

Introduction

Current personal protective equipment (PPE), especially protective suits, relies on the use of perfluoroalkyl substances (PFAS) for repellency of CWAs. As these chemicals are phased out due to environmental concerns, novel solutions are required for repellency. This research aims to develop PFAS-free omniphobic textiles and barriers through the incorporation of polyhedral oligomeric silsesquioxane (POSS)-treated metal organic frameworks (MOFs) onto elastomeric films and fibers that are active towards CWA degradation. POSS cubes, as shown in Figure 1a, have a cage-like structure and are small discrete particles of ~1-3 nm in diameter. They are very robust, chemical- and heat- resistant, nonvolatile, and more importantly environmentally friendly. On the other hand, MOFs have been of great interest with the CBRN community for the past decade due to their ability to capture/degrade CWAs, especially Zr-based MOFs which are also highly chemically and thermally stable. We chose UiO-66-NH₂ as a model MOF for the proof-of-concept study.

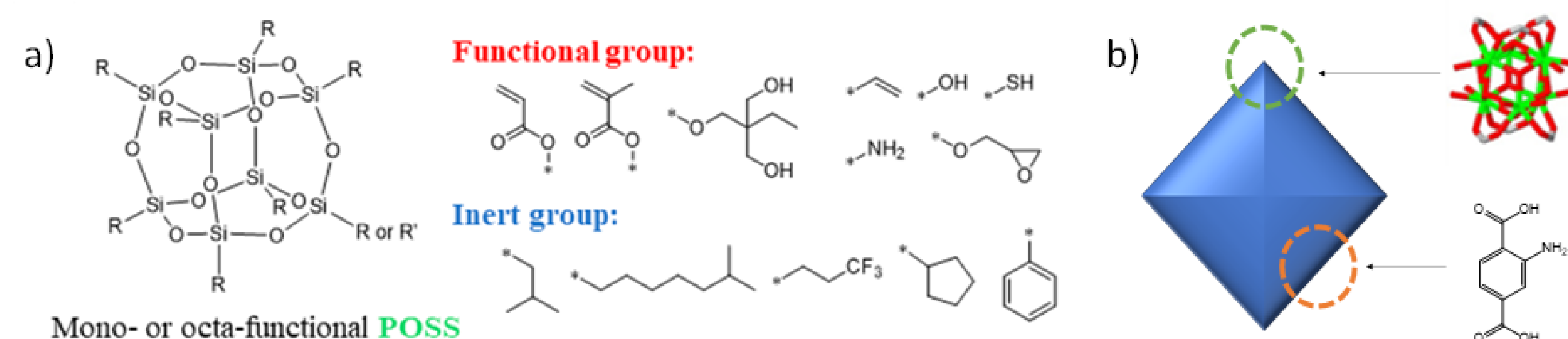
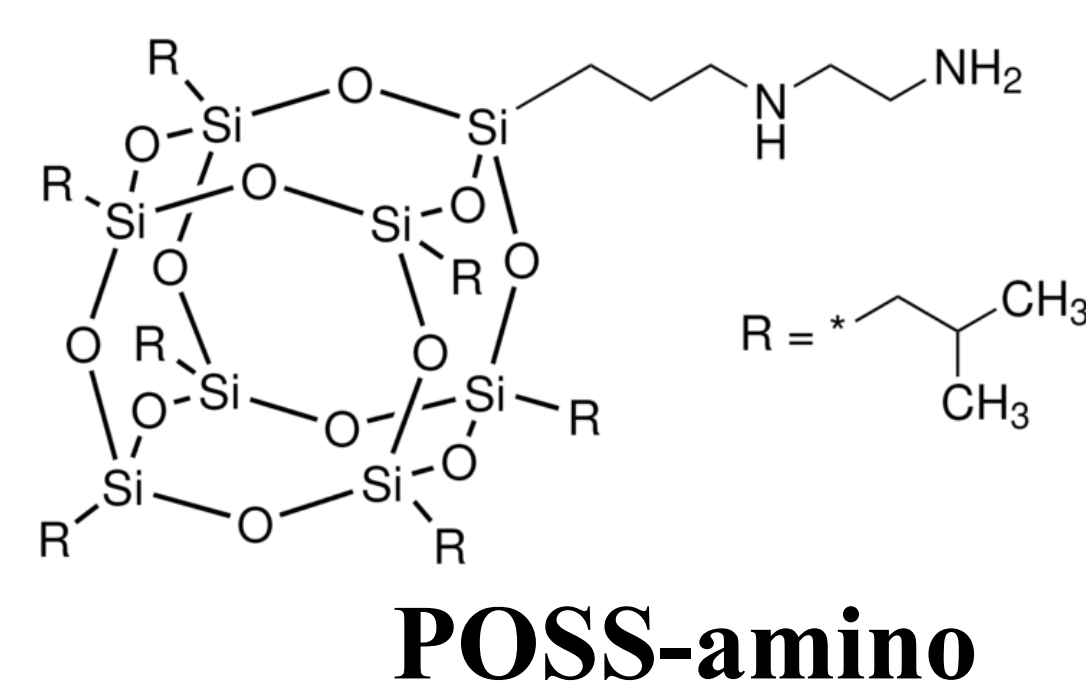


