Function through Form: The Development and Application of Polymer Composites of Metal-Organic Frameworks

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy

in

Chemistry

by

Michael Stephen Denny, Jr.

Committee in charge:

Professor Seth M. Cohen, Chair
Professor Olivia A. Graeve
Professor Tadeusz F. Molinski
Professor Jeffrey D. Rinehart
Professor Michael J. Sailor

2018
The Dissertation of Michael Stephen Denny, Jr. is approved, and it is acceptable in quality and form for publication on microfilm and electronically:

Chair

University of California San Diego

2018
To those that have spent their time and energy to foster my scientific curiosity and to teach me that there is a solution to every problem if we understand it properly, thank you. Especially to my first science teacher, VSD, who taught me the beauty of understanding the natural world and my first engineering teacher, MSD, who taught me that creative thinking can overcome even the most difficult problems, thank you.
Letting your mind play is the best way to solve problems. A playful mind is inquisitive, and learning is fun. If you indulge your natural curiosity and retain a sense of fun in new experience, I think you’ll find it functions as a sort of shock absorber for the bumpy road ahead.

Bill Waterson
TABLE OF CONTENTS

Signature Page........................................................................................................ iii

Dedication............................................................................................................. iv

Epigraph............................................................................................................ v

Table of Contents............................................................................................... vi

List of Figures..................................................................................................... ix

List of Tables...................................................................................................... xix

Acknowledgements............................................................................................ xx

Vita...................................................................................................................... xxii

Abstract of the Dissertation.............................................................................. xxv

Chapter 1............................................................................................................. 1

1.1 Metal-organic frameworks................................................................. 1

1.2 MOFs for Separation Technologies.................................................. 5

1.3 Membrane-based Separations......................................................... 8

1.4 MOF Membrane Fabrication Strategies....................................... 13

1.5 Scope of the Dissertation................................................................. 34

1.6 Acknowledgements.............................................................................. 35

1.7 References............................................................................................... 36
4.2 Co-cast MOF MMMs.......................................................... 122
4.3 Mixed MOF MMMs.......................................................... 123
4.4 Layered MOF MMMs........................................................ 128
4.5 Catalytic MOF Membranes............................................... 135
4.6 Conclusions........................................................................ 141
4.7 Appendix: Supporting Information.................................... 142
4.8 Acknowledgements............................................................ 160
4.9 References.......................................................................... 161

Chapter 5. ..................................................................................... 164

5.1 Introduction............................................................................ 164
5.2 Interfacial PSP of MOF-PA Composites.............................. 167
5.3 Prepolymer salt PSP of MOF-PA Composites...................... 180
5.4 Conclusions........................................................................... 189
5.5 Appendix: Supporting Information.................................... 190
5.6 References............................................................................. 193
LIST OF FIGURES

Figure 1.1. Metal-organic framework (MOF) diversity. The combination of multitopic ligands and inorganic SBUs gives rise to crystalline MOF structures. (Top) Combining Zn2+ (blue) with bdc (gray) gives the MOF-5 structure made up of Zn4 SBUs connected in a cubic arrangement, while the same metal combined with 2-methylimidazole... 3

Figure 1.2. Defects and dynamics in MOFs. a) Missing-linker type defects in MOFs are common and can lead to enlarged permeation pathways through the crystal network. b) Some MOFs exhibit flexible frameworks, allowing for differential pore size and shape based on environmental factors like temperature, pressure, and guest species........ 5

Figure 1.3. Membrane-based liquid separation processes. a) Filtration is driven by positive pressure on a mixed feed across a membrane, wherein species are rejected by the membrane that are too large to fit through the pore apertures. b) Pervaporation is a separation process by which species have different transport speeds across the...... 12

Figure 1.4. Fabrication methods for continuous MOF films. a) Solvothermal growth on a substrate immersed in the MOF precursor reaction mixture resulting in a surface-adhered MOF layer. b) A substrate is cycled between ligand and metal salt solutions, resulting in layer-by-layer growth of continuous MOF layers on the substrate surface............ 14

Figure 1.5. MOF MMM fabrication procedure. Typical MMM fabrication: a) An ink is prepared containing polymer solution and the MOF species. b) This ink is cast onto a surface via drawdown coating with a doctor blade. c) The casting solvent is removed via evaporation. d) The MMM is delaminated from the casting substrate to give a...... 22

Figure 1.6. Postsynthetic methods for MOF functionalization. a) Presynthetic functionalization incorporates a functional ligand into the MOF lattice during MOF crystal growth. b) Postsynthetic modification (PSM) uses organic chemistry techniques to functionalize a reactive handle on the MOF ligand within the preformed lattice. 28

Figure 1.7. Postsynthetic polymerization of MOFs. a) Membrane synthesis by PSP may be able to bridge the gap between pure-MOF membranes, which have near ideal selectivity, and MMMs, which are easily processed and have flexibility and durability from the polymer component. b) PSP requires MOFs that have chemically........ 32

Figure 2.1. MOF MMM fabrication process. A MOF/polymer ink is prepared and cast onto a substrate via drawdown coating with a doctor blade. The film is then heated to drive off casting solvent via evaporation. The resultant film is then delaminated from the substrate to give a free-standing MOF film................................................................. 49
Figure 2.2. MOF MMMs. a) Freestanding MMMs (~1 x 1 cm²) produced from a variety of canonical MOFs. b) Photographs demonstrating that large area (~3 x 5 cm²) HKUST-1, UiO-66, and MIL-53(Fe) MMMs are resilient to mechanical stress and can be easily handled.

Figure 2.3. SEM images of MMMs (~67% wt.). a) UiO-66, b) MIL-101(Cr), c) MIL-101(Fe), d) HKUST-1, e) MIL-53(Fe), f) ZIF-8.

Figure 2.4. SEM images of UiO-66 MMM (~67% wt.). a) UiO-66 MMM showing MOF microcrystal structure. b) Torn edge of UiO-66 MMM, clearly showing both the UiO-66 particles and PVDF polymer fibers. c) Cross section of UiO-66 MMM showing uniform thickness of approx. 35 μm. d) Higher magnification of cross section.

Figure 2.5. N₂ sorption isotherm of UiO-66 MMM. BET surface area: 693±4 m²/g. BET calculation based on only MOF content (~67% wt.): 1021±4 m²/g.

Figure 2.6. MOF MMM dye sorption. a) Dye sorption experiment for qualitative assessment of UiO-66 MMM (~67% wt.) porosity. Bottom: UiO-66 MMM as cast on Al foil, Left: UiO-66 MMM after soaking in Acid Orange 8 solution overnight, Top: UiO-66 MMM after soaking in Azure A solution overnight, Right: UiO-66 MMM after...

Figure 2.7. MOF MMM digestion. SEM images of: a) UiO-66 MMM; b) UiO-66 MMM after digestion with HF/DMSO solution to remove the MOF component, showing the intact porous polymer network with reliefs corresponding to the MOF microcrystals; c) Magnified section of 2.7b showing the clear relief of a polygonal MOF particle.

Figure 2.8. Postsynthetic reactions in MOFs. a) Postsynthetic exchange (PSE) of UiO-66 with NH₂-bdc. b) Postsynthetic modification (PSM) reaction of UiO-66-NH₂ with acetic anhydride. The octahedron is used to represent the MOF lattice, indicating that the reactions take place without degrading the overall MOF structure.

Figure 2.9. MOF MMM PSE. NMR spectrum of UiO-66 MMM (~67% wt.) after PSE with NH₂-bdc. Peak integration indicates 46% ligand exchange. (*) indicates peaks associated with NH₂-bdc product and (o) indicates peak of starting bdc ligand.

Figure 2.10. MOF MMM PSE PXRD spectra. PXRD spectra of UiO-66 MMM (67% wt.) before (red) and after (blue) PSE reaction with NH₂-bdc.

Figure 2.11. MOF MMM PSM. NMR spectrum of UiO-66-NH2 MMM (~67% wt.) after PSM with acetic anhydride. Peak integration indicates 75% modification to UiO-66-AM1. (*) indicates peaks associated with UiO-66-AM1 product and (o) indicates peak of starting NH₂-bdc ligand.
Figure 2.12. MOF MMM PSM PXRD spectra. UiO-66-NH$_2$ MMM (67% wt.) before (red) and after (blue) PSM reaction with acetic anhydride.

Figure 2.13. MOF MMM mechanical analysis. a) UiO-66 MMM (~67% wt.) during mechanical testing. 15 mm wide strip was tested in extension mode at 0.005 mm/s. b) Sample failure in mechanical testing. Failure point can be seen just below top clamp. c) Example of test strip after sample failure.

Figure 2.14. Ultimate tensile strength for MMMs with varying MOF % wt. Increasing MOF content reduces the ultimate tensile strength of the composite, giving a more brittle material.

Figure 2.15. Elastic modulus for MMMs with varying MOF % wt. The increase in elastic modulus with incorporation of 10-30% MOF is indicative of good adhesion between polymer and MOF particles.

Figure 2.16. Aqueous filtration with UiO-66 MMM. a) Removal of Coomassie Blue dye via filtration by a UiO-66 MMM. Top: Schematic showing the dye molecule in aqueous solution before filtration through the membrane and only water in the eluent. Bottom: Photograph of syringe pump driven experimental setup. The syringe contains......

Figure 2.17. Aqueous dye separation with UiO-66 MMM. a) Schematic for separation of Coomassie Brilliant Blue R-250 (blue) and Methyl Orange (orange) by filtration with a UiO-66 MMM. b) Separation of Coomassie Blue R-250 and Methyl Orange dye solution. The mixed solution is forced through a UiO-66 MMM syringe filter......

Figure 2S.1. Left: MMM prepared from direct dispersion of UiO-66 in PVDF/DMF solution shows poor MOF dispersion and agglomeration. Right: MMM prepared with predispersion of UiO-66 in acetone and subsequent addition of PVDF solution shows greatly enhanced uniformity and improved casting ability with reduced particle.....

Figure 2S.2. PXRD spectra of pristine UiO-66 and UiO-66-NH$_2$ MMM (~67% wt.).

Figure 2S.3. SEM images of UiO-66 MMM (67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.4. SEM images of UiO-66 MMM with 40% wt. MOF. a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.5. SEM images of UiO-66 MMM with 20% wt. MOF. a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.6. a) UiO-66-NH$_2$ MMM before PSM reaction, b) UiO-66-AM1 MMM after PSM reaction.

Figure 2S.7. PXRD spectra of pristine UiO-66 and UiO-66-NH$_2$ MMM (~67% wt.).
Figure 2S.8. $N_2$ sorption isotherm of UiO-66-NH$_2$ MMM. BET surface area: $430\pm 6$ m$^2$/g. BET calculation based on only MOF content (~67% wt.): $652\pm 9$ m$^2$/g. 

Figure 2S.9. SEM images of UiO-66-NH$_2$ MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications. 

Figure 2S.10. PXRD spectra of as-synthesized MIL-53(Fe) and MIL-53(Fe) MMM (~67% wt.). 

Figure 2S.11. SEM images of MIL-53(Fe) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications. 

Figure 2S.12. PXRD spectra of as-synthesized MIL-101(Fe) and MIL-101(Fe) MMM (~67% wt.). 

Figure 2S.13. SEM images of MIL-101(Fe) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications. 

Figure 2S.14. PXRD spectra of as-synthesized MIL-101(Cr) and MIL-101(Cr) MMM (~67% wt.). 

Figure 2S.15. $N_2$ sorption isotherm of MIL-101(Cr) MMM. BET surface area: $1323\pm 8$ m$^2$/g. BET calculation based on only MOF content (~67% wt.): $2002\pm 12$ m$^2$/g. 

Figure 2S.16. SEM images of MIL-101(Cr) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications. 

Figure 2S.17. PXRD spectra of as-synthesized HKUST-1 and HKUST-1 MMM (~67% wt.). 

Figure 2S.18. $N_2$ sorption isotherm of HKUST-1 MMM. BET surface area: $892\pm 6$ m$^2$/g. BET calculation based on only MOF content (~67% wt.): $1353\pm 9$ m$^2$/g. 

Figure 2S.19. SEM images of HKUST-1 MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications. 

Figure 2S.20. PXRD spectra of as-synthesized ZIF-8 and ZIF-8 MMM (~67% wt.). 

Figure 2S.21. $N_2$ sorption isotherm of ZIF-8 MMM. BET surface area: $870\pm 8$ m$^2$/g. BET calculation based on only MOF content (~67% wt.): $1317\pm 12$ m$^2$/g. 

Figure 2S.22. SEM images of ZIF-8 MMM. (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.
Figure 3.1. HKUST-1 MMM Fabrication.  a) 3-dimensional lattice structure of HKUST-1 and the coordinateively unsaturated sites on the Cu-paddlewheel SBU.  b) Schematic representing the MMM fabrication process, see Chapter 2 for details.  c) Photograph showing the flexibility of the HKUST-1 MMM.  d) Plan-view and e) cross...........  91

Figure 3.2. N\textsubscript{2} isotherms of HKUST-1 MMMs.  BET surface area and total N\textsubscript{2} capacity correlate to the MOF content of each MMM.  BET surface areas = HKUST-1 (1324 m\textsuperscript{2}/g), 67-HKUST-1 MMM (1025 m\textsuperscript{2}/g), 50-HKUST-1 MMM (861 m\textsuperscript{2}/g), and 30-HKUST-1 MMM (373 m\textsuperscript{2}/g)……………………………………………………….. 93

Figure 3.3.  PXRD spectra of HKUST-1 MMMs. The HKUST-1 MMM PXRD spectra are compared to HKUST-1 powder and PVDF……………………………………. 94

Figure 3.4. FTIR spectra of HKUST-1 MMMs. The FTIR spectra of the MOF MMMs are compared to HKUST-1 powder and PVDF……………………………………... 94

Figure 3.5. Microbreakthrough data. Microbreakthrough curves comparing PVDF polymer, HKUST-1 MMMs, and HKUST-1 powder……………………………………… 96

Figure 3.6.  PXRD spectra after ammonia exposure.  PXRD spectra of the HKUST-1 MMMs compared to HKUST-1 powder and PVDF after exposure to ammonia. The major reflections from the ammonia exposed HKUST-1 powder (green), are designated with lines at 2\textdegree = 14.8, 15.6, 16.2, 18.1, 19.9, 21.6, 22.1, 25.3, and 27.0°............. 98

Figure 3.7.  FTIR spectra after ammonia exposure.  FTIR spectra of the HKUST-1 MMMs compared to HKUST-1 powder and PVDF after exposure to ammonia..... 99

Figure 3.8 Ammonia sorption vs. aging.  Ammonia loading for HKUST-1 powder and HKUST-1 MMMs.  Different HKUST-1 loadings after aging at 90\% RH and 25 °C for various amounts of time are shown…………………………………………………… 101

Figure 3.9.  PXRD spectra vs. aging.  PXRD patterns of 30-HKUST-1, 50-HKUST-1, and 67-HKUST-1 MMMs, compared to HKUST-1,31 aged for 0, 1, 3, 7, 14, and 28 days at 90\% RH at 25 °C…………………………………………………………………… 102

Figure 3.10.  HKUST-1 FTIR vs. aging.  FTIR spectra of HKUST-1 powder before and after aging at 90\% RH at 25 °C for 1, 3, 7, 14, and 28 days………………………………….. 103

Figure 3.11.  30-HKUST-1 MMM FTIR vs. aging.  FTIR spectra of 30-HKUST-1 MMM before and after aging at 90\% RH at 25 °C for 1, 3, 7, 14, and 28 days……….. 103

Figure 3.12.  50-HKUST-1 MMM FTIR vs. aging.  FTIR spectra of 50-HKUST-1 MMM before and after aging at 90\% RH at 25 °C for 1, 3, 7, 14, and 28 days…………….. 104

Figure 3.13.  67-HKUST-1 MMM FTIR vs. aging.  FTIR spectra of 67-HKUST-1 MMM before and after aging at 90\% RH at 25 °C for 1, 3, 7, 14, and 28 days…………….. 104
Figure 3.14. Physical appearance vs. aging. Photographs of each HKUST-1 MMM after aging for 0, 1, 3, 7, 14, and 28 days at 90% RH and 25 °C .................................................. 105

Figure 3.15. Microscale appearance vs. aging. SEM images of each HKUST-1 MMM, on the outward-facing (MOF dominant) side and substrate-facing (polymer dominant) side, after aging for 0, 1, 3, 7, 14, and 28 days, at 90% RH and 25 °C ............................................... 106

Figure 3.16. Water isotherm data (uncorrected). Water isotherms collected at 25°C for HKUST-1 powder and the HKUST-1 MMMs ............................................................... 108

Figure 3.17. Water isotherm data (corrected). Water isotherms collected at 25°C for the HKUST-1 powder and the HKUST-1 MMMs. MMM data are adjusted for the amount of HKUST-1 present in the composite .................................................. 109

Figure S3.1. Ammonia breakthrough curved 30-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C .......................................................... 113

Figure S3.2. Ammonia breakthrough curved 50-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C .......................................................... 114

Figure S3.3. Ammonia breakthrough curved 67-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C .......................................................... 114

Figure 4.1. Strategies for multifunctional MOF MMMs. a) Co-casting different MOF inks results in MMMs with different MOF species spatially separated in the same monolithic MMM. The resulting MOF MMMs can be of two types: (left) simple discrete regions or (right) patterned MOF distribution. b) Mixing MOF species .................................................. 121

Figure 4.2. Mixed MOF MMMs. A variety of MOF MMMs have been fabricated from mixed MOF inks. The MMM in each cell is a mixture of the MOF species identified in the corresponding row and column. Each MMM is 60% wt. total MOF, combined in a 1:1 ratio by weight .................................................. 124

Figure 4.3. HKUST-1 + UiO-66 MMM. a) 60% wt. HKUST-1 MMM. b) 60% wt. UiO-66 MMM. c) Mixed HKUST-1 and UiO-66 MMM (60% wt. total MOF) in a 1:1 ratio. d) PXRD spectra of the UiO-66 MMM (black), HKUST-1 MMM (blue), and the mixed MOF MMM (cyan), which displays peaks from both the UiO-66 and HKUST-1... 125

Figure 4.4. Pore accessibility of the mixed MOF MMM. N₂ sorption isotherms of 50% UiO-66 MMM (black), 50% HKUST-1 MMM (blue), and the mixed MOF MMM (purple). BET surface areas = UiO-66 (577 m²/g), HKUST-1 (888 m²/g), and mixed MOF MMM (537 m²/g) .................................................. 127

Figure 4.5. SEM images of 50% wt. mixed MOF MMM. The 50% wt. HKUST-1 + UiO-66 mixed MMM was observed in the SEM. a) Plane-view images of the MMM surface show both MOF species are well distributed. b) A closer magnification of the MMM surface distinctly shows both the large HKUST-1 particles and the smaller .......... 128
Figure 4.6  Resolvation for multilayer MMMs.  a) Photograph of the top side of a two layer MOF MMM, UiO-66 first layer, HKUST-1 second layer.  b) Reverse image of the same film.  c) Cross section SEM of this film.  Smaller UiO-66 particles make up the bottom layer in this image, while larger HKUST-1 particles are exclusively in.......

Figure 4.7  Large area layered MMM.  a) Photograph of the top side of a two layer MOF MMM, ZIF-8 first layer, HKUST-1 second layer.  b) Reverse image of the same film.  c) Cross section SEM of this film.  Smaller ZIF-8 particles make up the bottom layer in this image, while larger HKUST-1 particles are exclusively in the top layer.............

Figure 4.8.  Triple-layer MOF MMM.  Cross section SEM of the triple layer MOF MMM. The bottom layer of this MMM is ZIF-8, followed by UiO-66, and the top layer is HKUST-1.  b) SEM-EDX Cu-map showing the Cu is localized in the top layer of the MMM, tracking with the HKUST-1 particles.  c) SEM-EDX Zr-map showing........

Figure 4.9.  MOF MMM catalyzed reactions.  (a) The conversion of benzaldehyde dimethylacetal to benzaldehyde is acid catalyzed.  (b) The Knoevenagel condensation of benzaldehyde with malonitrile

Figure 4.10.  Reaction monitoring by $^1$H NMR.  The reactions may be monitored by following the benzylic proton in each product (blue).  In the benzaldehyde dimethylacetal starting material, this proton is a singlet at 5.35 ppm (red trace).  After the acid catalyzed reaction, this proton on benzaldehyde is a singlet at 9.93 ppm (green trace)........

Figure 4.11.  UiO-66-NH$_3^+$Cl$^-$ MMM catalysis at 60 °C.  The reaction shows complete conversion of the starting material, with 87% of the desired product and 13% of the Knoevenagel condensation product............................................

Figure 4.12.  ZIF-8 MMM catalyzed Knoevenagel condensation at room temperature.  $^1$H NMR analysis of the eluent shows that 95% of the benzaldehyde successfully reacted with malonitrile, catalyzed by the ZIF-8 MMM at room temperature..............

Figure 4.13.  UiO-66-NH$_3^+$Cl$^-$ and ZIF-8 MMM catalyzed reactions at 60 °C.  $^1$H NMR analysis of the eluent shows that 53% of the starting material successfully reacted to form the final product over two steps in the membrane reactor..........................
Figure 4S.2. a) 60% wt. HKUST-1 MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. HKUST-1 + UiO-66 MMM. d) PXRD spectra for each MMM. e, f) SEM images of the HKUST-1 + UiO-66 MMM. The large particles are HKUST-1 and the small particles are UiO-66.

Figure 4S.3. a) 60% wt. HKUST-1 MMM. b) 60% wt. MIL-101(Fe) MMM. c) 60% wt. HKUST-1 + MIL-101(Fe) MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the HKUST-1 + MIL-101(Fe) MMM. The large particles are HKUST-1 and the small particles are MIL-101(Fe).

Figure 4S.4. a) 60% wt. HKUST-1 MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. HKUST-1 + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the HKUST-1 + MIL-53(Fe) MMM. The large, anisotropic particles are MIL-53(Fe) and the smaller, octahedral particles are HKUST-1.

Figure 4S.5. a) 60% wt. ZIF-8 MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. ZIF-8 + UiO-66 MMM. d) PXRD spectra for each MMM. e, g) Plan-view and f, h) cross section SEM images of the ZIF-8 + UiO-66 MMM.

Figure 4S.6. a) 60% wt. MIL-101(Fe) MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. MIL-101(Fe) + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the ZIF-8 + UiO-66 MMM.

Figure 4S.7. a) 60% wt. MIL-53(Fe) MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. MIL-53(Fe) + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the MIL-53(Fe) + UiO-66 MMM. The large particles are MIL-53(Fe) and the small particles are UiO-66.

Figure 4S.8. a) 60% wt. MIL-53(Fe) MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. MIL-53(Fe) + ZIF-8 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the MIL-53(Fe) + ZIF-8 MMM. The large particles are MIL-53(Fe) and the small particles are ZIF-8.

Figure 4S.9. a) 60% wt. MIL-101(Fe) MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. MIL-101(Fe) + ZIF-8 MMM. d) PXRD spectra for each MMM. e, g) Plan view and f, h) cross section SEM images of the MIL-101(Fe) + ZIF-8 MMM. The octahedral particles are MIL-101(Fe) and the small particles are ZIF-8.

Figure 4S.10. a) 60% wt. MIL-101(Fe) MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. MIL-101(Fe) + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e, g) Plan view and f, h) cross section SEM images of the MIL-101(Fe) + MIL-53 MMM. The large particles are MIL-53(Fe) and the small particles are MIL-101(Fe).

Figure 4S.11. a) 60% wt. UiO-66-NH₂ MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. UiO-66-NH₂ + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH₂ + UiO-66 MMM.
Figure 4S.12.  a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. UiO-66-NH$_2$ + ZIF-8 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + ZIF-8 MMM.

Figure 4S.13.  a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. HKUST-1 MMM. c) 60% wt. UiO-66-NH$_2$ + HKUST-1 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + HKUST-1 MMM.

Figure 4S.14.  a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. MIL-101(Fe) MMM. c) 60% wt. UiO-66-NH$_2$ + MIL-101(Fe) MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + MIL-101(Fe) MMM.

Figure 4S.15.  a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. UiO-66-NH$_2$ + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + MIL-53(Fe) MMM.

Figure 5.1. Postsynthetic polymerization. The MOF particles with reactive handles (blue) are integrated into the growing polymer chains during polymerization of the monomer (pink), forming a covalently integrated MOF-polymer composite.

Figure 5.2. Polyamides. a) Polyamide bond formation is typically achieved through reaction of a carboxylic acid with a primary amine (top) or the more reactive acyl chloride with a primary amine (bottom). b) Aliphatic amines can be prepared from a single, doubly functionalized monomer, as in PA-6, or by condensation.

Figure 5.3. MOF-PA fabrication. a) Reaction of UiO-66-NH$_2$ with adipoyl chloride yields a MOF particle decorated with acyl chlorides on the surface. Reaction of this species with HMDA elongates the aliphatic polymer chains via formation of a second amide bond, leaving the particle surface presenting the amine functionality.

Figure 5.4. MOF crystallinity. a) PXRD spectra of the MOF-PA series. b) 80 mg UiO-66-NH$_2$ sample. c) 160 mg UiO-66-NH$_2$ sample.

Figure 5.5. Non-uniform MOF incorporation. a) PXRD spectra of the MOF-polymer fiber at various points along the fiber length. b) TGA traces of the MOF-polymer fiber at various points along the fiber length. Both analyses show high MOF content at the beginning of the fiber and a consistent reduction of MOF content along its length.

Figure 5.6. MOF-PA composite porosity. The N$_2$ sorption isotherms are shown for UiO-66-NH$_2$ (black) and the 80 mg UiO-66-NH$_2$ sample. The composite sample shows extremely low accessible porosity (BET surface area = 25 m$^2$/g) vs. the native MOF (BET surface area = 1128 m$^2$/g).

Figure 5.7. SEM analysis of MOF-PA composites. SEM images of the surfaces of a) PA-66, b) 5 mg UiO-66-NH$_2$ sample, c) 10 mg UiO-66-NH$_2$ sample, d) 20 mg UiO-66-NH$_2$ sample, e) 40 mg UiO-66-NH$_2$ sample, and f) 80 mg UiO-66-NH$_2$ sample.
Figure 5.8. DSC analysis of MOF-PA composites. DSC traces for PA-66 and composite samples ranging from 5 mg MOF to 160 mg MOF heated to 300 °C at 10 °C/min. The pure PA-66 and samples up to 10 mg UiO-66-NH₂ show melting events; the remaining samples do not.

Figure 5.9. Ethyl acetate preparation. PXRD spectra of the MOF-PA series at different MOF loading levels.

Figure 5.10. SEM analysis of MOF-PA composites. SEM images of the surfaces of a) PA-66, b) 20 mg UiO-66-NH₂ sample, c) 40 mg UiO-66-NH₂ sample, d) 60 mg UiO-66-NH₂ sample, e) 80 mg UiO-66-NH₂ sample, and f) 1000 mg UiO-66-NH₂ sample.

