Supporting Information

Chemical Protective Textiles of UiO-66 Integrated PVDF Composite Fibers with Rapid Heterogeneous Decontamination of Toxic Organophosphates

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Materials

Poly(vinylidene fluoride) (PVDF) (d=1.74g/mL, Mn=107,000, Mw =275,000, melt viscosity 17,500.000-21,500.000 poise(100sec^{-1}, 230˚C), Melt index 7.00-15.00 g/10min (230˚C/12.5kg, ASTM D 1238)), titanium (IV) isopropoxide (TTiP), N,N-dimethylformamide (DMF) (anhydrous), 4-nitrophenyl phosphate (methyl paraoxon, DMNP), di-iso-propyl fluorophosphate (DFP), triethanolamine (TEA) and acetone were purchased from Sigma Aldrich and used without any further purification.

UiO-66 MOF

UiO-66 was synthesized by methods published previously.[1] In short, 19.068 mmoles of zirconium (IV) chloride and 19.068 mmoles of benzene dicarboxyalate were mixed in 742 ml of dimethyl formamide (DMF) at room temperature in a glass beaker. The resulting mixture was divided in equal parts into three 500 ml glass jars. The jars were placed in a preheated oven at 120 °C for 24 h. The solution was cooled to room temperate, and the resulting solid was repeatedly washed with DMF. DMF was subsequently exchanged with methanol and then activated in a vacuum oven for 24 h.
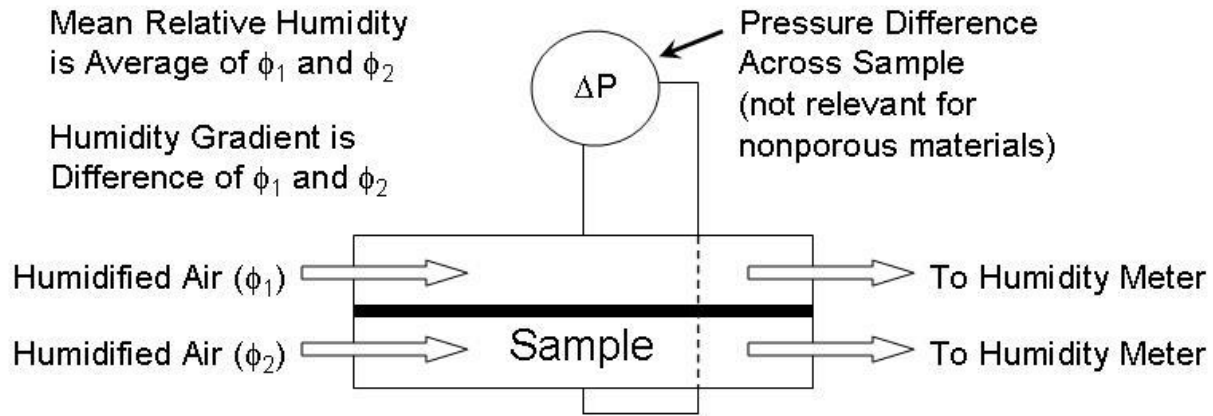
PVDF/Ti(OH)4/UiO-66/TEA nanofibers

PVDF/Ti(OH)4/UiO-66/Triethanolamine(TEA) NFs were fabricated by first dissolving 360 mg of PVDF in 2 mL of DMF (anhydrous) using a combination of sonication and heating at 50˚C. 194 mg of UiO-66 MOF was then added to the sol-gel and stirred for 30 min. 640 mg (0.67 mL) of titanium (IV) isopropoxide (TTiP) and 1 mL of acetone was added and the sol-gel was stirred for another 30 min. Finally, 0.70 mL (787 mg) of TEA base was added to the sol-gel and stirred for a final 30 min before electrospinning the sol-gel. Two vials of sol-gel were prepared and electrospun onto a single aluminum foil at 15.5 cm and voltage of 25 kV to create a thicker fiber mat that could be easily removed from the collector in one piece. The final NF mat was left out overnight to dry before testing. PVDF/Ti(OH)4/UiO-66 NFs were fabricated using the same procedure but without addition of the TEA base.

