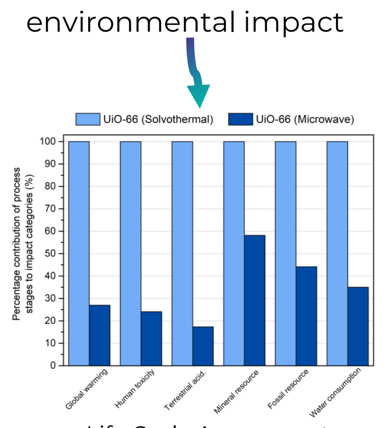
Different synthetic methods

Conventional (convection oven) 120 °C for 24h

Microwave (microwave oven) 120 °C for 1h

reduction of time and cost for synthesis

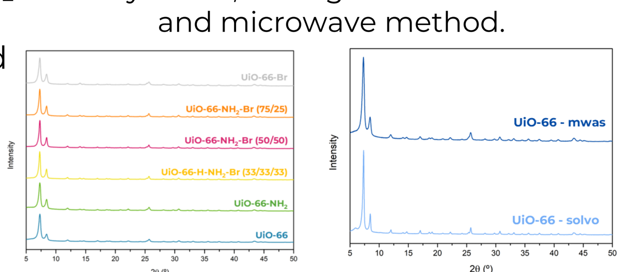
decrease of environmental impact



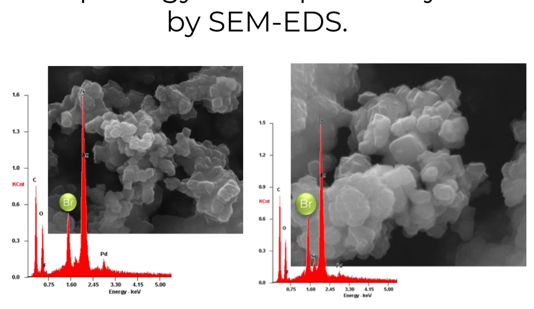

Life Cycle Assessment

**Characterization and confirmation of MOF formation and respective alterations**

Crystallinity of samples confirmed by PXRD, through conventional and microwave method.




Morphology of samples analyzed by SEM-EDS.

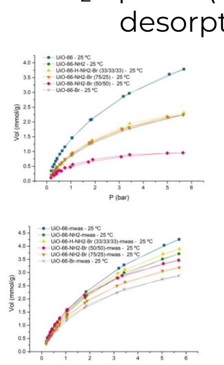



Porosity of different mixed-ligand samples, obtained through conventional and MWAS methods, determined by BET analysis.

| | Conventional | | | | Microwave | | | |
|---|---|---|---|---|---|---|---|---|
| | $S_{BET}$ ($m^2 \cdot g^{-1}$) | $S_{microp}$ ($m^2 \cdot g^{-1}$) | $S_{ext}$ ($m^2 \cdot g^{-1}$) | $V_p$ ($cm^3 \cdot g^{-1}$) | $S_{BET}$ ($m^2 \cdot g^{-1}$) | $S_{microp}$ ($m^2 \cdot g^{-1}$) | $S_{ext}$ ($m^2 \cdot g^{-1}$) | $V_p$ ($cm^3 \cdot g^{-1}$) |
| UiO-66-Br | 131.3 | 110,9 | 20,4 | 0.06 | 891.0 | 664.1 | 226.9 | 0.62 |
| UiO-66-$NH_2$-Br (75/25) | 658.2 | 570.5 | 87.7 | 0.27 | 947.5 | 743.4 | 204.1 | 0.57 |
| UiO-66-$NH_2$-Br (50/50) | 564.3 | 303.4 | 260.9 | 0.71 | 948.5 | 778.3 | 169.8 | 0.50 |
| UiO-66-H-$NH_2$-Br (33/33/33) | 780.8 | 455.6 | 325.2 | 0.98 | 998.5 | 797.1 | 201.4 | 0.56 |
| UiO-66-$NH_2$ | 835.7 | 733.5 | 102.1 | 0.36 | 1079.1 | 798.8 | 280.3 | 0.74 |
| UiO-66 | 1041.5 | 915.9 | 125.5 | 0.46 | 1276.4 | 948.0 | 328.4 | 0.82 |

**Adsorption studies**

$CO_2$ uptake ($mmol \cdot g^{-1}$) measure in a $CO_2$ adsorption-desorption equipment at URJC (Madrid).

