Expanding the Scope of MOF-Polymer Hybridization for the Synthesis of Water Stable Adsorbents

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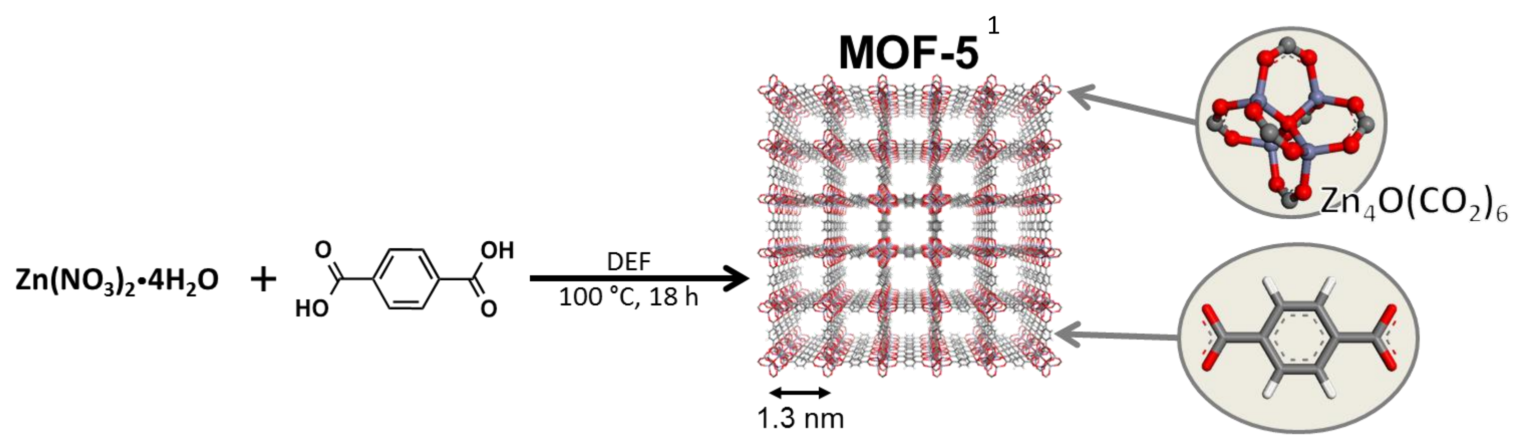
Background

- Metal-Organic Frameworks (MOFs), 3-D porous materials composed of metal nodes and organic linkers, have shown potential for use in industrial separation applications, particularly for the adsorption and separation of CO_2.

