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In Situ Modification of Metal–Organic Frameworks in Mixed-Matrix Membranes**

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Abstract: *Processable films of metal–organic frameworks (MOFs) have been long sought to advance the application of MOFs in various technologies from separations to catalysis. Herein, MOF–polymer mixed-matrix membranes (MMMs) are described, formed on several substrates using a wide variety of MOF materials. These MMMs can be delaminated from their substrates to create free-standing MMMs that are mechanically stable and pliable. The MOFs in these MMMs remain highly crystalline, porous, and accessible for further chemical modification through postsynthetic modification (PSM) and postsynthetic exchange (PSE) processes. Overall, the findings here demonstrate a versatile approach to preparing stable functional MMMs that should contribute significantly to the advancement of these materials.*

Metal–organic frameworks (MOFs) are an exciting class of crystalline materials that are of interest to synthetic chemists and materials scientists alike.[1] Because of their crystalline nature, MOFs are not as malleable as soft materials (e.g. organic polymers), which limits their manipulation and processability.[2] Films or membranes of MOFs are of potential interest for a wide variety of applications and technologies.[3] Despite broad interest in preparing MOF films, this area of study is still relatively new.[4]

Significant work has been applied toward the development of MOF membranes on porous substrates by either direct growth on the substrate or by secondary or seeded growth strategies to achieve monolithic MOF structures. These efforts have been catalogued in reviews by Shah et al.[4b] and Qiu et al.,[4c] demonstrating their suitability for some gaseous[5] and a limited number of liquid separations.[4a,6] Some work has also been done to achieve free-standing pure-MOF membranes, but only small areas can be achieved and delamination is difficult.[7] Membranes based on these processes have some inherent limitations, including: 1) the substrates must be stable to the conditions of MOF growth, 2) the selection of MOFs is largely limited to those grown under mild conditions, 3) the resulting membranes are rigid and brittle.[8]

To circumvent many of these issues, composite materials integrating MOF particles with a polymeric binder have been investigated;[9] several reviews on these MOF-based mixed-matrix membranes (MMMs) have been recently published.[4a,d] The majority of studies on MMMs have focused on their use in gas separations, but MMMs also are of value as a way to improve the processability and handling of MOFs, as well as performing liquid-phase separations or extractions. For example, a report by Basu et al.[9a] described a MOF/polymer composite membrane for the removal of an organic dye (Rose Bengal) from isopropanol. While promising results were obtained, introduction of the MOF species without surface modification with *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide resulted in decreased dye retention by the membrane when compared to the pure polymer (Matrimid). With modification of the MOF particle surface to improve MOF–polymer adhesion, increased dye retention was achieved, but this was attributed largely to reduced swelling of the polymer. A recent report by Zhang et al. described MOF composite membranes[10] that showed robust, recyclable separation of dye pollutants from water. Despite achieving an interesting hybrid material, their synthetic approach presented challenges with controlling crystallite size and MOF composition throughout the film. Additionally, these films were only prepared with a single MOF (ZIF-8) on a single substrate (polyacrylonitrile, PAN) in a laborious layer-by-layer approach. Finally, in another recent study, postsynthetic polymerization (PSP) was used to crosslink MOF particles to prepare a unique MMM that was investigated for heavy-metal sequestration.[11]

Overall, these studies, while encouraging, are limited in scope, utilizing only a handful of MOFs, with generally low MOF loading (in most reports <30 wt%).[4a,12] Moreover, the majority of studies of MOF-based MMMs have been focused on improving membrane characteristics by using the MOF as a polymer filler material, rather than exploring and exploiting the characteristics and chemistry of the included MOF. 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.[13] In this context, we have 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 fabricated on a large scale, easily handled, and readily manipulated. Importantly, distinctive from prior

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studies we are aware of, these MMMs retain the high specific surface areas of the parent MOFs and readily undergo postsynthetic modification (PSM) and postsynthetic exchange (PSE) by standard methods, thus demonstrating that the MOF component is functionally intact in the composite MMM.

A drawdown coating (e.g. bar-coating, doctor-blading) process was used for the fabrication of MMMs,[9a,b,14] using a MOF-based ink prepared by dispersion of MOF particles with a polymer binder (Scheme S1, Supporting Information). Note that "ink" in this study refers to a suspension of preformed MOF particles in a casting solution, not a MOF precursor solution.[15] The preparation of a homogeneous MOF dispersion and a uniform film was difficult by direct dispersion of MOF particles in a polymer solution (e.g. 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 the addition of the polymer solution to this dispersion (Figure S2). The films resulting from this ink were stable, free of cracks, and readily delaminated from the substrate by soaking in solvents (e.g. acetone, methanol). The resulting free-standing MMMs were mechanically robust, pliable, and free of macroscopic defects. Both glass (microscope slide) and aluminum (foil and sheet) substrates were used for casting with similar results.

