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Nylon-MOF Composites via Postsynthetic Polymerization

Mark Kalaj, Michael S. Denny Jr., Kyle C. Bentz, Joseph M. Palomba, and Seth M. Cohen *

Abstract: Hybridization of metal-organic frameworks (MOFs) and polymers into composites yields materials that display the exceptional properties of MOFs with the robustness of polymers. However, realization of MOF-polymer composites requires efficient dispersion and interactions of MOF particles with polymer matrices, which remains a significant challenge. Herein, we report a simple, scalable, bench-top approach to covalently tethered nylon-MOF polymer composite materials by an interfacial polymerization technique. The copolymerization of a modified UiO-66-NH_2 MOF with a growing polyamide fiber (PA-66) during an interfacial polymerization gave hybrid materials with up to ~29 weight percent MOF. The covalent hybrid material demonstrated nearly an order of magnitude higher catalytic activity for the breakdown of a chemical warfare simulant (dimethyl-4-nitrophenyl phosphate, DMNP) compared to MOFs that are non-covalently, physically entrapped in nylon, highlighting the importance of MOF-polymer hybridization.

Metal-organic frameworks (MOFs) are constructed from inorganic metal nodes, termed secondary building units (SBUs) and multitopic organic linkers, forming a highly porous three-dimensional lattice.[1] The large, open cavities form an interconnected porous network, and consequently, MOFs display exceptional sorption capacities across a broad range of applications. Coupled with catalytic activity deriving from functional units on the ligands and active metal sites at the SBU, MOFs have attracted great interest as functional, porous materials.[2] For example, Zr^{4+}-based MOFs have been investigated as sorbents that can also catalytically degrade chemical warfare agents (CWAs);[3] however, few examples have demonstrated this activity in a functional form factor.[4]

Assembly of composite materials with MOFs has proven to be an effective way to exploit the desired 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.[5] Previous work has shown that a polymer composite can actually enhance the characteristics of MOFs through framework stabilization[6] or enhanced uptake of a desired analyte.[7] Significant advances have been made in the field of MOF composites by achieving covalent integration of MOF and polymer components.[8] Despite these advances, the covalent integration of MOFs and polymers remains challenging. Two primary methodologies to produce these covalent composite materials has been pursued. The first method uses the solvothermal synthesis of MOFs from polymeric ligands resulting in MOF-polymer hybrid materials, termed polyMOFs.[9] An alternative approach termed postsynthetic polymerization (PSP)[8, 10] uses a reactive handle on the MOF that can combine with a monomer to form an interstitial polymer matrix around the MOF particles. PSP has been successfully used to prepare membranes and stable, highly connected monoliths.[8, 11]

Nylon 6,6 (PA-66), is a simple linear polyamide (PA) prepared from hexamethylenediamine (HMDA) and adipic acid. PA-66 remains one of the most widely used polymers today, especially in high-durability textiles. Given their utility, ubiquity, and facile preparation, polyamides are a natural choice for preparation of covalent composites with MOFs via PSP. However, no methods currently exist to create covalently linked nylon-MOF hybrid materials under mild conditions. Formation of amide bonds on ligands has been well established by postsynthetic modification (PSM) studies with MOFs.[8b, 10, 12] Indeed, many common MOFs can be prepared with amine functionalized ligands where the amine is amenable to chemical modification to amide groups.[1, 13] In related work by Choe et al., acyl chloride ligands were utilized to crosslink amine functionalized metal-organic polyhedral (MOPs).[14]

Herein, the first example of a mild, scalable, bench-stable preparation of nylon-MOF covalent hybridization is reported. Previously, only Yu and coworkers reported a method to covalently attach MOFs to nylon surfaces, but this method required the use of harsh γ-ray irradiation, and was limited only to the polymer surface.[15] The synthesis described here covalently attaches UiO-66-NH_2 to a growing PA-66 fiber (designated as PA-66-UiO-66-NH_2) via PSP. The Zr^{4+}-based UiO-series was selected due to its chemical stability and previously reported catalytic activity toward CWAs.[3a-c] The activity of this polymer-MOF hybrid toward CWA simulant degradation is reported, which are largely not available for polymer-MOF hybrids, with the vast majority of the literature reporting only on powdered samples.[3c] The PSP prepared materials show good activity compared to non-covalent, nylon-entrapped MOF particles.[3b]