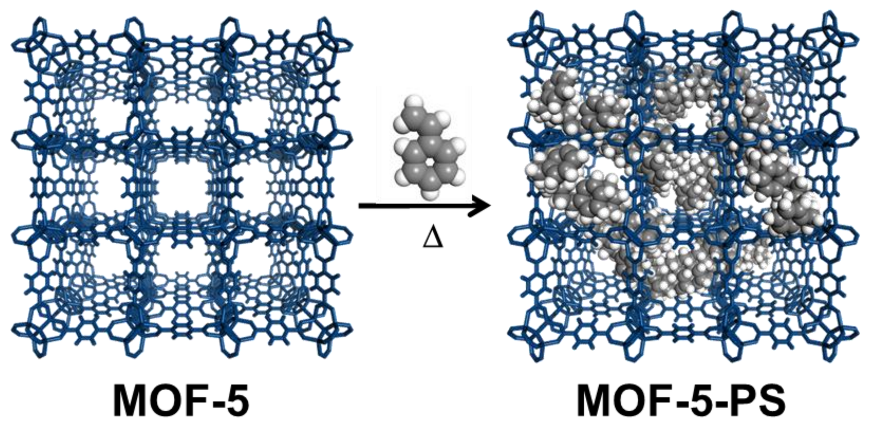


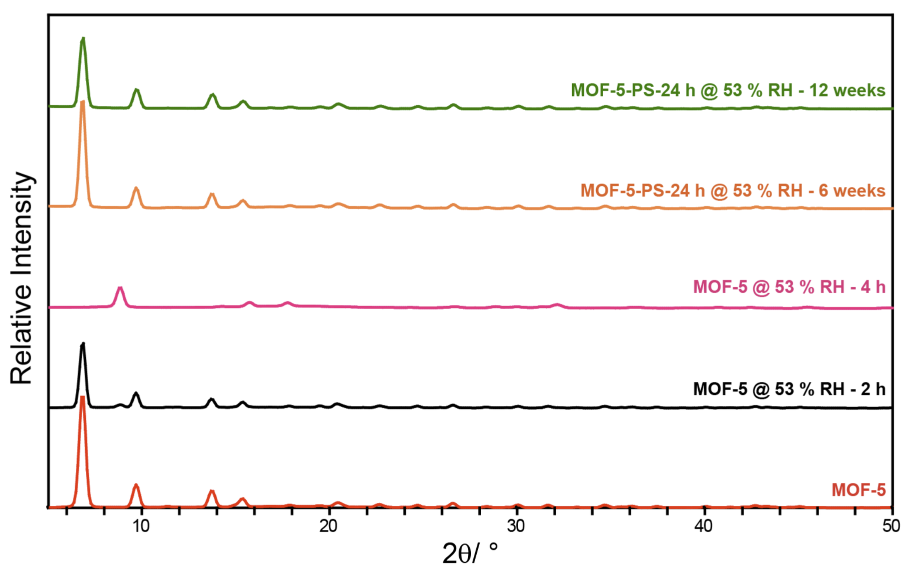
BET surface area: 3500 $m^2 g^{-1}$

- One drawback of these materials is that many suffer from ligand displacement by water in humid environments leading to framework decomposition.
- Hybridization of MOFs with organic polymers has recently shown promise in increasing the hydrolytic stability of MOFs.

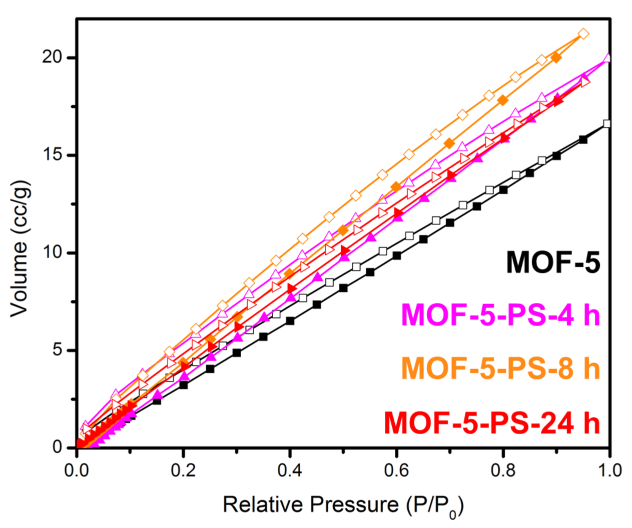
MOF-5-Polystyrene

- MOF-5-polystyrene was previously shown in our research group to have exceptional water stability and CO_2 adsorption capacity relative to the parent MOF-5. This hybridization method represents a conceptual precursor to enhancement of hydrolytic stability for known MOFs which have otherwise promising capacity for CO_2.[2]





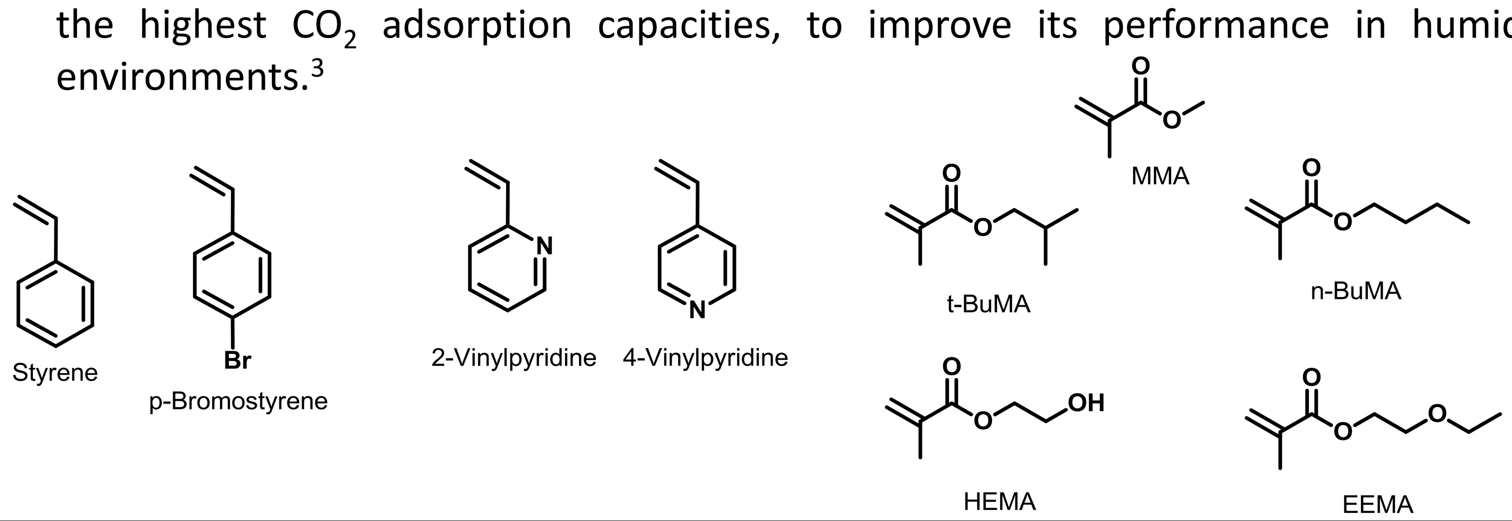
- Powder X-ray Diffraction (PXRD) shows that MOF-5-PS-24 h is stable under 53 % RH for greater than 12 weeks[2]