Figure 1. (a) Representative POSS cube with associated functional and inert groups. (b) A notional UiO-66-NH₂ MOF crystal with metal nodes and organic linkers.

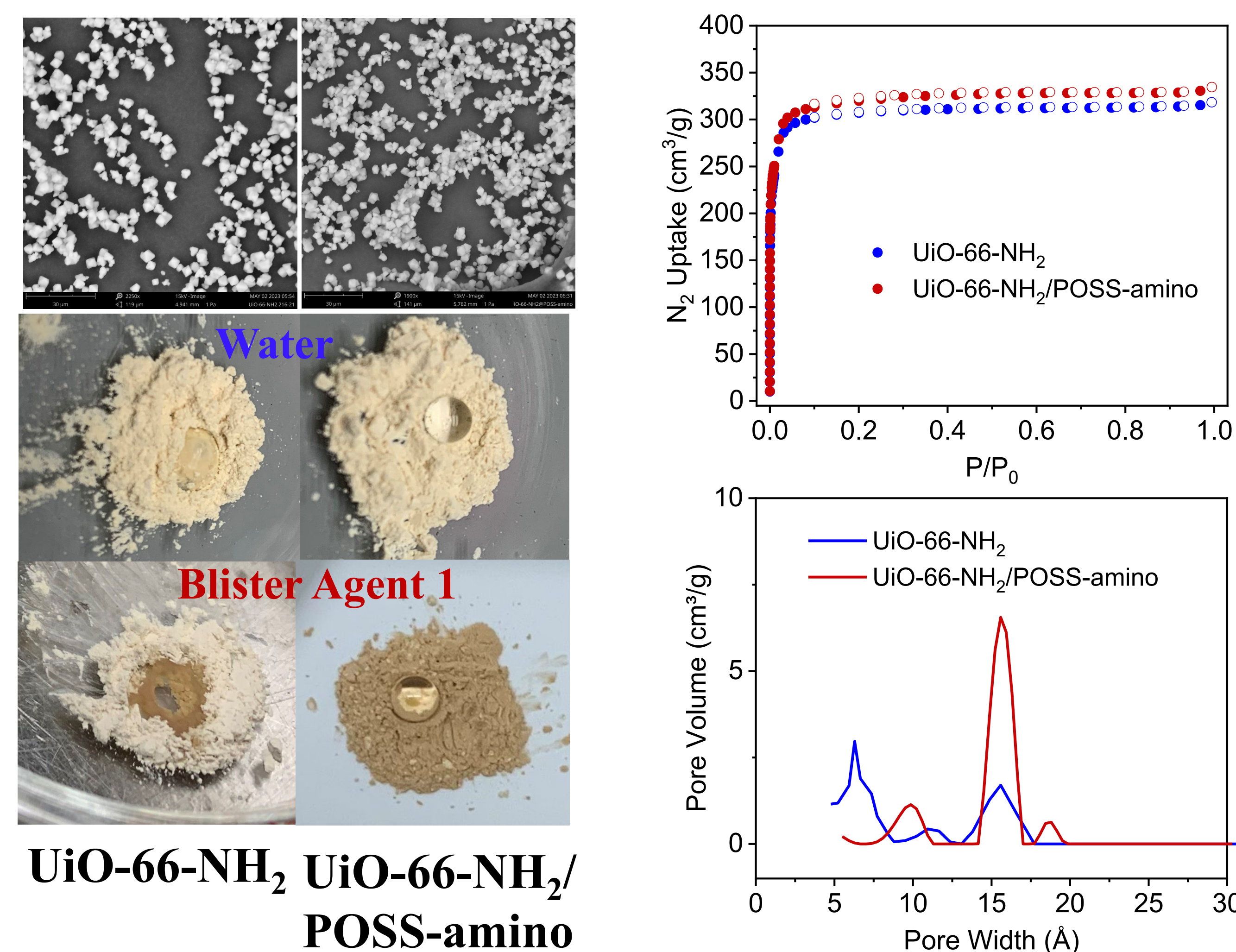


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POSS-Modified MOFs

POSS particles with various functionalities, including epoxide, thiol, and amino, were used to modify UiO-66-NH₂. Interestingly, UiO-66-NH₂ treated with POSS-amino showed the most promising results. POSS-amino modified UiO-66-NH₂ was able to repel both water and blister agent 1 liquid droplets. Nitrogen and water (data not shown) adsorption isotherms were similar before and after modification, suggesting POSS modification likely occurs on the MOF surface only. Its reactivities against CWAs were also retained after modification. It's still unclear to us how POSS-amino is bound to UiO-66-NH₂. We speculate it's a coordination bond between the amino group of POSS and the Zr-nodes of MOF.



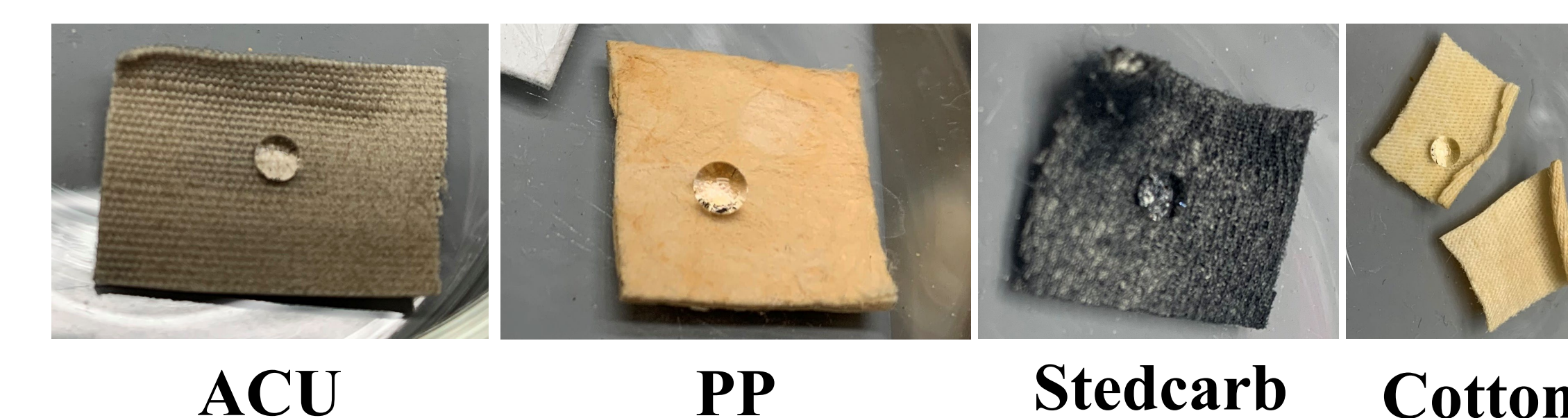
CWA REACTIVITIES

Conversion after 24 h	CEES	Nerve agent 1	Blister agent 1
UiO-66-NH ₂	100%	99%	100%
UiO-66-NH ₂ /POSS-amino	100%	99%	100%

MOF/POSS Composites

Various processing techniques, including dip-coating, drop-casting, electrospinning, covalent attachment, and in-situ MOF growth, were utilized to formulate MOF/POSS composites. All composites formed were able to repel water droplets. However, the best composites we obtained so far were MOF/POSS dip-coated polypropylene (PP) swatches, which were able to hold blister agent 1 droplets up to 4 h. We also fabricated dip-coated fabrics with polymer binders, including PEI, PeBax, and PDMS. However, they didn't perform as well as the ones without any polymers.

Water droplets on UiO-66-NH₂/POSS fabrics



Blister agent 1 droplets on UiO-66-NH₂/POSS dip-coated PP



Conclusions and Future Works

We have shown that POSS can be a viable strategy for creating PFAS-free surfaces that repel blister agent 1. In addition to UiO-66-NH₂, we also successfully modified other MOFs, including MOF-808, CuBTC, UiO-66, and UiO-67, with POSS particles. We will continue to focus on composites development and determine the effects of process and processing parameters on repellency of the composites.

Acknowledgements: We thank the Defense Threat Reduction Agency for funding this research under CB11222.