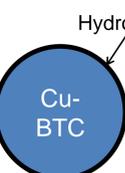
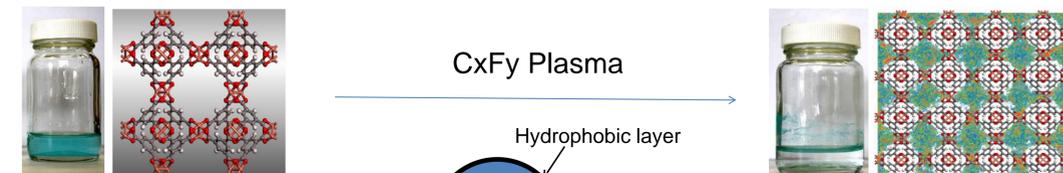


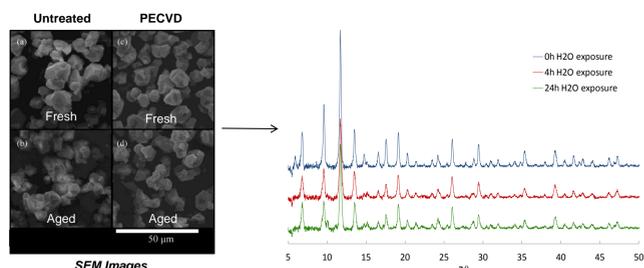
# Treatment of Metal-Organic Frameworks with Fluoroalkane Plasmas

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## Stabilization of CuBTC



Plasma enhanced chemical vapor deposition (PECVD) with perfluoroalkanes lead to stabilization of the structure. Fluorination of the organic linkers in conjunction with a hydrophobic coating prevent water clustering.



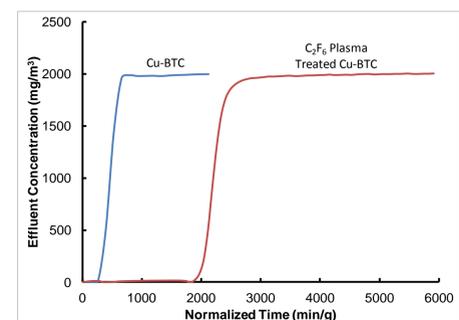
Untreated CuBTC immediately begins to degrade upon exposure to moisture, especially liquid water. Powder X-ray diffraction (PXRD) patterns show long range order peaks immediately degrade, with structural collapse occurring as well.

C<sub>6</sub>F<sub>14</sub>-treated CuBTC shows no degradation after 24 hours of exposure to liquid water. Scanning electron microscope (SEM) images show no structural degradation, whereas untreated CuBTC shows loss of structure and agglomeration occurring as well.

Ammonia loadings (fresh vs. aged) as a function of treatment time. Aging conducted at 45° C, 80% RH for 7 days

Sample	NH <sub>3</sub> Loading (mol/kg)	Aged NH <sub>3</sub> Loading (mol/kg)
CuBTC	6.0	1.1
CuBTC-CF <sub>4</sub> -5min	5.1	0.9
CuBTC-CF <sub>4</sub> -30min	4.3	1.7
CuBTC-CF <sub>4</sub> -60min	4.8	2.4
CuBTC-CF <sub>4</sub> -240min	4.7	3.6

Samples treated with CF<sub>4</sub> (above) and C<sub>2</sub>F<sub>6</sub> (left) exhibit slightly decreased loading for "fresh" materials; however, treated materials provide resistance to aging. Increasing treatment time with CF<sub>4</sub> plasma, for example, increases the resistance to aging through deposition of hydrophobic -CF polymeric groups.

