A Journal of the Gesellschaft Deutscher Chemiker

Angewandte Chemie

GDCh

International Edition

www.angewandte.org

Accepted Article

Title: Spray Coating of Catalytically Active MOF-Polythiourea through Postsynthetic Polymerization

Authors: Mark Kalaj and Seth Mason Cohen

To be cited as: *Angew. Chem. Int. Ed.* 10.1002/anie.202004205

Link to VoR: https://doi.org/10.1002/anie.202004205

WILEY-VCH

Spray Coating of Catalytically Active MOF-Polythiourea through Postsynthetic Polymerization

Mark Kalaj and Seth M. Cohen*

Abstract: Chemical warfare agents (CWAs) and more specifically, organophosphorous nerve agents, are some of the most acutely toxic chemicals to humans. Despite international treaties designed to ban nerve agents, they continually resurface to cause harm to both civilian and military personnel worldwide. Herein, we report the synthesis of a UiO-66-NCS MOF from postsynthetic modification (PSM) of UiO-66-NH_2. The UiO-66-NCS MOF displays a ~20-fold increase in activity against the chemical warfare agent simulant dimethyl-4-nitrophenyl phosphate (DMNP) compared to UiO-66-NH_2, making it the most active MOF materials as assessed using a previously validated high-throughput screening (HTS) method. More importantly, the -NCS functional groups provide reactive handles for postsynthetic polymerization (PSP) of these MOFs into functional materials. We show that these MOFs can be tethered to amine terminated polypropylene polymers (Jeffamines) through a facile room temperature synthesis with no byproducts. These MOFs are then crosslinked into a MOF-polythiourea (MOF-PTU) composite material that maintain the catalytic properties of the MOF and display the flexibility of the polymer. Furthermore, this MOF-PTU hybrid material was utilized as a spray coating onto Nyco textile fibers and displayed excellent adhesion to the fiber surface. Compared to physical mixture control experiments with UiO-66-PTU, the covalent UiO-66-NCS-PTU spray coating shows better compatibility and durability with the Nyco fibers. The spray coated fibers were screened for the degradation of DMNP and showed durable catalytic reactivity.

Introduction

Since their first use during World War I, chemical warfare agents (CWAs) have periodically resurfaced throughout most of the 20th and 21st century to cause mass destruction on both military personnel and civilians. While CWAs are broadly generalized as devastating weapons, they have been classified into nuanced categories based on their chemical composition. The most acutely toxic CWAs are organophosphorus nerve agents such as tabun, sarin, soman, and VX. As such, the design of materials with potential to chemically degrade organophosphorous nerve agents are heavily sought after to thwart the threat of these dangerous chemicals.

Over the last decade, metal-organic frameworks (MOFs) have emerged as a leading candidate for the degradation of CWAs. MOFs are a highly crystalline class of rigid two- or three-dimensional porous materials composed of inorganic metal centers, termed secondary building units (SBUs), linked by multitopic organic ligands.[1] The facile chemical tunability and of MOFs make them ideal candidates for screening a wide range of functional groups or metal centers in an effort to design the most catalytically effective material.[2] More specifically, Zr-based MOFs have shown promise for the catalytic degradation of organophosphorus based CWAs and their simulants, and this has been attributed to the Lewis acidic nature of the zirconium metal nodes.[3]

Two main approaches have been utilized for improving the activity of MOFs against CWAs and simulants: engineering more active sites or altering the functional groups on the organic linkers.[2a, 2b, 4] Density functional theory (DFT) calculations suggest the degradation of the CWAs occurs at the MOF SBU.[3b, 5] Thus, attempts to improve the catalytic activity of MOFs against CWAs have mainly focused on designing MOFs with experimentally induced defects or lower connectivity MOFs offering more active sites.[2b, 4a-c, 4f] Ligand-based effects, where addition of functional groups on the organic linkers results in increased catalytic activity, have also been described.[2a, 2b, 4e] Most notably, Farha et al. showed a ~20 fold increase in activity for the degradation of the CWA simulant dimethyl-4-nitrophenyl phosphate (DMNP) using UiO-66-NH_2 compared to UiO-66.[2b] This ligand effect was also observed in the Zr-based MOF NU-1000 (NU = Northwestern University) where the presence of amine groups at distinct positions of the organic linkers resulted in increased DMNP activity.[2a] The cause of this increased activity has been attributed to the amine group behaving as a Bronsted base as these results are only observed in very basic conditions (pH = 10) and have proven to be pH dependent.[6] For example, other studies have shown that UiO-66 degrades DMNP two times faster than the amine analogue under less basic conditions (pH = 8).[6-7] As such, our group has focused on improving the catalytic activity of these MOFs at pH = 8 in an effort to more closely emulate the conditions at which the MOF would come in contact with a CWA. In another report, we screened halogenated derivatives of UiO-66 using the same method and UiO-66-I displayed 4-fold increased activity compared to UiO-66. This increase was attributed to halogen bonding occurring between the iodine atom and the phosphoester bond of the DMNP molecule resulting in a more electrophilic and more readily hydrolysable phosphorous atom.[4d] While these results are interesting, the overarching goal of this research is to achieve a functional protective textile material as opposed to a crystalline powder.

