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XXXII Cycle

Development of 3D structures for energy applications: CO_2 capture and permeability control

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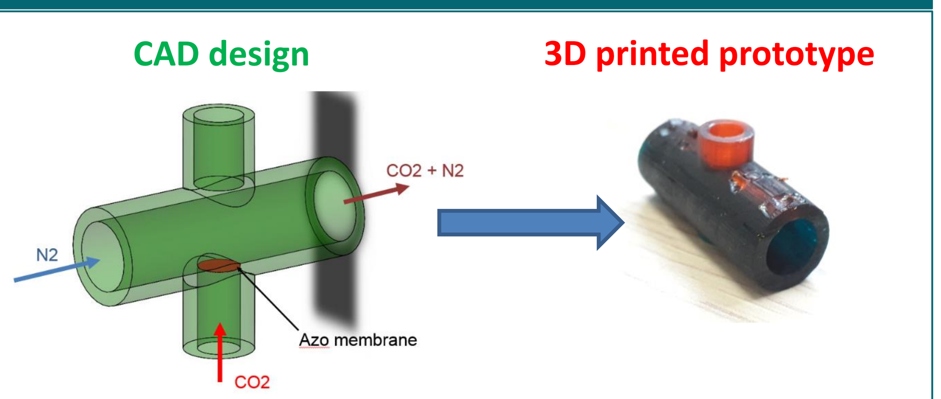
Research context and motivation

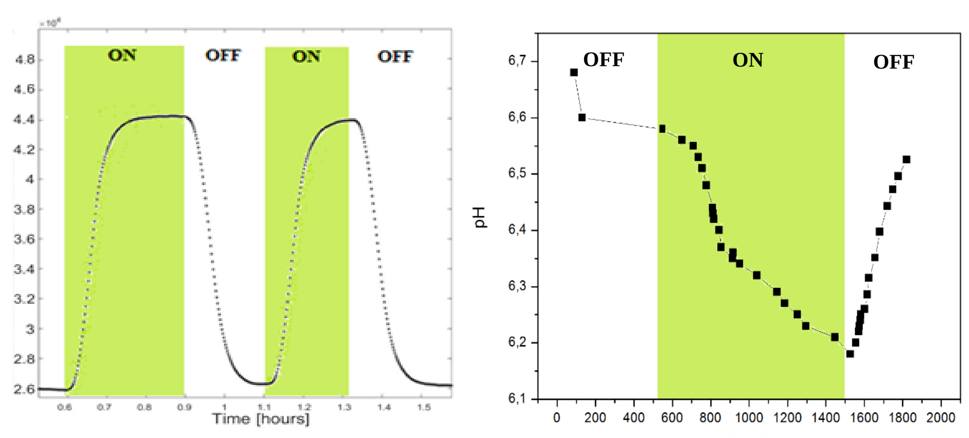
- In recent decades atmospheric concentration of **CO_2** has remarkably increased. This increase is due to natural and anthropogenic emissions, that include the iron and steel industry, gas flaring, and combustion of fossil fuels. A substantial reduction of the CO_2 emissions is required to slow down the global warming affecting our planet. Despite the urgency of the problem, in the last years, CO_2 emissions have not been decreased. The necessity for alternative or improved methods to reduce CO_2 emissions and to **capture and store** released CO_2 has stimulated intense research in academia and industry. Today the so-called absorbers are used in power plants for post-combustion CO_2 capture.
- **Polymeric solid absorbers** for CO_2 capture are in increasing interest, and many research have been made in this field, most of all related to membrane separation technology. Poly ionic liquids (**PILs**) have gained a lot of attention in CO_2 capture/release compared with other type of technologies and their liquid counterparts as well.
- **stimuli-responsive materials** are widely studied in polymeric membrane separation processes due to their ability to change specific properties by external stimuli.
- **3D printing** is a suitable technology for this purpose because it can produce complex objects directly from computer-aided design (CAD) and, skipping the slow and expensive lithography process of traditional manufacturing, it is a time-saving and cost-effective technique.
- Polymeric based **smart filters** could be created, containing CO_2-philic PILs or stimuli responsive molecules, exploiting 3D printing.

