Bottom-up Synthesis of 2D Polymers and Frameworks for Gas Separation

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MOTIVATION

Covalent organic frameworks (COFs) represent organized and intrinsically porous networks constructed using a variety of organic units. These materials are made of organic blocks containing light elements and are linked by strong covalent bond.[1] This study focused on the unit Tetrakis(4-aminophenyl) porphyrin(TAPP).This unit is porphyrin-based and forms vacancy zones in its polymer framework that are ideal for separations. The porphyrin center can be used to intercalate a metal ion and has been shown to be an effective catalyst for oxygen reduction [7]. Despite the promising properties of COFs, their applications are hindered by their processability.[2-7] This study measured permeability and selectivity of TAPP membranes for H2 separation and proposes a method of using vapor phase polymerization to increase processability and performance of TAPP based frameworks in separation and catalytic applications.

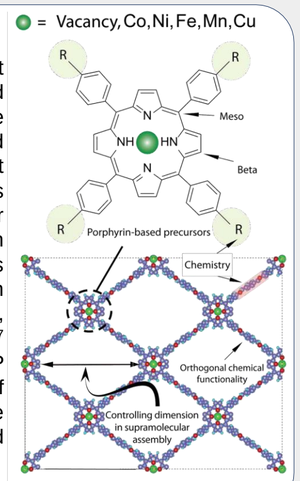

Figure 1. Porphyrins and their derivatives are among the building blocks of COFs.

SYNTHETIC METHODS

Electro-polymerization of TAPP

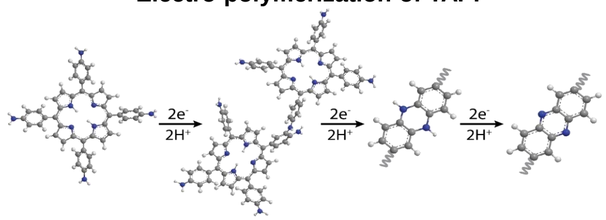

Figure 2. Polymerization mechanism of TAPP through amine coupling reactions.

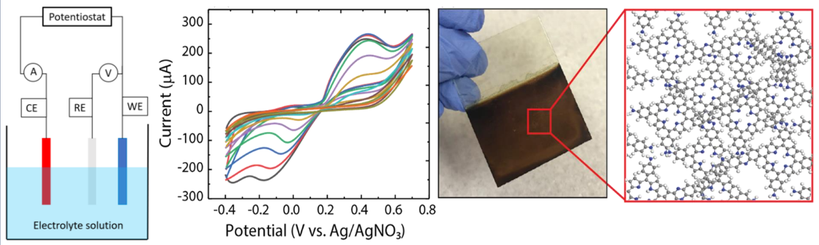

Figure 3. Preparation of pTAPP via electro-polymerization

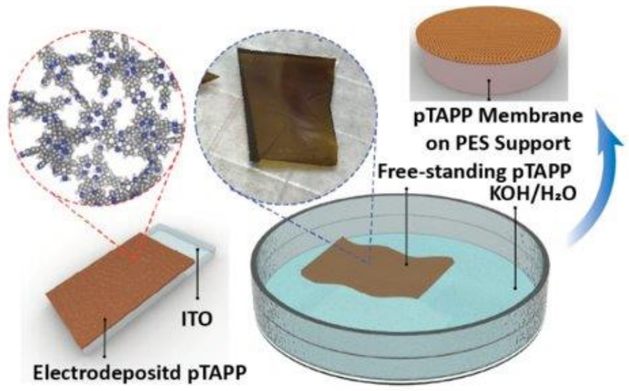

Figure 4. Schematic of pTAPP liftoff process on ITO substrate.