Figure 5.11. MOF-PA composite using suberoyl chloride and DETA monomers. a) Photograph showing that the product formed as thin ribbons of MOF-polymer composite. b-f) SEM images of the product showing a polymer ribbon decorated with the UiO-66-NH₂ particles at varying magnification. Low magnification shows that there.

Figure 5.12. Prepolymer salt preparation. Instead of progressing directly from co-monomers to the finished polymer by pathway A, the prepolymer salt is first prepared via pathway B. This salt can then be polymerized to the final product by pathway C.

Figure 5.13. PXRD spectra of co-precipitated MOF and nylon salt. The co-precipitation products of the nylon salt (black) and UiO-66-NH₂ (dark blue) are shown. The co-precipitation samples show peaks consistent with both species.

Figure 5.14. DSC traces of the co-precipitated MOF and nylon salt.

Figure 5.15. PXRD spectra of nylon salt and UiO-66-NH₂ before and after melting. The nylon salt upon polymerization displays two broad peaks at $2\theta = 20^\circ$ and $24^\circ$ which are also observed in the 50 mg UiO-66-NH₂ sample after polymerization along with the intact MOF peaks.

Figure 5.16. DSC traces of the ground UiO-66-NH₂/nylon salt mixtures.

Figure 5.17. SEM images of the ground UiO-66-NH₂/nylon salt mixtures. 5 mg UiO-66-NH₂ sample a) before and b) after thermal treatment. 10 mg UiO-66-NH₂ sample c) before and d) after thermal treatment. 25 mg UiO-66-NH₂ sample e) before and f) after thermal treatment. 50 mg UiO-66-NH₂ sample g) before and h) after thermal.
LIST OF TABLES

Table 2.1. MOF MMM mechanical properties. Mechanical properties of UiO-66 MMMs at various MOF loadings. 61

Table 3.1. Ammonia Loading Capacity. Experimentally measured and hypothetical ammonia loadings for the HKUST-1 powder, HKUST-1 MMMs, and PVDF control. 97

Table 3.2. Contact angle data. Contact angles for each HKUST-1 MMM measured on the outward facing (MOF dominant) and substrate facing (polymer dominant) side. 107

Table 5.1. MOF loading of co-precipitated nylon salt. 182

Table 5.2. Peak data for DSC traces in Figure 5.12. 184

Table 5.3. MOF content in the ground UiO-66-NH₂/nylon salt mixtures. 186

Table 5.4. Peak data for DSC traces in Figure 5.14. 187
ACKNOWLEDGEMENTS

I would first like to acknowledge Professor Seth M. Cohen for his support as my advisor and chair of my committee. His guidance and encouragement have helped me grow immeasurably as a scientist.

Secondly, I would like to acknowledge my many collaborators and coworkers in the Cohen lab. Their friendship and helpful discussion over the course of this work has made the work of science both exciting and enjoyable.

I would also like to acknowledge my external collaborators for helping to shape my science for real applications. Especially of note are Jared B. DeCoste and Gregory W. Peterson of the Edgewood Chemical Biological Center. They have been truly excellent scientists with whom to collaborate.

I wish to express my sincere gratitude to my wonderful friends which whom I have had the privilege of sharing this graduate school journey. You have made the journey so much more fun.

Finally, the unwavering support of K.M.G. has been a source of strength when the challenges seemed insurmountable. Thank you for being your silly, wonderful self.

Chapter 1, in part is a reprint of the material as it appears in “Metal-organic frameworks for membrane-based separations.” Nat. Rev. Mater., 2016, 1, 16078. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthors, Jessica C. Moreton, Lauren Benz, and Seth M. Cohen.
Chapter 2, in part is a reprint of the material as it appears in “In Situ Modification of Metal-Organic Frameworks in Mixed-Matrix Membranes.” *Angew. Chem., Int. Ed.*, 2015, 54, 31, 9029-9032. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthor and advisor, Seth M. Cohen.

Chapter 3, in part is a reprint of the material as it appears in “Enhanced aging properties of HKUST-1 in hydrophobic mixed-matrix membranes for ammonia adsorption.” *Chem. Sci.*, 2016, 7, 2711-2716. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthors, Jared B. DeCoste, Gregory W. Peterson, John J. Mahle, and Seth M. Cohen.

Chapter 4, in part is currently being prepared for submission for publication of the material. The dissertation author was the primary author of this material and gratefully acknowledges the contributions of his coauthor and advisor, Seth M. Cohen.
VITA

Education

2007 Bachelor of Chemistry, Villanova University
2007 Bachelor of Biochemistry, Villanova University
2008 Nanofabrication Manufacturing Technologies Certification, The Pennsylvania State University
2014 Master of Science, University of California San Diego
2018 Doctor of Philosophy, University of California San Diego

Professional Research


Honors and Awards

2016 Distinguished Graduate Student Fellowship
UC San Diego Department of Chemistry & Biochemistry
2015-2017 ARCS Scholar
2012-2013 Harold Urey Fellowship
Publications and Patents


Presentations


ABSTRACT OF THE DISSERTATION

Function through Form: The Development and Application of Polymer Composites of Metal-Organic Frameworks

by

Michael Stephen Denny, Jr.

Doctor of Philosophy in Chemistry

University of California San Diego, 2018

Professor Seth M. Cohen, Chair

Metal-organic frameworks (MOFs) are a diverse class of porous materials that hold great promise for providing low-cost solutions in a wide range of applications. Their native, powdered form, however limits their inherent utility. Through fabrication
of polymer composites, these materials can be prepared in engineered forms that exploit
the useful attributes of MOFs in application-ready forms.

MOFs that are fabricated into membranes are an especially useful form factor for
these engineered materials. Chapter 2 describes the development of mixed matrix
membranes (MMMs) with a variety of MOF species. The work shows that the inherent
porosity and chemical tunability of the MOFs is retained when prepared in the composite
MMM, providing a material that effectively exploits the MOF properties while enhancing
the ease of handling and implementation of the MOF material.

Chapter 3 shows that not only are the MOF properties retained in the MMM, but
that fabrication of the composite material can actually enhance the stability of the MOF
in the MMM. A copper-based MOF (HKUST-1) is explored for personal protection
against toxic industrial chemicals due to its strong ammonia adsorption behavior. While
the native MOF displays high uptake initially, it is unstable and degrades rapidly even in
ambient moisture. The MOF in the MMM, however, remains highly active even after
aging under harsh conditions for a month.

Chapter 4 details various methods for incorporating multiple MOF species into a
single MMM for multifunctional materials. Methodologies for fabricating spatially
segregated MOF species, fully mixed MOF species, and layered MOF species are
described, as well as incorporation ad activation of a cross-linking agent in the MMM
formulation to improve the range of solvent tolerance.
In Chapter 5, a method for producing melt-processable, covalently integrated MOF-polymer composites is described. Using a postsynthetic polymerization strategy, MOF particles are incorporated into polyamide chains to generate a next generation MOF-polymer composite material. Multiple polymer syntheses are investigated and the materials are shown to retain the MOF crystallinity and polymer melt characteristics in the composite materials.
Chapter 1

Introduction to Metal-Organic Frameworks and their Composite Materials

1.1 Metal-organic frameworks

Metal-organic frameworks (MOFs) are a class of porous, crystalline solids composed of inorganic nodes, termed “secondary building units” (SBUs) connected by multitopic organic ligands (Figure 1.1). These solids are prized for their regular and highly-tunable open-pore structures\(^1\) and can display enormous variability in SBU structure, linker topology, connectivity, and chemical functionality. First reported by Hoskins and Robson\(^2\) in 1990, early structures were formed from discrete metal-clusters linked via multitopic ligands, thus bridging the molecular species to form crystalline materials. Structures of this type were termed MOFs in 1995\(^3\) in a landmark publication by the Yaghi research group due to the hybrid nature of these regular, 3-dimensional structures. In the subsequent two decades, studies of these materials have moved beyond the simply synthesis and characterization of ever more diverse structures towards more applied research seeking to exploit the properties of MOFs for industrial processes. The variety of MOF topologies accessible (i.e. pore shapes and sizes) combined with relatively facile chemical modification makes MOFs attractive for a range of such applications, including, but not limited to, heterogeneous catalysis,\(^4\) gas storage,\(^5\) and drug delivery.\(^6\) Perhaps the most touted property of MOFs is their high surface area and consequent high capacity for storage of gasses. Indeed, MOF species are readily prepared with measured apparent surface areas of thousands of square meters per gram (m\(^2\)/g), the equivalent of multiple American football fields in a single gram of material.
The high capacity for gas storage in MOFs was famously exhibited in 2007 on a publicity tour by the EcoFuel World Tour team that completed a 28,000 mile journey across five continents in an automobile using MOF-enhanced fuel storage technology.\textsuperscript{7-8}

Figure 1.1 illustrates some of the key aspects of MOF materials. As stated above, MOFs are hybrid organic/inorganic crystalline materials, characterized by open, porous structures. Metal ions or metal ion clusters form the inorganic nodes (SBUs) of the MOF structure and these SBUs are bridged by multitopic organic ligands in regular, geometric patterns. MOF structures can thus be represented as simplified nets of connected nodes, as in Figure 1.1, to clearly show the repeating crystalline structures. In the figures below, SBUs are represented by colored spheres and the connecting ligands are depicted as lines. The high diversity of SBUs and ligand connectivity in MOFs allows for extremely variant networks from relatively simple components. For example, combining Zn\textsuperscript{2+} (blue) with 1,4-benzenedicarboxylic acid (H\textsubscript{2}bdc) (gray) yields MOF-5 (Figure 1.1, upper left), but the same metal with a different ligand (2-methylimidazole) (pale green) gives the ZIF-8 structure (Figure 1.1, upper right). Similarly, the same ligand (H\textsubscript{2}bdc) that leads to MOF-5 with Zn\textsuperscript{2+}, gives a completely different structure when combined with a Zr\textsuperscript{4+}-based SBU (green), known as UiO-66. Pore size can be controlled by changing the ligand size, but keeping the same metal-to-ligand connectivity, as in the UiO-66/67 pair (bottom), wherein the 4,4'-biphenyldicarboxylic acid (yellow) is used to expand the node-to-node distance of the structure. MOFs with the same connectivity but bearing different ligand functionality, metal-species, or pore size, like the UiO-66/67 pair, are said to be isoreticular.\textsuperscript{9} Isoreticular families of MOFs allow researchers to probe the effects of each
component of the MOF crystal individually. For example, MOF species that are structurally identical, but having different metal species in the SBU differ widely in their chemical and thermal stabilities and binding affinity for guest species, while appending functionality to the bridging ligand may add catalytic behavior to an otherwise inert MOF species.

**Figure 1.1. Metal-organic framework (MOF) diversity.** The combination of multitopic ligands and inorganic SBUs gives rise to crystalline MOF structures. *(Top)* Combining Zn$^{2+}$ (blue) with bdc (gray) gives the MOF-5 structure made up of Zn$_4$ SBUs connected in a cubic arrangement, while the same metal combined with 2-methylimidazole (pale green) results in a sodalite topology with SBUs consisting of a single Zn$^{2+}$ ion. *(Bottom)* Isoreticular expansion of the MOF structure is seen in the UiO-66/67 series. The same 12-connected Zr$_6$ SBU (green) is used to give the same structure in both species, but the ligand is elongated in the UiO-67, resulting in a larger framework with correspondingly larger pores. Figure reproduced from reference 12.
Judicious choice of SBU and ligand can give rise to relatively simple MOF structures, as shown here in MOF-5 (a.k.a IRMOF-1), or complex connectivity with multiple pore sizes and shapes. In one computational study, 137,953 possible MOF structures were predicted through a combination of different SBUs and ligands.\textsuperscript{13} Beyond the geometric design of the pores, functionalization at the SBU and the bridging ligands through chemical methods allows the MOF pore environment to be further tailored for a given application through pre- and postsynthetic means.

It is important to note that most MOFs synthesized under experimental conditions are not crystallographically perfect. While the overall structure may be mostly complete, defects within the lattice do happen during most crystal growth processes. In particular, missing-linker defects in MOFs are common in MOF syntheses that use chemical modulators to control crystal growth (Figure 1.2a). In short, these chemical modulators bind to the MOF SBUs during growth and remain bound, inhibiting attachment of the MOF ligand to the node, resulting in a missing connection between adjacent SBUs. If the lattice can tolerate this missing connection, the crystal continues to grow, leaving a defect site where the ligand should be. These missing linkers result in enlarged pore windows in the lattice that may allow entry to chemical species that would otherwise be too large to enter the pore. A high density of missing linkers will thus create enlarged permeation pathways through MOF crystals. These defects may be beneficial for catalytic processes, since they can provide additional reactive sites for chemical transformations.

Additionally, MOFs, while crystalline, can be dynamic structures. Indeed, ligand lability within the framework is routinely exploited to perform postsynthetic
functionalization\textsuperscript{14} of MOFs, giving modified versions of the parent framework while maintaining a crystalline architecture. Moreover, the entire crystalline network may exhibit flexibility or “breathing” modes.\textsuperscript{15} For example, flexibility in MOF pores is exhibited in the prototypical MIL-53 structure, which shows ready transition between narrow pore (Figure 1.2b, \textit{left}) and large pore (Figure 1.2b, \textit{right}) forms of the crystal. Flexibility in MOF structures can be induced through a variety of environmental factors like temperature, pressure, and guest species.\textsuperscript{15}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure12}
\caption{Defects and dynamics in MOFs. a) Missing-linker type defects in MOFs are common and can lead to enlarged permeation pathways through the crystal network. b) Some MOFs exhibit flexible frameworks, allowing for differential pore size and shape based on environmental factors like temperature, pressure, and guest species. Figure reproduced from reference 12.\textsuperscript{12}}
\end{figure}

1.2 MOFs for Separation Technologies

Technologies exploiting the activity of MOFs have tremendous potential for separation applications across various form factors. This has been successfully demonstrated using packed-bed systems for selective adsorption to effect chemical separations,\textsuperscript{16} particularly for CO\textsubscript{2} capture and storage.\textsuperscript{17-18} Although simple packed-beds
are a good system for adsorption-based separations wherein the species of interest is sequestered within the pressed-pellets and later released in the regeneration cycle, other types of separations are not possible with a packed-bed setup and require alternative technologies to exploit the separation abilities of the MOFs. MOF-based membranes provide an alternative separation platform with the potential for continuous separation processes. Continuous separations are advantageous because they could simplify system design by alleviating the requirement for cycling between adsorptive and desorptive states that are required for packed beds. This would consequently reduce infrastructure costs by eliminating the need for parallel redundant systems required for continuous operation while a bed is regenerated. Moreover, membranes are highly versatile, with filtration and pervaporation processes offering low-energy alternatives to current distillation technologies, providing a further opportunity for operating cost reduction.

In membrane-based separations, judicious selection of MOFs with pores of appropriate size, shape, and local chemical environment could allow for separations with high fidelity, while still permitting high membrane flux, i.e. rapid permeate transport across the membrane.

Compared to membranes based on other porous materials such as zeolites (porous aluminosilicates), the field of MOF-based membranes is not well developed. This is due, at least in part, to the comparatively more recent emergence of MOFs than zeolites as a field of study. Additionally, the majority of early MOFs were limited by poor chemical stability; even ambient moisture would result in degradation of many early frameworks. This shortcoming has now been largely resolved with many chemically-
robust, water-stable MOFs reported in the literature.\textsuperscript{22} Having overcome these deficiencies, MOFs may provide advantages for use in membrane separations compared to zeolites (all inorganic porous materials) or porous organic polymers (all organic porous materials). This is, in part, because MOFs offer greater structural diversity than zeolites and can exhibit surface areas greater than any other inorganic solid; indeed, MOF species with surface areas up to 7,000 m$^2$ g$^{-1}$ have been successfully synthesized.\textsuperscript{23} MOFs are thus well positioned to perform separations not readily achieved by other materials.\textsuperscript{5, 24}

In addition, the combination of organic and inorganic components that compose the MOF lattice, and the development of postsynthetic modification strategies,\textsuperscript{14} makes MOFs highly tunable with respect to physical and chemical properties. This tunable functionality is currently beyond the reach of either all-organic or all-inorganic porous materials. The rich diversity in MOF structure and functionality suggests that these hybrid materials will continue to offer advantages over other inorganic films and inorganic-doped membranes\textsuperscript{25} as the field is further developed.

MOFs can also provide a route to overcoming one of the more persistent hurdles plaguing separations in industrial settings. In short, separation technologies are typically plagued by a trade-off between performance and throughput; as separation performance improves, system throughput suffers and vice versa. In adsorption-based separations, this trade-off is between selectivity and adsorption capacity; more specifically, sorbents with a high capacity for a given species often do not demonstrate good selectivity for the preferred species over others in a mixture. In contrast, a highly selective sorbent will be
hindered by a low sorption capacity, and hence, although the separation of species is very clean, the system throughput suffers since each cycle has a low yield.

In membrane systems, this performance trade-off is between the permeability and the selectivity of the membrane. Often referred to as Robeson’s ‘upper bound,’\textsuperscript{26-27} those membranes that demonstrate high permeability often have poor selectivity for the preferred species over others in the mixture. Conversely, highly selective membranes will exhibit poor permeability overall, limiting system throughput, just as in the packed-bed systems. This concept was first developed in the context of polymer membranes, with rubbery polymers having inherently higher permeability and glassy polymers demonstrating better selectivity.\textsuperscript{28} Single-polymer and blended-polymer systems engineered to enhance one of these parameters almost always results in a loss in the other. Efforts to surpass Robeson’s upper bound have led researchers to investigate new membrane technologies using alternate porous materials or polymer composite systems, wherein additives enhance the membrane selectivity and/or permeability of the polymer membrane. The uniform porosity and open framework structure of MOF materials makes them an ideal candidate for composite membrane systems and should allow for effective membrane separations that have both high permeability and high selectivity, surpassing the upper bound.

1.3 Membrane-based Separations

Perhaps the most widely explored form factor for separations with MOFs and MOF-composite materials is in membrane technologies. Three main separation applications are outlined in the following pages to illustrate the applicability of MOF-
based membranes: gas separations, nanofiltration, and pervaporation. These categories are broadly described here and specific cases will be investigated later in a discussion of membrane fabrication technologies.

Gas separations. Porous membrane materials can separate gases based on differences in diffusion coefficients\(^\text{29}\) or by a molecular sieving effect between the gases and porous material.\(^\text{30-31}\) A variety of MOF species have been explored for gas separations,\(^\text{32}\) consisting of both pure MOF membranes and MOF-polymer composite systems, although the polymers used in these composites have largely been limited to polyimides due to these polymers already being widely used in these processes. Among the many gases of interest for separation by MOFs, the removal of CO\(_2\) from flue gas streams\(^\text{33}\) has emerged as a major area of interest because of its well documented role in climate change and the fact that many MOF species have shown high selectivity and capacity for CO\(_2\) uptake.\(^\text{18}\) Pure MOF-5 membranes, for example, have been shown effectively separate CO\(_2\) from CH\(_4\) and N\(_2\) with extremely high selectivity (ideal separation factors of 328 and 410, respectively) in a model flue gas system.\(^\text{34}\) Before being considered industrially viable, however, some improvements to MOF-based membranes for gas separations are required, including bolstering the stability of pure MOF thin-film membranes\(^\text{25, 30}\) and improving gas selectivity in MOF-composites, which requires improving the adhesion at the interface between the MOF particles and polymeric matrix.\(^\text{30, 35}\) Despite these challenges that remain, the best MOF-based membranes\(^\text{36}\) currently exhibit separation performances that are competitive with leading
commercial membrane materials, including microporous polymers\textsuperscript{37} and zeolites\textsuperscript{38} and with further exploration are likely to surpass them.

\textit{Nanofiltration: solvent nanofiltration and aqueous desalination.} MOF-based membranes have been investigated for a growing number of liquid separations. Among these, nanofiltration has enormous potential to impact both the chemical production market space via fine chemicals purification and society at large in desalination applications. Typical membrane systems for separations by liquid filtration are driven by positive pressure on the mixed feed liquid,\textsuperscript{20} forcing smaller species to permeate the porous membrane and rejecting species larger than the pore aperture (Figure 1.3a), effecting separations by a simple size-exclusion process. Although membrane-based separations have been gradually adopted industrially since the 1960s, MOFs are poised to greatly improve the performance and scope of membrane separations possible. MOF pore windows are highly variable and can range from 0.3 nm to over 10 nm depending on composition, placing MOF membranes squarely in the nanofiltration regime (~1-10 nm) and even capable of competing with reverse osmosis (RO) membranes for desalination processes. In principle, MOF-based membranes should not suffer from the trade-off between selectivity and permeability that plagues polymer membranes.\textsuperscript{26} In polymer membranes, high-pressure on the feed required to drive the separation can lead to pore deformation and loss of selectivity, effectively enlarging the pores under the high pressure. The crystalline nature of MOFs means that the pore window of many MOFs is not readily-deformable, so the selective permeability of a MOF membrane can achieve true molecular sieving.\textsuperscript{39-40} Additionally, the open framework nature of MOFs provides
more permeation pathways, when compared to denser polymer membranes, and should allow permeating species to transit the membrane more rapidly, resulting in high membrane-flux. This latter has been clearly demonstrate by the addition of MIL-101(Cr) to a polyamide matrix in a composite membrane, which shows a 6-fold increase in solvent (THF) permeance while maintaining 90% rejection of contaminant species.\textsuperscript{41} The combination of selective pores and high permeability in MOF membranes can thus lead to both high selectivity and high flux, which are necessary to make membranes that are competitive for industrial separations.\textsuperscript{42}

\textit{Pervaporation.} For some liquid mixtures filtration is not a suitable means of separation, but an alternative membrane separation method, pervaporation, can be used for effective separation. Pervaporation can be likened to distillation across the membrane, but instead of differential boiling points being the main separation driver, the membrane affinity for each different component of the feed takes precedence, resulting in differences in transport speeds of feed components across the membrane (Figure 1.3b).\textsuperscript{19} Negative pressure applied to the permeate side of the membrane partially vaporizes the feed components and the relative affinity of the membrane for one species over another results in faster transport of the preferred species across the membrane, resulting in separation.\textsuperscript{43} This process is especially attractive as a low-energy alternative to distillation and has proven effective in breaking azeotropes.\textsuperscript{44} For example, in the separation of water from ethanol, the hydrophilic MOF, HKUST-1, was employed in a 40\% wt. mixed-matrix membrane (MMM) pervaporation system to remove water from a mixed feed.\textsuperscript{45} The addition of the MOF component to the membrane nearly doubled the
flux versus the pure polymer membrane without decreasing selectivity, which is attributable to selective permeability of water in the membrane resulting from the preference of the HKUST-1 for water over ethanol.

**Figure 1.3. Membrane-based liquid separation processes.** a) Filtration is driven by positive pressure on a mixed feed across a membrane, wherein species are rejected by the membrane that are too large to fit through the pore apertures. b) Pervaporation is a separation process by which species have different transport speeds across the membrane in a partially evaporated state due to the affinity of the membrane for one species over another. Figure reproduced from reference 12.
Low membrane fabrication costs and energy requirements have led to pervaporation processes are already being employed commercially, with current membrane technologies using both polymers\textsuperscript{46} and zeolites.\textsuperscript{47} Introduction of MOFs for this application is a natural extension of the current industrial goals, given the chemical versatility and subsequent separation tunability more freely available with MOFs compared to polymers or zeolites.

1.4 MOF Membrane Fabrication Strategies

The form factor of a MOF-based material significantly affects its effectiveness in various separation applications. Most native MOF species form either as microcrystalline powders or, at their largest, small crystals in the sub-millimeter regime. Although these powders or small crystals can be effective in packed-bed systems, they are not suitable for membrane separation processes in their as-synthesized state. Thus, two main strategies have been developed for fabrication of membranes with MOF based technologies, in addition to some other less well explored methods. The first main membrane fabrication process involves the preparation of MOF films, composed of an uninterrupted, pure-MOF layer on a supporting substrate. This is achieved by growing this MOF film as a continuous layer on a support substrate, albeit with significant difficulty. The second major membrane fabrication method involves creating MOF composite systems, wherein the MOF is combined with a polymer, either as a mixed-matrix membrane (MMM) or in other form factors like pressed pellets.
Figure 1.4. Fabrication methods for continuous MOF films. a) Solvothermal growth on a substrate immersed in the MOF precursor reaction mixture resulting in a surface-adhered MOF layer. b) A substrate is cycled between ligand and metal salt solutions, resulting in layer-by-layer growth of continuous MOF layers on the substrate surface. Figure reproduced from reference. 12

Continuous growth MOF membranes. MOF membranes prepared by continuous growth methods can give pure MOF materials unadulterated by other filler components and thus the innate chemical properties and separation performances of the membrane can be modulated solely by tuning the MOF pore structure. Effective separation relies on
growth of defect-free membranes, wherein the MOF pores are the only trans-membrane routes. This defect-free growth becomes exponentially more difficult as scale increases, i.e. larger area membranes have a significantly greater chance of containing killer defects than smaller area membranes. Continuous growth methods result in either intergrown polycrystalline films or more-perfect epitaxial films (Figure 1.4). The most common methods for growing continuous MOF films are solvothermal/hydrothermal growth, and liquid-phase epitaxy (i.e. layer-by-layer growth).

Solvothermal, or hydrothermal when water is the solvent, growth of MOF films is analogous to the typical synthesis of most bulk MOFs described in literature: a precursor solution of metal salt and organic ligand are heated until the MOF forms. A MOF film is formed by this process via the simple addition of an appropriate substrate to the growth solution, on which the MOF nucleates and grows. When successful, the resultant films are continuous, usually intergrown polycrystalline structures with tight junctions between crystal grains. Because these membranes are pure-MOF species, the MOF pores are the only permeation pathway through the membrane in a defect free film, and so should demonstrate near-optimal selectivity in gas- and liquid-phase separations. In other words, strict molecular sieving with these membranes is possible via rejection of species larger than the pore aperture.

Computational modeling supports that this ideal separation performance is possible and experimental results have begun to corroborate these computational membrane models using ZIFs and other common MOF species. For example, computer models of ZIF membranes show that defect-free ZIF-100 membranes could
achieve significantly higher flux than current commercial reverse osmosis membranes while maintaining 100% salt rejection.\textsuperscript{50} If this modeling prediction can be validated by laboratory experiments, it would represent a significant advancement for desalination technology. Importantly though, it is far more difficult to create a crystallographically perfect ZIF membrane in the real world than in a computer model. However, a polycrystalline ZIF-8 membrane prepared solvothermally has been shown to successfully reject >99% of hydrated ions found in seawater, while maintaining high water flux in a pervaporation system.\textsuperscript{40} This is a promising start, despite this pervaporation experimental setup being somewhat more complicated than current reverse osmosis technologies.