Addressed research questions/problems

- **Light induced permeability control and 3D printing application**

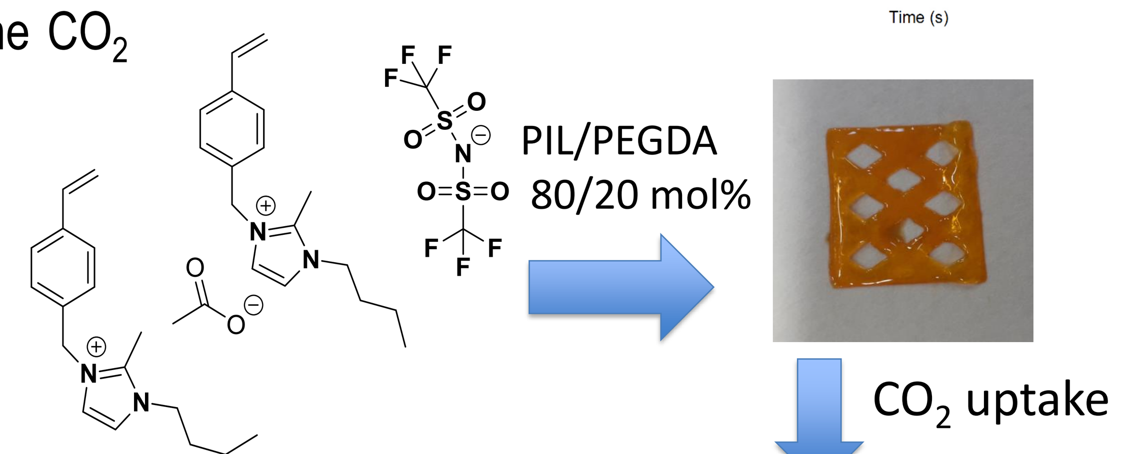
The CO_2 permeability of a membrane of PEGDA containing 0.2 phr of Methyl Red (**MR**) and Disperse Red 1 Methacrylate (**DR1M**) increased of about **70%** while irradiated with a LASER source. As a proof of concept and application, a 3D printed device was manufactured to photo-control the pH of a solution by monitoring the CO_2 flow.

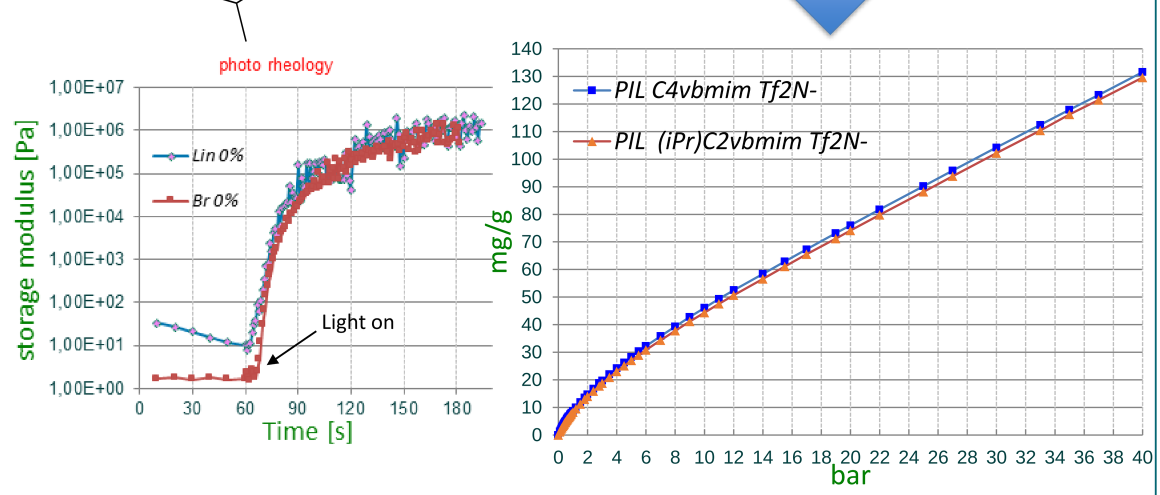




- **3D Printable Poly Ionic liquids(PIL) for CO_2 capture**

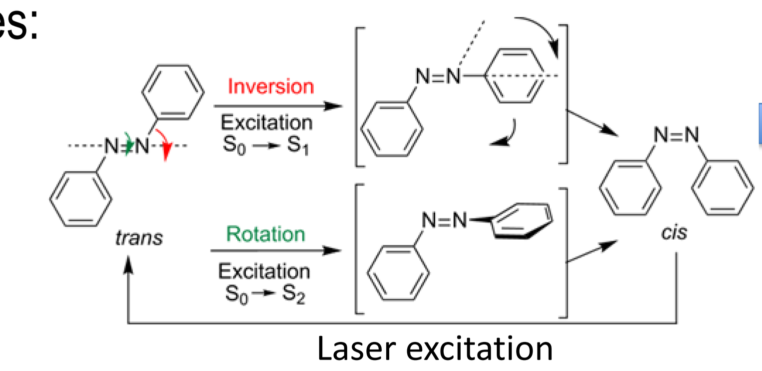
Imidazolium based PILs, suitable for DLP 3D printing, were synthesized modifying their cations and anions to increase CO_2 uptake. Self–standing structures with high content of PIL were successfully 3D printed with a DLP system.