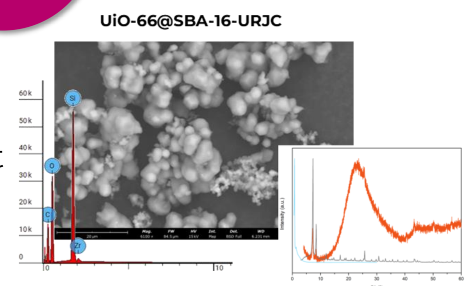


| | Conventional | | Microwave | |
|---|---|---|---|---|
| Description | 45 °C | 25 °C | 45 °C | 25 °C |
| UiO-66-Br | - | - | 2.13 | 2.88 |
| UiO-66-$NH_2$-Br (75/25) | 1.57 | 2.25 | 2.30 | 3.19 |
| UiO-66-$NH_2$-Br (50/50) | 1.63 | 2.24 | 2.53 | 3.47 |
| UiO-66-H-$NH_2$-Br (33/33/33) | 1.82 | 2.31 | 2.66 | 3.89 |
| UiO-66-$NH_2$ | - | - | 2.63 | 3.71 |
| UiO-66 | 2.84 | 3.79 | 3.13 | 4.26 |

**Current work**

Synthesis of MOF@silica hybrids through different methods.

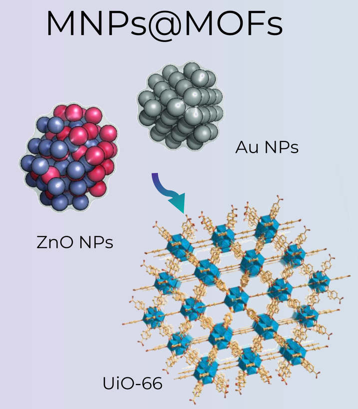
UiO-66@SBA-16-URJC



## FUTURE WORK

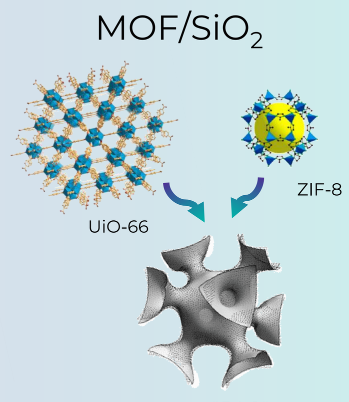
Preparation of MOF-based hybrids:

MNPs@MOFs




active catalyst MNPs in $CO_2$ conversion supported in MOFs of high $CO_2$ capture capacity

MOF/$SiO_2$

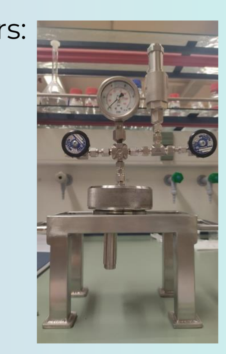


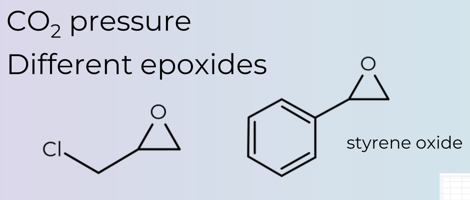

amine modified silicas combined with active catalytic DeMOFs

Study and optimization of catalytic performance

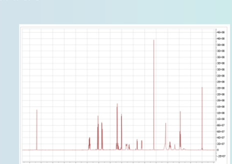
Study the effect of several parameters:

- Amount and nature of catalyst
- Presence of co-catalyst
- Temperature
- Time
- $CO_2$ pressure
- Different epoxides






Quantification by [1]H NMR

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