In addition to aqueous-based applications, continuous MOF membranes are a logical next step for gas separation applications due to the widely demonstrated high fidelity of gas separations and sequestrations in microcrystalline MOF powders. In fact, continuous MOF films have already been shown to be able to surpass the Robeson upper bound.\textsuperscript{27} This is because unlike polymers which are relatively soft and deformable, in rigid MOF crystals, the pore windows do not deform under pressure.\textsuperscript{30} This means that as long as the crystal remains intact, the pore window remains the same size regardless of the feed pressure. This rigidity, combined with open permeation pathways, allows for high flux under high-pressure conditions alongside the maintenance of high selectivity in the membrane. Indeed, in gaseous separations MOF-5 membranes have been shown to exhibit ‘sharp molecular sieving’ of CO\textsubscript{2} from both N\textsubscript{2} and CH\textsubscript{4}, with performance surpassing both the Robeson upper bound as well as other high-performing MOF and zeolite films\textsuperscript{34}. Similarly, polycrystalline ZIF membranes have successfully effected the
separation of an acetone, butanol, ethanol fermentation broth\textsuperscript{52} and solvent dehydration\textsuperscript{53} in pervaporation systems that outperform current technologies.

Despite these successful demonstrations of industrially-relevant separations using polycrystalline MOF membranes, there are notable drawbacks to films fabricated in a continuous MOF film. Most importantly, one major limitation is the formation of defects within the film (cracks and voids) arising from poor intergrowth of the polycrystalline film, incomplete substrate coverage,\textsuperscript{25,54} or inherent MOF defects like missing-linkers as described above. All of these can compromise the membrane performance by providing non-selective permeation pathways, reducing the selectivity for the desired product. Indeed, despite computer simulations predicting perfect rejection performance, a polycrystalline UiO-66 membrane (pore window ~6 Å) in a filtration-type desalination experiment successfully rejected only about 85% of large hydrated ions in aqueous solution, far short of the complete rejection of these species predicted.\textsuperscript{91} Although no cracks or pinhole defects were evident in the UiO-66 membrane by microscopy, the imperfect ion rejection can likely be explained by missing-linker and missing-cluster defects within the membrane. As shown in Figure 1.1c, missing-linker defects in a MOF crystal arise from the absence of a bridging ligand between SBUs, making the pore aperture larger than expected for an idealized framework. These defects typically result from the addition of modulators during MOF synthesis; these modulators are usually non-bridging ligands designed to coordinate to SBUs to control or slow crystal growth. In the synthesis of UiO-66, modulators such as acetic acid, benzoic acid, and HCl are commonly used and known to contribute to missing-linker defects. Simulations often
cannot, or do not, account for defects in the MOF,\cite{55-58} which can explain the mismatch between the ideal predictions of simulations and the good, but non-ideal selectivity observed in experimental studies.

Beyond defects like those in UiO-66, the impact of flexibility in some MOF lattices has also not been adequately addressed, which can similarly impact separation performance.\cite{15} For example, the linkers in ZIF-8 have been observed to undergo a ‘saloon-door’ motion\cite{59} that allows for the penetration of molecules such as benzene that are larger than the idealized, rigid pore window (3.4 Å) in the lattice. This effect arises from the inherent lability of MOF ligands. An opportunistic guest molecule (e.g. benzene) can gain access to the lattice interior when the saloon door (imidazolate ligand) swings open momentarily and remain trapped there after it closes again. This ligand lability is not inherently bad however, since it allows for processes like postsynthetic exchange (PSE) of the ligands for new MOF functionality. More sophisticated modeling will likely help understand and control these phenomena to bridge the gap between in silico and experimental membrane performance.

Another limitation is that large-area continuous MOF films are difficult and inefficient to prepare by solvothermal growth. Most MOF synthetic protocols have been determined empirically and optimized for microcrystalline MOF growth, meaning many protocols must be significantly re-optimized for film growth, especially to achieve defect-free films larger than a few centimeters in diameter. Even with optimization, MOF nucleation and growth occurs in free solution and on the reactor chamber walls in addition to on the intended substrate surface, resulting in a large amount of unusable,
microcrystalline by-product. Addition of seed crystals adhered to the intended substrate prior to solvothermal treatment improves MOF film coverage, but seeding is both time and reagent intensive and does not guarantee complete coverage. Crystal seeding works by providing a pre-nucleated crystal so that crystal growth can proceed without relying on chance nucleation on the substrate. The choice of membrane substrate is also not trivial to MOF growth and can dramatically alter the final film quality. For instance, in one study HKUST-1 films were shown to grow well on alumina surfaces but not at all on silica substrates under the same conditions. Similarly, MOF-5 was shown to readily grow on bare alumina substrates, but only grew on silica after the surface was treated with carboxylate-terminated self-assembled monolayers (SAMs) to which the nascent MOFs could anchor. Clearly, SAMs can help obviate the need for MOF-specific fabrication conditions for film growth and can be used to pattern MOF film growth on substrates to grow in certain areas but not others, but even with SAMs in use, a significant amount of process optimization will be required.

The second widely employed route to continuous MOF films is use of layer-by-layer methods such as liquid-phase epitaxy. These approaches can result in smoother, surface-attached metal-organic frameworks (SURMOFs), but can be similarly time intensive and somewhat tedious. Layer-by-layer methods expose the substrate to one MOF component at a time, in a repeating fashion to build up the lattice. A substrate is repeatedly cycled between metal-only and ligand-only solutions, with intermediate washing steps, adding MOF layers in a highly controlled manner (Figure 1.4b). As with solvothermal growth, layer-by-layer methods may require pre-treatment of the substrate
with a SAM to ensure MOF adhesion. Though application-ready films can be grown by this method, SURMOF films are more appropriate for research-scale (i.e. small) preparations because the growth process is time consuming, synthetically nontrivial, and presents scalability issues as the substrate is repeatedly cycled between metal and ligand solutions. Moreover, liquid-phase epitaxy has only been demonstrated with a handful of MOFs. For research purposes, though, these films are excellent candidates due to the high degree of control over thickness and low number of defects afforded by epitaxial growth.

In addition to solvothermal growth and layer-by-layer processes, some less common methods have shown promise for reducing the time and precursor volumes necessary for continuous MOF film growth. Most notably, a clever interfacial diffusion process has been successfully employed to selectively grow MOF films on a porous substrate. In a typical setup, separate solutions of the metal source and ligand are prepared and the two solutions are introduced to opposite faces of the porous substrate. As the two solutions diffuse through the substrate toward each other, they come into contact and react, forming a MOF film at the interface. A significant advantage of this synthetic approach is that it self-corrects defects; diffusion at open voids is faster than in areas already containing MOF, thus MOF will grow in these voids too, resulting in continuous films with good uniformity. Another advantage is that this interfacial diffusion strategy uses reagents more efficiently than solvothermal methods, because MOF nucleation and growth only occurs at the interface of the two solutions where both ligand and metal components are present, so smaller amounts of each are required and no
MOF powder is wasted. The major drawback, however, is that thus far, this technique has been demonstrated with only a few MOFs (HKUST-1, ZIF-8, ZIF-71)\textsuperscript{58-71} that form rapidly under mild conditions. Extending this method to a wider scope of MOFs, especially those that require high temperatures and primarily form discrete nano-sized crystallites, would greatly enhance the use of this approach for MOF film fabrication.

\textit{Composite Systems: MMMs and beyond.} Given that most MOF syntheses yield microcrystalline powder products, a strategy for membrane fabrication that uses these powders directly in a composite system without modification of the synthesis conditions is an attractive proposition to overcome many of the difficulties discussed above inherent to continuous MOF film fabrication. Mixed matrix membranes (MMMs) are composite materials composed of particles of a filler material embedded in a polymeric matrix. In this case, the filler material of interest is a MOF powder. These composites derive properties from both the polymer matrix and filler components; ideally, a membrane with the mechanical flexibility of the polymer binder and the high porosity of the MOF. In a typical MMM fabrication, the MOF species is dispersed in a polymer solution in a compatible solvent, forming a spreadable MOF ‘ink’ (or polymer dope) (Figure 1.5). This ‘ink’ is then cast into a film and finished by a curing process to remove the casting solvent. Common casting methods include by drawdown coating with a doctor blade, rod coating, and spin-coating. This process can yield both supported and free-standing membranes,\textsuperscript{72} unlike the continuous MOF films described above that require a supporting substrate. Free-standing MMMs mean greater functionality per unit weight (or volume)
compared to substrate-supported films, with the active species accounting for the entire material and not just a small portion, as in a supported membrane.

The biggest advantage of these materials comes from an economic perspective. Because MMMs use pre-formed MOF particles, they are able to use a wide variety of MOFs, regardless of the original MOF synthetic conditions required and without significant process reoptimization for each species. MMMs can even be formed with two or more mixed MOF species in the same composite for multifunctionality, something that would be almost impossible to achieve with solvothermal membrane growth processes. Although some of the canonical MOFs like MOF-5, HKUST-1, UiO-66, and ZIFs have established routes to continuous, polycrystalline films, many other important MOFs such as MIL-101, UiO-67, and NU-1000 are not known to form continuous MOF films, but do form monodisperse discrete particles, and thus lend themselves more readily to MMM formulations.

![Figure 1.5. MOF MMM fabrication procedure.](image)

Typical MMM fabrication: a) An ink is prepared containing polymer solution and the MOF species. b) This ink is cast onto a surface via drawdown coating with a doctor blade. c) The casting solvent is removed via evaporation. d) The MMM is delaminated from the casting substrate to give a freestanding film. Figure reproduced from reference 12.

MOF inclusion in MMMs is often intended to enhance the properties of polymer membranes, rather than harness a particular property of the MOF particles. MOFs can
add rigidity to the polymeric membrane by inhibiting polymer swelling and chain migration or they can provide enhanced flux via addition of less-inhibited through-MOF permeation pathways. The selectivity of the membrane, however, remains dictated by the porous polymer matrix. The relatively low MOF loading in many studies (<30% wt.) reflects this approach of enhancing polymer performance, rather than taking a MOF-focused approach to the composite. For example, in a recently reported reverse osmosis membrane composed of a MOF MMM thin-film-nanocomposite, the addition of as little as 0.4% wt. ZIF-8 led to a 162% increase in flux compared to pure polyamide membrane, while maintaining greater than 98% NaCl rejection. These findings indicate that the ZIF component serves to increase the membrane flux due to relatively unimpeded transit of water through the crystallites, but the selectivity of the membrane is still dictated by the polymer.

Similarly, enhanced single gas permeability was observed in ZIF-8/Matrimid® MMMs (up to 30% wt.) compared to the pure polymer with negligible loss of ideal selectivity with increasing MOF content. Again, the enhanced permeability was attributed to the relatively unimpeded movement of the permeate through the free-volume of the MOF component, but the MOF is not active in the membrane selectivity.

If the MOF content in MMMs is increased, such that the MOF rather than polymer is the dominant component, then the nature of the MMM changes. There is not only enhanced membrane permeability from the MOF, but also MOF-dictated selectivity properties, and the polymer takes on a supporting role as a binder. Some studies suggest a synergistic relationship, resulting in a membrane that is greater than the sum of
its parts. For example, work that will be described in Chapter 3 shows that MMMs composed of HKUST-1 and polyvinylidene difluoride (PVDF) were able to far outperform HKUST-1 powder in both ammonia uptake and stability over time at 30, 50, and 67% MOF by weight. Unlike the as-synthesized HKUST-1 powder, which degrades under humid conditions, the MMMs were stable under 90% relative humidity for over a month and retained their ammonia sorption capacity. The added stability of HKUST-1 within the MMMs is attributed, in part, to the hydrophobic PVDF polymer matrix.

The morphology of MOF particles in MMMs have also been shown to affect the overall performance of the membrane. For example, when MOF-74 nanoparticles of different sizes were combined with a polyimide matrix, 6FDA-DAM, membranes with smaller particles (~20 nm) successfully separated ethylene from ethane with selectivities far greater than the native polymer. However, larger particles (~100 nm) only slightly improved the permeability of the membrane compared to the native polymer, without improving selectivity. The MMMs containing the smaller particles also show increased stability to dissolution of the membrane in solvent compared to pure polymer and larger-particle MMMs, suggesting the presence of strong stabilizing interactions between MOF and polymer. Furthermore, these MMMs resist plasticization at industrially relevant feed temperatures and pressures, maintaining separation performance far above the pure polymer under the same conditions. This enhanced stability to dissolution and plasticization suggests that strong polymer-MOF interactions are reducing mobility of the polymer chains within the membrane. These stabilizing interactions could allow for
membrane separation applications that were not previously possible because the conditions were too harsh for polymer-only membranes. The MMMs prepared in this study also greatly exceeded the Robeson upper bound for polymer membranes when applied to the separation of ethylene from ethane.\textsuperscript{89}

MOF MMMs have also demonstrated good efficacy for organic solvent and aqueous nanofiltration. MOF MMMs have shown efficient removal of organic dyes\textsuperscript{72, 82-83, 75} from both water and organic solvents and removal of heavy-metal ions\textsuperscript{84} from water by means of filtration. These systems serve to model the downstream clean-up of industrial waste streams of various processes like refining, mining, and textile production. Upstream, styrene oligomers\textsuperscript{69, 85} and sulfurous species\textsuperscript{86} have been used as models for contaminants in organic systems, relevant for processes such as fuel refining and fine and commodity chemicals production.

Unlike these nanofiltration systems, which use the MOF component both to provide size-selective pores and a less-encumbered permeation pathway for solvent, pervaporation separations are primarily dependent on the chemical environment of the MOF pores. MOFs membranes are an ideal candidate for pervaporation systems because membrane-to-permeate affinity is the driving factor in these separations, and this can be readily tuned in MOFs via chemical modification. By combining MOFs with polysiloxanes\textsuperscript{70} to produce MMMs, small amounts of organic species (ethanol,\textsuperscript{87-89} butanol,\textsuperscript{90-91} and acetone\textsuperscript{92}) can be selectively removed from aqueous solution by pervaporation. For example, inclusion of different ZIFs from 10-60\% by weight yields MMMs that exhibit both greater flux and better selectivity than the native polymer
control membranes by increasing the organophilicity of the membrane due to the addition of the hydrophobic MOFs. Increasing the hydrophobic nature of the membrane increases the affinity of the organic component of the feed for the membrane, speeding its transit and repelling the aqueous component. These MMM composite systems for pervaporation have again been shown to outperform the demonstrated upper limit for single-component polymer membranes.

Inverting the experimental paradigm of the previous systems, ZIF MMMs are also being investigated for organic solvent dehydration by pervaporation. This solvent dehydration operates by the same process as above, but instead of removing trace organics from aqueous systems, the majority component of the feed liquid is organic solvent with a small volume of aqueous contaminant. As such, a membrane with high flux is essential because the majority of the feed must permeate the membrane, leaving behind a small amount of water. Thus, the huge improvements in membrane flux achievable with the addition of MOF to the polymer membranes are highly significant.

Despite their promise, MOF MMMs still face challenges and significant limitations that must be overcome. First, MOF MMMs generally have reduced permeability compared to their pure-MOF counterparts because of the non-porous nature of many polymer binders. This is not necessarily a major problem, as the permeability is still superior to pure-polymer membranes, but it highlights an opportunity for MMMs with high-MOF loading. As MOF MMM composition evolves from polymer-dominant to MOF-dominant composites with higher MOF loadings, permeability should correspondingly improve, approaching that of an all-MOF membrane. Another
significant challenge to MOF MMM fabrication is the tendency of the MOF and polymer components to phase segregate. This results in aggregation of the MOF particles and poor dispersion in the MMM, giving a membrane with non-uniform composition. This phase segregation is a leading source of void defects\textsuperscript{77} in the membranes; the aggregated particles contain voids between them that are not filled with polymer. These voids then provide nonspecific permeation pathways through the MMM that reduce the separation efficiency and compromise performance. A variety of fabrication techniques have been developed to overcome the tendency of MOF particles to aggregate in these MMMs, including a spray self-assembly technique,\textsuperscript{91} a sonication-enhanced synthetic process,\textsuperscript{88} and interfacial diffusion processes\textsuperscript{70} and any industrial production will need to contain engineering controls to address this issue. Alternatively, modifying the surface chemistry of the MOF particles themselves could alleviate aggregation, giving better dispersions, and hence inhibit macrovoid formation in MOF MMMs,\textsuperscript{35} however, a better molecular-level understanding of MOF surfaces and interfaces is required to improve integration of these two disparate materials.

\textit{Surface and post-synthetic modifications to MOF particles.} Studies aimed at integration of higher loadings of MOF species\textsuperscript{39, 72} into defect-free membranes\textsuperscript{69, 93} will continue to improve membrane flux and allow the high selectivity and permeability of continuous MOF films to be attained. Defects or macrovoids that arise from a mismatch in the chemical properties of the MOF and polymers used to prepare MMMs may be addressed by tailoring the surface chemistry of the MOF,\textsuperscript{35} representing a natural application for postsynthetic modification (PSM) strategies\textsuperscript{14} on the MOF lattice (Figure
1.6. Analogous to silylation methods used to improve the properties of zeolite-based MMMs, MOF modification offers far more chemical diversity in functionalization and can be used to achieve improved physical interactions between the materials to decrease macrovoid formation. Ultimately, when taken to their logical end, these postsynthetic processes can even be used to achieve a covalent integration of the MOF and polymer phases.

**Figure 1.6. Postsynthetic methods for MOF functionalization.** a) Presynthetic functionalization incorporates a functional ligand into the MOF lattice during MOF crystal growth. b) Postsynthetic modification (PSM) uses organic chemistry techniques to functionalize a reactive handle on the MOF ligand within the preformed lattice. c) Postsynthetic exchange (PSE) takes advantage of lability of the native MOF ligands in the framework to exchange them for functionalized ligands. d) Postsynthetic polymerization incorporates reactive ligands in the MOF lattice into growing polymers after MOF formation, creating a hybrid MOF-polymer material. Figure adapted from reference 95.
Indeed, postsynthetic methods have already been effectively used to enhance the MOF-polymer interface within MMMs. In a study of MMMs using multiple MOF species (HKUST-1, ZIF-8, MIL-47, and MIL-53(Al)) for the separation of organic dye molecules from isopropanol by nanofiltration, addition of each MOF species to the polydimethylsiloxane (PDMS) matrix led to improved membrane flux, but also greatly reduced selectivity versus the unfilled polymer membrane. This suggests that the MOFs were simply providing non-selective permeation pathways, likely macrovoid defects. Investigation of the MOF MMMs by scanning electron microscopy (SEM) revealed exactly that, voids surrounding the MOF particles, indicating poor MOF-polymer adhesion, and thus providing non-selective permeation pathways through the membrane. This poor adhesion was attributed to the non-polar polymer interacting poorly with the inorganic SBUs on the MOF surface. By employing PSM on the particle surface with non-polar molecules via silylation, the SBUs on the particle surfaces were effectively shielded in a more polymer-friendly coating. MMMs prepared with these modified MOFs still showed enhanced permeability for the isopropanol solvent, but now also had enhanced selectivity over the pure PDMS membrane even at 20% wt. MOF. SEM analysis showed that these membranes did not display the non-selective voids that were present in those made with untreated MOF particles.

The silylation reaction described above was shown to be an effective surface modification for improving polymer affinity, but given the rich body of literature on MOF PSM there are many MOF modifications waiting to be exploited for improvement of MMMs. A systematic exploration of MMM properties as a function of MOF particle
surface chemistry would be useful and would likely improve MMMs for use in separations by reducing defects, resulting from enhanced MOF-polymer interactions. Recently some progress has been made in this area as applied to gas separations, specifically for CO$_2$/N$_2$ mixtures.$^{35}$ In this study, hydrogen bonds and π-π interactions between phenyl acetyl surface groups on MOF particles and complementary chemical moieties on a Matrimid® polymer led to higher quality MMMs and better separations (200% better permeability and 25% better selectivity versus pure Matrimid®). Importantly, the enhanced selectivity did not occur for MMMs built from MOFs with non-complementary surface groups (decanoyl acetyl groups and succinic acid groups) suggesting that the selectivity enhancement is due to the formation of a defect-free interface between the Matrimid® polymer and MOF particles. In the case of decanoyl acetyl surface MOF groups, selectivity actually decreased, presumably because of defects at the interfaces of MOF particles and polymer, opening up non-selective diffusion pathways and contributing to mechanical brittleness in the membrane. Permeability increased with all three functional groups suggesting that MOF surface chemistry is not necessarily critical in maximizing permeability, if that is the only goal. Three MOF loadings of 12%, 23%, and 40% were examined in this study. Interestingly, even with favorable surface coatings, the 23%, rather than the 40% loading, gave the best overall results because at higher loadings particle agglomeration was observed to occur. As expected, agglomeration resulted in lower selectivity, but greater permeability. This suggests enhanced selectivity may only be partially achieved by increasing MOF loading and selectivity will suffer in cases where particle agglomeration occurs.
Finally, as a natural progression from MOF PSM, postsynthetic polymerization (PSP) has been developed as a method to integrate pre-formed MOF particles into films by building reactive chemical ‘tags’ on the surface of MOF crystals and polymerizing them with a co-monomer.\textsuperscript{84, 96} PSP has been artfully demonstrated by postsynthetically functionalizing UiO-66-NH\textsubscript{2} microcrystals with methacrylamide groups and subsequently copolymerizing them with butyl methacrylate to form a membrane (Figure 1.7).\textsuperscript{84} The mixture of functionalized MOF particles (20\% wt.) and monomer was polymerized via UV exposure, making this method rapid and readily scalable. The resultant membrane was elastic and defect-free and proved capable of removing Cr\textsuperscript{6+} ions from aqueous solution with 80\% retention.

More recently, a UiO-66-NH\textsubscript{2}/polyurethane PSP membrane system was developed and shown to effectively remove dye molecules from aqueous solution,\textsuperscript{97} using a membrane with 70\% wt. MOF.\textsuperscript{84} These membranes were challenged with different organic dye molecules in aqueous solution and separated the species based on a selective dye adsorption mechanism. Although this system falls short of true molecular sieving, improvement to the methodology is a promising path forward to obtain PSP membranes for separations. PSP MOF membranes have also been applied to pervaporation separations in an attempt to achieve molecular sieving; more specifically, SIM-1 was postsynthetically polymerized with ethylenediamine vapor to form a continuous MOF membrane.\textsuperscript{96} This membrane was challenged to separate water/ethanol mixtures by pervaporation, successfully showing only water permeation through the membrane over multiple cycles.
Figure 1.7. Postsynthetic polymerization of MOFs. a) Membrane synthesis by PSP may be able to bridge the gap between pure-MOF membranes, which have near ideal selectivity, and MMMs, which are easily processed and have flexibility and durability from the polymer component. b) PSP requires MOFs that have chemically reactive ‘tags’ on the particle surface. In this system, PSM of UiO-66-NH₂ was carried out with methacrylic anhydride to give the chemically reactive MOF. Reaction of this modified MOF with butylmethacrylate under UV irradiation gives a polymerized MOF composite. c) Stand-alone membranes can be formed via PSP by casting the MOF and reactive monomer into a film with subsequent polymerization. Figure reproduced from reference 12.
Membrane fabrication by PSP goes beyond traditional MMM fabrication and creates a covalently integrated composite structure. It is an excellent example of molecular-level design for membrane fabrication and with additional developments should be able to bridge the gap between the ease of fabrication of MMMs and the high flux and selectivity of continuous MOF films.

To maximally exploit the properties of MOFs in films and membranes, the development of improved amalgamation methods must be explored. As described above, pure MOF films can be prepared, but for many applications the fabrication methods for these membranes require improvement. A formulation that creates a seamless combination of MOFs and polymers, thereby merging the chemical and physical properties of the MOF with the mechanical and processing properties of the polymer, may be more desirable. This might be achieved by improved MMMs, but the inherent phase separation in MMMs may limit the seamless integration of both materials. Perhaps a better approach will be the PSP methods described above,\textsuperscript{84,96} where the MOF particles are polymerized to each other to form membranes. If crystallite size can be sufficiently reduced, with highly monodisperse particle sizes, then these materials may offer a very tight-knit hybrid with merged properties. Tuning the size and nature of the intervening polymer links should allow for tuning of membrane performance. Recent studies are examining even more intimate links between polymers and MOFs. For example, some metal-coordinating polymers can be coaxed into forming MOF-like structures, some of which form films.\textsuperscript{98-99} Further development of these ‘polyMOFs’ (and related polyMOCs, where MOCs are metal-organic cages)\textsuperscript{100} may prove capable of creating membranes that
combine MOFs and polymers at the molecular level, in such a way as to maximally exhibit the optimal properties of both. With ongoing efforts in synthesis and analysis of these new MOF structures, membranes of MOFs are expected to accelerate these materials from laboratory curiosities to important sensing and separations technologies, as well as functional coatings and materials.

1.5 Scope of the Dissertation

This dissertation will describe our efforts in MOF membrane and hybrid materials fabrication and the applications thereof. Chapter 2 describes the development of MOF MMMs using a PVDF binder and a wide scope of canonical MOF MMMs. The MOFs are shown to maintain their desirable properties in the MMM format, even being amenable to postsynthetic methods within the MMM matrix.

Chapter 3 describes the application of these MOF MMMs as a functional material for personal protection. HKUST-1 membranes are then shown to exhibit high uptake of the toxic industrial chemical, ammonia, while enhancing the chemical stability of the MOF within the matrix.

Chapter 4 describes the evolution of these MMM systems beyond single MOF MMMs. Multicomponent MOF MMMs and layered MOF MMMs are fabricated and characterized.

Chapter 5 describes our efforts to move beyond MMMs by using PSP methods to create a MOF-polymer composite material that is melt-processable. Polyamide-6,6 is
combined covalently integrated with the MOF materials and the resulting hybrid material is characterized.

1.6 Acknowledgements

Chapter 1, in part is a reprint of the material as it appears in “Metal-organic frameworks for membrane-based separations.” Nat. Rev. Mater., 2016, 1, 16078. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthors, Jessica C. Moreton, Lauren Benz, and Seth M. Cohen.
1.7 References


79. Song, Q. L.; Nataraj, S. K.; Roussenova, M. V.; Tan, J. C.; Hughes, D. J.; Li, W.;


50942-50954.