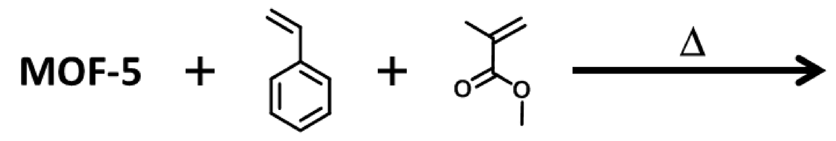
- CO_2 adsorption capacity is increased in MOF-5-PS[2]

Approach

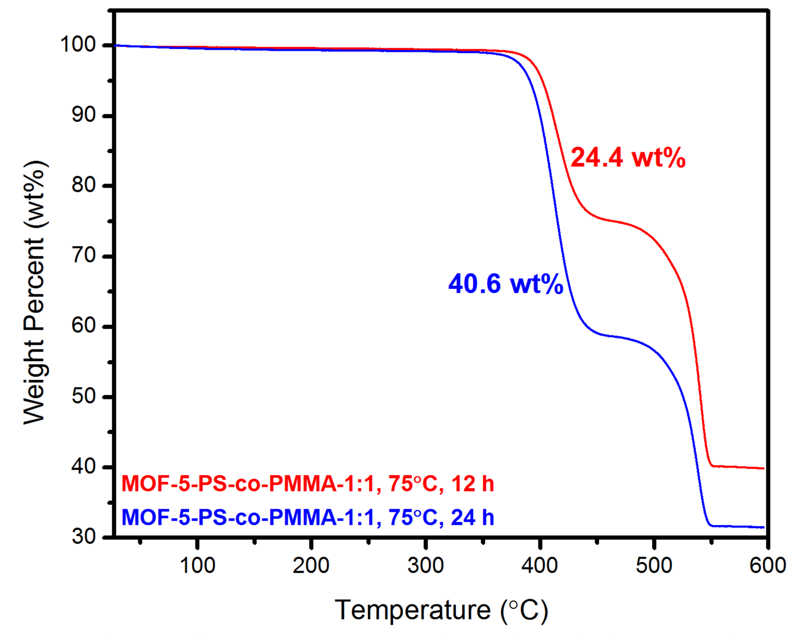
- Here, we expand this hybridization method to include copolymers resulting in varying functionality on the pore wall.
- Moreover, we examine the effects of the copolymer on the hydrolytic stability of the MOF-polymer hybrids.
- Finally, we extend this hybridization technique to Mg/DOBDC, a MOF with one of the highest CO_2 adsorption capacities, to improve its performance in humid environments.[3]