Figure 1 shows images of seven different MMMs fabricated by this technique (for cross-section images see the Supporting Information). A canonical, but diverse set of materials, including UiO-66 (UiO = University of Oslo),[16] HKUST-1 (HKUST = Hong Kong University of Science and Technology),[17] MIL-101 (MIL = Material Institute de Lavoisier),[18] MIL-53,[19] and ZIF-8 (ZIF = zeolite imidazolate framework),[20] all readily formed MMMs using this methodology. Different metal isoforms, such as MIL-101(Cr) and MIL-101(Fe), as well as functionalized versions of these MOFs (e.g. UiO-66-NH_2),[21] could also be prepared as MMMs. In addition, MMMs were prepared with a wide range of MOF loadings, from approximately 10 to 67 wt% of MOF (using UiO-66 as a representative material, Table S2, Figures S5–S7).[4a]

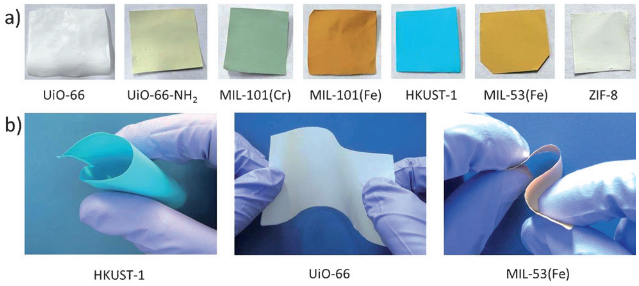

Figure 1. a) Free-standing MMMs (≈1 × 1 cm^2) produced from a variety of MOFs. b) Photographs demonstrating that large area HKUST-1, UiO-66, and MIL-53(Fe) MMMs (≈3 × 5 cm^2) are resilient to mechanical stress and can be easily handled.

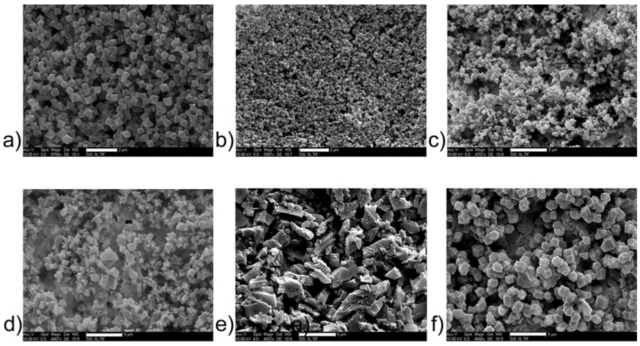

Figure 2. SEM images of MMM surfaces (≈67 wt%): a) UiO-66, b) MIL-101(Cr), c) MIL-101(Fe), d) HKUST-1, e) MIL-53(Fe), f) ZIF-8. Scale bars: a,b: 2 μm; c–f: 5 μm.

In addition to the different colors of the films indicating their composition (Figure 1), all of these materials were characterized by scanning electron microscopy (SEM, see the Supporting Information). At lower MOF loadings (Figure S5–S7), few macrovoids are observed between the MOF and polymer. At higher MOF loadings (≈67 wt%, Figure 2), the MMM composition is dominated by MOF crystallites, which result in apparent macrovoids. The characteristic morphology of the different MOF materials can be readily seen in the film matrices. PXRD (Figures S3, S15, S18, S20, S22, S25, and S28) showed that the crystallinity of these MOFs in the MMMs was maintained.

