Supporting Information for

MOFwich: Sandwiched Metal-Organic Framework-Containing Mixed Matrix Composites for Chemical Warfare Agent Removal

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Materials Preparation

Polymer/metal-organic framework (MOF) and metal oxide composites were prepared according to the following general procedure, and details for the MOFwiches are listed in Table S1. All MOFs and metal hydroxides were obtained from NuMat Technologies, Inc. and Guild Associates, Inc., respectively.

The MOF (or metal oxide) first was mixed with tetrahydrofuran (THF) (Sigma Aldrich, 99.5% purity) at amounts necessary to achieve the target wt%. For example, **M1** was made using three separate MOF/polymer mixtures. In the first mixture, 0.25 g UiO-66-NH$_2$ MOF was mixed with 5 mL THF and then tip-sonicated for 30 s. Next 1 g polystyrene-*block*-polyisoprene-*block*-polystyrene, SIS, (Sigma Aldrich, 20 wt% styrene) was added. The mixture was vortexed and then was magnetically stirred at room temperature for approximately 16 h. In the second mixture, 2.0 g HKUST-1 MOF was mixed with 5 mL THF. After sonication, 1 g SIS was added, and the mixture was magnetically stirred for approximately 16 h. The third mixture was prepared in an identical manner to the first mixture.

After approximately 16 h of mixing, the first mixture was poured onto a Teflon block, and a film was drawn using a National Institute of Standards and Technology (NIST)-certified 10 mil blade. The film was allowed to dry for approximately 1 min, at which point the second mixture was poured on top of the first film. The same NIST-certified 10 mil blade was used to draw down the film. This step was repeated using the third mixture resulting in **M1**, a layered mixed matrix composite (MMC) with two outer layers of 20 wt% UiO-66-NH$_2$ in SIS encasing a layer comprised of 67 wt% HKUST-1 in SIS.

Each subsequent composite was prepared using a similar procedure. All polymer solutions were 20% w/v (solvent basis) in this study except **M6** and **M9**. Due to the limited solubility of poly(ethylene oxide), PEO, a 5% w/v in chloroform (Sigma Aldrich, 99.5% purity) was used. For the composite **M9**, an electrospun nanofiber was used as the middle of the sandwich. Electrospinning of poly(vinylidene fluoride), PVDF, and UiO-66-NH$_2$ composite fibers was conducted using an MTI Corporation MSK-NFES-4 floor unit according to previously reported methods.[1] Briefly, PVDF and UiO-66-NH$_2$ were mixed together in a 40 wt% mixture (UiO-66-NH$_2$ mass to total mass) in a 80/20 dimethylformamide/acetone solution. Spinning was conducted at 40 °C, 15.5 kV, and 1 mL h^{-1} through an 18.5-gauge needle. Fibers were collected on a mandrel rotating at 300 rpm. After spinning, the resulting MOF/nanofiber composite was sandwiched between two polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polystyrene (SEBS)/UiO-66-NH$_2$(20%) layers to form **M9**.

Table S1. List of Prepared Mixed Matrix Composites.

Designation	Layer	Polymer	MOF	wt% MOF
M1	Outer 1	SIS	UiO-66-NH$_2$	20
	Middle	SIS	HKUST-1	67
	Outer 2	SIS	UiO-66-NH$_2$	20
M2	Outer 1	SIS	HKUST-1	20
	Middle	SIS	UiO-66-NH$_2$	67
	Outer 2	SIS	HKUST-1	20
M3	Outer 1	SEBS G1642*	HKUST-1	50
	Middle	None	None	n/a
	Outer 2	SEBS G1642	UiO-66-NH$_2$	50
M4	Outer 1	SEBS G1642	UiO-66-NH$_2$	50
	Middle	None	None	n/a
	Outer 2	SEBS G1642	Zr(OH)$_4$	50
M5	Outer 1	SIS	UiO-66-NH$_2$	20
	Middle	Polystyrene	HKUST-1	67
	Outer 2	SIS	UiO-66-NH$_2$	20
M6	Outer 1	SIS	UiO-66-NH$_2$	20
	Middle	PEO	HKUST-1	67
	Outer 2	SIS	UiO-66-NH$_2$	20
M7	Outer 1	SIS	UiO-66-NH$_2$	20
	Middle	Poly(methyl methacrylate)	HKUST-1	67
	Outer 2	SIS	UiO-66-NH$_2$	20
M8	Outer 1	SEBS G1642	UiO-66-NH$_2$	20
	Middle	None	None	n/a
	Outer 2	SEBS G1642	UiO-66-NH$_2$	80
M9	Outer 1	SEBS G1642	UiO-66-NH$_2$	20
	Middle	PVDF nanofiber	UiO-66-NH$_2$	40
	Outer 2	SEBS G1642	UiO-66-NH$_2$	20