Zr-MOFs display this excellent catalytic activity against CWAs; however, they are an inherently crystalline materials making their handling and processing somewhat difficult. Several approaches have been utilized for hybridizing MOFs and polymers into composite materials that contain the desired properties of MOFs with the flexibility and processability of polymers.[8]

In particular, some reports in the literature have attempted to synthesize MOF-polymer hybrid materials using textile polymers in an attempt to design fabrics for warfighter and civilian

---

[*] M. Kalaj, Prof. Dr. S. M. Cohen
Department of Chemistry and Biochemistry,
University of California, San Diego
La Jolla, California, 92093, USA
E-mail: scohen@ucsd.edu

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.

10.1002/anie.202004205

protection.[7, 9] The work of Parsons and coworkers has used atomic layer deposition (ALD) of metal oxides onto polymer fibers to provide MOF nucleation sites.[9b-d] While these results are promising, the ALD method has limitations as it is laborious, time consuming, and expensive. In an effort to develop a facile method for the synthesis of MOF-polymer hybrid materials, our group previously reported a nylon-MOF composite material through postsynthetic polymerization (PSP).[7, 10] These materials displayed activity for the degradation of the CWA simulant DMNP; however, the MOF used in this synthesis (UiO-66-NH$_2$) is inherently less active at pH 8. Thus, we aimed to synthesize a more active MOF that had reactive groups that could undergo PSP. Based on our aforementioned study, where halogen bonding increased catalytic activity,[4d] we set out synthesize a MOF containing a pseudohalogen functional group to improve the catalytic activity of the MOF. These pseudohalogen groups could also serve as reactive groups for polymerization of the MOF particles into a functional composite material.

Herein, we report the synthesis of UiO-66-isothiocyanate (UiO-66-NCS) via postsynthetic modification (PSM) of UiO-66-NH$_2$.[11] The MOF was characterized and screened for the degradation of the CWA simulant DMNP, displaying ~20-fold higher activity than the unmodified UiO-66-NH$_2$ at pH = 8, making it the most active MOF reported under these conditions. Additionally, the UiO-66-NCS MOF could be incorporated into a composite material via PSP through the formation of a thiourea bond (UiO-66-NCS-PTU).[12] Furthermore, the MOF-polymer hybrid material could be spray coated onto Nyco (nylon and cotton blend) fibers. Nyco fibers coated with the covalent UiO-66-NCS-PTU material display much better compatibility between the two materials whereas phase separation is evident in the physical UiO-66-PTU spray coating.

Results and Discussion

Synthesis and Characterization

MOF Synthesis. UiO-66-NH$_2$ was synthesized using an acetic acid modulated synthesis.[13] UiO-66-NCS was synthesized through PSM, where UiO-66-NH$_2$ (0.37mmol, 110mg) was reacted with thiophosgene in tetrahydrofuran (THF) at 55 °C for 18 h (**Error! Reference source not found.**, see ESI for complete procedure).[11]

MOF-PTU composite synthesis. Various amounts of MOF were added to achieve a membrane of desired MOF wt % (Table S2). For a ~8% wt MOF composite, UiO-66-NCS (100mg, 0.34mmol) are dispersed in 5 mL of CH_2Cl_2 for 15 min. Jeffamine T3000 (1.0 g, 0.33 mmol) was added to the mixture and the solution was sonicated for 10 min. In a separate vial, 1,4-phenylene diisocyanate (100 mg, 0.62 mmol) was dissolved in 2 mL of CH_2Cl_2 with the aid of sonication. The two solutions were added together, the material promptly vortexed, and the resulting mixture was cast into a glass petri dish. The solvent was then allowed to evaporate at room temperature for 1 h (see ESI for complete procedure).

MOF-PTU spray coating on Nyco fibers. In a 6-dram vial, 100 mg of MOF are dispersed in 10 mL of CH_2Cl_2 for 20 min. To that mixture, 250 mg of Jeffamine T3000 (Huntsman Corporation, material #247625) were added and the mixture was then sonicated for 10 min. In a separate 1-dram vial, 1,4-phenylene diisocyanate (25 mg, 0.16 mmol) is dissolved in 2 mL of CH_2Cl_2 with the aid of sonication. The 1,4-phenylene diisothiocyanate solution was then added to the MOF solution and the mixture was stirred for about 5 sec. The vial was then loaded into a Preval Sprayer (supplied by Preval, item model number: 268) and sprayed onto a swatch (~3 by 4 inches) of ACU (Army Combat Utility) Nyco fibers (50% cotton and 50% nylon provided by U.S. Army Natick Soldier Systems Center (NSSC)) all of the solution was used. The fibers were then allowed to dry in ambient air for 2 h.