84. Zhang, Y.; Feng, X.; Li, H.; Chen, Y.; Zhao, J.; Wang, S.; Wang, L.; Wang, B.,


90. Liu, X.-L.; Li, Y.-S.; Zhu, G.-Q.; Ban, Y.-J.; Xu, L.-Y.; Yang, W.-S., \textit{Angew. Chem.,


Chapter 2

Development of Metal-Organic Framework Mixed-Matrix Membranes and their In Situ Modification

2.1 Introduction

As described in Chapter 1, MOFs are an exciting class of crystalline materials that have garnered significant interest from synthetic chemists and materials scientists alike.\textsuperscript{1-3} Due to their crystalline nature, MOFs are naturally not as malleable as soft materials, such as organic polymers. This rigidity limits their manipulation and processability for engineered forms and industrial applications.\textsuperscript{4} Despite this difficulty of processing, films or membranes of MOFs are of significant potential interest for a wide variety of applications and technologies (see Chapter 1).\textsuperscript{5-10} Though there is broad interest in preparing MOF films, preparing such films presents significant technical challenges and this area of study, while growing, is still relatively new.\textsuperscript{11-14}

Some work has been applied toward the development of MOF membranes on porous substrates by either direct growth on the substrate or by secondary, seeded growth strategies to achieve monolithic MOF structures. These efforts have been catalogued in reviews by Shah et al.\textsuperscript{12} and Qiu et al.\textsuperscript{13} demonstrating suitability for some gaseous\textsuperscript{15} and a limited number of liquid separations.\textsuperscript{11, 16} Other work has also attempted to achieve free-standing pure-MOF membranes, but only small areas can be achieved and delamination of the resultant films remains difficult.\textsuperscript{17} Membranes based on these reported processes have some inherent limitations, including: (1) the substrates must be
stable to MOF growth conditions; (2) the selection of MOF is largely limited to MOFs grown under mild conditions; (3) the resulting pure-MOF membranes are rigid and brittle. Consequently, it is easy to see that while a pure-MOF membrane is an attractive proposition, the reality of the technical challenges they present calls for alternative technologies.

To circumvent many of these issues, composite materials integrating MOF particles with a polymeric binder have been investigated and several reviews on these MOF-based mixed matrix membranes (MMMs) have been recently published. The majority of MMM studies to date have focused on the application of these composites for gas separations. More recently, it has been recognized that MMMs are also of value for liquid phase separations, and more generally, as a way to improve the processibility and handling of MOFs. An excellent example of liquid phase application of MOF MMMs comes from a report by Basu et al. describing a MOF/polymer composite membrane for performing organic solvent nanofiltration, specifically removal of an organic dye (Rose Bengal) from isopropanol. While promising results were obtained, it is important to note that modification of the MOF surface was essential for good polymer-to-MOF adhesion. Introduction of the MOF without surface modification with $N$-methyl-$N$-(trimethylsilyl) trifluoroacetamide actually resulted in decreased dye retention by the membrane when compared to pure polymer (Matrimid®). With surface modification of the MOF particles to improve MOF-to-polymer adhesion, increased dye retention was achieved, but the mechanism of separation was attributed largely to
reduced swelling of the polymer. The loading of MOF in these membranes was also rather limited (20% wt.).

Similarly, a recent report by Zhang et al. described MOF composite membranes\textsuperscript{24} that showed robust, recyclable separation performance for removing dye pollutants from water. However, despite achieving an interesting hybrid material, their synthetic approach presents significant challenges with controlling crystallite size and MOF composition throughout the film. Moreover, these films were prepared with only a single MOF (ZIF-8) on a single substrate (polyacrylonitrile, PAN) in a laborious layer-by-layer approach. As highlighted in Chapter 1, while layer-by-layer methods can give films of excellent quality, their time and reagent requirements make them very unattractive for industrial scale production. Interestingly, the polymer binder used in this preparation (poly(sodium 4-styrene-sulfonate), PSS) also acts as a coordinating dopant in the synthesis, which can serve to stabilize the MOFs onto the polymer through coordination to the MOF SBUs. However, it may also perturb the purity of the MOF phase, making for non-ideal separation domains. In a different, promising approach to membrane fabrication, postsynthetic polymerization (PSP) was used to crosslink MOF particles to prepare a unique MMM that was investigated for heavy metal sequestration.\textsuperscript{25} While the PSP approach to membrane fabrication is no doubt of great interest, it also presents significant technical challenges around the in situ polymerization of the binder.

Overall, these studies, while encouraging, are largely limited in scope, utilizing only a handful of the many MOFs available, with generally low MOF loading (most reports <30% wt.).\textsuperscript{11, 26-27} Moreover, these studies are missing a significant opportunity
that MOFs offer relative to other porous materials that may be used to fill polymer composites. Specifically, the majority of studies of MOF-based MMMs have been focused on simple improvement of membrane characteristics by use of the MOF as a polymer filler material, rather than exploring and exploiting the characteristics and chemistry of the included MOF. Like other porous filler materials (e.g., zeolites), MOFs provide a way to improve membrane flux because they do not significantly impede permeating species, but the tunability of MOFs offers far more opportunity that is not currently being capitalized on. Pore shape, size, high specific surface area, and the potential for chemical modification of the MOF pores by postsynthetic methods are all attractive features worth capturing in a processable material.28

In this context, we sought to demonstrate the utility of a MOF-focused composite material that inverts the current paradigm. By making a composite that elevates the MOF to the forefront and reduces the polymer to a supporting role, we can demonstrate the utility of such a MOF-focused composite and explore ways to exploit the unique attributes of MOFs. We have successfully achieved the integration of MOF particles in a MMM with a high MOF content (~67% wt.), using a wide range of MOFs, producing MMMs that can be made on scale, easily handled, and readily manipulated. Importantly, distinctive from prior studies of which we are aware, these MMMs retain the high specific surface areas of the parent MOFs and have been shown to readily undergo postsynthetic modification (PSM) and postsynthetic exchange (PSE) by standard methods, demonstrating that the MOF component is functionally intact in the composite MMM.
2.2 MOF MMM Fabrication

A drawdown coating (bar coating, doctor blading, etc.) process was used for MMM fabrication, using a MOF-based ink prepared by dispersion of MOF particles with a polymer binder (Figure 2.1). Note that “ink” in this study refers to a suspension of preformed MOF particles in a casting solution, not a solution of MOF precursor components (i.e. free metal and ligand in solution). Importantly, we found that achieving a homogeneous MOF dispersion and uniform film was difficult by direct dispersion of MOF particles in a polymer solution composed of polyvinylidene fluoride (PVDF) polymer in N-methylpyrrolidone (NMP) or N,N-dimethylformamide (DMF); therefore, MOF particles were first dispersed in a less viscous solvent (acetone) followed by subsequent addition of the polymer solution to this dispersion (Figure 2S.1). This predispersion step proved highly effective in giving high-quality, uniform MOF films and was compatible with all MOF species used in this study. The films resulting from these inks were stable, free of obvious defects (i.e. cracks or pinholes), and readily delaminated from the casting substrate. Delamination is made easier by placing the film in solvents (e.g. acetone, methanol) that results in film swelling and facile release of the film. The resulting freestanding MMMs were mechanically robust and pliable, amenable to basic manipulations like bending and stretching. Both glass (microscope slide) and aluminum (foil and sheet) were used as supporting substrates with similar results. Properties of the final MOF films were not significantly affected by the supporting substrate.
Figure 2.1. MOF MMM fabrication process. A MOF/polymer ink is prepared and cast onto a substrate via drawdown coating with a doctor blade. The film is then heated to drive off casting solvent via evaporation. The resultant film is then delaminated from the substrate to give a free-standing MOF film.

Figure 2.2 shows images of seven different MMMs fabricated by this technique. A canonical, but diverse set of MOF materials including UiO-66 (University of Oslo), HKUST-1 (HKUST = Hong Kong University of Science and Technology), MIL-101 (MIL = Material Institute de Lavoisier), MIL-53, MIL-53 and ZIF-8 (ZIF = Zeolite Imidazolate Framework) all readily formed MMMs using the same methodology without modification. This set of MOFs represents a variety of SBU and ligand compositions. Different metal isoforms, such as MIL-101(Cr) and MIL-101(Fe), as well as functionalized versions of these MOFs (e.g. UiO-66-NH₂), could also be prepared as freestanding MMMs. To demonstrate adaptability of the final form, MMMs were prepared with a wide range of MOF loadings, from ~10-67% (by weight) of MOF (using UiO-66 as a representative material, Figures 2S3-5), all showing uniform MOF dispersion in the final film without evidence of particle aggregation that has led to macrovoid formation in other reports. To date, this approach is the most broadly demonstrated method for producing MMMs with different MOFs.
Figure 2.2. MOF MMMs. a) Freestanding MMMs (~1×1 cm²) produced from a variety of canonical MOFs. b) Photographs demonstrating that large area (~3×5 cm²) HKUST-1, UiO-66, and MIL-53(Fe) MMMs are resilient to mechanical stress and can be easily handled.

In addition to the different colors of the films indicating their composition (Figure 2.2), all of these materials were characterized by scanning electron microscopy (SEM) as shown in Figure 2.3 and the Supporting Information at the end of this chapter. At lower MOF loadings (Figures 2S.3-5) macrovoids between the MOF and polymer are not obvious in these SEM images. At higher MOF loadings (~67% by wt, Figure 2.3) the MMM composition is dominated by MOF crystallites, which results in apparent macrovoids in the film, but there is still excellent adhesion between the MOF and polymer components of the composite. The characteristic morphology of the different MOF materials can be easily seen in the film matrices, showing that film fabrication is not detrimental to the MOF integrity. Powder X-ray diffraction analysis (PXRD) confirms that the crystallinity of these various MOFs in the MMMs was maintained, as the characteristic pattern for each species remains intact in the films (Figures 2S.2, 2S.7, 2S.10, 2S.12, 2S.14, 2S.17 and 2S.20).
Figure 2.3. SEM images of MMMs (~67% wt.). a) UiO-66, b) MIL-101(Cr), c) MIL-101(Fe), d) HKUST-1, e) MIL-53(Fe), f) ZIF-8.

Figure 2.4 shows a series of more detailed SEM images of a UiO-66 MMM (67% wt.). The octahedral UiO-66 microcrystals clearly remain intact and are well integrated with the polymer binder. Figure 2.4b shows a torn edge of the MMM, highlighting the integration of MOF crystals with the PVDF strands. Figures 2.4c and 2.4d display cross section images of the UiO-66 MMM showing the dense packing of the MOF particles within the film. From these cross-section images, the film is determined to be approximately 35 μm thick, which was confirmed with film thickness calipers with micrometer resolution. SEM images of MMMs with lower UiO-66 loadings also show good adhesion between the MOF and polymer, with few apparent macrovoids in the imaged film (Figures 2S.3-5).
Figure 2.4. SEM images of UiO-66 MMM (~67% wt.). a) UiO-66 MMM showing MOF microcrystal structure. b) Torn edge of UiO-66 MMM, clearly showing both the UiO-66 particles and PVDF polymer fibers. c) Cross section of UiO-66 MMM showing uniform thickness of approx. 35 μm. d) Higher magnification of cross section, showing densely packed UiO-66 particles in the MMM interior.

Surface area analysis by N$_2$ sorption measurements reveal that high porosity of the MOF is retained in these MMMs. For example, a delaminated UiO-66 MMM, activated under dynamic vacuum at room temperature overnight, gave a Brunauer-Emmett-Teller (BET) surface area of 693±4 m$^2$/g (N$_2$, 77 K). If all of this surface area were attributed to just the MOF component, this is a remarkable retention of surface area. In fact, when accounting for the MOF/polymer composition of the MMM (~67% wt., according to the starting MOF/PVDF composition), the BET surface area of the MOF
component of the MMM can be estimated to be >1000 m$^2$/g (Figure 2.5), which is comparable to the value of pristine UiO-66 (~1110 m$^2$/g).\textsuperscript{41} This result was confirmed with several other MMMs incorporating different MOF species, which also gave high gas sorption capacities that are not significantly diminished versus their pristine state (Figure 2S.8, 2S.15, 2S.18, and 2S.21).

Figure 2.5. N$_2$ sorption isotherm of UiO-66 MMM. BET surface area: 693±4 m$^2$/g. BET calculation based on only MOF content (~67\% wt.): 1021±4 m$^2$/g.

To the best of our knowledge, these data are among the only direct measurements showing the preservation of surface area of MOF crystals in a MMM.\textsuperscript{11} To further assess the accessibility of the MOF pores in the MMM, dye uptake studies with Azure A, Acid Orange 8, and Acid Red 17 (Figure 2.6 with UiO-66 MMM) were performed. The gas sorption and dye uptake results indicate that the PVDF binder does not substantially penetrate the MOF lattice or occlude the pores of the MOF.
Digestion of the MOF component of MMMs revealed that in addition to being interesting as a composite material, these films may be used as templates for complex polymer film architectures. A UiO-66 MMM was subjected to UiO-66 digestion conditions with dilute HF (1.6% HF in DMSO v/v) to dissolve the MOF component, while leaving the non-soluble PVDF behind. During digestion, the MMM was observed to change from an opaque to a translucent material, indicating removal of the MOF. The remaining porous polymer film was extensively rinsed with methanol and dried under vacuum. The resultant film retained 32% mass of the original MMM, indicating full removal of the MOF component (and also verifying the % wt. composition of the original MMM). SEM analysis of the remaining film reveals a highly interconnected, lacy polymer network containing reliefs that retain the shape of the UiO-66 crystals (Figure 2.6).
2.7b), further suggesting good prior adhesion (e.g. minimal macrovoids) between the MOF filler and the polymer binder. This method of templating polymer films with MOF crystallites may be a route to achieving porous films with complex and unusual architectures, albeit an expensive one.

Figure 2.7. MOF MMM digestion. SEM images of: a) UiO-66 MMM; b) UiO-66 MMM after digestion with HF/DMSO solution to remove the MOF component, showing the intact porous polymer network with reliefs corresponding to the MOF microcrystals; c) Magnified section of 2.7b showing the clear relief of a polygonal MOF particle.

2.3 Postsynthetic Processing of MOF MMMs

Having proven that the MOF pores were still accessible after MMM fabrication, we set out to demonstrate another advantage of MOF-based MMMs that has significant potential to specifically tailor each membrane for a specific application. Demonstrating proof-of-concept PSM of the MOF in the MMM provides evidence that application-specific, reactive MMMs are possible. Despite being immobilized in a polymer matrix that could inhibit lattice access, the following experiments showed that the MOF particles were still accessible to chemical functionalization even within the MMMs (Figure 2.8).
Figure 2.8. Postsynthetic reactions in MOFs. a) Postsynthetic exchange (PSE) of Uio-66 with NH$_2$-bdc. b) Postsynthetic modification (PSM) reaction of Uio-66-NH$_2$ with acetic anhydride. The octahedron is used to represent the MOF lattice, indicating that the reactions take place without degrading the overall MOF structure.

To demonstrate these postsynthetic processes, a Uio-66 MMM was immersed in a solution of 2-amino-1,4-benzenedicarboxylic acid (NH$_2$-bdc) for 24 h at 55 °C. After the incubation period, it was shown that the MMM underwent a postsynthetic exchange (PSE) reaction, yielding a MMM that was converted to the Uio-66-NH$_2$ species, with ~33% of the bdc ligands in the starting MMM exchanged for NH$_2$-bdc (Figure 2.9). The MMM remained intact and the crystallinity of the MOF was preserved even after in situ PSE (Figure 2.10).
Figure 2.9. MOF MMM PSE. NMR spectrum of UiO-66 MMM (~67% wt.) after PSE with NH$_2$-bdc. Peak integration indicates 46% ligand exchange. (*) indicates peaks associated with NH$_2$-bdc product and (o) indicates peak of starting bdc ligand.

Figure 2.10. MOF MMM PSE PXRD spectra. PXRD spectra of UiO-66 MMM (67% wt.) before (red) and after (blue) PSE reaction with NH$_2$-bdc.
Similarly PSM could be achieved by immersing a UiO-66-NH$_2$ MMM in a solution of acetic anhydride for 24 h at 55 °C, resulting in ~75% conversion to UiO-66-AM1$^{41}$ (the methylamide derivative UiO-66-AM1, Figure 2.11). Again, the MMM maintained its integrity and the MOF material showed good crystallinity after this PSM reaction (Figure 2.12). We are unaware of any previous reports demonstrating the chemical accessibility of MOFs in a MMM. The ability to judiciously functionalize MOFs within a MMM in situ may prove highly beneficial for the function of these membranes, as well as providing a route for optimizing MOF-to-polymer interactions to eliminate membrane defects that are evident in many reported MMMs.$^{11}$

![Figure 2.11. MOF MMM PSM. NMR spectrum of UiO-66-NH$_2$ MMM (~67% wt.) after PSM with acetic anhydride. Peak integration indicates 75% modification to UiO-66-AM1. (*) indicates peaks associated with UiO-66-AM1 product and (o) indicates peak of starting NH$_2$-bdc ligand.](image)
Figure 2.12. MOF MMM PSM PXRD spectra. UiO-66-NH₂ MMM (67% wt.) before (red) and after (blue) PSM reaction with acetic anhydride.

2.4 Mechanical Properties of MOF MMMs

The effect of MOF loading on the mechanical properties of the films was assessed on a series of MMMs with UiO-66 content ranging from 10% wt. to 67% wt. Tensile strength data were acquired according to ASTM Standard D882-02 on an Instron® Universal Testing Machine (3342 Single Column Model) equipped with a 500N load cell in extension mode. The samples were loaded into the test cell and slowly elongated until failure, to generate stress-strain curves (Figure 2.13).
Figure 2.13. MOF MMM mechanical analysis. a) UiO-66 MMM (~67% wt.) during mechanical testing. 15 mm wide strip was tested in extension mode at 0.005 mm/s. b) Sample failure in mechanical testing. Failure point can be seen just below top clamp. c) Example of test strip after sample failure.

Tensile data (Table 2.1, Figure 2.14, and Figure 2.15) on these films show an increase in the film stiffness with increasing MOF content. This is coupled with decreasing ultimate tensile strength (UTS) in the materials. Despite a reduction in UTS, the freestanding MMMs even at high MOF loadings (~67% wt.) are robust enough to withstand mechanical stresses, such as bending and moderate tension (Figure 2.2c); indeed, the flexibility of these materials with the highest MOF loadings is quite
remarkable given that they are composed primarily of a rigid crystalline material.\textsuperscript{19, 22, 43-45} The data for elastic modulus do not display an obvious trend, as the UTS data do, but with MOF loading up to 30\% wt. there is an observed increase in elastic modulus, indicating that there is likely good adhesion between the MOF and polymer components of the membrane. Above 30\% wt. there is a reduction of elastic modulus, as the MOF component becomes dominant in membrane composition.

Table 2.1. \textbf{MOF MMM mechanical properties.} Mechanical properties of UiO-66 MMMs at various MOF loadings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOF % wt.</th>
<th>Elastic Modulus (MPa)</th>
<th>UTS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>768 ± 192</td>
<td>34.6 ± 2.7</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1474 ± 56</td>
<td>27.9 ± 1.4</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>1151 ± 358</td>
<td>17.6 ± 4.5</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>1274 ± 266</td>
<td>20.0 ± 4.9</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>421 ± 159</td>
<td>7.6 ± 1.5</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>236 ± 178</td>
<td>4.0 ± 0.9</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>283 ± 169</td>
<td>5.2 ± 0.6</td>
</tr>
<tr>
<td>7</td>
<td>67</td>
<td>654 ± 109</td>
<td>4.1 ± 0.9</td>
</tr>
</tbody>
</table>

\textbf{Figure 2.14.} \textbf{Ultimate tensile strength for MMMs with varying MOF \% wt.} Increasing MOF content reduces the ultimate tensile strength of the composite, giving a more brittle material.
2.5 Dye Separation with UiO-66 MMMs

To demonstrate a possible application of these MMMs, a UiO-66 MMM was employed to separate organic dye molecules in aqueous solution. Dye solutions were driven through a UiO-66 MMM immobilized in a Swinnex® syringe filter housing (0.95 cm² filter area) using a syringe pump. Swatches of the UiO-66 MMM were cut to form from a larger film, and could be easily handled for mounting in the syringe filter. The ability to employ this experimental setup (Figure 2.16) demonstrates the durability of these MMMs and how the MMM form factor improves the ease of handling of MOFs as a functional material. As a first test, the MMM was used to remove a single dye component from water. This MMM successfully demonstrated removal of 10 μM Coomassie Brilliant Blue R-250 from an aqueous solution as it passed through the membrane. Dye removal from the solution is easily observed both by eye, and more rigorously by spectroscopy; the eluent was analyzed by UV-Vis spectroscopy (λ = 552
nm) and showed >99% removal of the Coomassie dye (Figure 2.16a). In contrast, a pure-PVDF membrane did not allow passage of the analyte solution.

Figure 2.16. Aqueous filtration with UiO-66 MMM. a) Removal of Coomassie Blue dye via filtration by a UiO-66 MMM. Top: Schematic showing the dye molecule in aqueous solution before filtration through the membrane and only water in the eluent. Bottom: Photograph of syringe pump driven experimental setup. The syringe contains Coomassie Blue dye in solution and the eluent is clear, indicating dye removal. b) Demonstration of recyclability of the UiO-66 MMM. Top: The membrane after one filtration cycle covered in retained dye. Bottom: The same membrane after washing with MeOH to regenerate it for a second cycle of filtration.

After successful dye removal, the UiO-66 MMM was investigated for reusability in the filtration setup. The MMM was removed from the filter housing and washed with methanol to remove the collected Coomassie Blue dye, then replaced into the housing and the filtration process was repeated. The second filtration experiment demonstrated ~95% retention of the Coomassie dye, indicating good recyclability.

Beyond this simple process of single dye removal from aqueous solutions, these MMMs also demonstrate the ability to separate organic dye molecules in a mixed solution. An equimolar mixture of Coomassie Brilliant Blue R-250 and Methyl Orange
in water was driven through a UiO-66 MMM using the same process and apparatus as described as above (Figure 2.17).

**Figure 2.17. Aqueous dye separation with UiO-66 MMM.** a) Schematic for separation of Coomassie Brilliant Blue R-250 (blue) and Methyl Orange (orange) by filtration with a UiO-66 MMM. b) Separation of Coomassie Blue R-250 and Methyl Orange dye solution. The mixed solution is forced through a UiO-66 MMM syringe filter (~11 mm diameter) allowing permeation of Methyl Orange only. *Inset:* Retention of Comassie dye on the MMM film.

The pink solution was passed through the UiO-66 MMM giving an orange-colored eluent. Analysis of the eluent by UV-Vis shows near complete retention of the Coomassie Blue (95.6 ± 0.6%) while allowing ~80% of Methyl orange (20.1 ± 7.2% retention) across the MMM. Conveniently, the two dyes have distinct, non-overlapping
$\lambda_{\text{max}}$ wavelengths. Based on these simple, proof-of-concept experiments and given the extremely diverse range of pore environments and chemical tunability of MOFs, MMMs based on this MOF-forward approach offer the potential to tailor the membrane pore features for a specific separations application. This is further enabled by the ability to perform PSM or PSE on these MMMs, as described above.

### 2.6 Conclusions

In conclusion, we have developed a general, facile approach to the formation of MOF/polymer composite MMMs. These films can be made with a wide range of MOFs on various substrates and readily delaminated to yield durable, large-area, freestanding MMMs with good mechanical stability and flexibility. Characterization of the films shows the MOFs are highly crystalline and remain porous within the MMM. Moreover, the tunability of the component MOF by postsynthetic methods is retained in the MMM, resulting in MMMs that can be directly modified in situ with a range of chemical functional groups. We anticipate that PSM and PSE of the MOFs in the MMM can be employed to effect even greater functionality to these films, as well as a route to enhance the affinity between the MOF and polymer components of the MMM. Finally, our studies show the inherent utility of MMMs for formulating MOFs into an easily handled, readily usable form.
2.7 Appendix: Supporting Information

Starting Materials

Starting materials and solvents were purchased and used without further purification from commercial suppliers: Sigma-Aldrich, Alfa Aesar, EMD, and TCI. The PVDF used in these experiments was generously provided by Arkema Inc. and used without purification.

MOF Syntheses

**MIL-101(Fe).** Iron(III) chloride hexahydrate (FeCl$_3\cdot$6H$_2$O) (94 mg, 0.348 mmol) and terephthalic acid (58 mg, 0.348 mmol) were dissolved in 15 mL DMF. The solution was transferred to a 35 mL microwave reaction vessel and the reaction mixture was heated rapidly to 150 °C (Power = 300W) and held at 150 °C for 15 min. After cooling to room temperature, the red particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of each DMF and EtOH, and dried under vacuum at room temperature. BET surface area: 2494±186 m$^2$/g.$^{37}$

**MIL-101(Cr).** Chromium(III) nitrate nonahydrate (Cr(NO$_3$)$_3\cdot$9H$_2$O) (2.001 g, 5 mmol) and terephthalic acid (0.831 g, 5 mmol) were combined in a Teflon lined stainless steel Parr bomb with 25 mL water and 0.181 mL HF (48% soln. in water, 5 mmol). The sealed bomb was heated in an oven at 220 °C for 8 h. After cooling, the green precipitate was collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of each DMF and EtOH, and dried under vacuum at room temperature. BET Surface area: 3105±163 m$^2$/g.$^{36}$
**MIL-53(Fe).** Iron(III) chloride hexahydrate (FeCl$_3$·6H$_2$O) (0.540 g, 2 mmol) and terephthalic acid (332 mg, 2 mmol) were dissolved in 10 mL DMF. The solution was transferred to a Teflon lined stainless steel Parr bomb and heated to 150 °C (temperature ramped over 1 h, 2.5 °C/min) and held at temperature for 15 h. After cooling to room temperature, the yellow product was collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of each DMF and EtOH, and dried under vacuum at room temperature.$^{46}$

**UiO-66.** Zirconium(IV) chloride (ZrCl$_4$) (61 mg, 0.26 mmol) and terephthalic acid (43 mg, 0.26 mmol) were dissolved in 15 mL DMF with 0.447 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 h. After cooling to room temperature, the particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.$^{47}$

**HKUST-1.** Copper(II) nitrate hemipentahydrate (Cu(NO$_3$)$_2$·2.5H$_2$O) (1.22 g, 5.24 mmol) and 1,3,5-benzenetricarboxylic acid (0.58 g, 2.76 mmol) were dissolved in 5 mL DMSO. This solution was then added dropwise over 15 min to 250 mL of MeOH with magnetic stirring. Stirring was continued for 15 min after complete addition. The particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.$^{31}$

**ZIF-8.** Zinc(II) nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O) (0.30 g, 1.0 mmol) and 2-methylimidazole (0.66 g, 8.0 mmol) were each dissolved in 15 mL MeOH. The solutions were combined and stirred vigorously for 24 h. White ZIF-8 particles were collected by
centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.48

**MMM Fabrication**

**MOF/polymer mixed matrix membranes (MMMs).** In a typical formulation, 150 mg dry MOF powder was dispersed in 5 mL acetone with bath sonication for 30 min in a scintillation vial. 1 g of PVDF solution (7.5% wt. in DMF) was then added to the MOF suspension such that the final MOF:PVDF ratio was 2:1 w/w. The combined MOF/PVDF suspension was sonicated for 30 min in an ultrasonic bath, after which the acetone was removed by rotary evaporation, resulting in a MOF ‘ink’ of MOF and PVDF in DMF. Solutions of PVDF in NMP were also used with no significant difference in the cast films. The ink was cast by hand into films on Al foil, Al sheet, or glass (Fisherbrand Plain Microscope Slides, Catalogue #12-550C) substrates by drawdown coating with a glass rod using a spacer thickness of 300-400 μm. The coated films were then heated to remove solvent (1 h in an oven, 70 °C). Immersion in solvent (acetone or MeOH) resulted in rapid delamination of the MMMS. Delamination of the film in the aforementioned solvents is likely due to swelling of the PVDF, resulting in a morphological change at the MMM/substrate interface and consequent release. Sufficient roughening of the substrate surface prior to film deposition enhances substrate adhesion of the film, effectively inhibiting delamination (data not shown). The free-standing films were dried in air. Pure PVDF membranes were cast, heated, and delaminated by same procedure as MOF/polymer composite films.
**Characterization and Other Experiments**

**Postsynthetic Modification of UiO-66-NH₂.** UiO-66-NH₂ MMM (10.6 mg) was immersed in a solution of acetic anhydride (0.2 mmol in 2 mL CHCl₃) for 24 h at 55 °C. The sample was then rinsed several times with CHCl₃, and soaked in 10 mL CHCl₃ for 3 days with the solvent replaced every 24 h. Digestion of the MMM with HF solution and analysis by NMR determined that 75% of the bdc ligands had been modified by acetic anhydride.