Characterization

The materials were characterized using a Supra 55 VP field emission scanning electron microscope (SEM) from Zeiss equipped with energy dispersive X-ray spectroscopy (EDS) detector. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed using an IRAffinity-1S equipped with a MIRacle single reflection horizontal ATR accessory.

MVTR and air permeation

The moisture vapor transport rate (MVTR) and air permeation were measured with a dynamic moisture permeation cell (DMPC) according to ASTM F2298. A schematic of the permeation cell is shown in Figure S1. The humidity of the feed and sweep streams were set to 95% and 5%, respectively, for a mean relative humidity of 50%. Only one mean relative point is necessary to characterize the MVTR of the electrospun composite as the water transport through nanofibers is not dependent on concentration like polymer membranes.[2] To measure the MVTR of air permeable materials, the pressure drop across the sample is increased stepwise while the relative humidity of both feed and sweep streams remain constant. The MVTR is measured at each stepwise increase in pressure difference, and a linearization used to determine the MVTR at $\Delta P = 0$. Development and use of the DMPC test method has been documented by Gibson et al., 1995.[3]

Mean Relative Humidity is Average of ϕ_1 and ϕ_2

Humidity Gradient is Difference of ϕ_1 and ϕ_2

ΔP

Pressure Difference Across Sample (not relevant for nonporous materials)

Humidified Air (ϕ_1) → To Humidity Meter

Humidified Air (ϕ_2) → Sample → To Humidity Meter

Figure S1. Schematic of dynamic moisture permeation cell (DMPC).[3]

Aerosol filtration efficiency test

The materials were examined using a TSI Automated Filter Tester Model 3160 that measures particle penetration versus particle size at a set aerosol flow rate (face velocity). TSI 3160 can generate polydisperse dioctylphtalate (DOP, oil) and NaCl aerosol particles in the range of 0.015 to 0.8 microns using an atomizer. The TSI 3160 is capable of measuring efficiencies up to 99.999999%. The TSI 3160 is equipped with two TSI Model 3772 Condensation Particle Counters (CPCs). The Model 3772 CPC detects particles as small as 0.010 microns in diameter and employs single-particle-count-mode operation to measure concentrations up to 10,000 particles per cubic centimetre. The detector counts individual pulses produced as each particle (droplet) passes through the sensing zone. A high signal-to-noise ratio and continuous, live-time coincidence correction provides accuracy even at very low concentrations. The Model 3772 CPC uses a laser-diode light source and diode photodetector to collect scattered light from particles. The TSI 3160 is also equipped with a TSI Model 3302A Diluter to reduce the particle

concentration of high-concentration aerosols. The Diluter is calibrated for dilution ratios of 100:1 and 20:1 at a total flow rate of 5 standard litre per minute.

**Hydrolysis of methyl paraoxon (DMNP) simulant**

Degradation experiments were performed following a previously published procedure by Katz et al.[4] First, an aqueous buffer solution (pH 10) of N-ethyl morpholine (0.45 M) was prepared. In a 4 mL glass vial 12 mg of polymer/MOF catalyst was added to 1 mL of distilled water. The reaction was performed in distilled water to evaluate the self-buffering capability of the TEA in the NFs. The fiber was stirred in the solution for 30 min at a stir speed of 750 rpm. Next, 4 µL of DMNP simulant was added to the solution. 10 µL aliquots were taken from the reaction at specified times and diluted to 5 mL with the prepared buffer solution for analysis with UV-Visible spectroscopy using an Hewlett Packard Diode array spectrophotometer. Product formation was observed by tracking the 4-nitrophoxide product peak at 407 nm. The DMNP simulant and its degradation products are shown in Scheme 1.