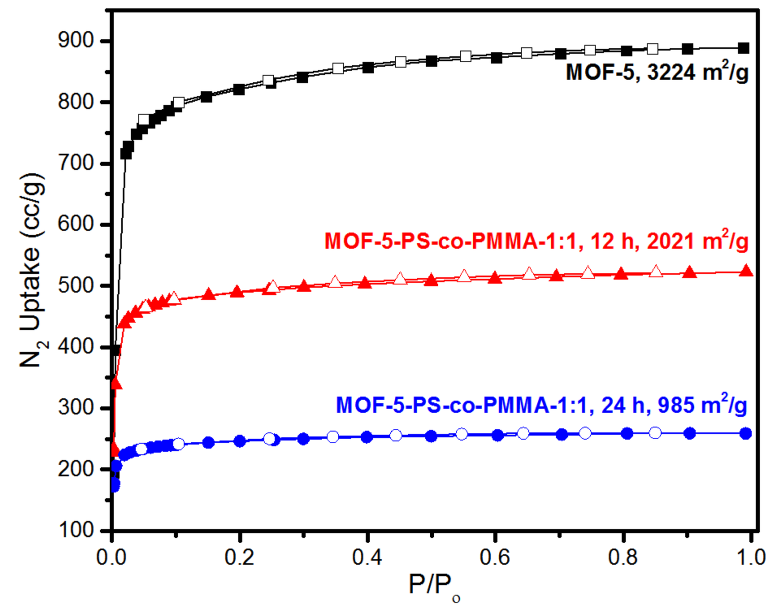
Results and Discussion



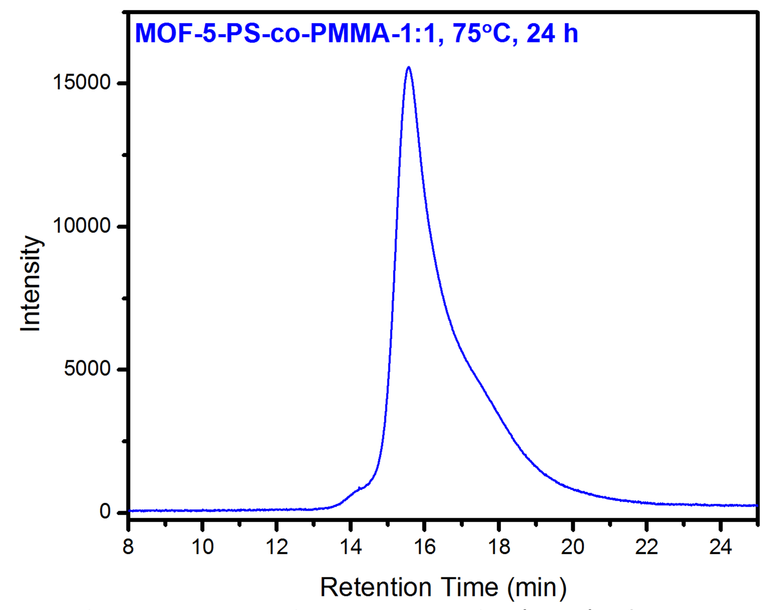
- PXRD shows a retention of the MOF-5 crystal structure after polymerization



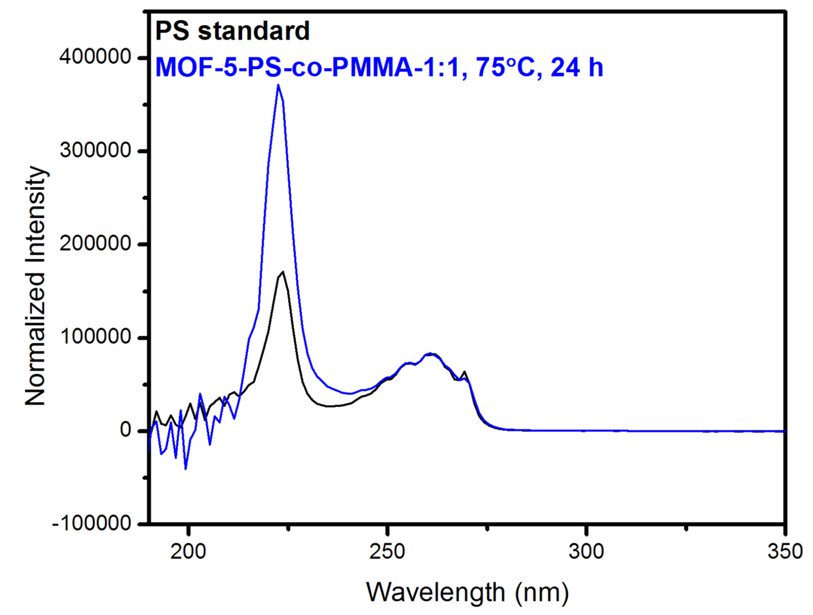
- Thermal Gravimetric Analysis (TGA) showing the depolymerization of PS-co-PMMA at ~400 C and subsequent thermal decomposition of MOF-5



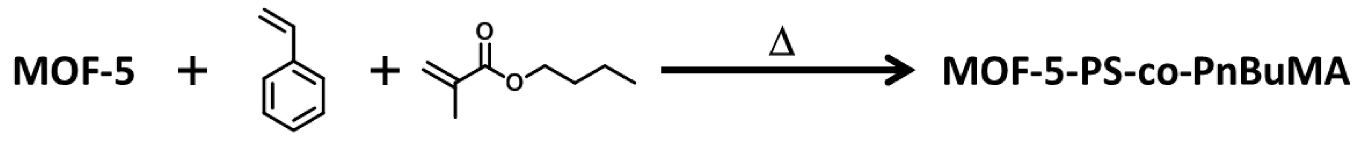
- N_2 adsorption isotherms and BET surface areas for MOF-5-PS-co-PMMA composites