**Postsynthetic Exchange of UiO-66.** UiO-66 MMM (8.3 mg) was immersed in a solution of 2-amino-1,4-benzenedicarboxylic acid (NH₂-bdc) (0.3 mmol in 2 mL H₂O) for 24 h at 55 °C. The sample was then rinsed several times with MeOH, and soaked in 10 mL of MeOH for 3 days with the solvent replaced every 24 h. The resultant film changed color from white to yellow, indicating incorporation of the NH₂-bdc ligand. Digestion of the MMM with HF solution and analysis by NMR determined a 46% of the bdc ligands exchanged for NH₂-bdc.

**MMM Digestion.** 12.1 mg of dry UiO-66 MMM was immersed in 1 mL DMSO. 50 μL of HF (48% soln. in H₂O) was added and the mixture was stored at room temperature overnight. Upon addition of the HF solution, the opaque MMM became transparent, indicating digestion of the MOF component. The supernatant was decanted and the sample was rinsed with 3×10 mL portions of MeOH. The sample was dried under vacuum overnight, giving a final mass of 3.9 mg, or ~32.2% of the original MMM mass.
**Powder X-Ray Diffraction (PXRD).** Approximately 50 mg of dry MOF powder or 0.5 cm$^2$ MMM was mounted on silicon sample holder for analysis by PXRD. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka ($\lambda = 1.5418$ Å), with a scan speed of 2 sec/step, a step size of 0.05° in 2θ, and a 2θ range of 2-50°.

**N$_2$ Sorption Analysis & BET Surface Area Analysis.** Samples for analysis were evacuated on a vacuum line overnight at room temperature prior to analysis. ~50 mg samples were then transferred to pre-weighed sample tubes and degassed at 105 °C (unless otherwise noted) on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. After degassing, the sample tubes were re-weighed to obtain a consistent mass for the samples. Sorption data and BET surface area (m$^2$/g) measurements were collected at 77 K with N$_2$ on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

**Scanning Electron Microscopy (SEM).** MMM films (approx. 3 mm$^2$) were transferred to conductive carbon tape on a sample holder disk, and coated using a Ir-sputter coating for 9 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum at a working distance at 10 mm.

**Mechanical Testing.** Tensile strength data were acquired according to ASTM Standard D882-02 on an Instron® Universal Testing Machine (3342 Single Column Model) equipped with a 500N load cell in extension mode. Sample thickness was measured using a Mutityo Digital Micrometer (0-25 mm range, 0.001 mm resolution, IP 54 standard) and averaged from 5 independent measurements from each sample. Tensile
measurements were acquired at an extension rate of 0.005 mm/s with a sampling rate of 500 ms to generate stress-strain curves. Ultimate tensile strength and elastic modulus were calculated from these curves using MS Excel. Tensile data were collected for at least 3 independent samples.

**Nuclear Magnetic Resonance.** Proton nuclear magnetic resonance spectra (\(^1\)H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. MMMs were digested for NMR analysis by immersion of ~8-10 mg MMM in 580 μL DMSO-\(d_6\) with 20 μL HF (48% in water). Samples were kept in this acidic solution at room temperature until the MOF component of the MMMs was fully dissolved.

**Separation Experiments.** As-prepared MMMs were fixed enclosed in a Swinnex® syringe filter housing (11 mm). 10 μM aqueous solutions of organic dyes were driven through the MMM at 250 μL/min with an infusion pump. The filtrate was collected and analyzed by UV-visible spectroscopy to determine dye content.

**UV-Visible Spectroscopy.** Absorption spectra were taken on a Perkin-Elmer Lambda 25 UV-visible spectrophotometer using quartz cuvettes over the range of 200 to 700 nm.
Supporting Figures

Figure 2S.1. *Left:* MMM prepared from direct dispersion of UiO-66 in PVDF/DMF solution shows poor MOF dispersion and agglomeration. *Right:* MMM prepared with predispersion of UiO-66 in acetone and subsequent addition of PVDF solution shows greatly enhanced uniformity and improved casting ability with reduced particle agglomeration. Films are shown as cast on Al foil substrate prior to delamination.

Figure 2S.2. PXRD spectra of pristine UiO-66 (black) and UiO-66 MMM (~67% wt., red).
Figure 2S.3. SEM images of UiO-66 MMM (67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.
Figure 2S.4. SEM images of UiO-66 MMM with 40% wt. MOF. a, b) plane-view; c,d) cross-section view at two different magnifications.
Figure 2S.5. SEM images of UiO-66 MMM with 20% wt. MOF. a, b) plane-view; c, d) cross-section view at two different magnifications.

Figure 2S.6. a) UiO-66-NH₂ MMM before PSM reaction, b) UiO-66-AM1 MMM after PSM reaction.
Figure 2S.7. PXRD spectra of pristine UiO-66 and UiO-66-NH$_2$ MMM (~67% wt.).

Figure 2S.8. N$_2$ sorption isotherm of UiO-66-NH$_2$ MMM. BET surface area: 430±6 m$^2$/g. BET calculation based on only MOF content (~67% wt.): 652±9 m$^2$/g.
Figure 2S.9. SEM images of UiO-66-NH₂ MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.10. PXRD spectra of as-synthesized MIL-53(Fe) and MIL-53(Fe) MMM (~67% wt.).
Figure 2S.11. SEM images of MIL-53(Fe) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.12. PXRD spectra of as-synthesized MIL-101(Fe) and MIL-101(Fe) MMM (~67% wt.).
Figure 2S.13. SEM images of MIL-101(Fe) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.14. PXRD spectra of as-synthesized MIL-101(Cr) and MIL-101(Cr) MMM (~67% wt.).
**Figure 2S.15.** N\textsubscript{2} sorption isotherm of MIL-101(Cr) MMM. BET surface area: 1323±8 m\textsuperscript{2}/g. BET calculation based on only MOF content (~67% wt.): 2002±12 m\textsuperscript{2}/g.

**Figure 2S.16.** SEM images of MIL-101(Cr) MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.
Figure 2S.17. PXRD spectra of as-synthesized HKUST-1 and HKUST-1 MMM (~67% wt.).

Figure 2S.18. N$_2$ sorption isotherm of HKUST-1 MMM. BET surface area: 892±6 m$^2$/g. BET calculation based on only MOF content (~67% wt.): 1353±9 m$^2$/g.
Figure 2S.19. SEM images of HKUST-1 MMM (~67% wt.). a, b) plane-view; c,d) cross-section view at two different magnifications.

Figure 2S.20. PXRD spectra of as-synthesized ZIF-8 and ZIF-8 MMM (~67% wt.).
Figure 2S.21. N$_2$ sorption isotherm of ZIF-8 MMM. BET surface area: 870±8 m$^2$/g. BET calculation based on only MOF content (~67% wt.): 1317±12 m$^2$/g.

Figure 2S.22. SEM images of ZIF-8 MMM. (~67% wt.). a, b) plane-view; c, d) cross-section view at two different magnifications.
2.8 Acknowledgements

Chapter 2, in part is a reprint of the material as it appears in “In Situ Modification of Metal-Organic Frameworks in Mixed-Matrix Membranes.” *Angew. Chem., Int. Ed.*, 2015, 54, 31, 9029-9032. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthor and advisor, Seth M. Cohen.

2.9 References


Chapter 3

Ammonia Adsorption and Enhanced Stability of HKUST-1 in MOF MMMs

3.1 Introduction

With an annual production over 200 million tons, ammonia is one of the most widely manufactured chemicals in the world.\textsuperscript{1} Ammonia has been identified as a chemical that frequently creates a high risk for accidental release that endangers the public through incidents such as spills at manufacturing facilities or explosions at fertilizer plants.\textsuperscript{2} Furthermore, the widespread availability and acute toxicity of ammonia make it a potentially highly effective chemical threat for opportunistic insurgents to utilize in asymmetric warfare. Indeed, in the 1990s, Serbian forces specifically targeted chemical plants during the war in Croatia to release ammonia into the environment as a means of attacking civilians.\textsuperscript{3} For these reasons, the development of engineered materials that can remove large amounts of ammonia for air purification applications is paramount for protection of warfighters and civilians alike.

As outlined in Chapter 1, MOF are porous materials built from inorganic metal nodes, known as secondary building units (SBUs), linked together by polydentate organic ligands.\textsuperscript{4-5} Various combinations of SBUs and organic linkers allow for tuning of the physical and chemical properties of the MOF. Importantly, the majority of MOFs are microporous, making them useful for gas storage,\textsuperscript{6-9} gas separations,\textsuperscript{10-11} molecular sensing,\textsuperscript{12-13} toxic chemical adsorption,\textsuperscript{14-15} and catalysis.\textsuperscript{16-17} While MOF materials have been examined extensively in their native powder form, there have been far fewer studies conducted on the properties of MOFs in engineered forms or as part of a composite matrix.\textsuperscript{18-22}
To incorporate MOFs into materials for applications in functional textiles, filters, or sensors, they must be fabricated into engineered forms, such as pressed pellets or films. Some Composite materials are preferred for these engineered forms because although pure-MOF membranes have been reported and are 100% active material by weight, they are only realistically achievable in small area samples and delamination from the support substrate typically proves difficult. MOF MMMs have the potential to enhance the utility of MOFs for personal protection by allowing for the facile fabrication of supported or freestanding films with variable material composition, while exhibiting mechanical and material properties beyond that of single crystals or free flowing powders that are more amenable to implementation in dynamic environments. Chapter 2 describes the preparation and characterization of a variety of MOF MMMs with polyvinylidene difluoride (PVDF) as the binding agent. PVDF-based MMMs of MOFs exhibited good chemical and mechanical stability, while allowing for high weight percent loading of MOFs as the active sorbent material. Furthermore, the crystallinity, surface area, and chemical reactivity of the MOFs were largely unperturbed in these composite membranes. MOF MMMs of this type then, were a natural choice for investigation as engineered materials for protection against chemical threats such as ammonia by incorporating MOFs that have proven activity against such threats in the native, powder form.

The MOF chosen for study in the engineered MMM is HKUST-1 (aka. Cu–BTC, Cu$_3$(BTC)$_2$, MOF-199, HKUST-1 = Hong Kong University of Science and Technology), a Cu-based MOF comprising Cu-paddlewheel SBUs linked together by benzene 1,3,5-tricarboxylate (btc) to form a 3-dimensional pore structure, as seen in Figure 3.1a.
HKUST-1 has a demonstrated affinity for ammonia, and has been shown to be superior to other MOFs for the adsorption of basic gases like ammonia, due to coordinatively unsaturated Cu-sites on the Cu-paddlewheel SBU.\textsuperscript{26-27} Recently, HKUST-1 was incorporated into biological chitin fibers at loadings up to 55\% wt., while maintaining approximately 75\% of its expected ammonia sorption capacity (based on HKUST-1 content), in an alternate approach to fabricating engineered forms of this MOF.\textsuperscript{28} Despite this study and the preliminary work on the native powder, this material’s potential remains largely unexploited.

\textbf{Figure 3.1. HKUST-1 MMM Fabrication.} a) 3-dimensional lattice structure of HKUST-1 and the coordinatively unsaturated sites on the Cu-paddlewheel SBU. b) Schematic representing the MMM fabrication process, see Chapter 2 for details. c) Photograph showing the flexibility of the HKUST-1 MMM. d) Plan-view and e) cross-section SEM images of the HKUST-1MMM.
Despite this MOF’s promise for mitigation of chemical threats from basic gases, one major obstacle to its widespread adoption: HKUST-1 is not stable in liquid water or high humidity conditions. Upon exposure to 90% RH at 25 °C, HKUST-1 exhibits a substantial loss of porosity and corresponding ammonia sorption capacity. This is accompanied by a transformation of the crystal structure that can be monitored by X-ray diffraction. However, it has been shown that the chemical stability of HKUST-1 can be improved via plasma enhanced chemical vapour deposition of perfluoroalkanes into the MOF structure. The hydrophobic nature of fluoroalkanes prevents water molecules from clustering in the pores and subsequently breaking the Cu–carboxylate linkages at the SBU of the MOF.

Despite the success of this approach, the product remains a powder and some degree of pore blocking is observed. Thus, while promising for improved stability, it does not address the myriad other issues required to make a suitable gas capture device from MOFs, including retaining fully accessible MOF surfaces, recyclability, mechanical stability, and facile processability. Fabrication of HKUST-1 into a MMM addresses all of these issues with a single solution, while also achieving enhanced chemical stability. In the following study, HKUST-1 MMMs of various loadings with PVDF are assessed for ammonia sorption as well as the effect of humidity on the performance of the MOF in the MMM. The data show that the ammonia removal performance of HKUST-1 in these MMMs is unprecedented, with greatly improved stabilization of the MOF toward both humidity and ammonia, when compared to HKUST-1 in the as-synthesized powder form.
3.2 HKUST-1 MMM Fabrication

The preparation and initial characterization of PVDF MMMs with a variety of MOFs is described fully in Chapter 2 and the same methodology was employed in this study.\textsuperscript{24} Fabrication of the HKUST-1 MMMs, described fully in Appendix of this chapter, is achieved through casting an ink composed of a solution of PVDF and HKUST-1 onto a suitable substrate, followed by solvent evaporation and delamination to give a freestanding MMM (Figure 3.1). The samples will be referred to by the code [\% wt.]-HKUST-1 MMM, where [\% wt.] = 30, 50, or 67, referring the \% wt. of MOF in the MMM. As the HKUST-1 content increases in the MMMs, so does the apparent surface area in the N\textsubscript{2} isotherm (Figure 3.2) and the intensity of the HKUST-1 peaks in the PXRD spectra (Figure 3.3). Likewise, the FTIR spectra (Figure 3.4) show that as the PVDF/HKUST-1 content varies for each sample, the corresponding infrared bands for PVDF and HKUST-1 vary in the same manner.

![Image of N\textsubscript{2} isotherms of HKUST-1 MMMs]

**Figure 3.2. N\textsubscript{2} isotherms of HKUST-1 MMMs.** BET surface area and total N\textsubscript{2} capacity correlate to the MOF content of each MMM. BET surface areas = HKUST-1 (1324 m\textsuperscript{2}/g), 67-HKUST-1 MMM (1025 m\textsuperscript{2}/g), 50-HKUST-1 MMM (861 m\textsuperscript{2}/g), and 30-HKUST-1 MMM (373 m\textsuperscript{2}/g).
Figure 3.3. PXRD spectra of HKUST-1 MMMs. The HKUST-1 MMM PXRD spectra are compared to HKUST-1 powder and PVDF.

Figure 3.4. FTIR spectra of HKUST-1 MMMs. The FTIR spectra of the MOF MMMs are compared to HKUST-1 powder and PVDF.
3.3 HKUST-1 MMM Ammonia Adsorption

A miniaturized breakthrough (microbreakthrough) apparatus was used to evaluate milligram-scale quantities of MOF samples for the adsorption of ammonia as described in depth elsewhere.\textsuperscript{33-34} Approximately 10-15 mg of material was loaded into a 4 mm inner diameter fritted glass tube that was subsequently loaded into a thermostated water bath for isothermal testing at 20 °C. Prior to testing, each material was pretreated for 1 h at 150 °C under flowing dry air to remove any physisorbed water from the sample. A ballast with a predetermined quantity of challenge gas was then mixed with a stream of dry (-40°C dew point) air at a rate necessary to achieve a challenge concentration of 2,000 mg/m\textsuperscript{3}. The contaminated air stream was then passed through the fritted glass sample tube at a flow rate of 20 mL/min, equivalent to a residence time of approximately 0.10 s. The effluent stream was sent through a photoionization detector to monitor the ammonia concentration in the stream. The data are shown in Figure 3.5, plotted as Normalized time (Normalized time = time/sample mass) verse the signal at a given time divided by the signal at saturation (C/C\textsubscript{0}). The corresponding breakthrough curves were integrated to determine the loading at saturation.

Using this apparatus, ammonia uptake capacities were measured for each material using dynamic microbreakthrough tests at a concentration of 2000 mg/m\textsuperscript{3}. The ammonia capacities, as determined from the breakthrough curves (Figure 3.5), for the HKUST-1 powder and HKUST-1 MMMs are shown in Table 3.1.
Figure 3.5. Microbreakthrough data. Microbreakthrough curves comparing PVDF polymer, HKUST-1 MMMs, and HKUST-1 powder.

The native HKUST-1 powder exhibited an ammonia sorption capacity of 7.4 mol/kg, which is commensurate with a loading of approximately 1.5 NH₃ molecules per Cu atom in the MOF. It has been shown that even at low pressures each Cu atom of HKUST-1 ligates one NH₃ molecule. The additional ammonia sorption is likely due to hydrogen bonding with the first, chemisorbed NH₃ molecules in the MOF pore. As expected, the ammonia capacity of each MMM varies proportionally with HKUST-1 content. Interestingly, as the HKUST-1 content increases in the MMM, the experimental ammonia capacity correlates very closely with the hypothetical capacity, as determined from the weight percent of HKUST-1 in each MMM. The good agreement between the experimental and hypothetical capacities, especially for 50-HKUST-1 and 67-HKUST-1 MMM, is strong evidence that the HKUST-1 crystals even within the interior of the MMM are accessible to the contaminated airstream, meaning that the entire MOF content of the MMM is available for chemical threat mitigation.
Table 3.1. **Ammonia Loading Capacity.** Experimentally measured and hypothetical ammonia loadings for the HKUST-1 powder, HKUST-1 MMMs, and PVDF control.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ammonia loading (mol kg(^{-1}))</th>
<th>Hypothetical ammonia loading (mol kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF polymer</td>
<td>0.1</td>
<td>N/A</td>
</tr>
<tr>
<td>30-HKUST-1 MMM</td>
<td>1.3</td>
<td>2.2</td>
</tr>
<tr>
<td>50-HKUST-1 MMM</td>
<td>3.2</td>
<td>3.7</td>
</tr>
<tr>
<td>67-HKUST-1 MMM</td>
<td>4.9</td>
<td>5.0</td>
</tr>
<tr>
<td>HKUST-1 powder</td>
<td>7.4</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The ammonia exposed HKUST-1 MMMs, HKUST-1 powder, and PVDF were then analyzed using PXRD (Figure 3.6) and FTIR (Figure 3.7) and compared to the pristine materials. The HKUST-1 powder exhibited a change in the PXRD pattern upon exposure to ammonia, with new reflections at \(2\theta = 18.1, 25.3,\) and \(27.0^\circ\), indicative of a substantial phase change and the loss of the HKUST-1 structure. In contrast, the PXRD patterns of each HKUST-1 MMM showed minimal change compared to Figure 3.3, indicating that HKUST-1 maintains its crystallinity better in the MMMs upon exposure to ammonia, when compared to the HKUST-1 powder.

The HKUST-1 powder exposed to ammonia also showed a loss of the FTIR band at 1646 cm\(^{-1}\), which is indicative of Cu–carboxylate bonding.\(^{31}\) These characteristics are consistent with degradation of the MOF structure by ammonia, as seen in earlier reports.\(^{26}\) The appearance of the bands at 1610 cm\(^{-1}\) in the FTIR spectrum upon the exposure of HKUST-1 to ammonia is characteristic N–H bending mode, indicative of the presence of ammonia.\(^{35}\)
Figure 3.6. PXRD spectra after ammonia exposure. PXRD spectra of the HKUST-1 MMMs compared to HKUST-1 powder and PVDF after exposure to ammonia. The major reflections from the ammonia exposed HKUST-1 powder (green), are designated with lines at $2\theta = 14.8$, 15.6, 16.2, 18.1, 19.9, 21.6, 22.1, 25.3, and 27.0°. There is no evidence of this change in the crystal structure in any of the ammonia exposed HKUST-1 MMMs.

The FTIR spectra of the HKUST-1 MMMs upon exposure to ammonia show that the Cu–carboxylate band is retained, which is consistent with the PXRD data confirming the retention of the HKUST-1 crystal structure. Furthermore, the HKUST-1 MMMs displayed an N–H bend at 1610 cm$^{-1}$ indicative of ammonia binding. The presence of Cu–carboxylate and N–H modes shows that even upon ammonia adsorption HKUST-1 can remain stable when confined within a PVDF MMM. Taken together, the microbreakthrough, PXRD, and FTIR data show that ammonia sorption in the native HKUST-1 powder induces rapid degradation of the structure, but that incorporation of HKUST-1 into a MMM stabilizes the MOF, without loss of ammonia sorption capacity.
**Figure 3.7. FTIR spectra after ammonia exposure.** FTIR spectra of the HKUST-1 MMMs compared to HKUST-1 powder and PVDF after exposure to ammonia.

Typically, engineered forms of sorbent materials display decreased activity toward an analyte of interest due to the occlusion of pores and/or active sites. However, that is not observed in this system, likely due to the vast majority of active sites being located within the micropores of the MOF, instead of on the outer surface as is typically the case with dense metal/metal oxide nanoparticles. Even though much of the outermost MOF surface is in contact with the polymer binder, many of these pores must still be accessible such that ammonia can still diffuse into the MOF crystallites, as evidenced by the high sorption capacities observed for HKUST-1 MMMs. Furthermore, based on the sorption capacity observed here, it is improbable that the PVDF polymer penetrates deeply into the inner pores of the MOF. Otherwise, it would impede the diffusion of adsorbates within the MOF.
3.4 Enhanced Aging Performance of HKUST-1 MMMs

It was previously found that HKUST-1 in its powder form degrades upon exposure to humid conditions over the course of a few weeks. The most aggressive aging condition was found to be 90% relative humidity (RH) at 25 °C, corresponding to an absolute humidity of 20.5 g/m, where HKUST-1 has a demonstrated water uptake of 32 mol/kg or 38% wt. These same conditions were used in this study to examine the moisture stability of HKUST-1 in the MMM form factor. The HKUST-1 MMMs were aged over 4 weeks under these conditions (90% RH, 25°C) and sampled at 1, 3, 7, 14, and 28 days. At each time point, the samples were analyzed again for ammonia sorption in the microbreakthrough apparatus as well as for changes in the PXRD and FTIR spectra.

The ammonia loading for each HKUST-1 MMM, compared to the HKUST-1 powder, after aging for various times is shown in Figure 3.8 (as determined from the microbreakthrough experiments in Figures S3.1-3). For the native HKUST-1 powder, approximately 90% of the ammonia capacity is lost within the first 7 days of aging, without much further change over the full 28 days of the experiment. In contrast, for the 50-HKUST-1 and 67-HKUST-1 MMMs the ammonia capacity over the full 28 days of aging varies less than 20%. 30-HKUST-1 MMM shows approximately 20% loss in ammonia capacity after aging for 14 days, and ~50% after aging for 28 days. Although 30-HKUST-1 MMM loses more ammonia capacity than higher loading MMMs, the relative loss in capacity of 30-HKUST-1 is still substantially less than the HKUST-1 powder.
Figure 3.8 Ammonia sorption vs. aging. Ammonia loading for HKUST-1 powder and HKUST-1 MMMs. Different HKUST-1 loadings after aging at 90% RH and 25 °C for various amounts of time are shown.

Upon examination of the PXRD spectra (Figure 3.9) of the HKUST-1 MMMs, it becomes more evident that the structures of 50-HKUST-1 and 67-HKUST-1 MMMs withstand the harsh aging conditions that HKUST-1 powder cannot. In general, the PXRD pattern remains unchanged over the 28 days studied for these materials. Furthermore, as expected from the loss in ammonia capacity of the 30-HKUST-1 MMM as it is aged, a degradation in the HKUST-1 crystal structure is observed as a loss of overall diffraction intensity. Interestingly, there is no formation of the secondary crystal structure in 30-HKUST-1 MMM that is seen upon degradation of the HKUST-1 powder, evidenced by reflections at 2θ = 7.9, 9.2, 12.1, and 14.3°. It should also be noted that the HKUST-1 PXRD reflections are observed in 30-HKUST-1 MMM after 28 days of aging, but they are significantly decreased in intensity.
Figure 3.9. **PXRD spectra vs. aging.** PXRD patterns of 30-HKUST-1, 50-HKUST-1, and 67-HKUST-1 MMMs, compared to HKUST-1, aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C.

In previous work, the breakdown of the HKUST-1 structure by water was identified to proceed mechanistically through the breaking of the Cu-carboxylate bond to form a carboxylic acid, evident as FTIR bands at 1708 and 1243 cm$^{-1}$. Over the course of the 28 days in this study we did not observe the appearance of these FTIR bands for any of the MMMs (Figures 3.10-13). Interestingly, FTIR bands at 1620 and 1540 cm$^{-1}$, which represent physisorbed water, were observed for 30-HKUST-1 MMM, which was also the only MMM that showed any signs of degradation. These same bands were observed in the powder form of HKUST-1 at the early stages of MOF degradation (days 1–3), with a modest decrease in the ammonia uptake, but no noticeable change in the crystal structure was observed. Conversely, these FTIR bands are not observed in 30-HKUST-1 MMM until day 14, nor are they observed in the 50-HKUST-1 and 67-HKUST-1 MMMs.
over the 28 day study. More importantly none of the HKUST-1 MMMs show the appearance of the carboxylic acid modes typically observed upon breakdown of HKUST-1.

![Figure 3.10. HKUST-1 FTIR vs. aging.](image)

**Figure 3.10. HKUST-1 FTIR vs. aging.** FTIR spectra of HKUST-1 powder before and after aging at 90% RH at 25 °C for 1, 3, 7, 14, and 28 days.