UiO-66-NCS was synthesized via PSM by treating UiO-66-NH$_2$ with thiophosgene (**Error! Reference source not found.**, Table S1-S2), as previously reported.[11] MOFs were characterized via powder X-ray diffraction (PXRD) to confirm retention of crystallinity. MOFs were digested in dilute acid and subsequently analyzed by ^1H NMR to confirm the presence of the -NCS functional group (Figure S1-S7). MOFs were also analyzed by scanning electron microscopy (SEM) to evaluate MOF particle size, and by N_2 gas sorption to measure surface areas (Figure S1-S8). Attenuated reflectance infrared spectroscopy (ATIR) was also used to detect the formation of the UiO-66-NCS MOF at the characteristic NCS vibrational frequency of ~2133 cm^{-1} (Figure S9).[11]

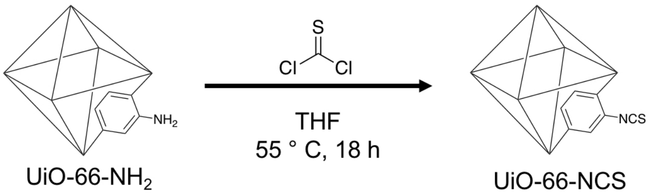
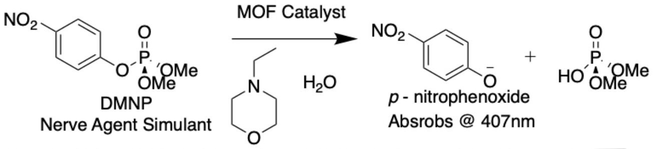


Figure 1. Chemical depiction for the synthesis of UiO-66-NCS via PSM.

DMNP Degradation

It is important to note that there is not a single, standardized assay for determining the rates of degradation of CWAs. Here, an approach based on an HTS methodology was used that has been shown to be a reproducible and reliable assay.[6, 14] All MOFs in this report were screened for the degradation of DMNP at pH = 8 using a previously validated HTS methodology.[6] UiO-66-NCS degrades DMNP at a rate of ~20-fold faster than UiO-66-NH$_2$ (Figure 2). To further probe this result, other MOFs were synthesized containing varying conversion of -NH$_2$ and -NCS functional groups (i.e. 15%, 25%, 50%, 75%, and 85%). The results show an increase in activity as a function of increasing -NCS present in the MOF with fully converted UiO-66-NCS being the best performing MOF (Figure 2). Of the >110 MOFs assayed by this HTS method, UiO-66-NCS displays the highest catalytic activity for DMNP hydrolysis.[4d, 4e, 6-7] The origin of this increased effect may be the result of the proximity of the polarizable -NCS pseudohalogen moiety to the secondary building unit during hydrolysis, as has been previously shown by our group with halogenated MOFs.[4d] This hypothesis is consistent with an increase in the rate of hydrolysis as the number of polarizable -NCS functional groups in increased in the material (Figure 2). To further test this, UiO-66-NCS was combined with hexylamine to produce a MOF with a thiourea substituent (Figure S10). The thiourea MOF displays about 10-fold slower activity when compared to UiO-66-NCS.



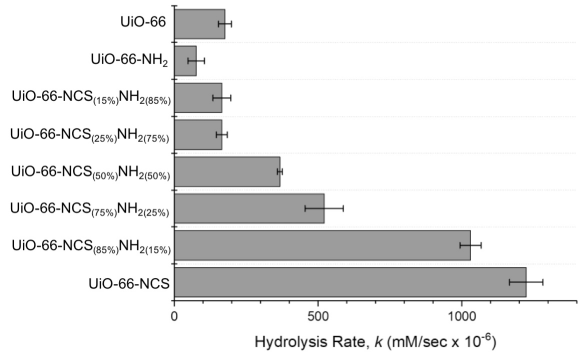


Figure 2. *Top*: DMNP degradation reaction. *Bottom*: Degradation of DMNP by UiO-66 MOFs with varying amounts of -NH_2 and -NCS functional groups as measured by UV-visible adsorption (407nm) at pH = 8.