*20 wt% polystyrene
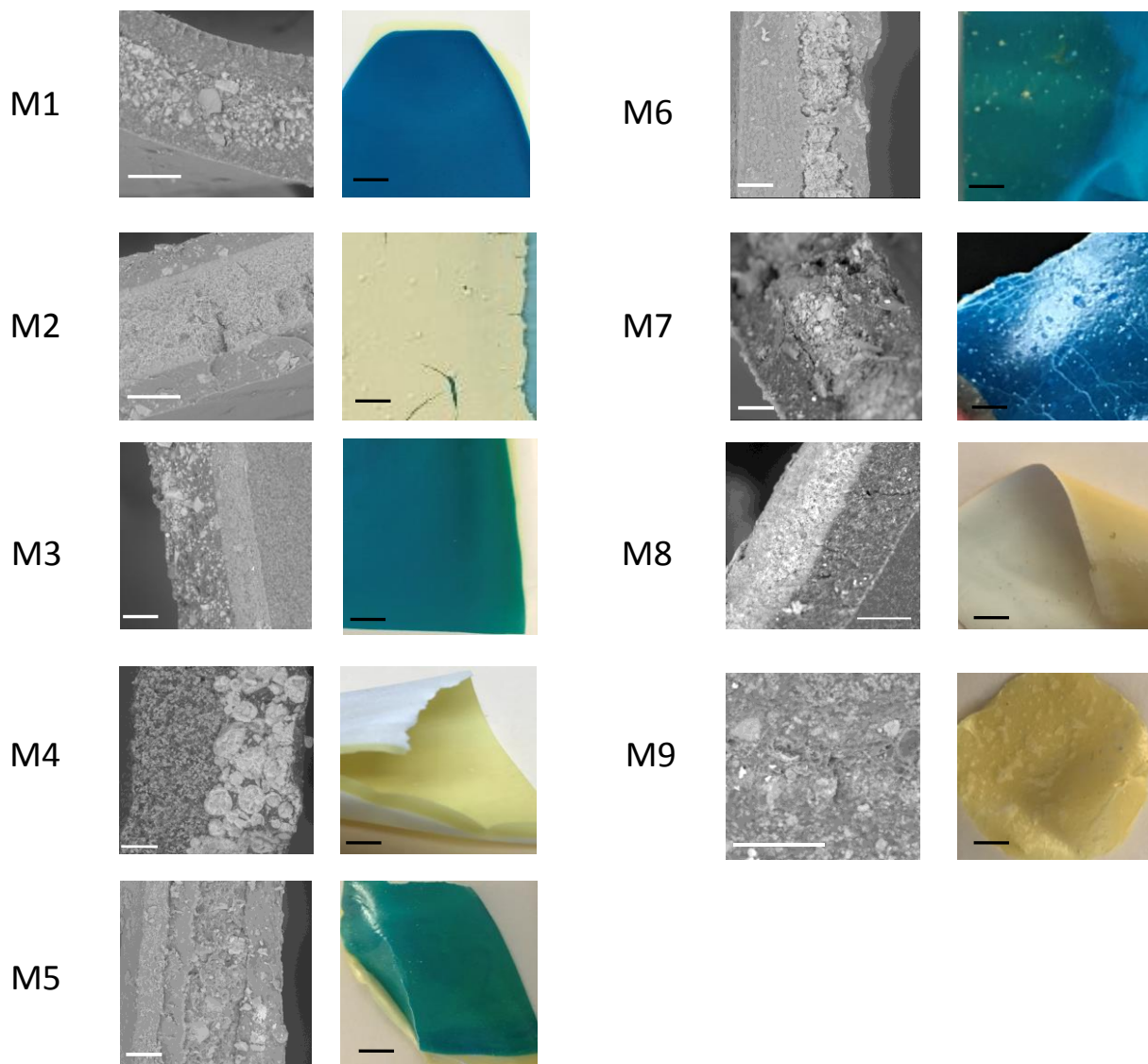
Figure S1. Scanning electron microscopy [SEM] (left hand column) and optical microscopy (right hand column) images for each MOFwich. Scale bar for scanning electron microscopy images = 50 μm. Scale bar for optical microscopy images = 1 cm.

Experimental Methods

Nitrogen isotherm. Nitrogen isotherms were measured using a Micromeritics ASAP 2040 analyzer at 77 K. Samples were degassed at 50 °C under vacuum for approximately 16 h. The BET method was used to calculate specific surface area in m^2 g^{-1}, and the t-plot method was used to calculate pore volume in cm^3 g^{-1}. Nitrogen uptake data are shown in Figure S2, and surface areas and pore volumes are listed in Table S2.

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (EDS). SEM images were obtained using a Phenom GSR desktop SEM. Samples were submerged in liquid nitrogen and cracked to form a clean break, and then mounted on double-sided carbon tape with the cracked edge facing upwards. EDS was used for elemental mapping of the MOFs within the composites and was conducted at an accelerating voltage of 15 kV.

Permeation. 2-chloroethyl ethyl sulfide (CEES) and bis 2-chloroethyl sulfide (distilled mustard) permeation testing was conducted in accordance with ASTM F739-12. Briefly, a 1.5" x 1.5" film was cut, weighed, and measured for thickness with a micrometer caliper and placed in a 1-inch-diameter Pesce PTC 700 permeation test cell. An equal countercurrent flow of 0% relative humidity and 300 (RH) mL min^{-1} air was applied to both sides of the swatch with a feed side concentration of 300 mg/m^3 CEES. The CEES concentration was monitored at 3 locations in the PTC 700 cell: the inlet stream to the cell apparatus (designated as the feed line), the outlet stream from the cell apparatus (designated as the retentate line), and the outlet stream from the cell apparatus on the opposite side of the swatch (designated as the permeate line). A schematic is shown in Figure S3. The test was considered complete when the two outlet stream concentrations summed to equal the value of the feed concentration, closing the mass balance and satisfying the condition of equation 1.

$$C_{feed} - C_{retentate} - C_{permeate} = 0 \qquad (1)$$

Adsorption Isotherms. Pure-component isotherms of carbon dioxide (CO_2), methane (CH_4), nitrogen (N_2), and oxygen (O_2) were measured on a Micromeritics 3Flex 3500 instrument from 0 to 1 bar at room temperature. Prior to measurement, approximately 300 mg of sample was degassed at 50 °C under vacuum. CO_2/N_2 separation factors approximating flue gas concentrations were calculated from pure-component isotherms. The equation used was:

$$\alpha = \frac{n_{CO_2} P_{N_2}}{n_{N_2} P_{CO_2}} \qquad (2)$$

in which α is the selectivity, P_{N2} and P_{CO2} are 0.75 bar and 0.15 bar respectively, and n_{N2} and n_{CO2} are the adsorbed quantities of each gas at the respective pressures.

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{31}P magic angle spinning (MAS) NMR spectroscopy was used to measure the disappearance of soman and VX nerve agents in the MMCs. Measurements were made using a Varian INOVA 400 Narrow Bore spectrometer equipped with a Doty Scientific solid-state probe. For soman tests, 3.5 µL was dispersed drop-wise on a 35 mg MMC, and MAS experiments were conducted at 1440 Hz. For VX, 4.5 µL was dispersed drop-wise on a 45 mg MMC, and MAS experiments were conducted at 2400 Hz.

Electrical Impedance Spectroscopy (EIS). EIS measurements were collected using a Solartron Analytical 1260 equipped with a 1296 dielectric interface and parallel plate sample holder. The voltage was set at 100 mV (alternating current) with a frequency sweep range from 10^{-2} to 10^{6} Hz.