![Figure 3.11. 30-HKUST-1 MMM FTIR vs. aging.](image)

**Figure 3.11. 30-HKUST-1 MMM FTIR vs. aging.** FTIR spectra of 30-HKUST-1 MMM before and after aging at 90% RH at 25 °C for 1, 3, 7, 14, and 28 days.
Figure 3.12. **50-HKUST-1 MMM FTIR vs. aging.** FTIR spectra of 50-HKUST-1 MMM before and after aging at 90% RH at 25 °C for 1, 3, 7, 14, and 28 days.

Figure 3.13. **67-HKUST-1 MMM FTIR vs. aging.** FTIR spectra of 67-HKUST-1 MMM before and after aging at 90% RH at 25 °C for 1, 3, 7, 14, and 28 days.
Physically no change was observed in the color or appearance of the 50-HKUST-1 and 67-HKUST-1 MMMs during the aging process; however, the 30-HKUST-1 MMM sample showed a fading of the characteristic blue color from what appeared to be visible degradation of the material (Figure 3.14).

**Figure 3.14. Physical appearance vs. aging.** Photographs of each HKUST-1 MMM after aging for 0, 1, 3, 7, 14, and 28 days at 90% RH and 25 °C.

The preparation of the MMMs results in the side against the substrate having greater apparent polymer content (referred to as substrate-facing side), while the other side is richer in MOF crystals dispersed throughout the PVDF (referred to as outward-facing side), which is more representative of the bulk MMM. SEM images (Figure 3.15) further show the physical state of the 50-HKUST-1 and 67-HKUST-1 MMMs remain essentially unchanged over the 28 days of aging.
Figure 3.15. Microscale appearance vs. aging. SEM images (magnification = 5000x) of each HKUST-1 MMM, on the outward-facing (MOF dominant) side and substrate-facing (polymer dominant) side, after aging for 0, 1, 3, 7, 14, and 28 days, at 90% RH and 25 °C.

The two different sides of the MMM have varying degrees of hydrophobicity, as do the MMMs with various amounts of HKUST-1, as determined by water contact angle measurements (Table 3.2). Two distinctive trends were observed in these contact angle data: 1) the contact angle increases as the HKUST-1 content of the MMM increases, and 2) the outward-facing side of the MMM has a higher contact angle than the substrate-facing side of the MMM. The water contact angle of a material is driven by not only the chemical make-up of the material, but also by the roughness of the material surface.\(^{36-37}\) The air trapped in the space between the MOF particles is an important contributor to the increased hydrophobicity as the water contact angle of air is
considered to be $180^\circ$.\footnote{37} Despite HKUST-1 being hydrophilic, the PVDF binder on the particle surface makes each particle hydrophobic, while the increased surface roughness from the individual MOF crystals in the polymeric matrix is the primary contributor to the increased contact angle of the outward facing-side (rounder) of the MMMs relative to the substrate-facing side (smoother). As expected, due to increased surface roughness, the HKUST-1 MMMs with a higher percentage of HKUST-1 exhibit an increased contact angle. Of particular significance, the water contact angle of an HKUST-1 pellet has been reported to be $59^\circ$,\footnote{33} much lower than that observed for any of the MMMs.

**Table 3.2. Contact angle data.** Contact angles for each HKUST-1 MMM measured on the outward facing (MOF dominant) and substrate facing (polymer dominant) side.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Side</th>
<th>Water contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF polymer</td>
<td>N/A</td>
<td>$82^\circ \pm 3$</td>
</tr>
<tr>
<td>30-HKUST-1 MMM</td>
<td>Outward</td>
<td>$84^\circ \pm 1$</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td>$80^\circ \pm 1$</td>
</tr>
<tr>
<td>50-HKUST-1 MMM</td>
<td>Outward</td>
<td>$101^\circ \pm 1$</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td>$83^\circ \pm 2$</td>
</tr>
<tr>
<td>67-HKUST-1 MMM</td>
<td>Outward</td>
<td>$110^\circ \pm 1$</td>
</tr>
<tr>
<td></td>
<td>Substrate</td>
<td>$107^\circ \pm 0$</td>
</tr>
</tbody>
</table>

The increased hydrophobicity of the MMMs compared to HKUST-1 powder results in a significant decrease in the total water uptake as observed in the water isotherms performed at 25 °C (Figure 3.16). When corrected for MOF content (Figure 3.17), the water loading is similar for each of the MMMs, not increasing with MOF content. It has been shown elsewhere that hydrolysis of HKUST-1 requires the clustering of water molecules near the Cu–carboxylate bonds, in order for hydrolysis to occur.\footnote{29} The decreased water uptake of the
MMM results in less water per SBU, significantly decreasing the potential for degradation of the MOF lattice via hydrolysis.

Figure 3.16. Water isotherm data (uncorrected). Water isotherms collected at 25°C for HKUST-1 powder and the HKUST-1 MMMs.
Figure 3.17. Water isotherm data (corrected). Water isotherms collected at 25°C for the HKUST-1 powder and the HKUST-1 MMMs. MMM data are adjusted for the amount of HKUST-1 present in the composite.

The PXRD and FTIR data, along with the ammonia sorption capacities of the HKUST-1 MMMs, clearly show that the 50-HKUST-1 and 67-HKUST-1 are quite stable to humid environments over the 28 day period studied here. As seen previously, the presence of hydrophobic fluoroalkanes enhance the water stability of HKUST-1.\textsuperscript{32-33} Curiously, in humid environments 30-HKUST-1 begins to lose its crystallinity and consequently its ammonia adsorption capacity over time, due to the early stages of MOF degradation, which can be observed through the sorption of water in the FTIR spectra, and loss of the HKUST-1 crystal diffraction in the PXRD spectra. 30-HKUST-1 MMM contains the highest ratio of the PVDF polymer, which in the case of the MMM acts as
a binder and supplies hydrophobic -CF₂ groups. Intuitively, one might hypothesize that the 30-HKUST-1 MMM would withstand the humid environment that the materials were subject to better than the MMMs with a higher HKUST-1 content; however, this was not the case. It was observed that the 30-HKUST-1 MMM sample had much lower contact angles (similar to that of PVDF) than the other MMMs, likely due to the increased surface roughness of the 50-HKUST-1 and 67-HKUST-1 MMMs. In the SEM images of the higher HKUST-1 content MMMs, it can be observed that the MOF crystals dominate the surface of the MMM, which is not the case for 30-HKUST-1 MMM. In turn, the flattened surface of 30-HKUST-1 MMM does not repel condensed water droplets as well as the other MMMs, and over the course of 28 days may attract more water into the MOF structure, promoting eventual degradation of the MOF, even though this was not observed on the timescale of the water isotherm. Nevertheless, the degree of degradation for the 30-HKUST-1 MMM is much less than is observed for the pure HKUST-1 powder. In fact, after 7, 14, and 28 days of aging, the 30-HKUST-1 MMM even has a higher ammonia capacity than the HKUST-1 powder, despite 30-HKUST-1 MMM only having 30% of the material being the active HKUST-1 MOF by weight.

3.5 Conclusions

HKUST-1 MMMs are strong candidates for use in gas filtration applications, due not only to the high ammonia capacities of the engineered form of the MOF, but also the increased water and ammonia stability of the MOF over the primitive powder form. Furthermore, the MMMs can easily be shaped or molded into useful forms for a given application. PVDF acts as an effective binder for HKUST-1, while still allowing the pores to
be permeable and accessible to adsorbates such as ammonia, giving ammonia sorption capacities that are directly scalable to the HKUST-1 content of the MMM.

Remarkably, no degradation was observed over the course of 28 days for the 50-HKUST-1 and 67-HKUST-1 MMMs upon exposure to 90% RH at 25 °C. Furthermore, the ammonia capacity for these samples was relatively constant over the period studied. The increased water stability of HKUST-1 in the MMM results from the increased chemical hydrophobicity stemming from the fluorocarbon groups of the PVDF polymer and the surface roughness created by the MOF crystals bound in the matrix, making these materials resistant towards both water vapor and liquid water. Overall the findings here strongly support the use of MOF MMMs as a means to enhance the utility, processability, stability, and performance of MOFs in gas sorption applications in a comprehensive manner that has not been demonstrated before.
3.6 Appendix: Supporting Information

Material Synthesis

HKUST-1 was synthesized by dissolving copper(II) nitrate hemipentahydrate (Cu(NO$_3$)$_2$·2.5H$_2$O) (1.22 g, 5.24 mmol) and 1,3,5-benzenetricarboxylic acid (0.58 g, 2.76 mmol) in 5 mL DMSO. This solution was then added dropwise at room temperature to 250 mL of MeOH with magnetic stirring over the course of 15 min. Stirring was continued for 15 min after complete addition. The particles were collected by centrifugation, washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.$^{38}$

Mixed Matrix Membrane Fabrication

The resulting dry HKUST-1 powder was dispersed in 5 mL acetone with sonication for 30 min. A PVDF solution (7.5 % wt. in DMF) was then added to the MOF suspension giving the desired HKUST-1: PVDF ratio, and sonicated for 30 min. The acetone was removed via rotary evaporation, resulting in a MOF ‘ink’. The ink was cast into films on Al substrates by drawdown coating with a doctor blade (blade height = 400 µm). The resulting film was heated at 70°C for 1 h to remove solvent. The resulting membranes were delaminated via immersion in solvent (acetone, MeOH). The free standing films were air dried.$^{24}$
**Powder X-ray diffraction (PXRD)**

Each MOF sample was analyzed using powder X-ray diffraction (PXRD). PXRD measurements were taken using a Rigaku Miniflex 600 X-ray powder diffractometer with a D/Tex detector. Samples were scanned at 40 kV and 15 mA, using Cu Ka radiation ($\lambda = 1.54 \text{ Å}$), and a scan rate of 5° min$^{-1}$ over a 20 range of 3 to 50°. Double-sided tape on zero-background discs were used to affix the MMM and minimize background scattering. A background correction was performed in the Rigaku PDXL software (version 2.1.3.6).

**Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)**

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of each MOF were taken using a Bruker Tensor 27 FTIR with a Bruker Platinum ATR accessory equipped with a single reflection diamond crystal. Sixteen scans were averaged over a range of 4000 to 400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$.

![Figure S3.1. Ammonia breakthrough curved 30-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C.](image-url)
Figure S3.2. Ammonia breakthrough curved 50-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C.

Figure S3.3. Ammonia breakthrough curved 67-HKUST-1 MMM aged for 0, 1, 3, 7, 14, and 28 days at 90% RH at 25 °C.
3.7 Acknowledgements

Chapter 3, in part is a reprint of the material as it appears in “Enhanced aging properties of HKUST-1 in hydrophobic mixed-matrix membranes for ammonia adsorption.” Chem. Sci., 2016, 7, 2711-2716. The dissertation author was the primary author of this paper and gratefully acknowledges the contributions of his coauthors, Jared B. DeCoste, Gregory W. Peterson, John J. Mahle, and Seth M. Cohen.

3.8 References


Chapter 4

Evolution of MOF MMMs to Multifunctional Membranes

4.1 Introduction

Now that MOF research is entering its third decade, significant efforts are being made toward actual implementation of MOF-based materials for various applications, including protection from chemical threats, as described in Chapter 3. Strategies for mitigation of chemical threats with MOF-based materials include both selective sorption of toxic species and catalytic degradation of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs). Selective sorption of the threat can serve to sequester and contain the threat, while catalytic degradation effectively removes the threat. While some MOFs have shown excellent performance against individual toxic species, it can easily be envisioned that multiple MOF species in the same material can exploit the best properties of each to achieve broad spectrum protection.

The inherent high surface areas, tunable porosities, and diverse functionalities that define this class of materials make MOFs appealing for personal protection from toxic species and others like gas and liquid separations. Despite their promise in this field, there have been two major hurdles to their implementation. First, many MOFs are relatively unstable when exposed to these toxic agents, humidity, or mildly caustic conditions. The second challenge is that MOFs form as a microcrystalline powder, which limits the handling, implementation, and processing of the MOF materials. Previous work, described in Chapters 2 and 3, has shown that both of these issues can be overcome.
Unstable MOFs can be effectively shielded from degradation by moisture through inclusion in a polymeric matrix, with the added benefit of being incorporated into an engineered form factor that makes their handling and implementation much easier than the native powder form. Engineered MOF composites for MOF applications, such as pressed pellets and mixed matrix membranes (MMMs) have become an area of increasing interest, although the field remains nascent. Indeed, compared to other inorganic materials, such as zeolites, the development of MOF-polymer composites is still in its infancy. Composites of MOFs and polymeric binders is a promising route to obtaining functional fibers, textiles, and films that exploit the extraordinary gas sorption, sensing, and catalytic properties of MOFs.

After successfully developing the methodology to prepare a wide range of MOF composites as MMMs, we demonstrated that HKUST-1, a copper-based MOF, shows significantly enhanced chemical stability vs. the native (i.e., microcrystalline powdered) MOF when fabricated into a MMM form factor with PVDF, while maintaining nearly unhindered capacity for ammonia. Having thus demonstrated that the composite material can not only maintain, but enhance the performance of MOFs, we sought to explore the ways in which multiple MOF species could be combined in a single composite material with a focus toward multifunctional materials. These multiple MOF materials should allow a single material to be used for applications like broad spectrum protection from chemical threats and multistep catalytic membranes. For example, incorporation of multiple MOFs can add to the functionality of the HKUST-1 MMM
above by inclusion of Zr^{4+}-based MOFs that have been shown to have excellent performance in catalytic degradation of chemical warfare agents (CWAs, e.g., Sarin). This combined material should display protection against ammonia and CWAs.

Figure 4.1. Strategies for multifunctional MOF MMMs. a) Co-casting different MOF inks results in MMMs with different MOF species spatially separated in the same monolithic MMM. The resulting MOF MMMs can be of two types: (left) simple discrete regions or (right) patterned MOF distribution. b) Mixing MOF species together to generate a single, blended ink results in fully integrated MMMs of mixed MOF species. c) Repeating the casting process with subsequent MOF layers results in layered MOF MMMs of different MOF species.

As indicated above, multifunctional MOF composites are of significant interest for various applications, but the specific form that the multifunctional composite takes will
be highly dependent on the intended use. To this end, we have prepared a series of mixed MOF composites in multiple forms (Figure 4.1). First, we explored combined materials wherein the MOF species are separated into discrete regions within a single composite material. We then prepared a range of mixed MOF MMMs, wherein the MOF species are fully integrated throughout the membrane. Finally, we developed a method to prepare layered MOF MMMs with use of a cross-linking agent to inhibit redissolution of the polymeric binder. Each type of multifunctional MOF MMM will be described in the following sections. Using these techniques for the combination of MOF species in a single composite material further advances the development and implementation of MOF-based materials tailor made for real-world applications.

4.2 Co-cast MOF MMMs

The first strategy employed was to cast inks of different MOF species into the same monolithic film. The result of this relatively simple strategy is a large area sample that has discrete regions of each MOF type. To produce films of this type, individual inks are applied side-by-side onto the same substrate, followed by simultaneous draw-down casting such that the inks contact each other during casting and the polymer matrix is contiguous. The MOF film is then heated to drive off the casting solvent and delaminated from the substrate just as the single MOF formulations are.

Figure 4.1a shows the process and results of this strategy. The resultant films are monolithic with no obvious weakness at the seam between the MOF types. Moreover, because of the viscosity of the casting inks, there is not a large degree of mixing of the MOF types at the interface, so the two species stay well separated. Two of these films
are shown in Figure 4.1a, using similar strategies. The film on the left is composed of a 
UiO-66 domain (white) and a HKUST-1 domain (right). Just as in the single MOF films, 
each of these domains retains the crystallinity and porosity of the MOF in the composite, 
while joining the two into a unified MOF MMM.

A modification of this process allows for creation of more complex designs, as 
demonstrated in the right image in Figure 4.1a. The ‘Triton’ logo of UC San Diego 
athletics was created by selectively applying HKUST-1 (blue) and MIL-53(Fe) (yellow) 
to the same substrate. In this case, the doctor blade was not used to spread these inks. 
Instead, each ink was simply applied to selected areas of the substrate with a pipette to 
form the pattern. Similarly, this sample remains intact after solvent removal as a single 
MMM, bearing discrete domains of HKUST-1 and MIL-53(Fe). While this technique of 
pattern creation is somewhat crude, this technology should be readily adaptable to 
processes like inkjet printing to apply MOFs into complex patterns with high spatial 
resolution on a variety of substrates for applications like sensing arrays.

4.3 Mixed MOF MMMs

The second approach to producing integrated composites with multiple MOF 
functionalities was to fabricate fully mixed MOF MMMs. In this type of MMM, two or 
more MOF species are fully mixed throughout the membrane. Fabrication of these mixed 
MOF MMMs is similar to production of the single MOF MMMs, with a single ink being 
formulated containing multiple MOF species in equal proportions. This ink is then cast 
and heated to removal solvent as per the normal MMM synthetic procedure. Figure 4.1b 
depicts this process and shows the result of a MMM produced from an ink containing
MIL-53(Fe) and HKUST-1. The single MOF MMMs are shown on the left, where the HKUST-1 MMM is blue and the MIL-53(Fe) MMM is orange. The combined MMM is green, as would be expected from mixing these two colors, showing evidence of good integration of the two species at the macroscale. This process is versatile, just as the single MOF formulation is, and can be applied to a variety of mixed MOF MMMs (Figure 4.2). Moreover, just as in the single MOF system, the total MOF content is easily tailored in the ink formulation up to approximately 70% wt., above which the films become brittle.

<table>
<thead>
<tr>
<th>MOF</th>
<th>HKUST-1</th>
<th>ZIF-8</th>
<th>UiO-66</th>
<th>UiO-66-NH₂</th>
<th>MIL-101(Fe)</th>
<th>MIL-53(Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UiO-66</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UiO-66-NH₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIL-101(Fe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MIL-53(Fe)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.2. Mixed MOF MMMs.** A variety of MOF MMMs have been fabricated from mixed MOF inks. The MMM in each cell is a mixture of the MOF species identified in the corresponding row and column. Each MMM is 60% wt. total MOF, combined in a 1:1 ratio by weight.

Closer examination of these MMM films shows that the characteristics of the component MOFs remain intact, just as in the single MOF systems. Figure 4.3 shows
MMMs of UiO-66, HKUST-1, the mixed MOF MMM, and their corresponding PXRD pattern. The total MOF content of each film is 60% wt. with equal parts (30% wt. each) of HKUST-1 and UiO-66. The mixed MOF system does not appear to have detrimentally affected the properties of the MMM, as it is easily handled and macroscopically behaves the same as the single MOF systems.

Figure 4.3. HKUST-1 + UiO-66 MMM. a) 60% wt. HKUST-1 MMM. b) 60% wt. UiO-66 MMM. c) Mixed HKUST-1 and UiO-66 MMM (60% wt. total MOF) in a 1:1 ratio. d) PXRD spectra of the UiO-66 MMM (black), HKUST-1 MMM (blue), and the mixed MOF MMM (cyan), which displays peaks from both the UiO-66 and HKUST-1 spectra.

Indeed, the film shows clear indication of good incorporation of both MOF components in a complementary way. The color of the film is a slightly lighter blue than the pure HKUST-1 film, as would be expected by blending a white species with the blue species, but the HKUST-1 still demonstrates the characteristic color change (light blue to
deep violet) on heating of the MMM that indicates dehydration of the HKUST-1 paddlewheel SBUs (data not shown).

Examination of the films by PXRD show diffraction peaks in the mixed system attributable to both of the pure species with good fidelity. Figure 4.3d shows such a mixed PXRD spectrum for the mixed UiO-66 and HKUST-1 MMM. The PXRD spectrum for the mixed MOF MMM (cyan) contains peaks consistent with both the UiO-66 MMM spectrum (black) and the HKUST-1 MMM spectrum (blue). This combined diffraction in the PXRD spectra is true for the remainder of the mixed MOF MMMs shown in Figure 4.2, which can be found in the Supporting Information.

Analysis of the N\textsubscript{2} sorption isotherm of the 50% wt. mixed MOF MMM of the same MOFs (Figure 4.4) shows good uptake performance, on par with the individual MOF MMMs, indicating that the porosity of both MOF species are still accessible in the mixed system. The BET surface area and total N\textsubscript{2} uptake are slightly lower than would be expected for the mixed MOF system, but still comparable to single MOF MMMs. Taken together with the PXRD spectra, it is clear that in the mixed MOF MMMs, the MOF crystallinity of each species is intact and the pores of each species are accessible, so the mixed system should perform well as a multifunctional material.
Figure 4.4 Pore accessibility of the mixed MOF MMM. N₂ sorption isotherms of 50% UiO-66 MMM (black), 50% HKUST-1 MMM (blue), and the mixed MOF MMM (purple). BET surface areas = UiO-66 (577 m²/g), HKUST-1 (888 m²/g), and mixed MOF MMM (537 m²/g).

Additional confirmation of good dispersion of the two MOF species in the mixed MOF MMM was obtained by SEM imaging. Figures 4.5 a and b show the surface of the mixed MOF film. Two distinct crystallite sized are clearly visible: large crystals ca. 2 μm in diameter are HKUST-1, and smaller crystals, ca 200 nm in diameter are UiO-66. From these images, it can be seen that there is good dispersion of the two species, without significant clustering of one versus the other. A cross-section image of the film (Figure 4.5c) shows a good distribution of both species throughout the thickness of the film, with the smaller UiO-66 particles serving to fill in gaps between the larger HKUST-1 crystals in a brick-and-mortar fashion. Such integration of MOF particles of disparate sizes may
even be beneficial for a mixed MOF system by helping to fill voids between the larger species that would otherwise be present. This same thorough integration of the mixed species holds true for the remainder of the MOF formulations shown in Figure 4.2; SEM analysis can be found in the Supporting Information.

**Figure 4.5 SEM images of 50% wt. mixed MOF MMM.** The 50% wt. HKUST-1 + UiO-66 mixed MMM was observed in the SEM. a) Plane-view images of the MMM surface show both MOF species are well distributed. b) A closer magnification of the MMM surface distinctly shows both the large HKUST-1 particles and the smaller UiO-66 particles in the film. c) The cross section image of the MMM shows that both MOF species are well integrated throughout the thickness of the membrane, with the smaller UiO-66 particles filling in the gaps between the larger HKUST-1 particles.

### 4.4 Layered MOF MMMs

The third strategy employed to make multifunctional MOF MMMs outlined in Figure 4.1c was to layer the MOF species in the MMM. The idea is quite simple, but achieving intact layered MOF MMMs proved to be non-trivial; indeed, apart from one recent report from Peterson et al.,\(^{23}\) there is little literature precedent for such composite materials. Utilizing PVDF as the binder matrix in a layered system presents a significant challenge resulting from the solubility characteristics of the polymer. PVDF is soluble in a limited range of high-boiling solvents, which is beneficial to the long-term stability of PVDF based systems, but effectively eliminates most common solvents from formulation, especially those that are easily removed at low temperatures.
In previous work, we found that MOF inks formulated in DMF were excellent for fabricating MMMs with PVDF. The boiling point of DMF is 153 °C, so the film dries quite slowly unless high temperatures are used. Trying to prepare a multi-layer MOF MMMs by simply casting a second layer on top of a pre-formed MMM results in swelling of the MMM as the polymer resolvates and ultimately dissolution of the PVDF in the first layer by the ink of the second layer. This process effectively destroys the MOF MMM, resulting in a cracked, non-continuous film. This technical hurdle was overcome by employing a crosslinking agent in the ink formulation and adjusting the fabrication procedure to limit the volume changes in the polymer due to solvation.

Crosslinking MOF MMMs

To overcome the solvent-induced dissolution of PVDF in the MMMs, the PVDF was crosslinked after casting by the addition of a small amount of a polyamine to the ink formulation. The MOF inks were first prepared in the typical fashion: 1) MOF was dispersed in acetone, 2) PVDF solution in DMF was added, 3) the mixture is sonicated to ensure homogeneity, and 4) acetone is removed from the mixture by rotary evaporation. At this point, hexamethylene diamine (HMDA) a short chain, linear diamine was added to the MOF ink and the mixture was further sonicated to ensure homogeneity. The inks were then cast into MMMs via doctor blade as before, but the baking conditions were changed from 1 hour at 70 °C to 12 hours at 100 °C to ensure full reaction of the HMDA with the PVDF.

Only a small amount of HMDA was needed to achieve polymer crosslinking in the MMMs made from UiO-66, UiO-66-NH₂, ZIF-8, and MIL-53(Al)-NH₂. 5 mol%
HMDA (relative to the PVDF monomer) was sufficient to inhibit redissolution of the MMM when fully immersed in DMF for over 24 hours. A MMM prepared by the same method without HMDA in the casting ink formulation disintegrated as the PVDF dissolved in the DMF within 10 minutes (data not shown). Analysis of the crosslinked films by PXRD and SEM shows no obvious difference from the typical MOF MMMs. Addition of more crosslinking agent (10 mol%) to a casting ink of UiO-66 also inhibited dissolution of the MMM, but also caused the membrane to be noticeably more brittle than that prepared with 5% crosslinking agent. One important caveat to this methodology is that HMDA is reactive toward HKUST-1, causing a color change in the MOF (blue to green) and degradation of crystallinity at high concentrations of HMDA. For this reason, HMDA was not added to any HKUST-1 ink formulations.

_Casting Conditions_

The addition of a crosslinking agent to the casting formulation noticeably enhanced the stability of the films such that a second MOF layer could be applied to the MMM without degradation of the first layer. However, the casting area of the second layer is limited to 1-2 cm$^2$ when applied to the dry MMM. The reason for this is that while the HMDA crosslinking successfully inhibits dissolution of the PVDF, the polymer still swells as a result of resolvation by the casting solvent from the second layer.

To enable casting of multi-layer films larger than 1-2 cm$^2$, we attempted to pre-swell the MMM prior to deposition of the second layer. The first layer of the MMM was resolvated after casting and heating, by immersion in various solvents (vide infra). The solvated MMM is then used as the substrate for casting a subsequent MMM layer.
Solvation with low boiling solvents like acetone sufficiently swell the MMM, but gave a short working time in which to apply the second MOF layer because of rapid evaporation, which results in uneven application of the second layer and insufficient quality of the final MMM. Resolvating the MMM with a high boiling solvent like DMF gave a longer working time and further expanded the available size of the casting area on the MMM. Use of the HMDA crosslinking agent was essential in this process to ensure that the first MOF layer remained intact during the resolvation step. Figure 4.6 shows the results of using this resolvation process to achieve a two layer MOF MMM. In this example, HKUST-1 has been cast as the second layer after solvating the UiO-66 MMM with DMF. The SEM cross section of the MMM is shown in Figure 4.6c, where a clear demarcation is evident in the membrane between the smaller UiO-66 particles on the bottom half and the larger HKUST-1 particles on the top half of the film.