- Gel Permeation Chromatography (GPC) of extracted PS-co-PMMA (Mn = 375 kDa, Đ = 2.07)



- UV-Visible spectra from the GPC at ~15.4 min showing increase in the adsorption at ~222 nm indicative of the presence of a PMMA copolymer unit



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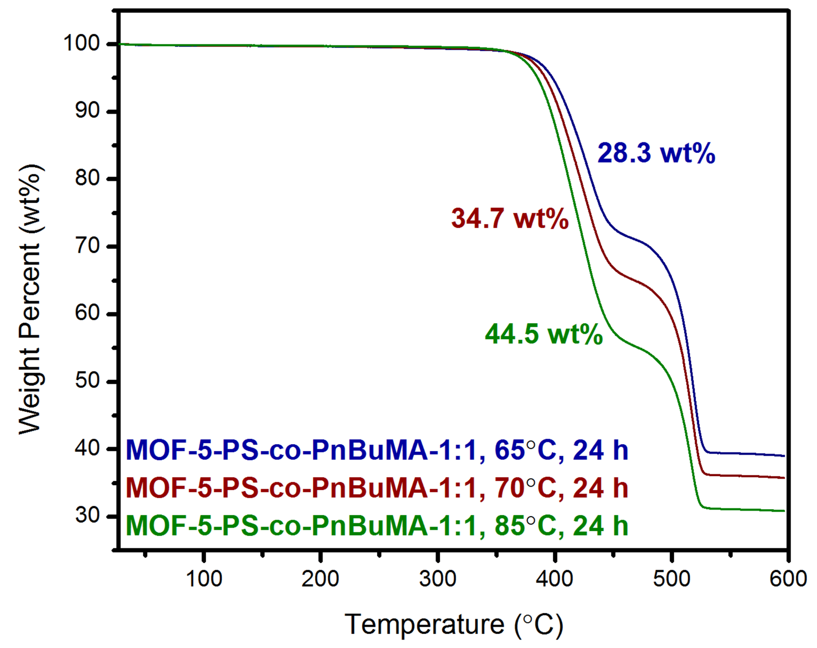
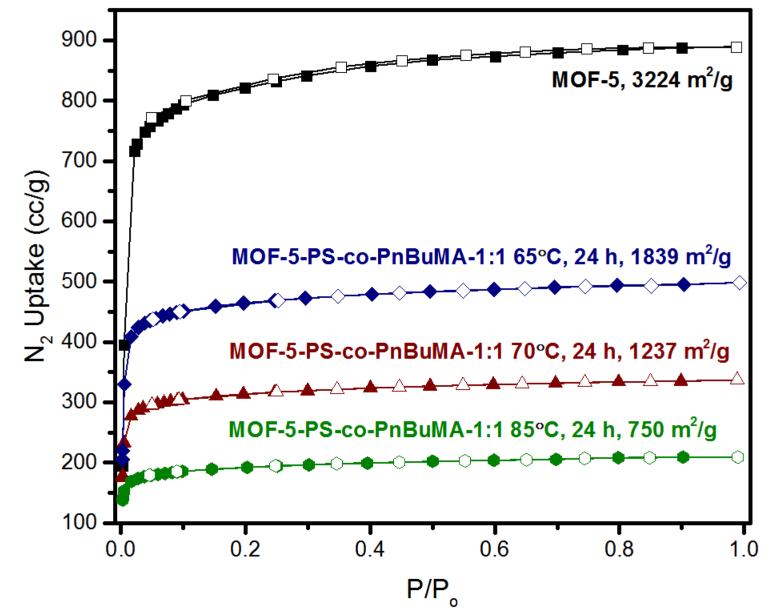
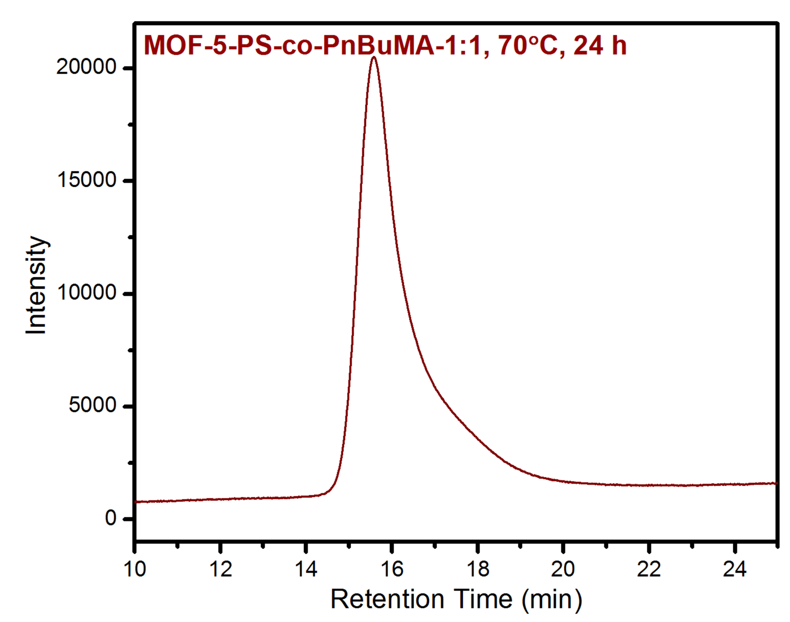