Figure 3 shows a series of more detailed SEM images of a UiO-66 MMM. The octahedral UiO-66 microcrystals clearly remain intact and are well integrated with the polymer binder. Figure 3b shows a torn edge of the MMM, highlighting the integration of MOF crystals with the PVDF strands. Figure 3c and 3d 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. SEM images of MMMs with

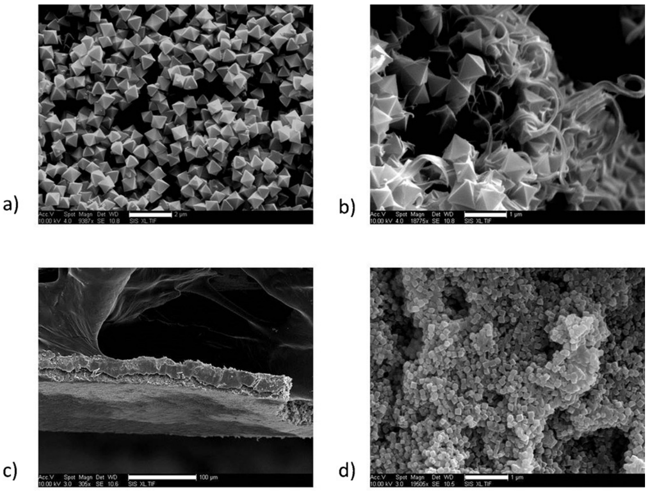

Figure 3. SEM images of UiO-66 MMM (≈67 wt%): a) UiO-66 MMM showing MOF microcrystal structure. b) Torn edge of UiO-66 MMM, clearly showing both the UiO-66 particles and PVDF polymer fibers. c) Cross-section of UiO-66 MMM showing uniform thickness of approximately 35 μm. d) Higher magnification of the cross-section, showing densely packed UiO-66 particles in the MMM interior. Scale bars: a: 2 μm; b,d: 1 μm; c: 100 μm.

lower UiO-66 loadings also show good contacts between the MOF and polymer (Figures S5–S7).

Surface area analysis by N_2 sorption measurements show that the porosity of the MOFs is retained in these MMMs. For example, delaminated UiO-66 MMM, activated under vacuum at room temperature overnight, gave a Brunauer–Emmett–Teller (BET) surface area of $693\pm4\ m^2g^{-1}$ (N_2, 77 K). When accounting for the MOF/polymer composition of the MMM ($\approx$67 wt%, calculated from starting MOF/PVDF composition), the BET surface area of the MOF component of the MMM can be estimated to be $>1000\ m^2g^{-1}$, which is comparable to the value of pristine UiO-66 ($\approx1110\ m^2g^{-1}$)[21] (Figure S3). This result was confirmed with several other MMMs using different MOF fillers, which also gave high gas-sorption capacities (Table S1; Figures S16, S23, S26, and S29).[4a] In addition, dye-uptake studies with azure A, acid orange 8, and acid red 17 (Figure S8 with UiO-66 MMM) also confirmed the porosity of the MOFs in the film. The gas-sorption and dye-uptake results indicate that the PVDF binder does not substantially penetrate or occlude the pores of the MOF.

Despite being immobilized in a polymer matrix, experiments showed that the MOF particles were still accessible to chemical functionalization even within the MMMs. For example, immersion of a UiO-66 MMM in a solution of 2-amino-1,4-benzenedicarboxylic acid (NH_2-bdc) for 24 h at 55 °C resulted in a postsynthetic exchange (PSE) reaction to give UiO-66-NH_2 MMM, with approximately 33 % of the bdc ligands exchanged for NH_2-bdc (Figure S9). The MMM remained intact and the crystallinity of the MOF was preserved even after in situ PSE (Figure S10). Similarly, immersion of UiO-66-NH_2 MMM in a solution of acetic anhydride for 24 h at 55 °C resulted in approximately 75 % conversion to UiO-66-AM1[21] (the methylamide derivative of the same MOF, Figure S11). Again, the MMM maintained its integrity and the MOF material showed good crystallinity after this PSM reaction (Figure S12). We are unaware of any reports demonstrating the chemical accessibility of MOFs in a MMM. The ability to functionalize MOFs within a MMM in situ may prove highly beneficial for the function of these membranes and for optimizing MOF-polymer interactions in order to eliminate macrovoids in many reported MMMs.[4a]

The effect of MOF loading on the mechanical properties of the resulting films was assessed on a series of MMMs with UiO-66 content ranging from 10 wt % to 67 wt %. Tensile data (Table S3, Figure S31–S33) on these films show an increase in the film stiffness with increasing MOF content coupled with decreasing ultimate tensile strength (UTS) in the materials. Despite a reduction in UTS, the free-standing MMMs even at high MOF loadings ($\approx$67 wt %) are robust enough to withstand mechanical stresses, such as bending and moderate tension (Figure 1 c); indeed, the flexibility of these materials with the highest MOF loadings is quite remarkable (Supporting Information, Video S1).[9a,d,22]