Di-iso-propyl Fluorophosphate (DFP) simulant testing

Catalytic activity against the simulant DFP was evaluated by cutting a 1 cm^2 sample of composite fabric and preconditioning at 100% RH for at least 24 hours. The sample was then spiked with 1 µL of DFP. The reaction was monitored using ^{31}P high resolution (HR) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy on a Bruker Advance 400 MHz spectrometer.

GD agent testing

GD agent testing was performed using the same procedure published in Lu et al.[5] Swatches of 1x2 cm size were cut and placed into a Thunder Scientific Corporation Series 2500 Humidity Chamber at 25 °C. The samples were conditioned at 50% RH for at least 16 h. Next, a 2.6 μl drop of soman (GD) was deposited onto the inside surface of the fabric sample in the rotor. ^{31}P NMR spectra were obtained over time at ambient temperature (25 °C) without spinning using a Varian INOVA 400 NB NMR spectrometer equipped with a Doty Scientific 10-mm NMR probe to monitor the reaction and identify products.
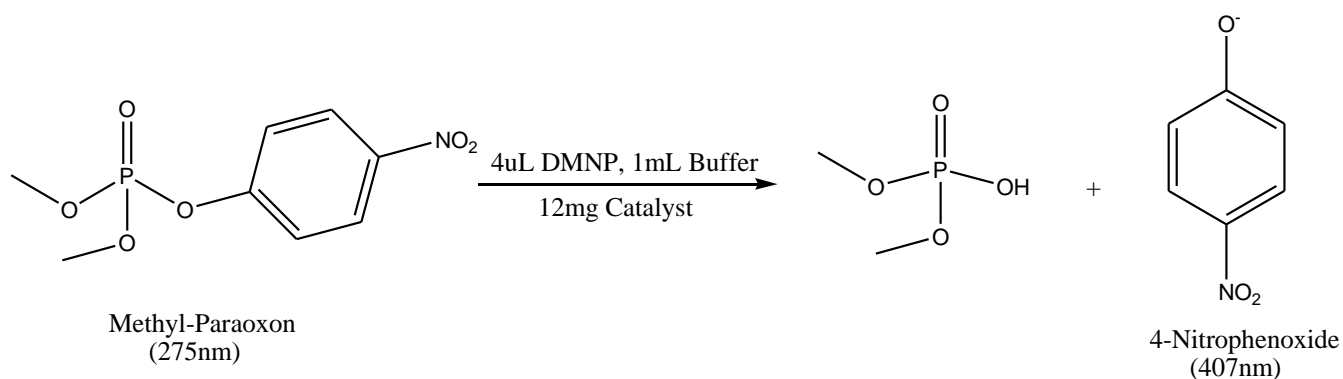
Scheme S1. Reaction of DMNP simulant with catalyst in buffered solution.

Table S1. MVTR and air permeation of FR fabric 1, carbon-based material and PVDF composite fibers.