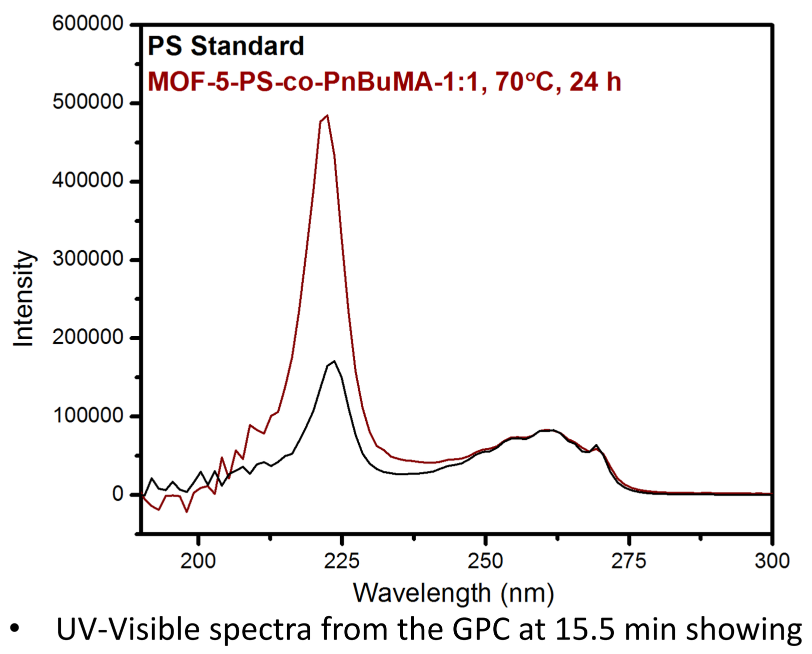
- TGA showing the depolymerization of PS-co-PnBuMA at ~400 C and subsequent thermal decomposition of MOF-5



- N_2 adsorption isotherms and BET surface areas for MOF-5-PS-co-PnBuMA composites

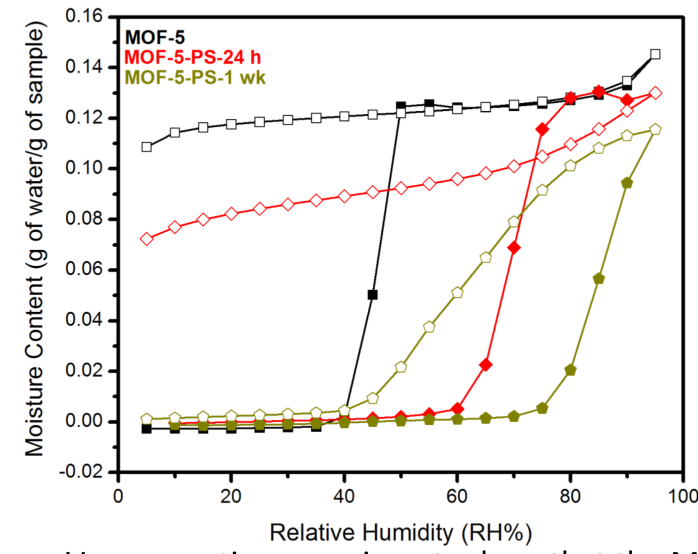


- GPC of extracted PS-co-PnBuMA (Mn = 595 kDa, Đ = 1.44)