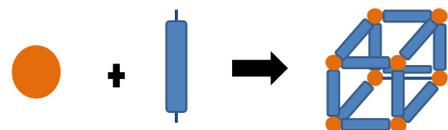


Ammonia microbreakthrough of C<sub>2</sub>F<sub>6</sub>-treated CuBTC vs. untreated CuBTC after aging

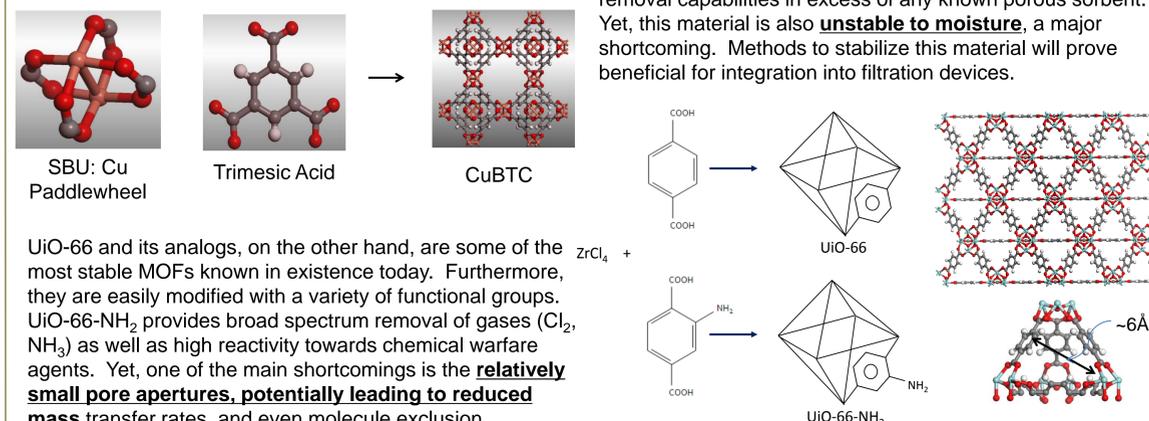
**Status & Future Work:** Materials have been transitioned to prototype filters as polishing layers for ammonia removal. Currently working on scaling technique for technology transition at TRL 6.

## Introduction

Metal-organic frameworks (MOFs) are a promising class of porous materials currently under investigation for enhanced air purification (filtration) systems. MOFs consist of metal oxide secondary building units linked by organic ligands to form reticulated, porous, 3-dimensional structures. The ability to tailor the type of metal, type of organic linker, and functional groups on the organic linker make MOFs prime candidates for nanostructured materials for targeted reactions against toxic chemicals.



Of particular note are CuBTC (aka HKUST-1) and the UiO-66 series of MOFs. CuBTC has been shown to provide ammonia removal capabilities in excess of any known porous sorbent. Yet, this material is also **unstable to moisture**, a major shortcoming. Methods to stabilize this material will prove beneficial for integration into filtration devices.



UiO-66 and its analogs, on the other hand, are some of the most stable MOFs known in existence today. Furthermore, they are easily modified with a variety of functional groups. UiO-66-NH<sub>2</sub> provides broad spectrum removal of gases (Cl<sub>2</sub>, NH<sub>3</sub>) as well as high reactivity towards chemical warfare agents. Yet, one of the main shortcomings is the **relatively small pore apertures, potentially leading to reduced mass transfer rates**, and even molecule exclusion.

## Experimental Design

Fluoroalkane plasmas can be used to both etch surfaces and incorporate functional groups onto surfaces. In particular, fluorinated precursors develop reactive radicals in the plasma and forming a variety of fluorine and carbon-fluorine functional groups that react with the surface, drastically changing the properties of the substrate.

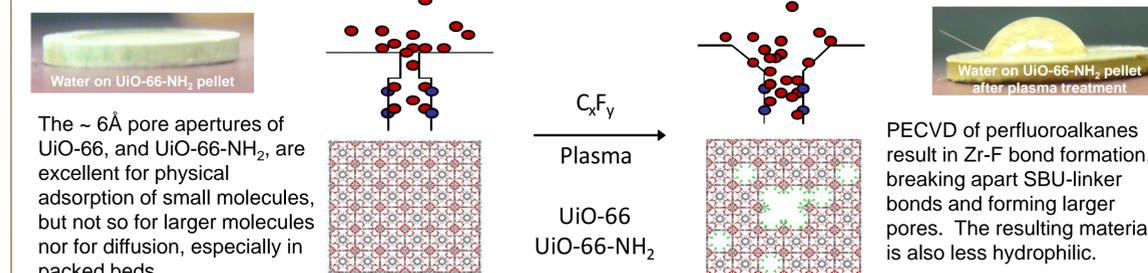
In this effort, we studied a variety of precursor materials and their effect on the structures of CuBTC and UiO-66-NH<sub>2</sub>.