Moisture Vapor Transport Rate (MVTR). MVTR measurements through the swatches were conducted in accordance with the Water Method outlined in ASTM E-96-16. Briefly, a swatch of material was sealed over a 1.75 in-diameter container filled to a headspace of 0.5 in with distilled water and placed in an environmentally-controlled chamber at 25 °C and 50% RH for 24 h. The total mass of the apparatus was weighed before and after the exposure, and the mass difference was divided by the cross-sectional area of the top of the container and the exposure time to generate a MVTR value. The MVTR value was reported in units of grams of water lost per square meter of surface area exposed to the humidity gradient in the test system per hour of exposure time. MVTR data are shown in Table S3.
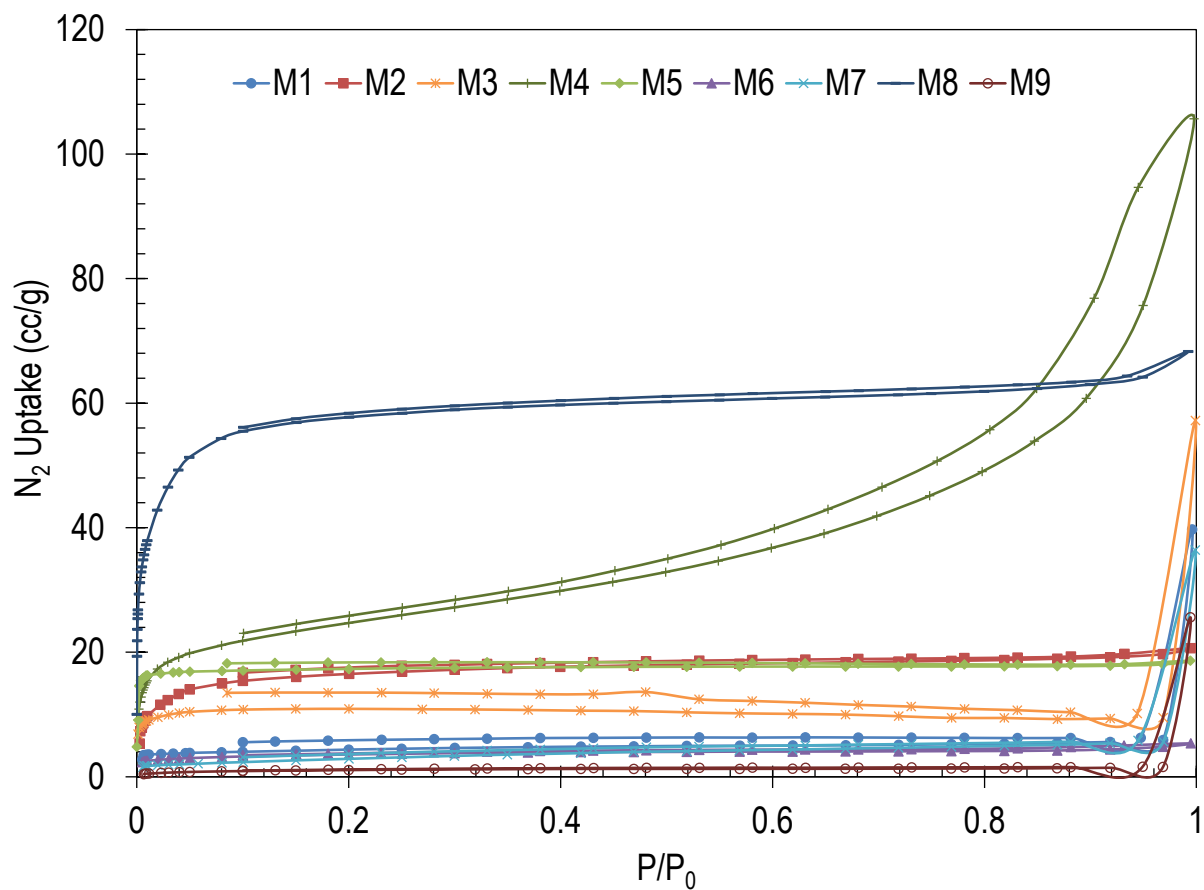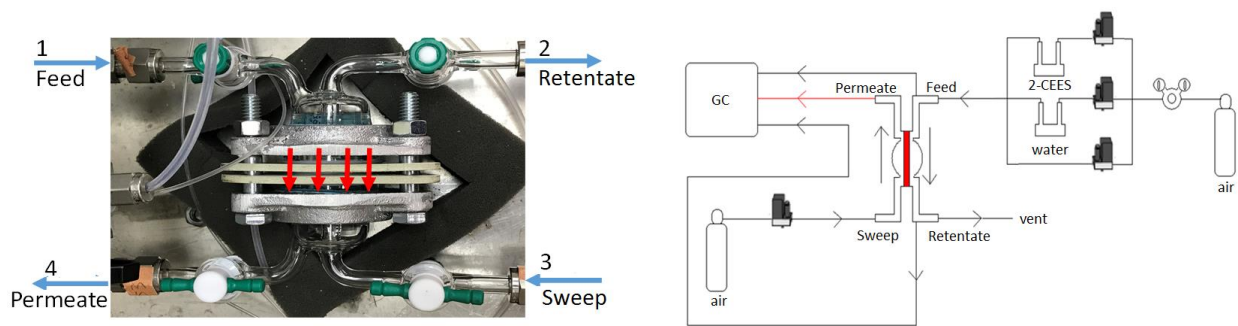
Figure S2. Nitrogen uptake as a function of relative pressure for MOFwiches. Composites **M1-M9** are defined in Table S1.

Table S2. Surface area measurements for **M1-M9**.