While the SEM cross section is clean and the bilayer area of the MMM is defect free, Figure 4.6a shows that the edges of the UiO-66 film deformed during the second heating step, likely due to the different rates of contraction during desolvation between this area and the bilayer film. Ultimately this method was deemed unsatisfactory because especially in larger areas, many of these layered MMMs showed evidence of defects like tears and buckling after the second heating step that affected the overall film quality. This pre-swelling approach worked for producing larger samples, roughly doubling the size of the castable area relative to casting a second layer on a dry MMM, but ultimately was insufficient for practical production because it is overly complicated and handling the MMM during the resolvation step can lead to MMM defects.
Figure 4.6 Resolvation for multilayer MMMs. a) Photograph of the top side of a two layer MOF MMM, UiO-66 first layer, HKUST-1 second layer. b) Reverse image of the same film. c) Cross section SEM of this film. Smaller UiO-66 particles make up the bottom layer in this image, while larger HKUST-1 particles are exclusively in the top layer. Each layer is 60% wt. MOF.

Uniform deposition of multiple MOF layers was ultimately achieved by deposition of subsequent MOF layers after only a partial drying of the previous layer. A similar methodology was independently developed in a concurrent study.\textsuperscript{23} In short, the film is dried at elevated temperature until the majority of the casting solvent is removed, but the film is still solvated, and thus has not contracted. When the second layer is then applied to this film and the composite is fully dried, the layers can dry together and thus, contract at the same rate, so as not to buckle or tear from differential rates of contraction.

In a typical multilayer MOF MMM the MOF inks are prepared in parallel since the coating process happens rather quickly. The first layer is cast via the normal process and placed in a 70 °C oven for 3-5 minutes. During this time, the solvent front can be clearly observed in the drying film. At the point when the surface of the film takes on a matte appearance, but is still solvated, the sample is removed from the oven and the second MOF ink is cast on top of it. This process can then be repeated if subsequent
layers are required, or the MMM can be heated for 12 hours at 100 °C to complete the process. Addition of HMDA as a crosslinking was used in these films to further enhance their integrity and ensure that the MOF layers are well adhered. Figure 4.7 shows the result of this process with a two layer film of ZIF-8 and HKUST-1.

**Figure 4.7** Large area layered MMM. a) Photograph of the top side of a two layer MOF MMM, ZIF-8 first layer, HKUST-1 second layer. b) Reverse image of the same film. c) Cross section SEM of this film. Smaller ZIF-8 particles make up the bottom layer in this image, while larger HKUST-1 particles are exclusively in the top layer. Each layer is 60% wt. MOF.

Like Figure 4.6, the two-layer MOF MMM in Figure 4.7c shows a clean cross section in the SEM with a clear demarcation between the ZIF-8 on the bottom and the larger HKUST-1 particles on top. In this case, the coating was achieved on a larger scale and does not show degradation of the first layer upon deposition of the second. The squares in the underlying grid in both sets of images are 1 cm² each, showing that the possible casting area is larger using this methodology, and indeed seems to be tolerated regardless of sample size.
As indicated earlier, this methodology for creating multilayer films can be extended to produce films with multiple subsequent layers applied on top of the first and is not limited to two-layer films. Figure 4.8 shows a cross section of a triple-layer MMM fabricated from ZIF-8, UiO-66, and HKUST-1. The SEM-EDX maps for Cu, Zr, and Zn are shown in Figure 4.8b, c, and d, respectively. As seen earlier, the larger HKUST-1 sits on the top side of the membrane as the final layer added to the composite. The Cu EDX map confirms this, with the Cu signal clearly localized to the top layer of the membrane.

**Figure 4.8. Triple-layer MOF MMM.** Cross section SEM of the triple layer MOF MMM. The bottom layer of this MMM is ZIF-8, followed by UiO-66, and the top layer is HKUST-1. b) SEM-EDX Cu-map showing the Cu is localized in the top layer of the MMM, tracking with the HKUST-1 particles. c) SEM-EDX Zr-map showing the Zr signal is localized to a thin band in the middle of the MMM, corresponding to the UiO-66 layer. d) SEM-EDX Zn-map showing the Zn signal maps to the bottom layer of the MOF MMM in the ZIF-8 layer. Each layer is 60% wt. MOF.

The demarcation between the ZIF-8 and UiO-66 is more difficult to discern in the cross section image because the two species have similar particle sizes, both being significantly smaller than the HKUST-1 particles. However, the EDX maps clearly show
that the Zr-based UiO-66 is localized in the middle layer of the MMM, and the Zn-based ZIF-8 is the bottom layer, with no significant overlap between the different layers.

The utility of layered MOF membranes of this type has yet to be fully realized, but two applications hold significant promise. First, just as the single MOF MMMs show potential utility for protection against chemical threats, the layered MOF system may show similar utility. The order of the layers determines the sequence in which a toxic species would encounter the MOFs in the membrane, beginning with the outermost MOF layer and progressing across the membrane. This may allow for the design of protective layers such that threats are ranked; e.g., most likely threat is mitigated with the top layer, or a combination of MOFs is used in tandem such that the outermost layer rapidly sequesters a toxic species and a subsequent layer catalytically degrades it.\textsuperscript{22-23} Such a design can effectively remove a threat from being an immediate hazard even if the degradation is not instantaneous.

\section*{4.5 Catalytic MOF Membranes}

The second application of layered MOF membranes is as membrane reactors for chemical transformations. Crucially, the addition of the HMDA crosslinking agent expands the list of compatible solvents of the MMM to include even those that would dissolve the PVDF. There is a significant body of literature exploring MOFs as heterogeneous catalysts for chemical reactions.\textsuperscript{10, 12, 24-26} With crosslinked PVDF and a MOF with demonstrated stability under the desired reaction conditions, we can produce
immobilized catalysts with MOFs to the point that the reaction mixture is simply passed through the active catalyst and the product is recovered from the eluent.

We chose a set of model reactions to demonstrate the utility of MOF MMMs as membrane reactors, as shown in Figure 4.9. First, the deprotection of benzaldehyde dimethylacetal yields benzaldehyde (a) on reaction with water in an acid catalyzed reaction. Second, a Knoevenagel condensation between benzaldehyde and malonitrile employs a basic catalyst (b). The chemical diversity of MOFs allows fabrication of MMMs that are capable of catalyzing these transformations as the reaction mixture transits the membrane using either a mixture of MOFs or a single, bifunctional MOF catalyst.

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{acid} & \quad \text{base}
\end{align*}
\]

**Figure 4.9. MOF MMM catalyzed reactions.** (a) The conversion of benzaldehyde dimethylacetal to benzaldehyde is acid catalyzed. (b) The Knoevenagel condensation of benzaldehyde with malonitrile is base catalyzed.

Conveniently, these reactions can be easily followed by $^1$H NMR, as there is a dramatic shift in the position of the benzylic proton in each molecule, as seen in Figure 4.10. In the benzaldehyde dimethyl acetal starting material, this proton is a singlet at 5.35 ppm (red trace). After the acid catalyzed reaction, this proton on benzaldehyde is a singlet at 9.93 ppm (green trace). After the base catalyzed reaction, the benzylic proton of the product appears as a singlet at 8.36 ppm (blue trace).
Figure 4.10. Reaction monitoring by $^1$H NMR. The reactions may be monitored by following the benzylic proton in each product (blue). In the benzaldehyde dimethylacetal starting material, this proton is a singlet at 5.35 ppm (red trace). After the acid catalyzed reaction, this proton on benzaldehyde is a singlet at 9.93 ppm (green trace). After the base catalyzed reaction, the benzylic proton of the product appear as a singlet at 8.36 ppm (blue trace).

AUiO-66-NH$_2$ derived species is used for the acid catalyzed step of this reaction, utilizing acidic sites within the MOF, showing good catalytic activity under elevated temperatures in the catalytic membrane system. This species was generated in situ in the membrane by PSM. A 67% wt. UiO-66-NH$_2$ MMM was prepared by the standard method described in Chapter 2 with 5 mol% HMDA crosslinking agent as described above. After delamination, a 4.3 mg section of the membrane was immersed in 5 mL of
5% HCl in CH$_3$OH for 1 hour. This membrane was then transferred to 10 mL fresh CH$_3$OH for another hour. The MMM was then removed from the CH$_3$OH, dried at room temperature and placed in a Swinnex® syringe filter housing.

The reaction solution containing 30 μL benzaldehyde dimethylacetal (0.20 mmol), 12 μL malonitrile (0.22 mmol), 0.5 mL D$_2$O, and 2.5 mL DMSO-d$_6$ was then passed through the MMM at a rate of 25 μL/min at 60 °C. The reaction product was analyzed by $^1$H NMR to determine the extent of conversion (Figure 4.11). The reaction shows complete conversion of the starting material, with 87% of the desired product and 13% of the Kneovenagel condensation product.

**Figure 4.11.** UiO-66-NH$_3^+$Cl$^{-}$ MMM catalysis at 60 °C. The reaction shows complete conversion of the starting material, with 87% of the desired product and 13% of the Kneovenagel condensation product.
As indicated above (Figure 4.9), the second reaction in this set is the base catalyzed Knoevenagel condensation of benzaldehyde with malonitrile. This is a widely studied reaction and multiple studies have shown that it is readily catalyzed by ZIF-8 at room temperature.\textsuperscript{27, 29-30, 32, 34} As expected, based on these reports, a ZIF-8 MMM (60% wt.) performs well for this catalytic transformation at room temperature in the membrane reactor. A solution of benzaldehyde (20 μL, 0.20 mmol) and malonitrile (12 μL, 0.22 mmol) in 3 mL DMSO-\textit{d}_6 was passed through the 60% wt. ZIF-8 MMM (3.9 mg MMM) at a rate of 25 μL/min at room temperature. The \textsuperscript{1}H NMR shows high conversion of the starting material, with only 5% of the benzaldehyde remaining unreacted, based on the benzylic proton (Figure 4.12).

![NMR Spectrogram](image.png)

**Figure 4.12.** ZIF-8 MMM catalyzed Knoevenagel condensation at room temperature. \textsuperscript{1}H NMR analysis of the eluent shows that 95% of the benzaldehyde successfully reacted with malonitrile, catalyzed by the ZIF-8 MMM at room temperature.
After demonstrating that each reaction is successfully catalyzed by a MOF MMM, the two independent MOF MMMs were stacked in the syringe filter housing, such that the reaction mixture would encounter them in a sequential manner. A UiO-66-NH$_3^+$Cl$^-$ MMM (67% wt., 4.3 mg MMM) and a ZIF-8 MMM (60% wt., 3.9 mg MMM) were placed in the syringe filter housing and the reaction solution containing 30 μL benzaldehyde dimethylacetal (0.20 mmol), 12 μL malonitrile (0.22 mmol), 0.5 mL D$_2$O, and 2.5 mL DMSO-d$_6$ was then passed through the MMMs at a rate of 25 μL/min at 60 °C. The eluent was analyzed by $^1$H NMR (Figure 4.13). Analysis of the benzylic proton shows that the starting material is not fully converted in this system (47% unreacted), but as expected, the intermediate benzaldehyde is almost completely absent from the eluent.

Figure 4.13. UiO-66-NH$_3^+$Cl$^-$ and ZIF-8 MMM catalyzed reactions at 60 °C. $^1$H NMR analysis of the eluent shows that 53% of the starting material successfully reacted to form the final product over two steps in the membrane reactor.
4.6 Conclusions

MOF-based composite materials have the potential to find utility in myriad industrial, commercial, and military applications. Indeed, work described in Chapters 2 and 3, demonstrates the early development and promise of MOF-based materials. To fully exploit the chemical diversity of MOFs in these composite materials, however, methodologies for incorporation of different MOF species are needed.

In the work described here, we have developed methods for incorporation of multiple MOF species in co-cast, fully mixed, and layered systems that can be tailored for a specific system based on need. We have also investigated the addition of a crosslinking agent (HMDA) to the MOF ink formulation to expand the scope of solvents compatible with these MMMs beyond what was previously possible.

Finally, we have demonstrated some proof-of-concept catalytic systems with MOF MMMs. These catalytic demonstrations are sufficient to show that 1) a catalytic MOF system can be encapsulated and used in a truly heterogeneous form for adaptation to flow reaction systems, and 2) more fundamentally, that the MOF is intimately reacting with species as they transit the membrane. Marriage of MOF membranes with highly catalytic MOFs for industrially relevant transformations has high potential to simplify flow reactor design and bring down manufacturing costs.
4.7 Appendix: Supporting Information

Materials Synthesis

UiO-66. Zirconium (IV) chloride (ZrCl$_4$) (61 mg, 0.26 mmol) and terephthalic acid (43 mg, 0.260 mmol) were dissolved in 15 mL DMF with 0.447 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 hours. After cooling to room temperature, the particles were collected by centrifugation (Rotor: FO685, RPM: 6200, Time: 15 mins) and washed three times with 10 mL portions of each DMF and methanol and dried under vacuum at room temperature. The procedure was repeated 10 times in parallel and all products were combined. 35

UiO-66-NH$_2$. Zirconium (IV) chloride (ZrCl$_4$) (61 mg, 0.26 mmol) and 2-amino terephthalic acid (47 mg, 0.260 mmol) were dissolved in 15 mL DMF with 0.447 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 hours. After cooling to room temperature, the particles were collected by centrifugation (Rotor: FO685, RPM: 6200, Time: 15 mins) and washed three times with 10 mL portions of each DMF and methanol and dried under vacuum at room temperature. The procedure was repeated 10 times in parallel and all products were.

HKUST-1. Copper (II) nitrate hemipentahydrate (Cu(NO$_3$)$_2$·2.5H$_2$O) (1.22 g, 5.24 mmol) and 1,3,5-benzenetricarboxylic acid (0.58 g, 2.76 mmol) were dissolved in 5 mL DMSO. This solution was then added dropwise over 15 min to 250 mL of MeOH with magnetic stirring. Stirring was continued for 15 min after complete addition. The
particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.\textsuperscript{36}

**ZIF-8.** Zinc (II) nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O (0.30 g, 1.0 mmol) and 2-methylimidazole (0.66 g, 8.0 mmol) were each dissolved in 15 mL MeOH. The solutions were combined and stirred vigorously for 24 h. White ZIF-8 particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of MeOH, and dried under vacuum at room temperature.\textsuperscript{37}

**MIL-101(Fe).** Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O) (94 mg, 0.348 mmol) and terephthalic acid (58 mg, 0.348 mmol) were dissolved in 15 mL DMF. The solution was transferred to a 35 mL microwave reaction vessel and the reaction mixture was heated rapidly to 150 °C (Power = 300W) and held at 150 °C for 15 min. After cooling to room temperature, the red particles were collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of each DMF and EtOH, and dried under vacuum at room temperature.\textsuperscript{38}

**MIL-53(Fe).** Iron (III) chloride hexahydrate (FeCl$_3$·6H$_2$O) (0.540 g, 2 mmol) and terephthalic acid (332 mg, 2 mmol) were dissolved in 10 mL DMF. The solution was transferred to a Teflon lined stainless steel Parr bomb and heated to 150 °C (temperature ramped over 1 h, 2.5 °C/min) and held at temperature for 15 h. After cooling to room temperature, the yellow product was collected by centrifugation (fixed-angle rotor, 6500 rpm, 15 min), washed with 3×10 mL portions of each DMF and EtOH, and dried under vacuum at room temperature.\textsuperscript{39}
MOF MMM ink formulation. Dry MOF powders of an appropriate amount for the desired final MOF % wt. were dispersed in 5 mL acetone with sonication for 30 min in a scintillation vial. For example, a typical 60% wt. MMM uses 120 mg total MOF. For mixed MOF MMMs, the component MOFs were added in equal quantities: 60 mg of each for a 60% wt. MMM. A PVDF solution (7.5 wt% in DMF) was then added to the MOF suspension such that the desired final MOF:PVDF ratio was achieved; 1.067 g for a 60% wt. MMM. The suspension was sonicated for 30 min. The acetone was then removed by rotary evaporation, resulting in a MOF ‘ink.’

Crosslinked MMM ink formulation. Inks for crosslinked MOF MMMs were prepared as above. After removal of the acetone by rotary evaporation, HMDA was added to the ink formulation at 5 mol% relative to the PVDF monomer in the ink. In the above formulation for a 60% wt. MOF, this is 8.5 μL HMDA. The ink was again sonicated for 30 minutes to homogenize the mixture.

MOF MMM fabrication. The ink was cast into films on Al foil substrates by drawdown coating using a 400 μm doctor blade at 25 mm/s. The coated films were then heated to remove solvent (1 h in an oven set to 70 °C; 12 h at 100 °C for crosslinked MMMs). Immersion in solvent (CH₃OH) resulted in rapid delamination of the MMMs. The free-standing films were dried in air.
Materials Characterization

**Scanning Electron Microscopy (SEM).** MMM films (approx. 3 mm²) were transferred to conductive carbon tape on a sample holder disk, and coated using a Ir-sputter coating for 9 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum at a working distance at 10 mm.

**Powder X-Ray Diffraction (PXRD).** Approximately 50 mg of dry MOF powder or 0.5 cm² MMM was mounted on silicon sample holder for analysis by PXRD. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka (λ = 1.5418 Å), with a scan speed of 2 sec/step, a step size of 0.05° in 2θ, and a 20 range of 2-50°.

**N₂ Sorption Analysis & BET Surface Area Analysis.** Samples for analysis were evacuated on a vacuum line overnight at room temperature prior to analysis. ~50 mg samples were then transferred to pre-weighed sample tubes and degassed at 105 °C (unless otherwise noted) on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. After degassing, the sample tubes were re-weighed to obtain a consistent mass for the samples. Sorption data and BET surface area (m²/g) measurements were collected at 77 K with N₂ on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

**Nuclear Magnetic Resonance.** Proton nuclear magnetic resonance spectra (¹H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for
TMS. MMMs were digested for NMR analysis by immersion of ~8-10 mg MMM in 580 μL DMSO-\textsubscript{d_6} with 20 μL HF (48% in water). Samples were kept in this acidic solution at room temperature until the MOF component of the MMMs was fully dissolved.

**Supporting Figures**

![Figure 4S.1](image)

**Figure 4S.1.** a) 60% wt. HKUST-1 MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. HKUST-1 + ZIF-8 MMM. d) PXRD spectra for each MMM. e, f) SEM images of the HKUST-1 + ZIF-8 MMM. The large particles are HKUST-1 and the small particles are ZIF-8.
Figure 4S.2. a) 60% wt. HKUST-1 MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. HKUST-1 + UiO-66 MMM. d) PXRD spectra for each MMM. e, f) SEM images of the HKUST-1 + UiO-66 MMM. The large particles are HKUST-1 and the small particles are UiO-66.
Figure 4S.3. a) 60% wt. HKUST-1 MMM. b) 60% wt. MIL-101(Fe) MMM. c) 60% wt. HKUST-1 + MIL-101(Fe) MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the HKUST-1 + MIL-101(Fe) MMM. The large particles are HKUST-1 and the small particles are MIL-101(Fe).
Figure 4S.4. a) 60% wt. HKUST-1 MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. HKUST-1 + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the HKUST-1 + MIL-53(Fe) MMM. The large, anisotropic particles are MIL-53(Fe) and the smaller, octahedral particles are HKUST-1.
Figure 4S.5. a) 60% wt. ZIF-8 MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. ZIF-8 + UiO-66 MMM. d) PXRD spectra for each MMM. e, g) Plan-view and f, h) cross section SEM images of the ZIF-8 + UiO-66 MMM.
Figure 4S.6. a) 60% wt. MIL-101(Fe) MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. MIL-101(Fe) + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan-view and f) cross section SEM images of the ZIF-8 + UiO-66 MMM.
Figure 4S.7. a) 60% wt. MIL-53(Fe) MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. MIL-53(Fe) + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the MIL-53(Fe) + UiO-66 MMM. The large particles are MIL-53(Fe) and the small particles are UiO-66.
Figure 4S.8. a) 60% wt. MIL-53(Fe) MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. MIL-53(Fe) + ZIF-8 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the MIL-53(Fe) + ZIF-8 MMM. The large particles are MIL-53(Fe) and the small particles are ZIF-8.
Figure 4S.9. a) 60% wt. MIL-101 (Fe) MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. MIL-101(Fe) + ZIF-8 MMM. d) PXRD spectra for each MMM. e, g) Plan view and f, h) cross section SEM images of the MIL-101(Fe) + ZIF-8 MMM. The octahedral particles are MIL-101(Fe) and the small particles are ZIF-8.
Figure 4S.10. a) 60% wt. MIL-101 (Fe) MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. MIL-101(Fe) + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e, g) Plan view and f, h) cross section SEM images of the MIL-101(Fe) + MIL-53 MMM. The large particles are MIL-53(Fe) and the small particles are MIL-101(Fe).
Figure 4S.11. a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. UiO-66 MMM. c) 60% wt. UiO-66-NH$_2$ + UiO-66 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + UiO-66 MMM.
Figure 4S.12. a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. ZIF-8 MMM. c) 60% wt. UiO-66-NH$_2$ + ZIF-8 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + ZIF-8 MMM.
Figure 4S.13. a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. HKUST-1 MMM. c) 60% wt. UiO-66-NH$_2$ + HKUST-1 MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + HKUST-1 MMM.
Figure 4S.14. a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. MIL-101(Fe) MMM. c) 60% wt. UiO-66-NH$_2$ + MIL-101(Fe) MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + MIL-101(Fe) MMM.
Figure 4S.15. a) 60% wt. UiO-66-NH$_2$ MMM. b) 60% wt. MIL-53(Fe) MMM. c) 60% wt. UiO-66-NH$_2$ + MIL-53(Fe) MMM. d) PXRD spectra for each MMM. e) Plan view and f) cross section SEM images of the UiO-66-NH$_2$ + MIL-53(Fe) MMM.

4.8 Acknowledgements

Chapter 4, in part is currently being prepared for submission for publication of the material. The dissertation author was the primary author of this material and gratefully acknowledges the contributions of his coauthor and advisor, Seth M. Cohen.
4.9 References


Chapter 5

Melt-processable, Covalently Integrated MOF-Polyamide Composites

5.1 Introduction

Fabrication of composite materials with metal-organic frameworks has proven to be an effective way to exploit the desirable properties of MOFs, such as porosity and catalytic activity, in a form factor that makes their handling and implementation considerably easier than in the native, powder form. Moreover, previous work has shown that a composite can actually enhance the characteristics of MOFs through stabilization of an unstable framework or even enhanced uptake of a desired analyte. Recently, some reports have begun to take the field of MOF composites to the logical end by covalently integrating the MOF and polymer components.

There are two primary means of covalently integrating MOFs and polymers. The first of these is to synthesize the MOFs using polymeric ligands in a bottom-up approach to composite fabrication. The resulting MOF-polymer hybrid materials, termed polyMOFs, have only recently been described and, despite their promise for molecular level control of MOF-polymer connectivity, there remains a great deal of exploration before this field produces functional composites for a market-ready application. The alternative, top-down approach has been termed ‘postsynthetic polymerization’ (PSP). PSP uses a reactive handle on the MOF that is complementary to a reactive monomer species that forms the interstitial polymer. Through mixing of the MOF and monomer species prior to polymerization, the
preformed MOF particles are covalently integrated into the growing polymer chains during polymerization event (Figure 5.1).\textsuperscript{8-9,15} PSP has been successfully used to prepare membrane form factors and typically results in stable, highly connected monoliths.\textsuperscript{8-9,16}

![Figure 5.1. Postsynthetic polymerization.](image)

**Figure 5.1. Postsynthetic polymerization.** The MOF particles with reactive handles (blue) are integrated into the growing polymer chains during polymerization of the monomer (pink), forming a covalently integrated MOF-polymer composite.

Despite successful demonstrations of PSP,\textsuperscript{8-9,16} the true power of covalently integrated MOF-polymer hybrid materials has not yet captured one of the properties that makes polymeric materials so ubiquitous and adaptable: melt-processing. The ability of polymers to melt and be processed as liquids allows them to be extruded, spun into fibers, and cast into complex three-dimensional shapes. Among these ubiquitous polymers in the modern world, polyamides have proven to be one of the most versatile classes of polymers and, depending on their chemical composition, can be made to be soft, pliant fabrics or rigid, structural materials.\textsuperscript{17-19}

Nylon 6,6 (PA-66) was among the earliest useful polyamides to find widespread market applications.\textsuperscript{20} First hinted at by Wallace Carothers in 1929,\textsuperscript{21} and patented in 1937,\textsuperscript{22} this simple linear polyamide (PA) prepared from hexamethylene diamine and adipic acid (Figure 5.2b), remains one of the most widely used polymers today.
Continued evolution of polyamide technologies has given rise to aromatic polyamides, termed Aramids (Fig 5.2c), which serve as high-performance polymers for personal protection (Kevlar®) and fire protection (Nomex®).\(^{23}\)

**Figure 5.2. Polyamides.** a) Polyamide bond formation is typically achieved through reaction of a carboxylic acid with a primary amine (*top*) or the more reactive acyl chloride with a primary amine (*bottom*). b) Aliphatic amines can be prepared from a single, doubly functionalized monomer, as in PA-6, or by condensation polymerization of diamine and diacid comonomers, as in PA-66. c) Aromatic polyamides, known as Aramids, are built from aromatic monomers. d) Interchain hydrogen bonding is responsible for the strength of polyamides, illustrated here with PA-66.

Figure 5.2 shows some of the main characteristics of polyamides. Polyamides are linear condensation polymers typically formed through reaction of doubly functionalized comonomers, diamines and diacids, though they can be prepared from a single monomer containing both functionalities as in PA-6 (Fig 5.2b). Often, acyl chlorides are used instead of carboxylic acids in polyamide synthesis (Fig 5.2a) because their enhanced reactivity allows for rapid polymer formation, which is required for interfacial polymer synthesis (vide infra). One of the most important attributes that lends strength to nearly
all polyamide formulations is the ability to form extensive hydrogen bonding networks between adjacent polymer chains (Figure 5.2d).

5.2 Interfacial PSP of MOF-PA composites

Given their utility, ubiquity, and facile preparation, polyamides are a natural choice for preparation of covalent composites with MOFs by PSP. With appropriate loading, the MOF-PA composites should incorporate functionalized MOF crystallites into the PA chains to give a product that can still be melt-processed like the parent polymer. Moreover, once the basic composite preparation methodology is developed, it should be broadly applicable to a whole range of polyamide compositions beyond PA-66 to tailor the materials properties of the composites.

Conveniently, formation of amide bonds with MOF ligands has been well demonstrated in the MOF PSM literature. Indeed, many of the most common MOFs can be prepared with amine functionalized ligands without detriment to the MOF structure or the accessibility of the amine for chemical modification. Thus, we can expect integration of an amine functionalized MOF into polyamide chains through formation of an amide linkage between the carboxylic acid moiety of the polymer with the amine-functionalized ligand. In this work, we take advantage of this demonstrated amine ligand reactivity with acyl chlorides to incorporate the amine functionalized MOF, UiO-66-NH$_2$, with the forming polymer chains of PA-66.