MOF-Polythiourea (PTU) Composite Materials by Postsynthetic Polymerization

The reactive -NCS functional groups on UiO-66-NCS were utilized to synthesize a MOF-polymer hybrid material through PSP. To synthesize the composite, UiO-66-NCS was dispersed in CH_2Cl_2 and an excess of branched amine terminated polypropylene, namely Jeffamine T3000 (Figure 3 and Figure S11), was added to the mixture to promote formation of thiourea bonds. The thiourea bonds were allowed to form for about 10 minutes. Subsequently, 1,4-phenylene diisothiocyanate was added to the mixture to form extended polymer chains from the MOF surface, resulting in linking of discrete MOF particles (Figure 3 and Figure S11, colored figures are provided in the ESI). The solution was then vortexed and cast out into a glass petri dish. The solvent was allowed to evaporate, and the resulting MOF-PTU composite was delaminated from the dish after swelling the polymer with ethanol (see ESI for details). The composite material contains very well dispersed MOF particles and is flexible. MOF loading for the membranes was varied with the highest achieved loading being about 13 wt% MOF as determined by TGA (Table S2, Figure S12-S17).

The same synthetic procedure was followed for the synthesis of PTU membranes using UiO-66 and UiO-66-NH_2. Using the exact procedure as outlined above, UiO-66-NH_2 MOF was suspended in CH_2Cl_2 and Jeffamine T3000 was subsequently added to the mixture. Upon addition of 1,4-phenylene diisothiocyanate and evaporation of the solvent in a petri dish, the composite material failed to form resulting in a non-solid substance (Figure S18). This suggests the amine terminated polymer and UiO-66-NH_2 were competitive in the formation of the thiourea bond with the 1,4-phenylene diisothiocyanate linker resulting in no composite material. The same procedure was followed with UiO-66. In this control experiment, a solid composite material was formed upon addition of the 1,4-phenylene diisothiocyante molecule. The UiO-66-PTU composite displays a distinct phase separation between the MOF and polymer components (Figure S18). PXRD of the top and bottom side of the composite materials clearly indicate UiO-66 settles to the bottom of the petri dish (Figure S19-S21). Furthermore, SEM and EDX images of the MOF-PTU composite cross sections clearly show phase separation of the MOF and polymer materials (Figure 4, Figure S22 Figure S23). BET surface area measurements of the UiO-66-NCS-PTU and UiO-66-PTU composite materials display almost no porosity (data not shown). This suggests that the crosslinked polymer network could potentially be blocking access to the MOF pores. The UiO-66-NCS-PTU composite displays more uniform incorporation of MOF throughout as evidenced by PXRD, SEM, and EDX (Figure 4, Figure S22-S27). This suggests the chemically reactive -NCS functional groups forming covalent linkages with the polymer are crucial for the formation of a uniform composite material. To further asses the applicability of these hybrid materials, we turned to a facile spray coating technique onto Nyco fibers.

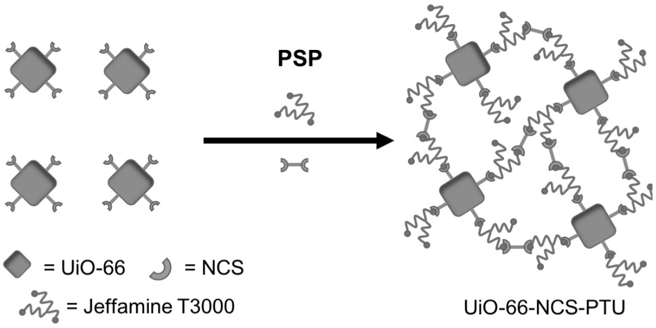


Figure 3. Scheme displaying the synthesis of MOF-PTU composite material. An amine terminated polypropylene polymer (Jeffamine T3000) is combined with UiO-66-NCS forming a thiourea linkage. Addition of 1,4-phenylene diisocyanate acts to further extended the thiourea polymers and crosslink MOF particles together resulting in a MOF-PTU membrane.

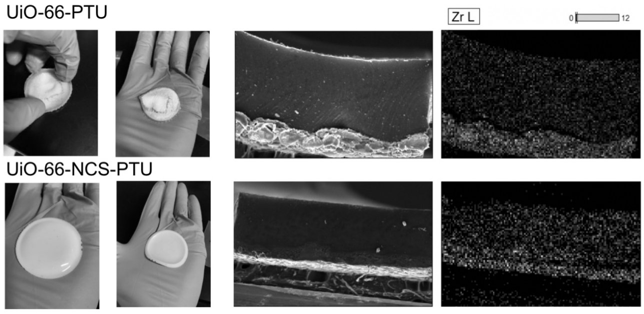


Figure 4. *Top*: Images of UiO-66-PTU membranes viewed from top (*left*) and bottom (*right*) faces. SEM and EDX images of the UiO-66-PTU cross section highlighting the phase separation of MOF and polymer components. *Bottom:* Images of UiO-66-NCS-PTU composite materials viewed from top and bottom, left and right, respectively. SEM and EDX images of the cross section highlighting well dispersed MOF as evidenced by the presence of Zr throughout the membrane.