Designation	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)
M1	16	0.00
M2	65	0.02
M3	42	0.02
M4	87	0.01
M5	73	0.02
M6	13	0.00
M7	11	0.00
M8	226	0.09
M9	4	0.00

Figure S3. Permeation test cell (left) and permeation piping and instrumentation diagram (right). The MMC was placed in the center of the glass cell which then was tightened. Contaminated air streams flowed into the cell in the top left and out of the cell in the top right. A sweep stream entered the bottom right and exited the bottom left. Detectors were placed in the streams to monitor 2-CEES and mustard concentrations.
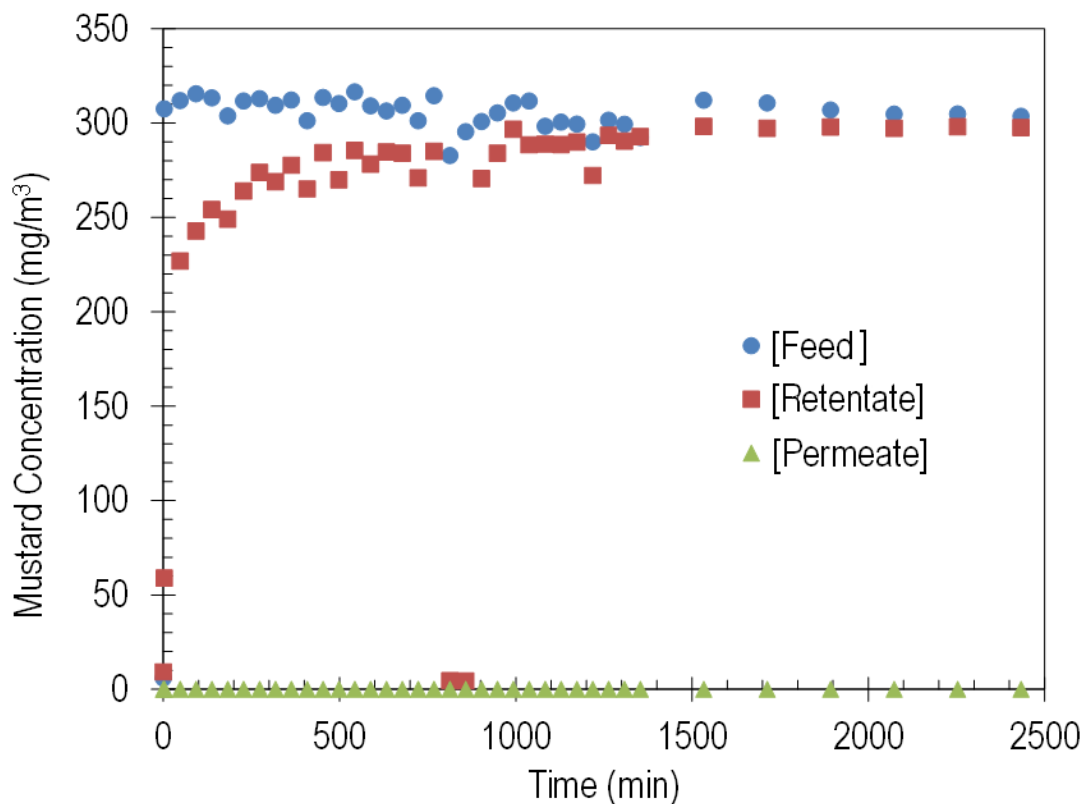
Figure S4. Mustard permeation through **M3**. "Feed" is a constant 300 mg/m^3 of mustard. "Retentate" represents the mustard that does not permeate the MMC. "Permeate" is the concentration of mustard that permeates the MMC – in this graph there is almost no measureable mustard that permeates. *Note: the effluent data points that appear near zero at ~800 min were due to a temporary malfunction in the detector; when the malfunction was corrected the data points returned to their 'pre-malfunction' trend.*
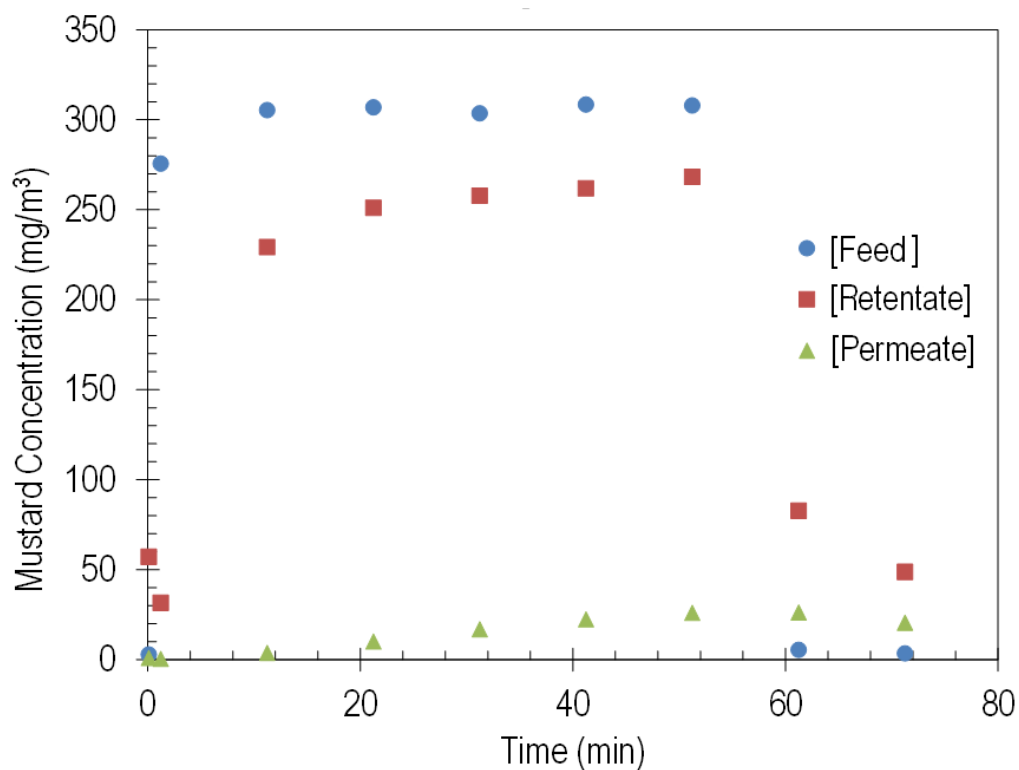
Figure S5. Mustard permeation of latex. "Feed" is a constant 300 mg/m^3 of mustard. "Retentate" represents the mustard that does not permeate the MMC. "Permeate" is the concentration of mustard that permeates the MMC.