To demonstrate the possible utility 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 cm^2 filter area) using a syringe pump. Swatches of MMM were readily cut from a larger film, and could be easily handled for mounting in the syringe filter (Figure 4). This MMM successfully removed 10 μM Coomassie brilliant blue R-250 from an aqueous solution. Dye removal from the solution is readily observed; the eluent was analyzed by UV/Vis spectroscopy ($\lambda=552$ nm) and showed more than 99 % removal of the Coomassie dye. In contrast, a pure-PVDF membrane did not allow passage of the analyte solution. After dye removal, the UiO-66 MMM was investigated for reusability. The MMM was washed with methanol to remove the collected Coomassie and the process was repeated. The second run demonstrated more than 95 % retention of the Coomassie dye. Beyond the simple removal of dyes from aqueous solutions, these MMMs achieved a separation of organic dye molecules. An equimolar mixture of Coomassie brilliant blue R-250 and methyl orange in water was driven through the UiO-66 MMM using the same process and apparatus as described above (Figure 4). The pink solution was passed through the UiO-66 MMM, resulting in an orange-colored eluent. Analysis of the eluent by UV/Vis spectroscopy shows near complete retention of the Coomassie blue (95.6 ± 0.6 %), while allowing approximately 80 % of methyl orange (20.1 ± 7.2 % retention) across the MMM. The mechanism of the separation is still under investigation, but given the extremely diverse range of pore environments, surface areas, and chemical tunability of MOFs, these MMMs offer the potential to adjust the pore features for specific separations. This is further enabled by the ability to perform PSM or PSE on these MMMs, as described above.

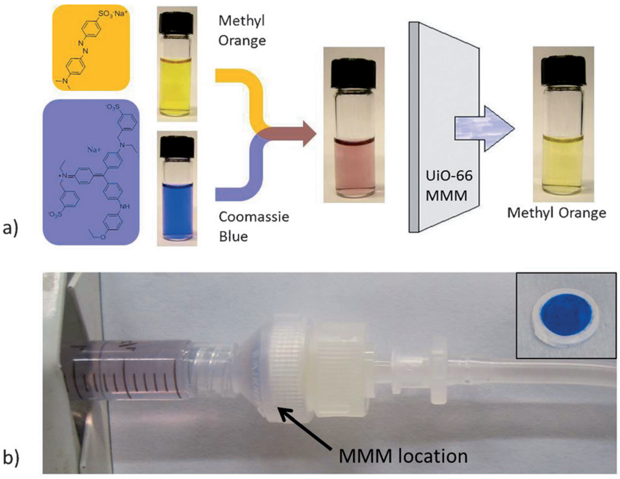

Figure 4. Aqueous dye sequestration with UiO-66 MMM. a) Separation of Coomassie brilliant blue R-250 (blue) and methyl orange (orange) by filtration with a UiO-66 MMM. b) Separation of Coomassie blue R-250 and methyl orange dye solution. The mixed solution (left) is forced through a UiO-66 MMM syringe filter ($\approx$11 mm diameter), allowing permeation of methyl orange only (right). Retention of Comassie dye on the MMM film (inset).

Digestion of the MOF component of MMMs showed that these films may be used as templates for complex polymer-film architectures. UiO-66 MMM was subjected to standard UiO-66 digestion conditions with dilute HF (1.6% HF in DMSO v/v) to dissolve the MOF component. During digestion, the MMM changed from an opaque to a translucent material. 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. SEM analysis of the remaining film showed a highly interconnected, lacy polymer network containing reliefs that retain the shape of the UiO-66 crystals (Figure S14), suggesting good prior contact (e.g. minimal macrovoids) between the MOF filler and the polymer binder. This method, by templating polymer films with MOFs, may be a route to obtaining porous films with complex and unusual architectures.

In conclusion, we have developed a facile approach for the formation of homogenous MOF–polymer composite MMMs with high MOF incorporation. These PVDF films can be prepared with a wide range of MOFs on various substrates and readily delaminated to give durable, large-area, free-standing MMMs with good mechanical stability and flexibility. Characterization of the films showed that the MOFs are highly crystalline and remain porous within the MMM. Moreover, the tunability of the component MOF through postsynthetic methods is retained in the MMM, resulting in MMMs that can be directly modified in situ with a wide 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.

Keywords: metal–organic frameworks · mixed-matrix membranes · polymers · postsynthetic modifications · separation methods

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