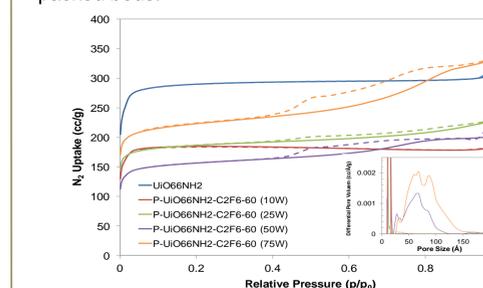
PECVD treatment was performed using a Diener Femto-BR-PCCE-c plasma system with a 100 W 13.56 MHz RF Generator

Parameter	Value
Precursor	CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub> , C <sub>6</sub> F <sub>14</sub>
Atmosphere	Vacuum, neat gas
Pressure	0.3 mbar
Power	10, 25, 50, 75 W
Time	5, 30, 60, 120, 240 min

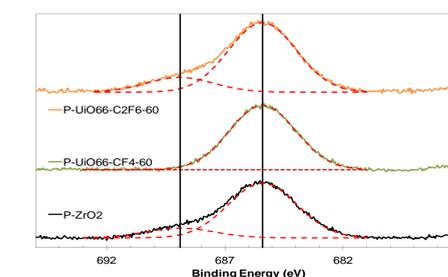
## Mesopore Creation in UiO-66-X



The ~ 6 Å pore apertures of UiO-66, and UiO-66-NH<sub>2</sub>, are excellent for physical adsorption of small molecules, but not so for larger molecules nor for diffusion, especially in packed beds.



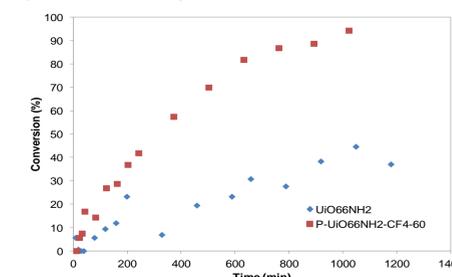
Nitrogen isotherm data show formation of mesopores (hysteresis) at higher wattages. A higher power results in more mesopores



UiO-66 treated with C<sub>2</sub>F<sub>6</sub> was found to create both Zr-F and C-F bonds, as shown via X-ray photoelectron spectroscopy (XPS). In fact, this corresponds quite well to treatment of ZrO<sub>2</sub>, which shares similarities with the SBU of UiO-66. CF<sub>4</sub> primarily showed formation of Zr-F bonds. Similar trends were seen for UiO-66-NH<sub>2</sub>.

**Status & Future Work:** mesopore formation appears to be tunable – we plan to optimize for V, G, & H agents, as well as scale technology for increased mass transfer rates in packed beds (filters). Focus on Cl<sub>2</sub> and NH<sub>3</sub> optimization.

Although there is localized bond-breaking, as seen through the formation of mesopores, the long range and even short range order remains intact for both CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub>-treated samples, as shown by PXRD.



Treatment of UiO-66-NH<sub>2</sub> with a CF<sub>4</sub> plasma results in formation of mesopores large enough to allow diffusion of VX into the pores. Resulting catalytic hydrolysis provides a 60% improvement in half-life. Further optimization is underway to re-hydrolyze the SBU, thus increasing reaction rates even more.

**Acknowledgements:** The authors thank the Defense Threat Reduction Agency/Joint Science and Technology Office for their assistance and funding of this work under Project CB2198. The views expressed in this presentation are those of the authors and do not necessarily reflect official policy or the position of the Department of Defense or the U.S. Government.

(1) Decoste, J.B. et al. *J. Am. Chem. Soc.* **2012**, *134*, 1406. (2) Decoste, J.B. & Peterson, G.W. *J Vis Exp* **2013**, e51175, doi: 10.3791/51175