**Table S3**. MVTR calculations and data.

| Material	Initial jar mass (g)	Final jar mass (g)	Mass lost (g)	Cross-sectional area (m^2)	Exposure Time (h)	MVTR (g/m^2/h)
M1	197.08	196.95	0.13	0.001552	24.0	3.66
M2	197.52	197.31	0.21	0.001552	24.0	5.61
M3	199.82	199.23	0.58	0.001552	23.5	16.00
M4	194.47	194.19	0.28	0.001552	24.0	7.53
M5	198.90	198.84	0.06	0.001552	24.5	1.66
M6	199.08	198.98	0.01	0.001552	24.5	2.61
M7	200.01	199.94	0.07	0.001552	24.5	1.89
M8	199.84	199.57	0.27	0.001552	24.0	7.28
M9	194.77	194.69	0.08	0.001552	23.5	2.21
Latex	197.81	197.78	0.03	0.001552	22.0	1.02
Butyl Rubber	198.30	198.30	0.00	0.001552	20.5	0.13
PVDF Nanofiber with 40% MOF	197.21	195.33	1.89	0.001552	20.5	59.34
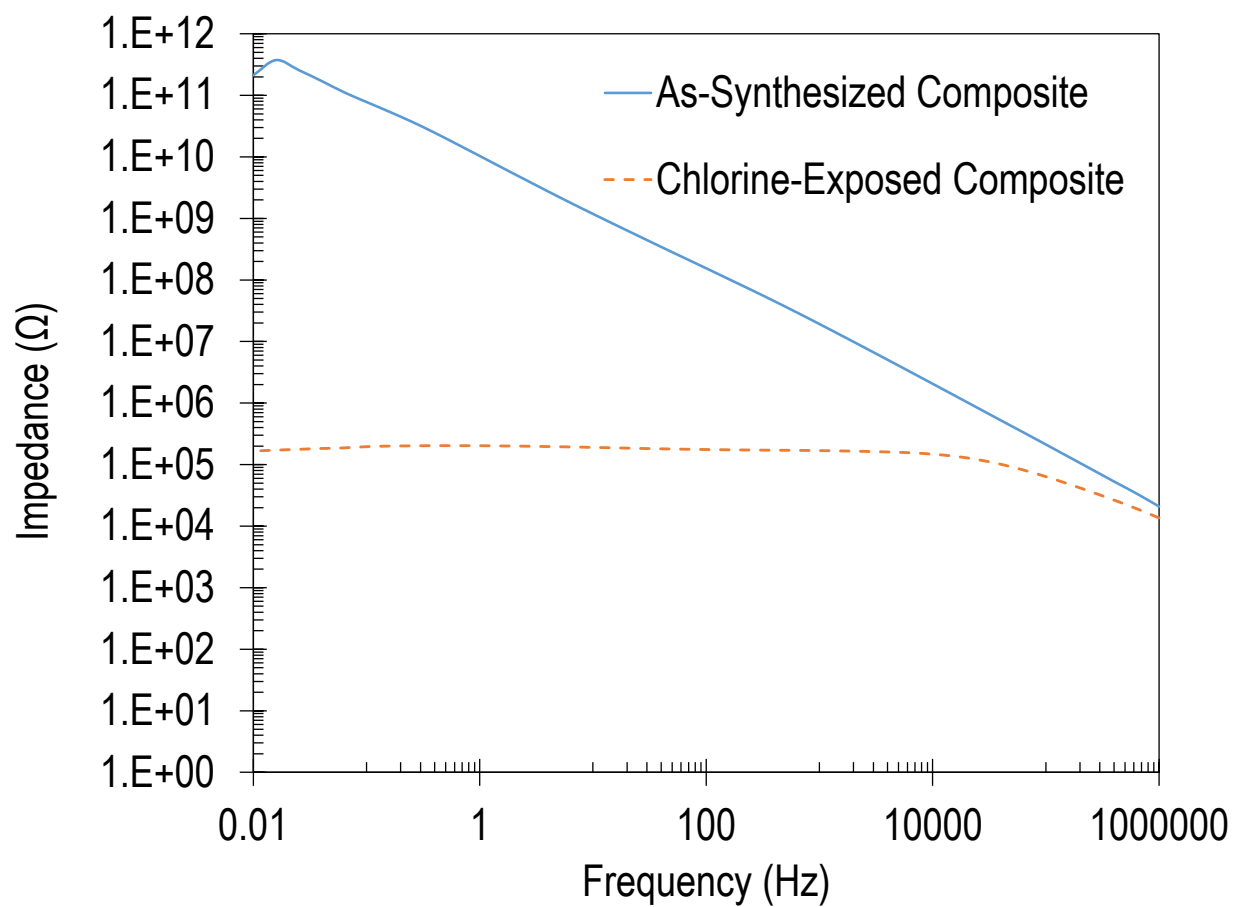