MOF-PTU Spray Coating on Nyco Fibers

While polyurea polymers are not commonly used textiles, they are utilized as commercial spray coating products. Moreover, spray coating of MOFs onto substrates has been demonstrated as well.[15] These spray coating techniques have shown promise for a number of applications including catalytically active surfaces.[16] To test the spray coating ability of MOF-PTU materials the composites were applied to common warfighter textiles known as Nyco (nylon and cotton blended fibers). Similar to the preparation of the MOF-PTU composite material, MOF was suspended in CH_2Cl_2 and Jeffamine T3000 was added to the solution, coupling the polymer to the MOF. Next, 1,4-phenylene diisothiocyanate was added to the mixture and the mixture was quickly loaded into a Preval Sprayer (see ESI for more details). The MOF-PTU solution was promptly sprayed onto a swatch of Nyco fibers which were subsequently dried under ambient conditions.

UiO-66-NCS-PTU spray coating onto Nyco fibers resulted in good adhesion to the fibers, with the Nyco material indistinguishable from uncoated fibers (Figure 5 and Figure S28). TGA analysis was performed on the spray coated Nyco fibers giving a MOF loading of 8.3±0.7 wt% MOF loading (Table S4). PXRD on the fibers indicate the presence of MOF (Figure S29). To determine the extent of MOF adhesion to the Nyco fibers, we conducted a tape test (see ESI for details), where two-sided tape was used to examine if particles are easily removed from the Nyco surface.[17] The tape test of UiO-66-NCS-PTU Nyco fibers indicated there was no MOF removed from the Nyco surface (Figure S30). Coated Nyco fibers were also scratched with a laboratory spatula and no MOF was observed falling from the swatch (Video S1). SEM images of the fibers after spray coating with UiO-66-NCS-PTU display a consistent layer of a MOF-polymer coating onto the fibers with little to no MOF aggregation (Figure S31). The SEM images clearly indicate the presence of MOF embedded in polymer on the Nyco surface (Figure 5, Figure S28, and Figure S31).

Several control experiments were conducted to further analyze the significance of the MOF-polymer covalent linkage as well as the presence of polymer in the spray coating. First, pure PTU was spray coated on Nyco fibers and the SEM images and PXRD results indicate a cohesive polymer layer on the fibers (Figure S32). Crystalline UiO-66-NCS was also sprayed on the fibers and the powdery material is shown to easily fall off the fibers after drying (Figure S33 and Video S2). The tape test was conducted for these materials and the results clearly indicate abundant MOF removal from the Nyco surface (Figure S34). Control experiments were also performed with UiO-66-PTU sprayed onto Nyco fibers. PXRD indicates the presence of MOF on the surface of the fibers (Figure S35). TGA analysis was performed on the Nyco fibers and the results indicate a MOF loading of 9.1±1.3 wt% MOF loading, nearly identical to that of the UiO-66-NCS-PTU sprayed fibers (Table S4). Optical images of the fibers after spray coating indicate a clear phase separation between the MOF, polymer and Nyco fibers (Figure 5). SEM images of the UiO-66-PTU Nyco coating display clear aggregation of the MOF particles and phase separation between the MOF particles and the polymer on the Nyco Fibers (Figure 5 and Figure S36). Further, the tape test was performed on this material and the results indicate that MOF is removed from the Nyco surface as evidenced by optical images and PXRD (Figure S37). Similar to the MOF-PTU composites, BET measurements of all the spray coated MOF-PTU on Nyco fibers show almost no porosity, which may result from partial pore blockage by the crosslinked polymer network.

Spray coated Nyco fibers and MOF-PTU composites were screened for the degradation of DMNP using a previously reported method (Figure 6 and Figure S38.[7] UiO-66-NCS-PTU fibers displayed similar activity to that of the UiO-66-PTU fibers (Figure 6). Pure Nyco and PTU spray coated Nyco fibers displayed no catalytic activity. The catalytical activity of the as-synthesized MOF powders (Figure 2) displayed a 10-fold increase in activity for UiO-66-NCS compared to UiO-66. However, when coated on Nyco, the activity of UiO-66-NCS-PTU and UiO-66-PTU are approximately equal. The reduction in activity between the MOF-PTU hybrids when compared to the polycrystalline MOF may be the result of the crosslinked polymer limiting access to some of the active sites within the MOF pores.

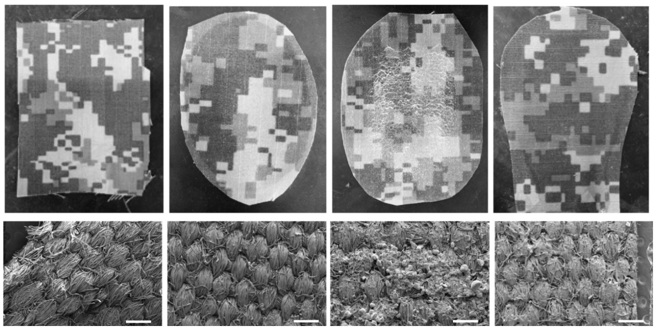


Figure 5. *Top:* Optical images of swatches of Nyco fibers (left to right): pure Nyco, PTU on Nyco, UiO-66-PTU on Nyco, and UiO-66-NCS-PTU on Nyco. *Bottom:* Corresponding SEM images of Nyco fibers. Scale bars are 500 μm.