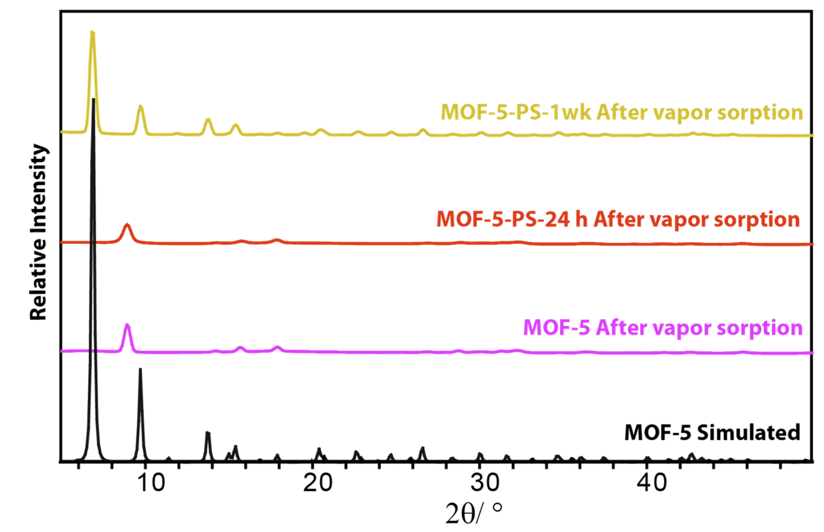


- UV-Visible spectra from the GPC at 15.5 min showing increase in the adsorption at ~221 nm indicative of the presence of a PnBuMA copolymer unit

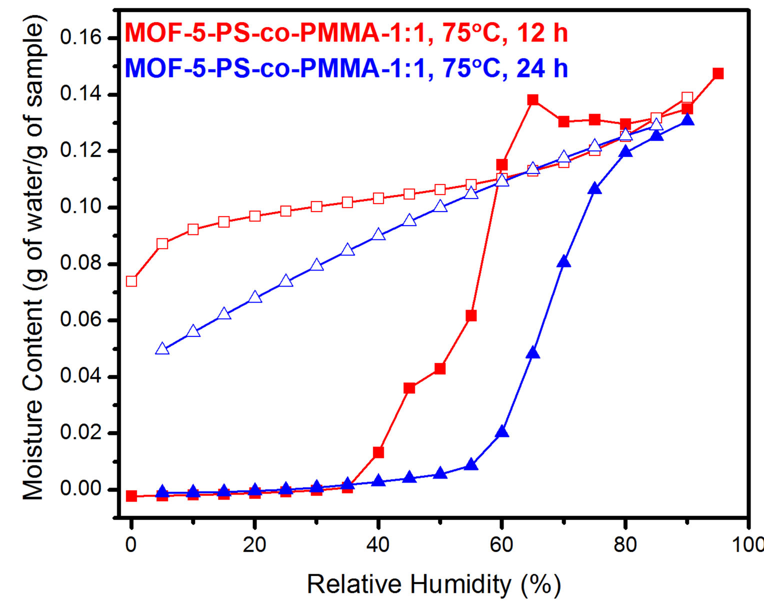
Water Stability



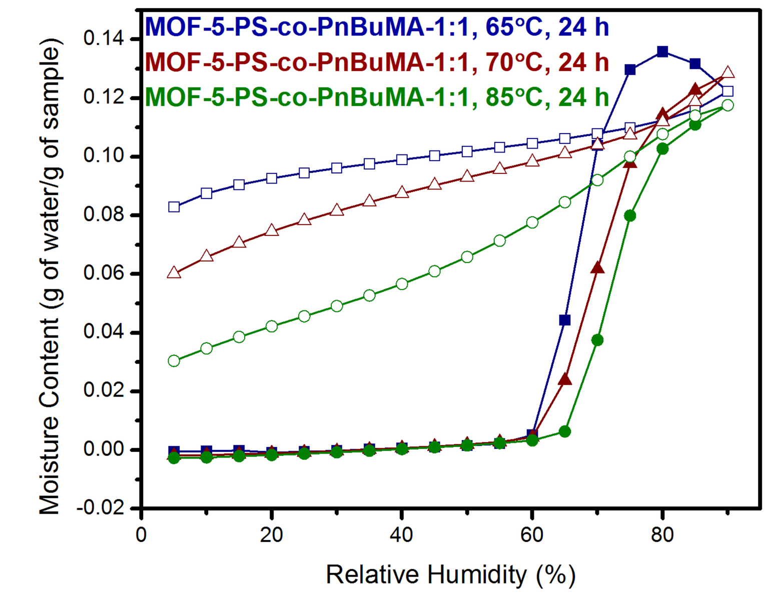
- Vapor sorption experiments show that the MOF-5-PS composites are significantly more hydrophobic than MOF-5



- PXRD confirms that only when the mass of adsorbed water is fully desorbed with decreasing relative humidity, the crystal structure is retained.