The amine functionalized MOF, UiO-66-NH_2, was covalently incorporated as part of the growing polymer

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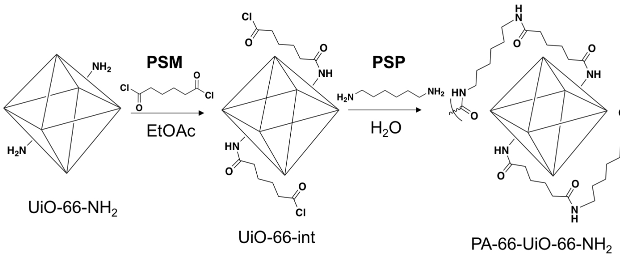
chains of PA-66, by pre-treating the MOF with adipoyl chloride (Scheme 1). PSM prefunctionalization of UiO-66-NH_2 with adipoyl chloride generated reactive acyl chloride groups on the MOF, which was followed by a PSP reaction via interfacial polymerization with an aqueous layer containing HMDA.



Scheme 1. PSM and PSP scheme used to prepare PA-66-UiO-66-NH_2

To synthesize the nylon composite, UiO-66-NH_2 was dispersed in ethyl acetate and PSM was performed with ten equivalents of adipoyl chloride. This forms the acid chloride UiO-66-int (int = intermediate, Scheme 1). Samples of UiO-66-int were isolated and analyzed by ^1H NMR to determine the extent of amine functionality. Exposure of UiO-66-NH_2 to adipoyl chloride for 10 min resulted in ~25% functionalization (Table S1). The ^1H NMR spectra suggested the formation of two different amide linked products, as well as free adipic acid (from hydrolyzed adipoyl chloride, a byproduct of the workup, Figure S4). One amide product is the desired condensation of amino-benzene dicarboxylic acid (NH_2-bdc) with adipoyl chloride, while the second product is a bis(amide) wherein the adipoyl chloride has linked two NH_2-bdc ligands (Figure S5). The ^1H NMR data revealed that after 10 min of PSM, 25% of the ligands in the MOF were functionalized with a ~1:1 ratio of the two amide products (Table S2). To interrogate the possibility of inter- (vs. intra-) particle cross-linking, dynamic light scattering (DLS) experiments were performed. DLS shows essentially identical particle hydrodynamic radii for UiO-66-NH_2 and UiO-66-int during the PSM reaction, indicating that intraparticle crosslinking is the predominant source of the aforementioned bis(amide) product (Figure S9).

After PSM with adipoyl chloride, a suspension of UiO-66-int in EtOAc (containing ten equivalents of adipoyl chloride) was carefully layered on top of an aqueous solution of HMDA. Polymerization occurs at the interface of the two layers, during which UiO-66-int is covalently incorporated into the forming polyamide, resulting in the desired PA-66-UiO-66-NH_2 hybrid material (Figure 1). The resulting PSP product retains the flexibility of the PA-66 fiber after incorporation of MOF (Video S1). The presence of the MOF throughout the length of the fiber was confirmed by powder X-ray diffraction (PXRD) patterns and scanning electron microscopy (SEM) images. Pieces of the composite material were cut every ~12 inches and analyzed by PXRD and SEM, which showed evidence of MOF particles throughout the fiber (Figure S10, S16) for up to 36 inches. Some degree of MOF aggregation is observed by SEM (Figure 1). TGA analysis showed that the MOF content throughout the fiber was relatively consistent at ~29 wt% (Figure S19, Table S3).