Results for Electro-Polymerized COF Membranes

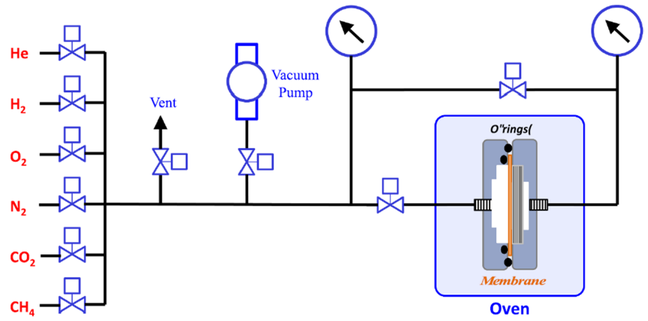

Figure 5. Process flow diagram for gas permeation system

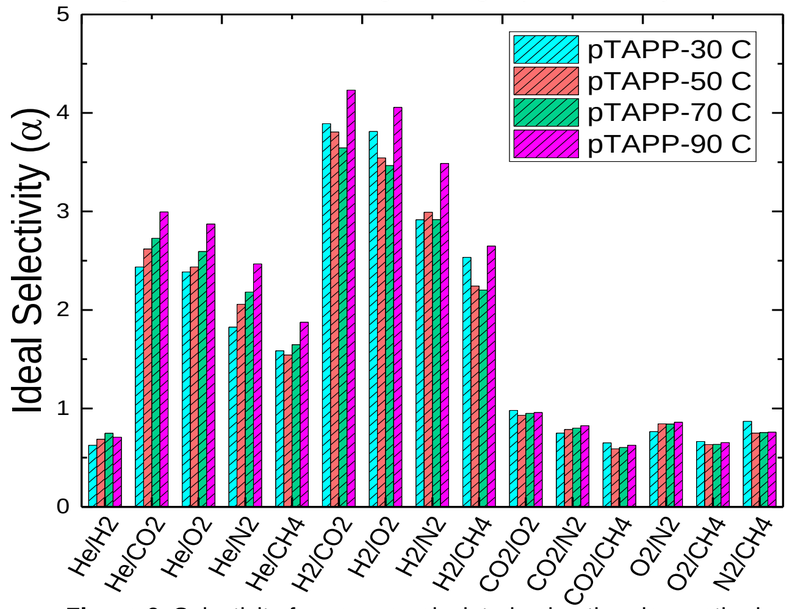

Figure 6. Selectivity for gasses calculated using time-lag method

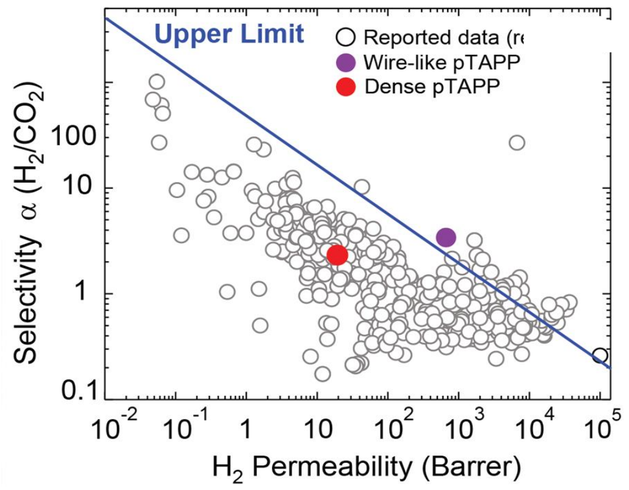

Figure 7. Performance comparison of reported separation membranes

Preliminary Results of oMLD pTAPP

Solvent stability, thickness and morphology

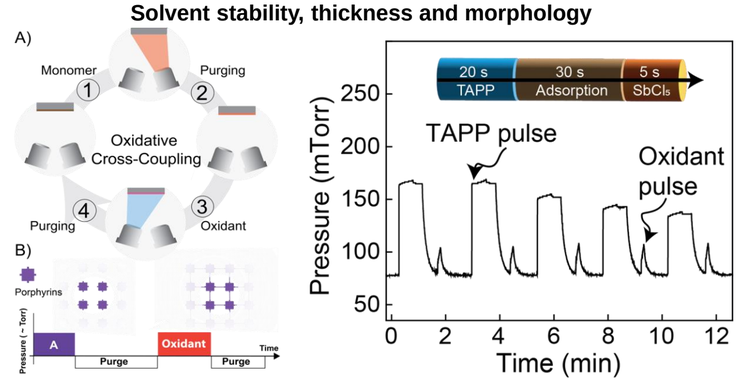

Figure 8. Schematic of oxidative molecular layer deposition (oMLD) and pressure trajectory.

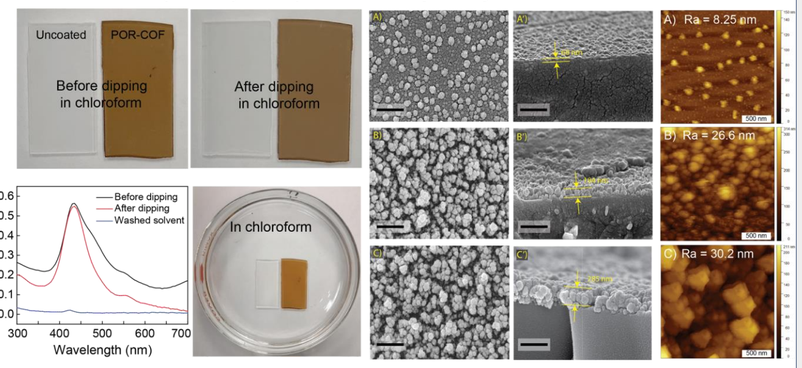

Figure 9. Solvent stability, thickness and morphology of POR-COF

CONCLUDING REMARKS

We report an electrochemical process on oxidative polymerization of porphyrin macrocyclic monomers to fabricate porous, self-standing, flexible, and defect-free polymer thin films. The prepared membranes illustrated promising gas separation performance and exceeded the upper bound toward H2/CO2 separation.

ACKNOWLEDGEMENTS

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