To test the durability of these fibers, Nyco UiO-66-NCS-PTU and UiO-66-PTU fibers were subjected to a wash test where Nyco swatches were stirred in a beaker containing water and soap for 3 h (see ESI for details). This test was done as a proof of concept to mimic laundry conditions that these fibers would be exposed to if incorporated into fielded uniforms. PXRD of the UiO-66-NCS-PTU and UiO-66-PTU spray coated fibers show MOF is still present after the laundry test. SEM images of the UiO-66-NCS-PTU spray coated fibers display no difference in the fibers before and after the laundry simulation test (Figure S39). SEM images of the UiO-66-PTU spray coated fibers display a significant loss of large MOF aggregates on the surface of the Nyco fibers compared to the prewashed swatches; however, some MOF aggregates are still observed (Figure S40). The fibers were then screened for their DMNP activity after the wash test. The Nyco UiO-66-PTU fibers displayed a substantial decrease in activity whereas the UiO-66-NCS-PTU fibers showed no decrease. This result indicates that when these fibers are subjected to physical agitation the non-covalent composite materials are less durable when compared to the covalent UiO-66-NCS-PTU material.

While MOF powders have extensively been screened for the degradation of DMNP, significantly fewer reports have screened MOF-polymer hybrid materials. Existing reports are mainly from the work of Parsons and co-workers using MOF-polymer composites synthesized by ALD for the degradation of the DMNP simulant and CWAs.[9c, 9d] While these materials have shown promise in rapid degradation of both simulants and agents, the ALD methodology is time consuming and expensive. Moreover, the ALD materials lack covalent attachment to the polymer backbone making them potentially susceptible to physical agitation. Recently, Farha and coworkers also reported a method for coating textiles with Zr-based MOFs.[9a] These materials displayed good activity for the degradation of nerve agents; however, tests for the physical durability, such as a laundry simulation test, of these MOFs on the textile fiber were not described. The method described here is a facile route to synthesizing highly functional MOF-polymer textiles that can endure physical agitation and maintain catalytic activity.

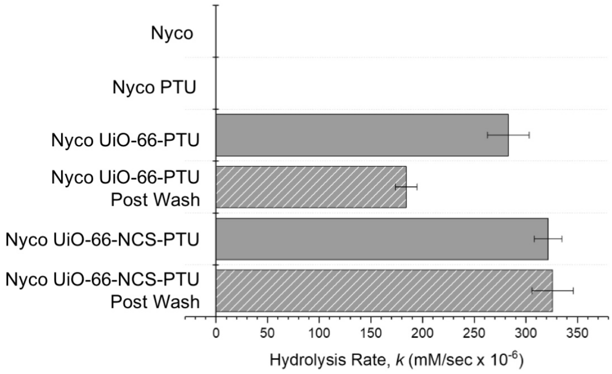


Figure 6. DMNP hydrolysis rates by Nyco spray coated fibers before and after conducting the laundry wash simulation. Data shown is an average of three different swatches run in triplicate.

Conclusion

PSP has been shown to be an effective way of applying a catalytically active MOF-polymer spray coating onto textile fibers. UiO-66-NH_2 was first subjected to PSM yielding UiO-66-NCS. Using the HTS conditions reported above, this MOF displayed the highest catalytic activity to date for the degradation of the CWA simulant DMNP. The -NCS reactive handles on the MOF were further utilized to covalently connect the MOF to an amine terminated polymer. Through PSP a MOF-polymer hybrid material was synthesized under mild conditions. The MOF-polymer hybrid material was spray coated onto Nyco textile fibers and display good adhesion to the surface of the material compared to control experiments. More importantly, the MOF maintains catalytic activity against DMNP while coated on the Nyco fibers. Another notable feature of this material is the durability of the covalent MOF-polymer hybrid, which shows enhanced physical durability when compared with other formulations that do not result in PSP materials. This is a useful and facile way of synthesizing a catalytically active textile fiber for protection from CWAs. We believe this method of PSP will open the door to tethering various amine terminated polymers to the surface of MOFs.

Acknowledgements

We acknowledge financial support from the Army Research Office, Department of Army Material command, under Award No. W911NF-16-2-0106. This work was performed in part at the San Diego Nanotechnology Infrastructure (SDNI) of U.C. San Diego, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542148). We thank the group of Dr. Natalie Pomerantz at US Army Natick Soldier Research, Development and Engineering Center for providing us with Nyco Fibers. M.K. is supported by the Department of Defense (DoD) through the National Defense Science and Engineering Graduate (NDSEG) Fellowship Program and is the recipient of an Achievement Rewards for College Scientists (ARCS) Foundation Fellowship.