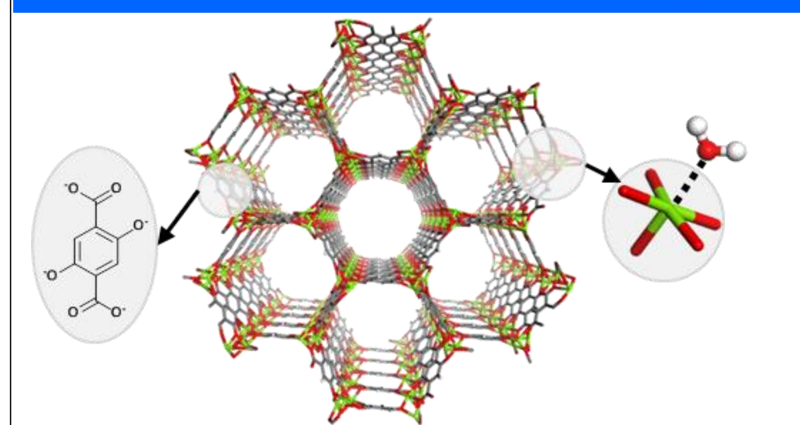


- Vapor sorption experiments of MOF-5-PS-co-PMMA show that the 24 h composite is more hydrophobic than the 12 h composite, consistent with more polymer incorporation

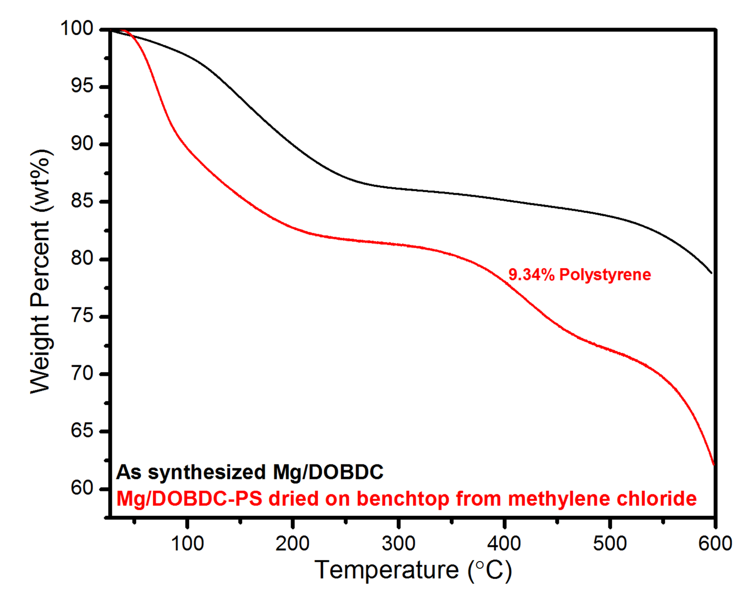


- Vapor sorption experiments of MOF-5-PS-co-PnBuMA show that the 85°C composite is slightly more hydrophobic that the other composites

Mg/DOBDC-PS



- Preliminary trials are in progress to synthesize a Mg/DOBDC-PS composite that is more hydrolytically stable. Mg/DOBDC has the highest CO_2 adsorption capacity among MOFs, but suffers from poor regeneration when exposed to humid environments[3]



- The presence of a peak at 1001 cm^{-1} by Raman Spectroscopy indicates that the aromatic breathing mode of PS is present

Conclusions and Future Directions

- We have shown that we can extend this polymer-MOF hybridization method to include copolymers
- This extension enables the generation of composites with varying functionality on the pore wall
- Further polymer characterization will verify the copolymer structure
- Future work will focus on copolymerizing styrene with other monomers to further enhance hydrolytic stability
- Optimize the approach to hybridization of Mg/DOBDC

Acknowledgements

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References:
[1]Li, H.; Eddaoudi, M.; O'Keefe, M.; Yaghi, O. M. Nature, 1999, 402, 276.
[2]Gamage, N.-D. H.; McDonald, K. A.; Matzger, A. J. Angew. Chem. Int. Ed. 2016, 55, 12099.
[3]Kizzie, A. C.; Wong-Foy, A. G.; Matzger, A. J. Langmuir 2011, 27, 6368.