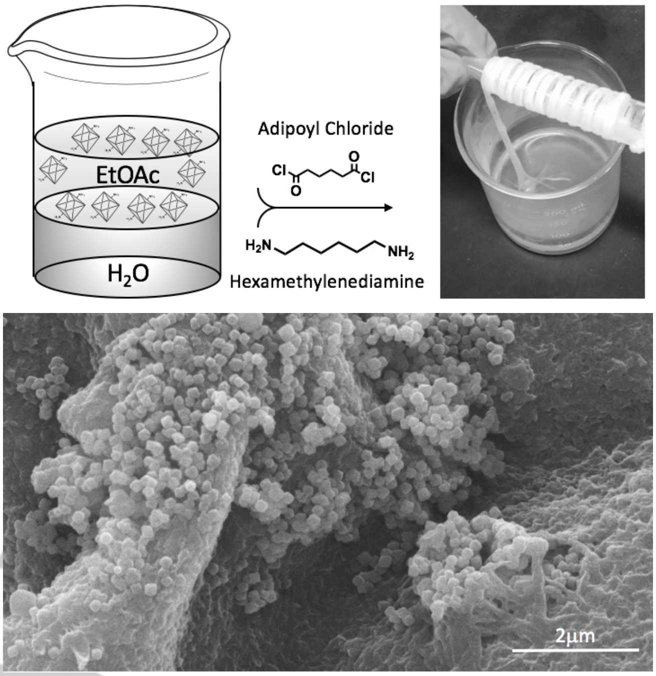


Figure 1. ,*Top:* Interfacial fabrication of PSP. *Bottom:* SEM image of PA-66-UiO-66-NH_2.

Control studies were performed with three different MOFs to confirm that covalent linkages between UiO-66-NH_2 and PA-66 was achieved, as opposed to physical entrapment of the MOF particles within or onto the polymer. The parent UiO-66 material and two UiO-66 derivatives (UiO-66-AM6, UiO-66-AM6COOH) were investigated to compare with UiO-66-NH_2 (Figure 2). Consistent with an inability to covalently integrate with PA-66, interfacial polymerization with control MOFs proved to be less robust. For example, with UiO-66 only a ~30 cm continuous fiber could be pulled from the interface under identical conditions as used with UiO-66-int (generated from UiO-66-NH_2, which gave >100 cm as described above). This is likely due to the UiO-66 interfering with the polymerization at the interface (detailed synthesis and characterization of these control materials can be found in the ESI). Distinct differences can be seen between the PSP product and noncovalent hybrids, for example, the noncovalent PA-66@UiO-66 material is extremely thin and brittle compared to the PA-66-UiO-66-NH_2 PSP product (Figure S17).

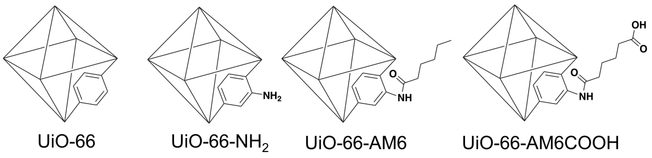


Figure 2. Four different MOFs used for PSP in nylon composites.

Thermogravimetric and differential scanning calorimetry (TGA/DSC) analysis of the PSP product (PA-66-UiO-66-NH_2), as well as all three control materials (PA-66@UiO-66, PA-66@UiO-66-AM6COOH, and PA-66@UiO-66-AM6), were conducted in an effort to determine the extent of MOF incorporation into the polymer as well as the melting point of the materials. TGA data indicates 29% by weight of MOF incorporation for the PSP product (PA-66-UiO-66-NH_2) compared to 20% incorporation for PA-66@UiO-66, 27% incorporation for PA-66@UiO-66-AM6COOH, and 23% incorporation for PA-66@UiO-66-AM6 (Table S3).

Covalent crosslinking of the polyamides in PA-66-UiO-66-NH_2 is supported by DSC melting point data (Table 1). Specifically, samples were heated to 280 °C at 10 °C/min, then cooled to 100 °C at 10 °C/min, and finally heated to 600 °C at 10 °C/min to determine the thermal characteristics of the composite materials. The initial heating step is performed to clear the thermal history of the material whereas the second heating step is used to determine the accurate melting point of the material. Melt curves were integrated and assessed by the onset and peak of the curve (ESI). Pure PA-66 has an experimental second melt point onset of 237 °C and melt peak of 252 °C. The PA-66@UiO-66 material shows a very similar second melt suggesting that the PA-66 and UiO-66 are phase segregated after the first melt leading to a nearly pure nylon-like second melt (Table 1). PA-66@UiO-66-AM6COOH shows a second melting point depression of ~5 °C at the onset and ~5 °C at the peak, relative to PA-66. PA-66@UiO-66-AM6 has a second melting point depression of ~5 °C at the onset and ~4 °C at the peak. In contrast, the same melt with PA-66-UiO-66-NH_2 results in a depression of the melting point by ~20 °C at the onset and ~12 °C at the peak, when compared to pure PA-66. This large melting point depression suggests the covalent attachment of MOF as part of the nylon fibers, which significantly disrupts the ability for polymer crystallization. These results are consistent with other findings where covalent attachment of large inorganic particles disrupt polymer crystallinity and results in reduced melt temperature.[16]