Keywords: metal-organic framework • postsynthetic polymerization • chemical warfare agent

[1] a) H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444; b) H. Li, M. Eddaoudi, M. O'Keeffe, M. Yaghi, *Nature* **1999**, *402*, 276-279; c) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature* **2003**, *423*, 705-714.

[2] a) T. Islamoglu, M. A. Ortuño, E. Proussaloglou, A. J. Howarth, N. A. Vermeulen, A. Atilgan, A. M. Asiri, C. J. Cramer, O. K. Farha, *Angew. Chem., Int. Ed.* **2018**, *57*, 1949-1953; b) M. J. Katz, S.-Y. Moon, J. E. Mondloch, M. H. Beyzavi, C. J. Stephenson, J. T. Hupp, O. K. Farha, *Chem. Sci.* **2015**, *6*, 2286-2291; c) T. Islamoglu, A. Atilgan, S.-Y. Moon, G. W. Peterson, J. B. DeCoste, M. Hall, J. T. Hupp, O. K. Farha, *Chem. Mater.* **2017**, *29*, 2672-2675.

[3] a) N. S. Bobbitt, M. L. Mendonca, A. J. Howarth, T. Islamoglu, J. T. Hupp, O. K. Farha, R. Q. Snurr, *Chem. Soc. Rev.* **2017**, *46*, 3357-3385; b) J. E. Mondloch, M. J. Katz, W. C. Isley Iii, P. Ghosh, P. Liao, W. Bury, G. W. Wagner, M. G. Hall, J. B. DeCoste, G. W. Peterson, R. Q. Snurr, C. J. Cramer, J. T. Hupp, O. K. Farha, *Nat. Mater.* **2015**, *14*, 512.

[4] a) H. J. Park, J. K. Jang, S.-Y. Kim, J.-W. Ha, D. Moon, I.-N. Kang, Y.-S. Bae, S. Kim, D.-H. Hwang, *Inorg. Chem.* **2017**, *56*, 12098-12101; b) S.-Y. Moon, Y. Liu, J. T. Hupp, O. K. Farha, *Angew. Chem., Int. Ed.* **2015**, *54*, 6795-6799; c) Y. Zhang, X. Zhang, J. Lyu, K.-i. Otake, X. Wang, L. R. Redfern, C. D. Malliakas, Z. Li, T. Islamoglu, B. Wang, O. K. Farha, *J. Am. Chem. Soc.* **2018**, *140*, 11179-11183; d) M. Kalaj, M. R. Momeni, K. C. Bentz, K. S. Barcus, J. M. Palomba, F. Paesani, S. M. Cohen, *Chem. Commun.* **2019**, *55*, 3481-3484; e) M. Kalaj, J. M. Palomba, K. C. Bentz, S. M. Cohen, *Chem. Commun.* **2019**, *55*, 5367-5370; f) G. W. Peterson, M. R. Destefano, S. J. Garibay, A. Ploskonka, M. McEntee, M. Hall, C. J. Karwacki, J. T. Hupp, O. K. Farha, *Chem. Eur. J.* **2017**, *23*, 15913-15916.

[5] a) M. R. Momeni, C. J. Cramer, *Chem. Mater.* **2018**, *30*, 4432-4439; b) M. R. Momeni, C. J. Cramer, *ACS Appl. Mater. Interfaces* **2018**, *10*, 18435-18439; c) E. López-Maya, C. Montoro, L. M. Rodríguez-Albelo, S. D. Aznar Cervantes, A. A. Lozano-Pérez, J. L. Cenís, E. Barea, J. A. R. Navarro, *Angew. Chem., Int. Ed.* **2015**, *54*, 6790-6794.

[6] J. M. Palomba, C. V. Credille, M. Kalaj, J. B. DeCoste, G. W. Peterson, T. M. Tovar, S. M. Cohen, *Chem. Commun.* **2018**, *54*, 5768-5771.

[7] M. Kalaj, M. S. Denny Jr, K. C. Bentz, J. M. Palomba, S. M. Cohen, *Angew. Chem., Int. Ed.* **2019**, *58*, 2336-2340.

[8] a) T. Kitao, Y. Zhang, S. Kitagawa, B. Wang, T. Uemura, *Chem. Soc. Rev.* **2017**, *46*, 3108-3133; b) M. Kalaj, K. C. Bentz, S. Ayala, J. M. Palomba, K. S. Barcus, Y. Katayama, S. M. Cohen, *Chem. Rev.* **2020**, *10.1021/acs.chemrev.9b00575*.