Figure S6. Impedance magnitude as a function of frequency for **M3** before and after exposure to chlorine gas.
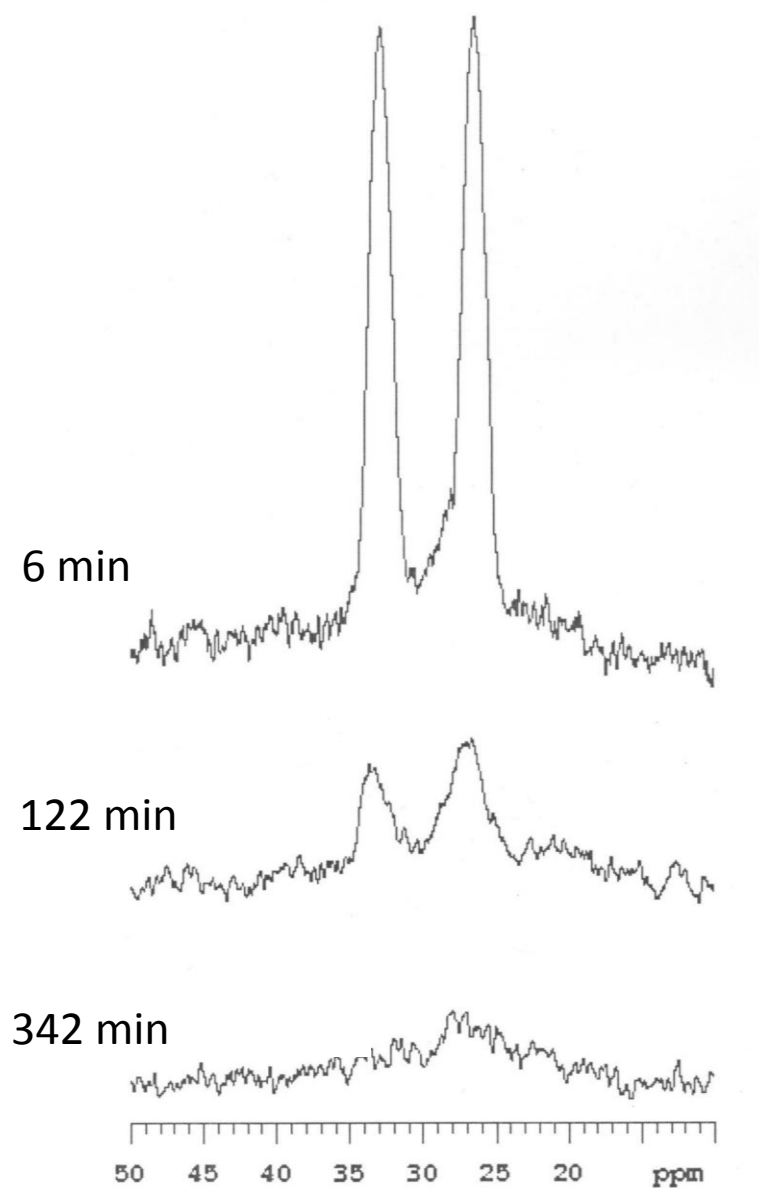
Figure S7. ^{31}P MAS NMR spectra of soman dosed to **M4** as a function of time. Pinacolyl methyl phosphonic acid (PMPA) is generated from the hydrolysis of soman in small quantities but is difficult to discern due to adsorption effects in the substrate. The signature peak for PMPA is the small hump located between 25-30 ppm in the above spectrum at 342 min.
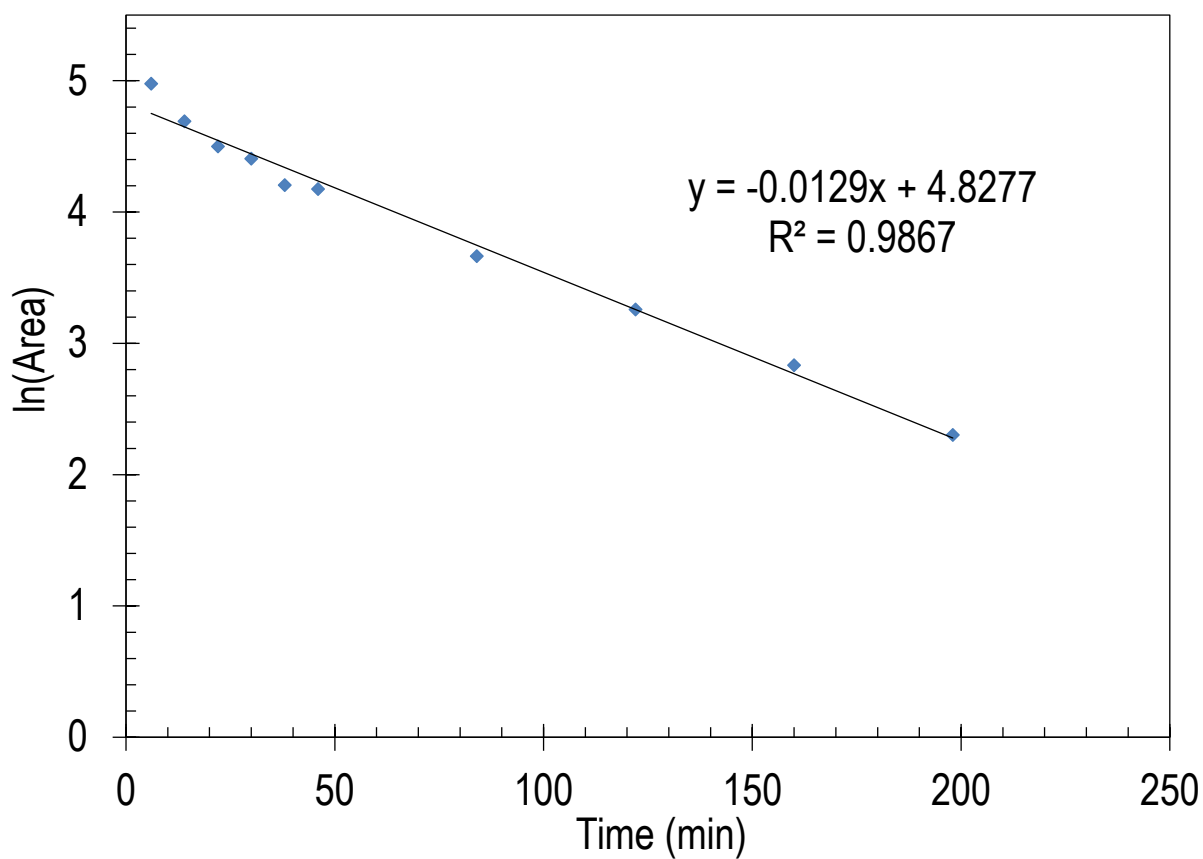
Figure S8. Natural log of soman peak area as a function of time for **M4** tested using ^{31}P MAS NMR. The representative data from Figure S7 (along with additional time points) were integrated to determine the area under the peaks. The slopes of the curves in this figure were used to calculate half-life of soman exposed to the MMC **M4**.