Table 1. Second melting point of PA-66 and PA-66-MOF hybrid materials highlighting the melting point depression of PA-66-UiO-66-NH_2.

Material	2nd MP Onset (°C)	2nd MP peak (°C)
PA-66	236 ± 2	252 ± 1
PA-66@UiO-66	238 ± 3	252 ± 2
PA-66@UiO-66-AM6	231 ± 1	248 ± 1
PA-66@UiO-66-AM6COOH	232 ± 1	247 ± 1
PA-66-UiO-66-NH_2	216 ± 5	240 ± 2

Pore accessibility of the hybrid materials was determined by measuring the BET surface area of the composites. Surface area analysis by N_2 gas sorption measurements show that the porosity of the MOFs is better retained in the covalent PSP hybrid material relative to the non-covalent materials. BET surface area measurements were performed on all free MOF powders (Figure S31). Based on the percent MOF content in the composite materials, the expected BET surface area of the composites was calculated. If the MOF component is completely accessible the BET surface areas are calculated to be ~290 m^2/g and ~220 m^2/g, for PA-66-UiO-66-NH_2 (29 wt%) and PA-66@UiO-66 (20 wt%), respectively. However, the measured surface areas were found to be 107±2 m^2/g and 35±1 m^2/g for the PA-66-UiO-66-NH_2 and PA-66@UiO-66, respectively (Figure S32). Whereas pore accessibility is decreased for both samples compared to the free MOF particles, the BET surface area shows that pore accessibility is better retained in the PSP product (37%) compared to the non-covalent product (16%, Table S4).

Covalent attachment of MOFs into processable polymer materials is critical for the utilization of MOFs in real-world applications. To assess the applicability of the materials as functional textiles, the PA-66-MOF hybrid materials were screened for catalytic activity against the nerve agent simulant, dimethyl 4-nitrophenyl phosphate (DMNP) (Figure 3). DMNP has been employed as a safer alternative to study the hydrolysis of phosphoester linkages that are present in nerve agents, although the authors note that this is still a high-hazard species and should be handled with extreme care. A high-throughput screening (HTS) approach using UV-visible spectroscopy was used to detect degradation of the DMNP simulant,[3b, 17] at pH = 8 using UiO-66, UiO-66-NH_2, UiO-66-AM6, and UiO-66-AM6COOH, as both nylon composites and powders. As shown in Figure 3, UiO-66 and UiO-66-AM6 powders are approximately three times more active than the UiO-66-NH_2 and UiO-66-AM6COOH MOFs, which is consistent with literature reports.[17] Incorporation of the various functionalized MOFs into PA-66 composites had a dramatic effect on the catalytic degradation of DMNP. The covalently attached hybrid material, PA-66-UiO-66-NH_2, was nearly an order of magnitude more active than any of the non-covalent incorporated PA-66 composites. Composite materials were recycled and reused, displaying no loss in catalytic activity toward DMNP degradation after four catalytic cycles (Figure S30). These results, along with the gas sorption analysis, demonstrate that the MOF particles in the PA-66-UiO-66-NH_2 composite are more accessible and active than in the nylon-entrapped materials (i.e., PA-66@UiO-66, PA-66@UiO-66-AM6COOH, and PA-66@UiO-66-AM6).