[9] a) K. Ma, T. Islamoglu, Z. Chen, P. Li, M. C. Wasson, Y. Chen, Y. Wang, G. W. Peterson, J. H. Xin, O. K. Farha, *J. Am. Chem. Soc.* **2019**, *141*, 15626-15633; b) J. Zhao, D. T. Lee, R. W. Yaga, M. G. Hall, H. F. Barton, I. R. Woodward, C. J. Oldham, H. J. Walls, G. W. Peterson, G. N. Parsons, *Angew. Chem., Int. Ed.* **2016**, *55*, 13224-13228; c) D. T. Lee, J. Zhao, C. J. Oldham, G. W. Peterson, G. N. Parsons, *ACS Appl. Mater. Interfaces* **2017**, *9*, 44847-44855; d) D. T. Lee, J. Zhao, G. W. Peterson, G. N. Parsons, *Chem. Mater.* **2017**, *29*, 4894-4903; e) Z. Chen, K. Ma, J. J. Mahle, H. Wang, Z. H. Syed, A. Atilgan, Y. Chen, J. H. Xin, T. Islamoglu, G. W. Peterson, O. K. Farha, *J. Am. Chem. Soc.* **2019**, *141*, 20016-20021.

[10] Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang, B. Wang, *Angew. Chem., Int. Ed.* **2015**, *54*, 4259-4263.

[11] C. Volkringer, S. M. Cohen, *Angew. Chem., Int. Ed.* **2010**, *49*, 4644-4648.

[12] a) Y. Zhang, X. Feng, H. Li, Y. Chen, J. Zhao, S. Wang, L. Wang, B. Wang, *Angew. Chem., Int. Ed.* **2015**, *54*, 4259-4263; b) D. Nam, J. Huh, J. Lee, J. H. Kwak, H. Y. Jeong, K. Choi, W. Choe, *Chem. Sci.* **2017**, *8*, 7765-7771.

[13] M. S. Denny Jr, S. M. Cohen, *Angew. Chem., Int. Ed.* **2015**, *54*, 9029-9032.

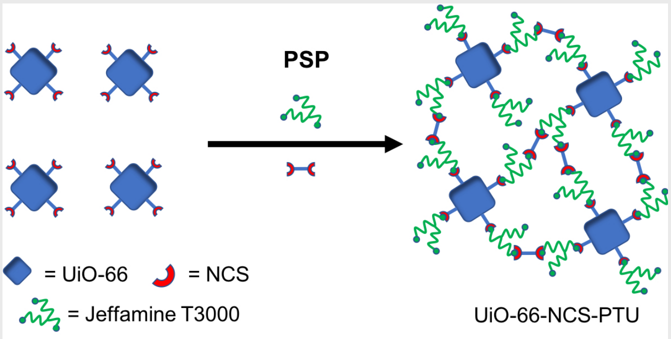
[14] R. Chen, C.-a. Tao, Z. Zhang, X. Chen, Z. Liu, J. Wang, *ACS Appl. Mater. Interfaces* **2019**, *11*, 43156-43165.

[15] a) J.-O. Kim, J. Y. Kim, J.-C. Lee, S. Park, H. R. Moon, D.-P. Kim, *ACS Appl. Mater. Interfaces* **2019**, *11*, 4385-4392; b) R. Ameloot, E. Gobechiya, H. Uji-i, J. A. Martens, J. Hofkens, L. Alaerts, B. F. Sels, D. E. De Vos, *Adv. Mater.* **2010**, *22*, 2685-2688; c) H. K. Arslan, O. Shekhah, J. Wohlgemuth, M. Franzreb, R. A. Fischer, C. Wöll, *Adv. Funct. Mater.* **2011**, *21*, 4228-4231.

[16] a) D. Zacher, O. Shekhah, C. Wöll, R. A. Fischer, *Chem. Soc. Rev.* **2009**, *38*, 1418-1429; b) S. T. Meek, J. A. Greathouse, M. D. Allendorf, *Adv. Mater.* **2011**, *23*, 249-267.

[17] C. Zhang, Y. Li, H. Wang, S. He, Y. Xu, C. Zhong, T. Li, *Chem. Sci.* **2018**, *9*, 5672-5678.

COMMUNICATION



*Mark Kalaj and Seth M. Cohen**

Page xx. – Page xx.

Spray Coating of Catalytically Active MOF-Polythiourea through Postsynthetic Polymerization

We report the synthesis of metal-organic framework-polythiourea hybrid materials through the postsynthetic polymerization of a UiO-66 derivative bearing isothiocyanate groups (UiO-66-NCS). These materials were characterized and screened for the degradation of a chemical warfare agent simulant. UiO-66-NCS was nearly 20-times better than the parent amine-bearing MOF (UiO-66-NH_2). Furthermore, the MOF-polythiourea materials were spray coated onto textile fibres and displayed activity against a chemical warfare agent simulant and maintained activity even after substantial physical agitation.