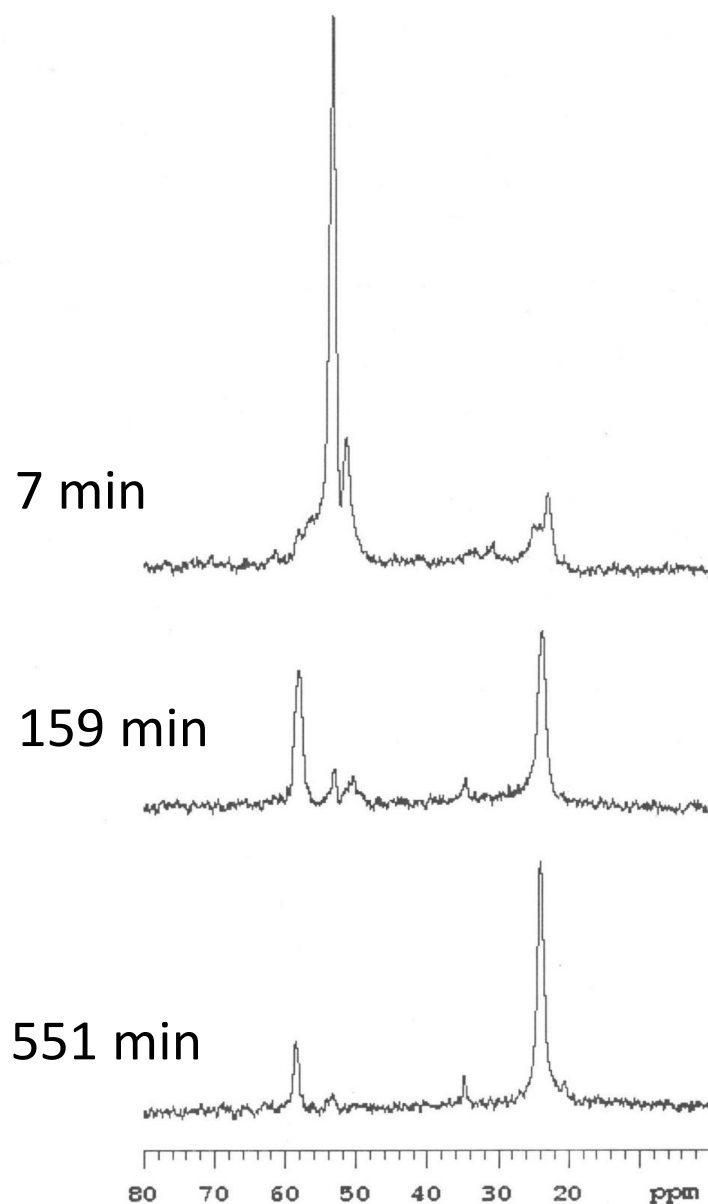
Figure S9. ^{31}P MAS NMR spectra of VX (58 ppm) dosed to **M4** as a function of time. Ethyl methyl phosphonic acid (EMPA) is generated from the hydrolysis of VX and is present at 24 ppm in the spectra above. Spectra shifted slightly over time due to adsorption onto the substrate.
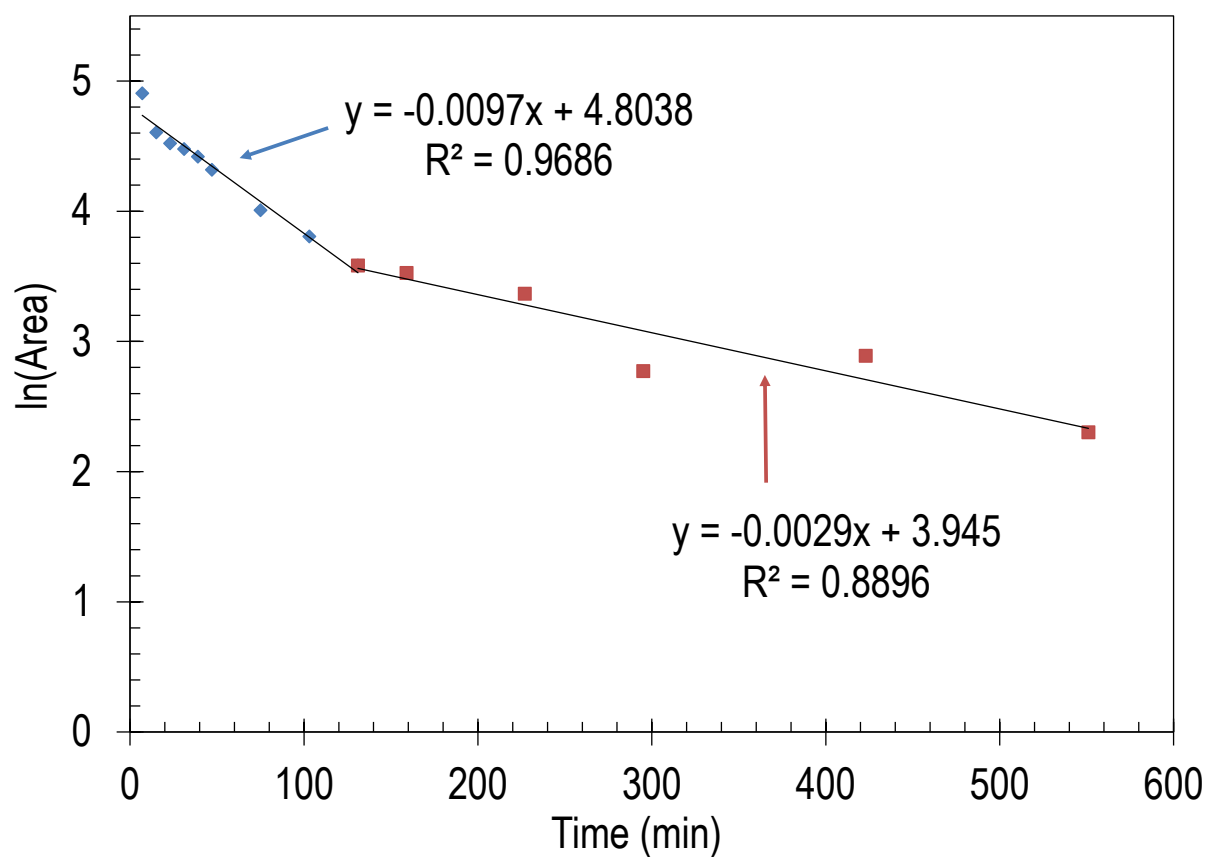
Figure S10. Natural log of VX peak area as a function of time for **M4** tested using ^{31}P MAS NMR. The representative data from Figure S9 (along with additional time points) were integrated to determine the area under the peaks. The slopes of the curves in this figure were used to calculate half-life of VX exposed to **M4**.