Several MOF materials in powder form have been screened for CWA catalysis, there are only a few examples in the literature of CWA screening via polymer-MOF hybrid materials.[4] Recent studies by Parsons et al. have utilized atomic layer deposition (ALD) by coating polymer fibers with an intermediate metal oxide layer that provides a nucleation site for MOF synthesis.[4] DMNP hydrolysis (pH = 10) using the ALD generated materials indicated decreased performance compared to the pure MOF powders.[4a] When comparing fibers with different ALD coatings, increased activity was observed when using ALD films that promoted a higher quality of MOF crystal growth.[4a] Expectedly, their studies showed the MOF was required for catalytic activity when compared to the polymer alone.[4b] The ALD composite materials displayed a loss of activity after the materials were recycled only two times, whereas PA-66-UiO-66-NH_2 showed retention of activity through at least four catalytic cycles (Figure S30).[4b] Our materials provide a straightforward, covalent alternative to catalytically active, MOF-containing polymer fibers.

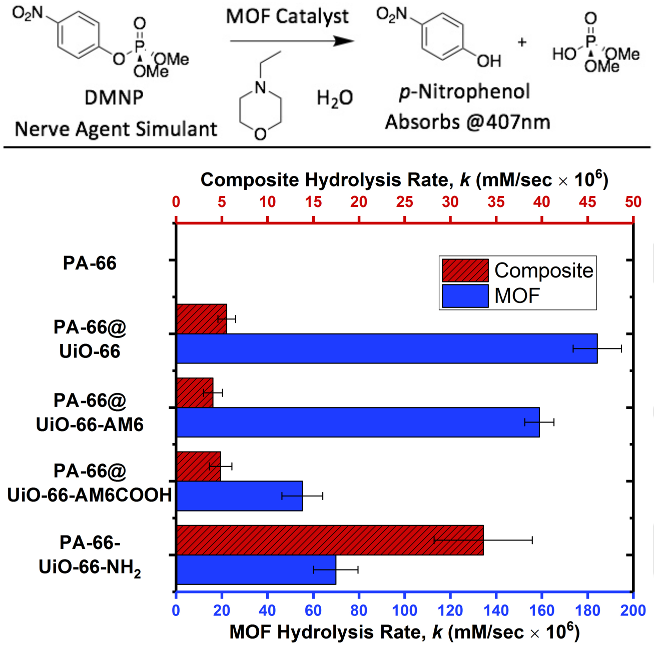


Figure 3. *Top:* DMNP degradation reaction. *Bottom:* Rate of catalytic degradation of DMNP by MOF powders of PA-66-MOF composites measured by UV-visible adsorption at 407nm.

In conclusion, PSP is shown to be an efficient method to incorporate UiO-66-NH_2 into nylon (PA-66) polymer fibers. MOF materials were subjected to PSM to modify the ligand components, after which PSP was used to generate PA-66-MOF hybrid materials. ^1H NMR studies on small molecule models, melting point measurements through DSC, and surface area determination, were all indicative of a covalent link between the MOF particles and the nylon fibers. The covalently linked hybrid material showed significantly higher activity against CWA simulant degradation compared to MOF particles that were simply physically entrapped in the polymer. This result underscores the benefits of PSP over physical adhesion or entrapment of MOFs to polymer materials. This is a rare example of examining CWA degradation in a polymer-MOF hybrid material that is closer to a usable form factor. Current experiments are focusing on engineering of this material for potential textile incorporation.

Keywords: metal-organic framework • MOF-polymer hybrid material • chemical warfare agent

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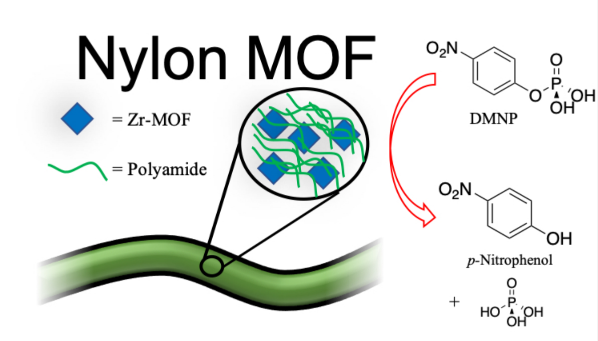

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We report hybridization of metal-organic frameworks (MOFs) and nylon polymers into composites via postsynthetic polymerization. This simple, scalable, bench-top approach provides a new method to design hybrid materials containing MOFs and polymers while maintaining the desired properties of both materials.