Development of Grafted Poly(ionic Liquid)/ionic liquid Membranes for CO_2/Light Gas Separations

Carbon dioxide separation is a key step in several energy-related industrial applications, including natural gas purification (CH_4/CO_2) or clean-up of combustion exhaust gases (CO_2/N_2). In competition with amines, ionic liquids (ILs) are known to interact strongly and reversibly with acid gases, making supported IL-materials versatile materials for use in adsorptive or membrane separation applications.[1] Conventional PIL/ion gels composite membranes have attracted a lot of interest due to the excellent performances of these membranes.[2] These membrane are composed of a selective "active layer" which contains a PIL (figure 1), a free ionic liquid, and in some case a cross-linking agent or a facilitated transport group. This layer sits on a highly permeable gutter layer or a porous polymeric support. Up to now, nanoporous polymer supports have been favored for preparing such kind of membranes, in spite of their relative instability during continuous separation processes at high temperature.

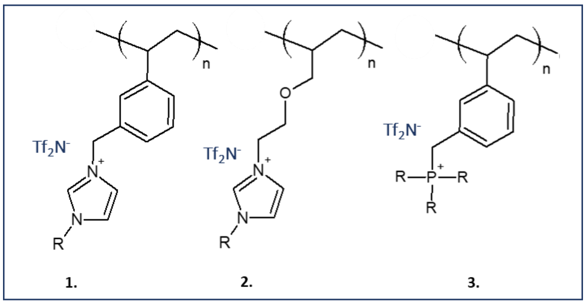

Figure 1. *Chemical structures of 1. Imidazolium-based styrene PIL, 2. Imidazolium-based acrylate PIL and 3. Phosphonium-based styrene PIL with R representing an organic group such as alkyl, alkyl ethers, alkylnitrile, disiloxane.*[1,2]

In this project, the aim is to demonstrate the possibility to polymerize the PIL monomer directly on the surface and in the pores of a porous ceramic support. A recent procedure developed in the IM group enables the growth of brushes from the pore surface of a γ-Al_2O_3 porous ceramic support. The candidate will benefit of the expertise and equipment of the Inorganic membrane group to:

1. **Synthesize PILs monomers** from protocol described in literature and developed in the IM group.
2. **Prepare PILs-grafted membranes on commercial ceramic supports**. This method implies in a first step the vapor phase deposition of the commercial initiator on the γ-Al_2O_3 porous ceramic support, followed by the blocking of the remaining hydroxyl surface group by surface modification. The last step consists of the Surface-initiated atom-transfer radical polymerization (SI-ATRP) to grow PIL chain from the γ-Al_2O_3 pore surface.
3. **Characterize the as-prepared membranes** by various techniques like FTIR, AFM, permporometry, electron microscopy, XPS, HR-MAS NMR, etc…
4. ***Find key parameters** (initiator and monomer concentration, influence of monomer composition, etc.)* ***that control membrane properties.***
5. ***Evaluate the performance of the membranes for CO_2/N_2 and CO_2/CH_4 gas separation.***

Skills which will be developed during the Master assignment:

- Synthesis of PIL monomers, porous ceramic membranes and grafted-PILs membranes
- Characterization of the as-prepared monomer molecules (liquid NMR, FTIR), and of the grafted membranes (*SEM, FE-SEM, EDX, XPS, FTIR, HR-MAS NMR, permporometry, N_2 sorption, TGA-DSC)*
- Evaluation of the membrane performances in single gas permeation (CO_2, N_2 and CH_4)

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1. L.C. Tomé, I.M. Marrucho, Ionic liquid-based materials: a platform to design engineered CO_2 separation membranes, *Chem. Soc. Rev*., **2016**, 45, 2785-2824. **2.** M.G. Cowan, D.L. Gin, R.D. Noble, Poly(ionic liquid)/Ionic Liquid Ion-Gels with High "Free" Ionic Liquid Content: Platform Membrane Materials for CO_2/Light Gas Separations, *Acc. Chem. Res.,* **2016**, 49, 724−732. **3.** Xin, B.; Hao, J. Imidazolium-based ionic liquids grafted on solid surfaces. *Chem. Soc. Rev*., **2014**, 43, 7171–7187.