# Exploration of the metal-organic framework/polymer interface in Mixed Matrix Membranes

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## Abstract

**Statement of the Problem**: Mixed matrix membranes (MMMs) composed of polymers and metal-organic frameworks (MOFs) have attracted a great interest for potential application in the field of gas/liquid separations[1,2,3]. One of the main challenges to overcome in this field is the fabrication of uniform and defect-free MMMs. Therefore, understanding what makes a MOF/polymer pair compatible is essential to advance the development and utility of these composites. To this end, the microscopic origins of the MOF/polymer compatibility must be investigated. Recently, the interfacial properties of PIM-1 (Polymer of Intrinsic Microporosity)/UiO-66 (MOF) nanocomposite were investigated by means of a joint experimental-theoretical exploration[4]. Compared to the use of other flexible polymers, e.g. PVDF and PEG, this nanocomposite presents a rather poor compatibility, with the presence of substantial microvoids at the interface[4]. The functionalization of PIM-1 would be a feasible way to circumvent this problem. Hence, a theoretical exploration consisting of investigating three functionalized forms of PIM-1 was proposed in order to anticipate a better compatibility of the corresponding MMMs. **Methodology & Theoretical Orientation**: A hybrid methodology integrating quantum- and force field-based simulations was used to construct and characterize the different PIM-1/UiO-66(Zr) models[4,5]. **Findings:** The three investigated functionalizations led to the improvement of the overlap length between the polymer and the UiO-66, thus leading to a better compatibility compared to the PIM-1/UiO-66 nanocomposite. We evidenced that a strong hydrogen bonding between the polymer and the MOF surface favors this compatibility enhancement. Furthermore, the aliphatic chains are able to penetrate the MOF pockets (Figure 1), increasing even more the interactions between the composite components. **Conclusion & Significance**: The simulations of the three polymer modifications clearly indicated that a better compatibility can be achieved by the presence of strong hydrogen bonds with the terminal hydroxyls of the MOF surface and by long aliphatic chains, being able to interpenetrate the surface pockets.

## Image

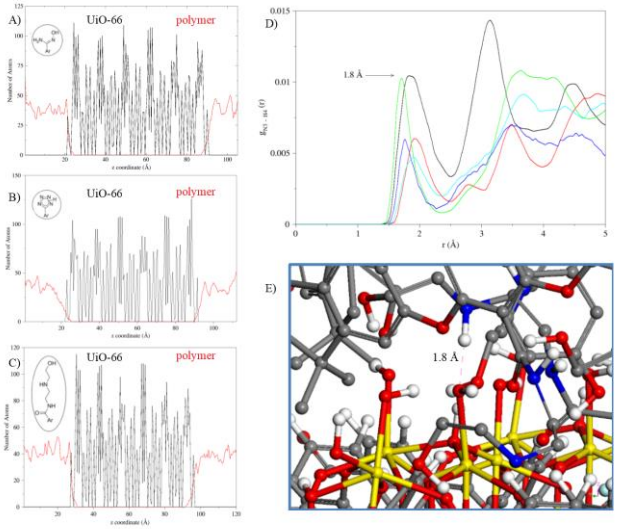



Figure 1: A) Atomic z density of UiO-66/PIM-1 mod(1) B) Atomic z density of UiO-66/PIM-1 mod(2) C) Atomic z density of UiO-66/PIM-1 mod(3) D) Pair distribution function of N atom of PIM-1 mod(3) and H atom of the surface hydroxyls. E) Snapshot of the hydrogen bond between PIM-1 mod(3) and UiO-66.

## Recent Publications

1. Lin R *et al.* (2016) Ionic Liquids as the MOFs/Polymer Interfacial Binder for Efficient Membrane Separation. Appl. Mater. Interfaces 8:32041-32049
2. Friebe S *et al.* (2016) MOF-Based Mixed-Matrix Membranes in Gas Separation – Mystery and Reality. Chemie Ingenieur Technik 88:1788-1797
3. Lin R et al. (2018) Metal Organic Framework based Mixed Matrix Membranes: an Overview on Filler/Polymer Interfaces. Journal of Materials Chemistry A 6:293-312
4. Semino R *et al.* (2018) Understanding the origins of Metal-Organic Framework/Polymer Compatibility. Chemical Science 9:315-324
5. Semino R *et al.* (2015) Microscopic model of the MOF/Polymer interface: a first step towards understanding the compatibility in Mixed Matrix Membranes. Applied Materials & Interfaces 8:809-819

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