Novel contributions

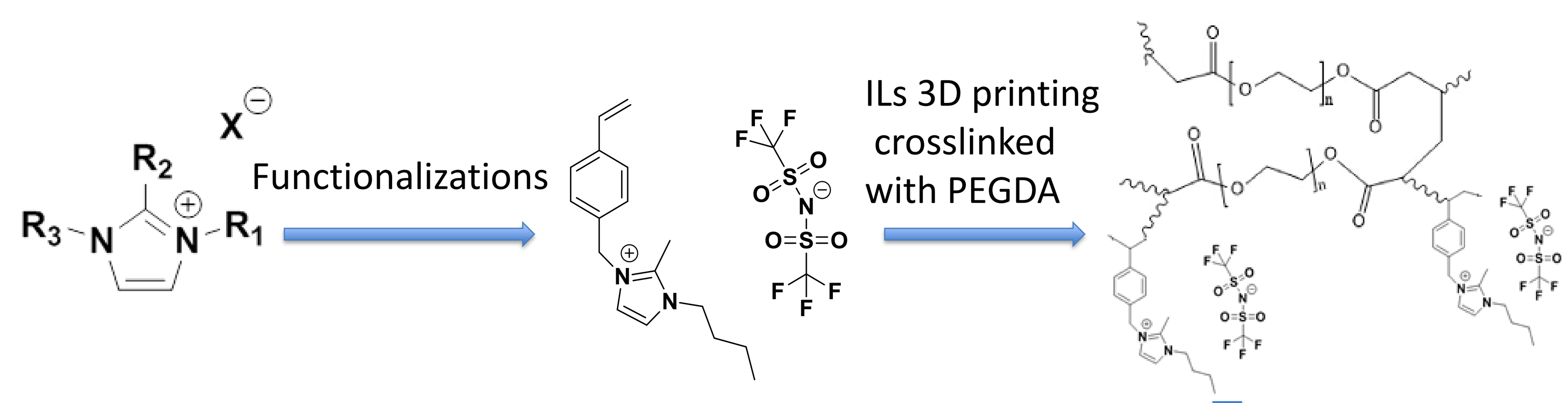
- **3D printing** is carried out in order to create structures composed of new materials capable to adsorb carbon dioxide from air.
- **Light responsive materials** are studied to control the CO_2 permeability in polymer membranes:



Increase of free volume in polymer matrix

PERMEABILITY CONTROL

- **Poly Ionic liquids** are used to create polymer matrices crosslinked with PEGDA functionalized with species able to interact physically and/or chemically with CO_2.



CO_2 CAPTURE

Adopted methodologies

- **3D printing (DLP)** : the methodology consists in preparing a liquid formulation containing monomers, a photoinitiator to activate the photo-induced polymerization and functional species/fillers suitable for the final application.The DLP printer creates the 3D object by illuminating the resin layer by layer with a digital projector, while a support basement lifts the attached structure generating the structure. The main control parameters are the thickness of the irradiated layers and the time of exposure. The formulation contains also a dye necessary to confine the light inside the exposed layer with a concentration that allows a precise printability without over-exposures.

Future work

- CO_2 capture reactor for 3D structures in dynamic flow
- CO_2 adsorption by PIL coupled with light controlled CO_2 release
- Engineering of the filter to maximize the capture by introducing controlled porosity
- Possibility of 3D printing implementation related to CO_2 (i.e. supporting structures for catalyzed CO_2 reduction)

List of attended classes

01MOUKI	Nanocomposite polymeric materials	4	21/04/2017
02LWHRV	Communication	1	16/02/2017
02RHPRV	Intellectual Property Rights, Technology Transfer and Hi-tech Entrepreneurship (Theoretical course)	6	23/03/2017
01QORRV	Writing Scientific Papers in English	3	23/03/2017
01MOVKI	Polymers and radiations	5	16/02/2018
01SDDKI	Polymeric additive manufacturing	4	11/07/2018
01TGTKI	Physical Chemistry of Materials for Nanotechnologies	7	09/09/2019
Winter school: Innovative approaches for material synthesis and characterization		5	23/01/2017
Summer school: CO_2oling the earth - CO_2 conversion path explained through EU funded projects		3	05/09/2019

Submitted and published works

- **Polymeric 3D Printed Functional Microcantilevers for Biosensing Applications** Stefano Stassi, Erika Fantino, Roberta Calmo, Annalisa Chiappone, Matteo Gillono, Davide Scaiola, Candido Fabrizio Pirri, Carlo Ricciardi, Alessandro Chiadò, and Ignazio Roppolo. ACS Applied Materials & Interfaces 2017 9 (22), 19193-19201. DOI: 10.1021/acsami.7b04030
- **In situ generation of silver nanoparticles in PVDF for the development of resistive switching devices** Chiappone, A.; Gillono, M.; Castellino, M.; Bejtka, K.; Rajan, K.; Roppolo, I.; Perrone, D.; Bocchini, S.; Ricciardi, C.; Pirri, C. F.; Chiolerio, A Applied Surface Science, Volume 455, 15 October 2018, Pages 418-424. DOI 10.1016/j.apsusc.2018.06.001
- **CO2 permeability control in 3D printed light responsive structures** Gillono, Matteo; Roppolo, Ignazio; Frascella, Francesca; Scaltrito, Luciano; Pirri, Candido; Chiappone, Annalisa. Applied Materials Today 2019.