A general synthetic scheme for this PSP strategy is depicted in Figure 5.3a, showing the step-growth of polyamide chains on the MOF surface, taking advantage of
the rapid kinetics and strong bond formation of the reaction of amines with acyl chlorides. Reaction of UiO-66-NH₂ with an excess of the bifunctional adipoyl chloride [COCl(CH₂)₄COCl] in hexanes results in an amide linkage between the MOF particle and the alkyl chain (Figure 5.3a). Because a large excess of acid chloride is used, only one side of the bifunctional molecule is likely to be tethered to the MOF, leaving the other end free to react. This effectively changes the external surface of the MOF from being amine-functionalized to acyl chloride-functionalized. Subsequent introduction of these modified particles to an excess of the bifunctional HMDA forms a second amide linkage, now leaving a free amine on the exterior of the MOF. By cycling between these two conditions, the growing polyamide oligomers on the MOF exterior are extended one block at a time.

Figure 5.3c shows the application of this methodology in practice. Instead of individually cycling the MOF particles between solutions of each co-monomer, the same end is accomplished rapidly through interfacial polymerization. In this process, UiO-66-NH₂ is first dispersed in an adipoyl chloride solution in hexanes. This results in the first reaction between the adipoyl chloride with the UiO-66-NH₂, as described above. This mixture is then carefully layered on top of an aqueous solution of HMDA, which introduces the MOF to the amine comonomer. Polymerization occurs rapidly at the interface of the aqueous and organic phases to form PA-66, while incorporating MOF particles that lie at this reactive interface. The polymer composite continues to form as it is drawn off the interface, resulting in composite fibers, as seen in the photograph in Figure 5.3c.
Figure 5.3. MOF-PA fabrication. a) Reaction of UiO-66-NH$_2$ with adipoyl chloride yields a MOF particle decorated with acyl chlorides on the surface. Reaction of this species with HMDA elongates the aliphatic polymer chains via formation of a second amide bond, leaving the particle surface presenting the amine functionality. b) Continued repetition of this process results in polyamide chains that contain the covalently integrated MOF particles. c) Interfacial polymerization: UiO-66-NH$_2$ is dispersed in an adipoyl chloride solution in hexanes. This mixture is layered on top of an aqueous solution of HMDA. Polymerization occurs rapidly at the interface of the aqueous and organic phases to form PA-66, incorporating the MOF particles (c). The polymer composite continues to form as it is drawn off the interface, resulting in MOF-polymer fibers.

A series of MOF-PA composites were prepared by this method and the materials were characterized to assess the integrity of the MOF component after fabrication. In a typical preparation, a quantity of UiO-66-NH$_2$ ranging between 0 and 160 mg (0 to 5.33 mmol equivalents of MOF ligand) was dispersed in 10 mL hexanes with ultrasonication for 20 minutes. Adipoyl chloride (3.45 mmol, 0.630 g, 0.50 mL) was then added to this dispersion and further sonicated for 10 minutes. Upon addition of the adipoyl chloride, a reaction is evident by a color change of the MOF particles to a paler shade of yellow.
Separately, a solution of HMDA (3.45 mmol, 0.400 g, 0.45 mL) was prepared in 10 mL H₂O. 0.5 mL of a 5% NaOH solution was added to this mixture to neutralize the HCl generated during the polymerization. The hexanes dispersion was then carefully layered on top of the aqueous layer. Polymerization occurred at the interface of the two layers and the MOF-PA product was slowly pulled from the interface, forming a continuous fiber (Figure 5.3b). The product was removed until fiber formation became non-continuous, indicating a depletion of the monomer feedstocks. The product was washed with water and dried at 70 °C overnight, then dried under vacuum at room temperature for 24 h.

The resulting samples clearly incorporated the MOF particles, as evidenced by a corresponding yellow color in the product from the MOF. PXRD spectra of the samples reveal that increasing MOF content in the precursor mixture results in a corresponding increase in intensity of peaks associated with the UiO-66-NH₂ structure (Figure 5.4a, peaks = 7.46° and 8.60°). This is accompanied by decreased intensity of the peaks associated with the PA-66.

The increasing MOF content in the composite was also evident in the macroscale characteristics of the product. Increasing MOF content in the precursor mixture resulted in more obvious yellow coloration in the composite. The products up to and including 80 mg of UiO-66-NH₂ formed as continuous MOF-polymer fibers (Figure 5.4b), but MOF loading above this point (100 mg, 120 mg, 140 mg, and 160 mg) results in discontinuous masses of the MOF-polymer composite (Figure 5.4c) and are noticeably slower to form.
Figure 5.4. MOF crystallinity. a) PXRD spectra of the MOF-PA series. b) Photograph of the 80 mg UiO-66-NH$_2$ sample. c) Photograph of the 160 mg UiO-66-NH$_2$ sample.

The flaky nature of the high-loading MOF samples is likely the result of depletion of the adipoyl chloride from interaction with the MOF by two mechanisms. First, because each MOF contains many reactive amine groups, the reaction of these with the adipoyl chloride removes this species from free solution, so it cannot participate in formation of extended chains between MOF particles. However, 160 mg UiO-66-NH$_2$ equates to only 0.5 mmol of the bdc-NH$_2$ ligand, which would only sequester about 15% of the available adipoyl chloride if every MOF ligand were to react. Instead, the porous MOF may simply be adsorbing the reactive species inside the lattice, thus further reducing the available monomer.

The second reason for the non-continuous fiber is likely that the MOF species does not remain fully suspended in the hexanes solution during polymer formation and tends to settle at the interface with the water. This locally concentrated MOF can disrupt formation of long polymer chains in favor of short connections between particles, which
results in a highly crosslinked mass that does not favor continuous fiber production. Notably, samples prepared with UiO-66, the non-reactive analogue of UiO-66-NH₂, readily form continuous polymer fibers with all MOF loadings up to 160 mg. The resulting fibers contain evidence of incorporated MOF as well, but readily shed this MOF as a white residue, while the UiO-66-NH₂ samples do not show evidence of MOF detachment after preparation with normal handling. This difference is presumably due to covalent integration of UiO-66-NH₂ and only physical adhesion of UiO-66.

Unfortunately, poor suspension of the UiO-66-NH₂ in the hexanes solution also results in uneven distribution of MOF along the length of the growing fiber, giving a product that is ‘front loaded’ with MOF. PXRD spectra were collected for sections of the MOF-polymer fiber at 12 inch increments (Figure 5.5a). These spectra show that the peaks associated with the UiO-66-NH₂ decrease in intensity from the beginning (0 inches) to the end (36 inches) of the sample, consistent with reducing MOF content along the length. This conclusion is confirmed by TGA analysis of the same samples. Each sample degrades around the same point in the heating cycle (ca. 380 °C), but there is less residue after this degradation for the each sample than for the one before it (Figure 5.5b). The MOF content of each sample was determined from these TGA data. They are 0 in = 74% wt., 12 in = 68% wt., 24 in = 65% wt., and 36 in = 47% wt. Indeed, the more pronounced mass loss on degradation for the 36 in sample relative to the 0 inch sample shows how dramatically this MOF content can vary from the beginning to the end of the composite synthesis by this method.
Figure 5.5. Non-uniform MOF incorporation. a) PXRD spectra of the MOF-polymer fiber at various points along the fiber length. b) TGA traces of the MOF-polymer fiber at various points along the fiber length. Both analyses show high MOF content at the beginning of the fiber and a consistent reduction of MOF content along its length.

Unfortunately, the composites fabricated by this method do not show an appreciable retention of porosity by N\textsubscript{2} sorption isotherms at 77 K. Figure 5.6 shows the N\textsubscript{2} sorption isotherm of the 80 mg UiO-66-NH\textsubscript{2} sample vs. the UiO-66-NH\textsubscript{2} powder. Clearly the composite shows very little porosity under these conditions, indicating pore occlusion in the composite. It is possible that porosity is not in fact fully occluded, but instead this is an artifact of the analysis conditions. The glass transition temperature of PA-66 is ca. 343 K, so it is possible that the PA-66 chains in the composite are frozen in place during testing at 77 K and they would be more mobile at higher temperature to allow pore access. Further analyses of porosity at higher temperature are needed going forward.

Analysis of the products by SEM reveals a thin polymer ribbon decorated with MOF particles. Figure 5.7 shows the SEM images corresponding to the PA-66 and the composites samples up to 80 mg UiO-66-NH\textsubscript{2}. These images appear to show increasing
MOF coverage of the PA-66 surface as the MOF content in the precursor suspension increases, consistent with the PXRD and TGA results.

Figure 5.6. MOF-PA composite porosity. The N₂ sorption isotherms are shown for UiO-66-NH₂ (black) and the 80 mg UiO-66-NH₂ sample. The composite sample shows extremely low accessible porosity (BET surface area = 25 m²/g) vs. the native MOF (BET surface area = 1128 m²/g).

Figure 5.7. SEM analysis of MOF-PA composites. SEM images of the surfaces of a) PA-66, b) 5 mg UiO-66-NH₂ sample, c) 10 mg UiO-66-NH₂ sample, d) 20 mg UiO-66-NH₂ sample, e) 40 mg UiO-66-NH₂ sample, and f) 80 mg UiO-66-NH₂ sample.
As stated above, a main goal of this project is to achieve a MOF-polymer composite that is melt-processable. Analysis of the samples by DSC allows investigation of the effect of the MOF component on the polymer melting behavior. As Figure 5.7 shows, PA-66 has a melt temperature at 255 °C (black trace). The samples containing 5 mg (red) and 10 mg (blue) of MOF show depression of the melting temperature of PA-66 by about 25 °C as a result of the addition of the UiO-66-NH$_2$. Curiously, all MOF loadings above this temperature do not show any evidence of melting in the DSC trace, indicating that the MOF content is inhibiting polymer melting at everything but the lowest loadings. This may be due to the MOF particles acting as crosslinking points for the polyamide, creating a highly interconnected PA network that is not prone to melting.

![DSC analysis of MOF-PA composites](image)

**Figure 5.8. DSC analysis of MOF-PA composites.** DSC traces for PA-66 and composite samples ranging from 5 mg MOF to 160 mg MOF heated to 300 °C at 10 °C/min. The pure PA-66 and samples up to 10 mg UiO-66-NH$_2$ show melting events; the remaining samples do not.
As stated above, the UiO-66-NH₂ particles do not form a stable suspension in hexanes solution. Indeed the MOF settles out of suspension quite rapidly, which is likely to be the cause of the non-uniform MOF incorporation. To address this, several attempts were made to achieve a better MOF suspension, which would give more uniform products. First, suspension of the MOF in the aqueous layer instead of the organic layer was investigated. CH₂Cl₂ was substituted for hexanes so that the MOF-containing aqueous layer would be the top of the interfacial system. UiO-66-NH₂ disperses very well in water to form a suspension that is stable on the bench top for hours without significant settling. However, addition of HMDA to the aqueous suspension results in rapid degradation of the MOF. Indeed the PXRD spectrum of UiO-66-NH₂ recollected from this solution by centrifugation shows no apparent crystallinity. As expected, composite fibers from this system also show no apparent MOF crystallinity.

Ultimately, substitution of ethyl acetate for hexanes as the organic solvent was found to give stable MOF suspensions in the organic layer without inhibition of the polymerization reaction or degradation of the MOF crystallinity. The resultant fibers display far more uniform MOF incorporation than their hexanes counterparts, though MOF incorporation is still not easily controlled. Figure 5.9 shows the PXRD spectra of a sample set prepared with increasing MOF in the synthesis. The PXRD spectra, however, show that the MOF incorporation does not track with the intended content. The peaks associated with UiO-66-NH₂ do not increase in intensity with added MOF, as would be expected with increasing MOF incorporation.
Figure 5.9. Ethyl acetate preparation. PXRD spectra of the MOF-PA series at different MOF loading levels.

As with the samples prepared from hexanes, the composite materials show incorporation of the UiO-66-NH$_2$ into the polymer fiber (Figure 5.10). In these SEM images, the MOF content appears to be better distributed in the PA fiber, but it is still far from uniform. Further optimization of this procedure will be required to generate composites with truly uniform MOF incorporation.
Finally, a second set of acid chloride and diamine reagents were used in a similar process as above to demonstrate the applicability of this method to other polyamide systems. Suberoyl chloride \([\text{COCl(CH}_2\text{)_6COCl}]\) and diethylene triamine (DETA) were substituted for the monomer reagents and again complexed with UiO-66-NH\(_2\) via interfacial synthesis. In this system, 25 mg UiO-66-NH\(_2\) were dispersed in 5 mL water with DETA (200 \(\mu\)L, 191 mg, 1.85 mmol). This mixture was then layered on top of a solution of suberoyl chloride (200 \(\mu\)L, 234 mg, 1.11 mmol) in 5 mL CH\(_2\)Cl\(_2\). As expected, the condensation polymer formed at the interface of the aqueous and organic layers, incorporating the MOF species in the forming polymer. This polymer was continuously removed from the interface, giving an off-white, feathery polymer ribbon (Figure 5.11a). Figure 5.11b-f show that the polymer surface completely covered by MOF crystallites that is able to bend and fold like a film.
Figure 5.11. MOF-PA composite using suberoyl chloride and DETA monomers. a) Photograph showing that the product formed as thin ribbons of MOF-polymer composite. b-f) SEM images of the product showing a polymer ribbon decorated with the UiO-66-NH$_2$ particles at varying magnification. Low magnification shows that there is dense surface coverage with MOF particles, while high magnification shows that the MOF particles are intimately integrated with the polymer.

These analyses show that interfacial polymerization is a promising method to prepare covalently integrated MOF-PA composites, though more work needs to be done to optimize the process. The preparation is easy and can be applied broadly to a variety of polyamides. However, even distribution of MOF within the polymer must be achieved before this technology yields a market-ready composite. This can likely be solved by engineering controls and reformulation of the interfacial polymerization system.
5.3 Prepolymer salt PSP of MOF-PA composites

To explore routes to more even distributions of MOF in the composite, we turned to an alternative approach to production of aliphatic polyamides, preparation of a prepolymer salt of the co-monomers, which will be termed ‘nylon salt’. Unlike interfacial polymerization which requires rapid reaction between acyl chloride and amine co-monomers, this method first combines the diacid and diamine into a single precursor species. To generate the nylon salt, a proton transfers from the acid to the amine monomer at elevated temperature in solution (Figure 5.12). The solution is then cooled, resulting in precipitation of the salt. This isolated salt is then heated to melting and polymerizes via dehydration. Typically, this method yields longer, more uniform polymers than interfacial polymerization because the salt, by necessity, has an exact stoichiometric balance of the comonomers, unlike interfacial polymerization. Additionally, prepolymer salts of polyamides are shelf stable and can be stored and transported much more easily than the individual acid and amine monomers.

![Diagram showing prepolymer salt preparation](image)

**Figure 5.12. Prepolymer salt preparation.** Instead of progressing directly from co-monomers to the finished polymer by pathway A, the prepolymer salt is first prepared via pathway B. This salt can then be polymerized to the final product by pathway C.
Two strategies were attempted to achieve integration of UiO-66-NH$_2$ with the nylon salt and subsequent PSP product. In the first approach, the MOF was dispersed in the co-monomer solution so that it would have a chance to participate in proton transfer process and co-precipitate with the salt. In the second approach, the nylon salt was pre-formed and the UiO-66-NH$_2$ was introduced by grinding the two species together with a mortar and pestle. The products of each approach were then polymerized by heating above the melting temperature of the nylon salt (ca. 190 °C) under N$_2$.

For both methods, preparation of the nylon salt followed the same procedure. First, adipic acid (512 mg, 3.5 mmol) was dissolved in 2 mL MeOH. A separate solution of HMDA (406 mg, 3.5 mmol) in 2 mL MeOH was then prepared. Both solutions were independently heated to 60 °C, then combined and kept at temperature for 15 minutes. The solution was then cooled to room temperature and left to rest overnight. The precipitated nylon salt was collected by filtration, washed with MeOH, and dried under vacuum.

For composites prepared via the co-precipitation method, the MOF (ranging from 10 to 50 mg UiO-66-NH$_2$) was dispersed in the adipic acid solution by sonication prior to proceeding with nylon salt formation. The MOF loading of the resulting products was determined from the total mass of the collected precipitate (Table 5.1). Overall yields for the products in this series are quite low and because of the high variability in the amount of nylon salt that precipitated in each sample, the MOF loading in the product does not track very well with the expected amount. For example, sample 4 has the highest calculated MOF loading simply because the amount of total product was the lowest of the
sample set. The PXRD spectra for the samples, however, show increasing UiO-66-NH$_2$ peak intensity with the increasing MOF mass in the sample (Figure 5.13).

Table 5.1. MOF loading of co-precipitated nylon salt.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOF mass (mg)</th>
<th>Mass (mg)</th>
<th>MOF loading (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon salt</td>
<td>0</td>
<td>442</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>314</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>353</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
<td>308</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>284</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>422</td>
<td>12</td>
</tr>
</tbody>
</table>

Figure 5.13. PXRD spectra of co-precipitated MOF and nylon salt. The co-precipitation products of the nylon salt (black) and UiO-66-NH$_2$ (dark blue) are shown. The co-precipitation samples show peaks consistent with both species.
The samples were then analyzed by DSC to determine the effect of the MOF component on the melting temperature of the polymer (Figure 5.14). The samples were cycled between heating and cooling steps, both at a rate of 10°C/min. The peak positions are noted in Table 5.2. Step 1 shows a melting event for each sample at the same temperature, which is the melting of the nylon salt and polymerization event. Upon cooling the samples in Step 2, the recrystallization peak shows movement toward lower temperatures with increasing MOF in the samples. Finally, on heating again in Step 3, the melting temperature of the composites also shows a lower melting temperature for the samples with increased MOF content.

Finally, the highest MOF loaded sample of this series (50 mg UiO-66-NH₂) was investigated by PXRD after the melting and polymerization of the nylon salt. Upon melting and polymerization, the highly crystalline nylon salt becomes largely amorphous with two broad peaks at $\theta = 20^\circ$ and $24^\circ$. Upon melting the co-precipitated product with 50 mg UiO-66-NH₂, this same transition occurs in the PXRD spectrum, but the UiO-66-NH₂ peaks are still present on top of this amorphous spectrum, indicating that the MOF remains intact through the melting process (Figure 5.15).
Figure 5.14. DSC traces of the co-precipitated MOF and nylon salt.

Table 5.2. Peak data for DSC traces in Figure 5.12.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt 1 (°C)</th>
<th>Recrystallization (°C)</th>
<th>Melt 2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>Peak</td>
<td>Onset</td>
</tr>
<tr>
<td>PA-66</td>
<td>229.0</td>
<td>250.8</td>
<td>231.0</td>
</tr>
<tr>
<td>1</td>
<td>229.2</td>
<td>242.8</td>
<td>220.0</td>
</tr>
<tr>
<td>2</td>
<td>231.9</td>
<td>243.4</td>
<td>212.7</td>
</tr>
<tr>
<td>3</td>
<td>233.7</td>
<td>243.4</td>
<td>208.9</td>
</tr>
<tr>
<td>4</td>
<td>234.8</td>
<td>244.1</td>
<td>206.3</td>
</tr>
<tr>
<td>5</td>
<td>232.5</td>
<td>242.7</td>
<td>204.2</td>
</tr>
</tbody>
</table>
Figure 5.15. PXRD spectra of nylon salt and UiO-66-NH₂ before and after melting. The nylon salt upon polymerization displays two broad peaks at $\theta = 20^\circ$ and $24^\circ$ which are also observed in the 50 mg UiO-66-NH₂ sample after polymerization along with the intact MOF peaks.

Despite the success of integrating the MOF particles with the nylon salt and subsequent melting of the mixture, the preparation method described above does not provide a reliable method for obtaining a specific MOF loading in the product. To address this, we next used a much simpler approach for integrating the MOF with the nylon salt. The nylon salt was independently prepared and dried first, then ground with the desired amount of UiO-66-NH₂ with a mortar and pestle. A series of samples were prepared by this method with 50 mg nylon salt according to Table 5.3.
Table 5.3. MOF content in the ground UiO-66-NH₂/nylon salt mixtures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MOF mass (mg)</th>
<th>MOF loading (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-66</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>16.7</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

These samples were treated to the same thermal cycling analysis by DSC as the co-precipitated samples above, and they show similar behavior (Figure 5.16, Table 5.4). Again the melting peak for the nylon salt is conserved in all samples during Step 1 and the subsequent recrystallization and melting temperatures in Steps 2 and 3 are shifted to lower temperatures for samples up to 25 mg MOF (33% wt.). The 50 mg MOF sample (50% wt.), however shows very different behavior. In Step 1, it undergoes the melting and polymerization of the nylon salt, just as the other samples. In the subsequent cooling and heating steps, though, it shows no recrystallization or melting events, indicating that the polymer is no longer able to behave normally. This is likely because the MOF content is so high that the polymer is adhered to the MOF particles and not localized in polymer-only domains of any significant size. This different melting behavior of the 50 mg MOF sample is also evident at the macroscale. After thermal treatment, the rest of the samples are monolithic composites, held together by the polymer. The 50 mg MOF sample, though, remains a powder after thermal treatment.
Figure 5.16. DSC traces of the ground UiO-66-NH$_2$/nylon salt mixtures.

Table 5.4. Peak data for DSC traces in Figure 5.14.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Melt 1 (°C)</th>
<th>Recrystallization (°C)</th>
<th>Melt 2 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Onset</td>
<td>Peak</td>
<td>Onset</td>
</tr>
<tr>
<td>PA-66</td>
<td>229.0</td>
<td>250.8</td>
<td>231.0</td>
</tr>
<tr>
<td>5</td>
<td>242.4</td>
<td>248.0</td>
<td>218.9</td>
</tr>
<tr>
<td>10</td>
<td>236.2</td>
<td>244.0</td>
<td>219.4</td>
</tr>
<tr>
<td>25</td>
<td>232.7</td>
<td>246.3</td>
<td>209.8</td>
</tr>
<tr>
<td>50</td>
<td>236.5</td>
<td>242.6</td>
<td>--</td>
</tr>
</tbody>
</table>

Finally, the samples were imaged by SEM before and after thermal treatment to determine whether the MOF particles and the polymer were well integrated (Figure 5.17). All samples show distinct MOF particles before melting and an integrated composite after melting, except the 50 mg UiO-66-NH$_2$ sample that remains a powder, and after melting, show features consistent with the size of the UiO-66-NH$_2$ particles, indicating that they are well distributed and remain intact.
Figure 5.17. SEM images of the ground UiO-66-NH$_2$/nylon salt mixtures. 5 mg UiO-66-NH$_2$ sample a) before and b) after thermal treatment. 10 mg UiO-66-NH$_2$ sample c) before and d) after thermal treatment. 25 mg UiO-66-NH$_2$ sample e) before and f) after thermal treatment. 50 mg UiO-66-NH$_2$ sample g) before and h) after thermal treatment.
5.6 Conclusions

This work demonstrates two distinct routes toward development of MOF-polyamide composites via PSP. The first route incorporates the MOF into the polyamide via interfacial polymerization. Though promising, obtaining uniform distribution of MOF in the final composite is difficult by this method. It is likely that with sufficient engineering controls and reformulation of the experimental conditions, uniform MOF incorporation will be achieved. This method is applicable to a wide range of polyamides, most notably Aramids.

The second route to MOF-polyamide composites is through the combination of MOF particles and a polyamide prepolymer salt. Thorough mixing of these species followed by polymerization of the prepolymer salt yields composite materials that display melting events with MOF content up to 33% wt. Importantly, the MOF crystallinity remains intact throughout the polymerization process, as assessed by PXRD. Refinement and utilization of both of these methods will lead to the development of melt-processable, covalently integrated MOF-polymer composites that can be utilized as functional textiles.
5.7 Appendix: Supporting Information

Materials Synthesis

UiO-66. Zirconium(IV) chloride (ZrCl$_4$) (61 mg, 0.26 mmol) and terephthalic acid (43 mg, 0.26 mmol) were dissolved in 15 mL DMF with 0.45 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 h. After cooling to room temperature, the particles were collected by centrifugation (Rotor: FO685, RPM: 6200, Time: 15 min) and washed three times with 10 mL portions of DMF and methanol, followed by drying under vacuum at room temperature. This procedure was repeated 10 times in parallel and all of the isolated products combined.$^{28}$

UiO-66-NH$_2$. Zirconium (IV) chloride (ZrCl$_4$) (61 mg, 0.26 mmol) and 2-amino terephthalic acid (47 mg, 0.26 mmol) were dissolved in 15 mL DMF with 0.45 mL glacial acetic acid in a 20 mL vial. The capped vial was placed in an oven and heated to 120 °C for 24 hours. After cooling to room temperature, the particles were collected by centrifugation (Rotor: FO685, RPM: 6200, Time: 15 min) and washed three times with 10 mL portions of DMF and methanol, followed by drying under vacuum at room temperature. This procedure was repeated 10 times in parallel and all of the isolated products combined

Materials Characterization

Scanning Electron Microscopy (SEM). MMM films (approx. 3 mm$^2$) were transferred to conductive carbon tape on a sample holder disk, and coated using a Ir-sputter coating
for 9 sec. A Philips XL ESEM instrument was used for acquiring images using a 10 kV energy source under vacuum at a working distance at 10 mm.

**Powder X-Ray Diffraction (PXRD).** Approximately 50 mg of dry MOF powder or 0.5 cm$^2$ MMM was mounted on silicon sample holder for analysis by PXRD. PXRD data was collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka ($\lambda = 1.5418$ Å), with a scan speed of 2 sec/step, a step size of 0.05° in 2θ, and a 2θ range of 2-50°.

**N$_2$ Sorption Analysis & BET Surface Area Analysis.** Samples for analysis were evacuated on a vacuum line overnight at room temperature prior to analysis. ~50 mg samples were then transferred to pre-weighed sample tubes and degassed at 105 °C (unless otherwise noted) on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. After degassing, the sample tubes were re-weighed to obtain a consistent mass for the samples. Sorption data and BET surface area (m$^2$/g) measurements were collected at 77 K with N$_2$ on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

**Thermogravimetric analysis and differential scanning calorimetry (TGA/DSC).** ~10 mg of the sample were and placed in a 100 μL aluminum crucible. The samples were analyzed on a Mettler Toledo Star TGA/DSC using a temperature range of 30-600 °C scanning at 5 °C/min under an N$_2$ atmosphere (75 cm$^3$/min N$_2$ flow rate) for sample degradation measurements and a heat-cool-heat procedure at 10 °C/min for melting point determination.
**Nuclear Magnetic Resonance.** Proton nuclear magnetic resonance spectra ($^1$H NMR) were recorded on a Varian FT-NMR spectrometer (400 MHz). Chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. MMMs were digested for NMR analysis by immersion of ~8-10 mg MMM in 580 μL DMSO-$d_6$ with 20 μL HF (48% in water). Samples were kept in this acidic solution at room temperature until the MOF component of the MMMs was fully dissolved.
5.8 References