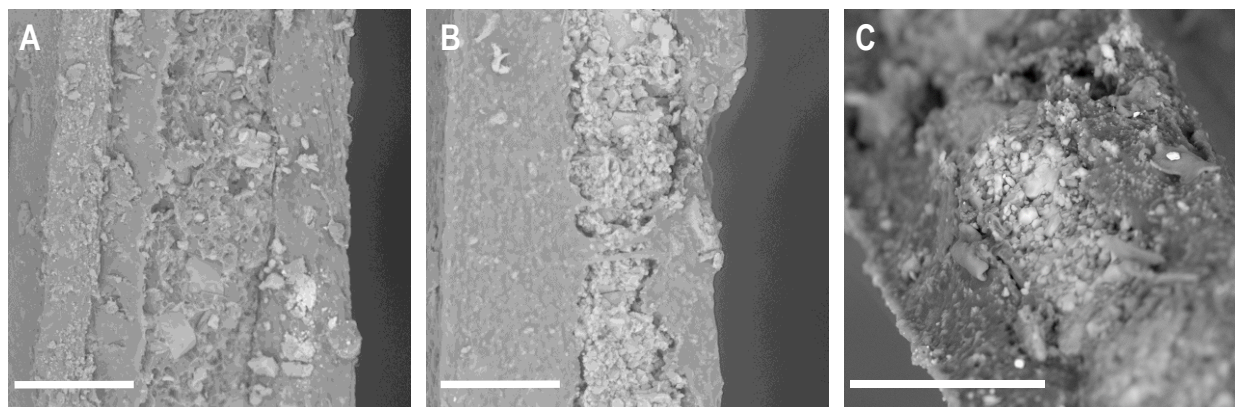
Figure S11. SEM images for (A) **M5**, (B) **M6**, and (C) **M7**. Scale bar = 50 µm and applies to all images.
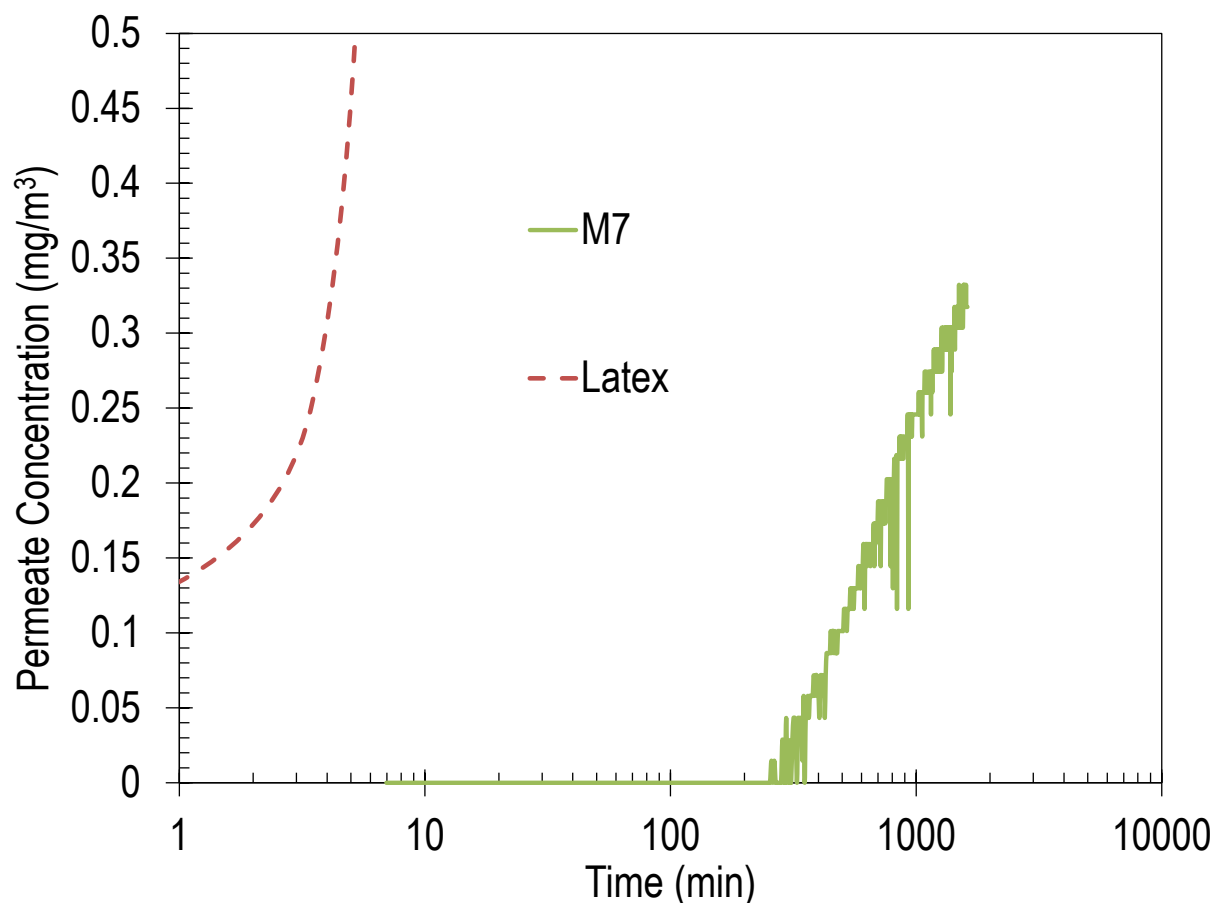
Figure S12. 2-CEES permeation through **M7**. The MOFwich was cracked before testing to determine residual permeation properties. Several hundred minutes of protection exists after cracking the composite. The noise in the **M7** data is associated with integration errors due to proximity to the limit of detection.

References

1. Lu, A. X.; McEntee, M.; Browe, M. A.; Hall, M. G.; DeCoste, J. B.; Peterson, G. W., MOFabric: Electrospun Nanofiber Mats from PVDF/UiO-66-NH$_2$ for Chemical Protection and Decontamination. *ACS Appl. Mater. Interfaces* **2017,** *9* (15), 13632-13636.