Sample	MVTR (g/m^2/day)	Air Perm. (ft^3/min/ft^2)
PVDF/Ti(OH)$_4$	18100	5.2
PVDF/Ti(OH)$_4$/UiO-66	15800	5.7
PVDF/Ti(OH)$_4$/UiO-66/TEA	14200	2.8
Carbon based material	4300	12.1
FR Fabric 1	13300	61.6
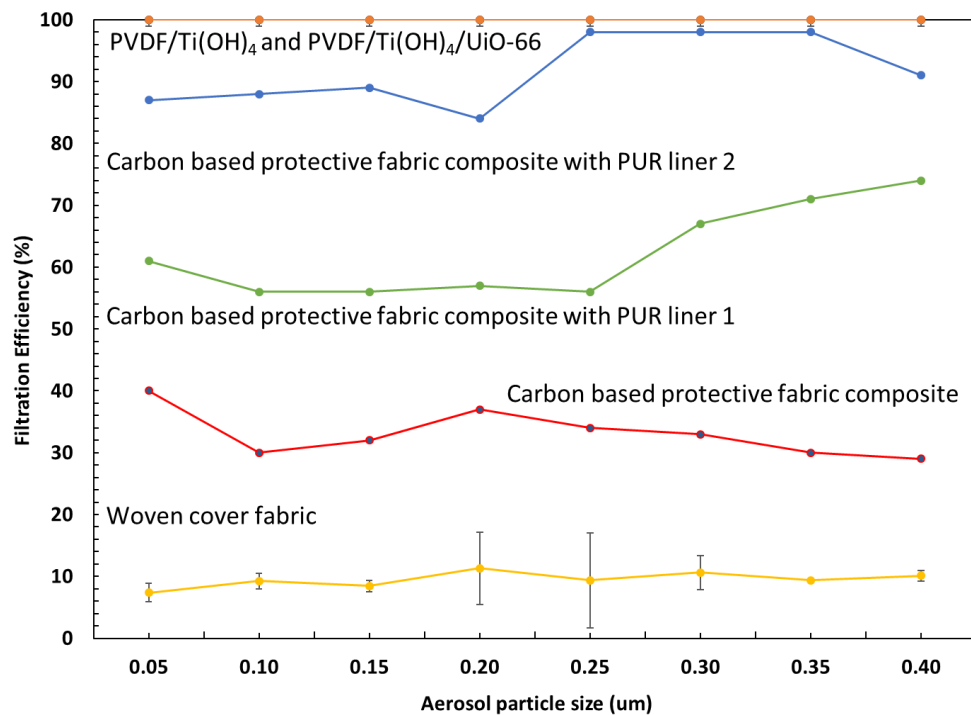
Figure S2. Filtration efficiency of PVDF/Ti(OH)$_4$ and PVDF/Ti(OH)$_4$/UiO-66 compared to other fabric and carbon-based materials.
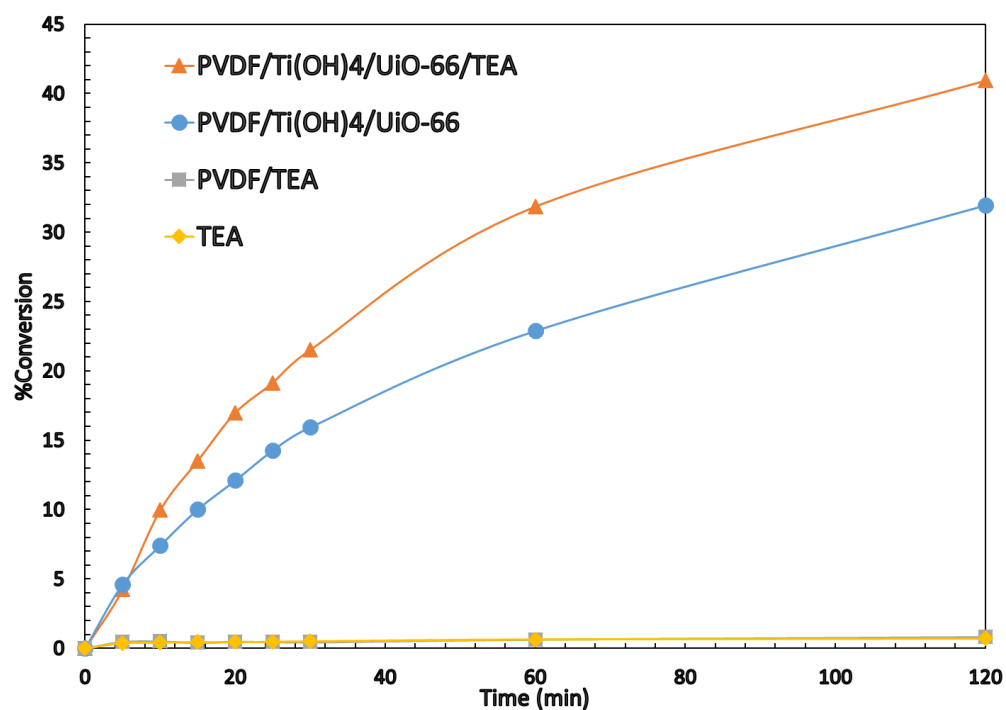
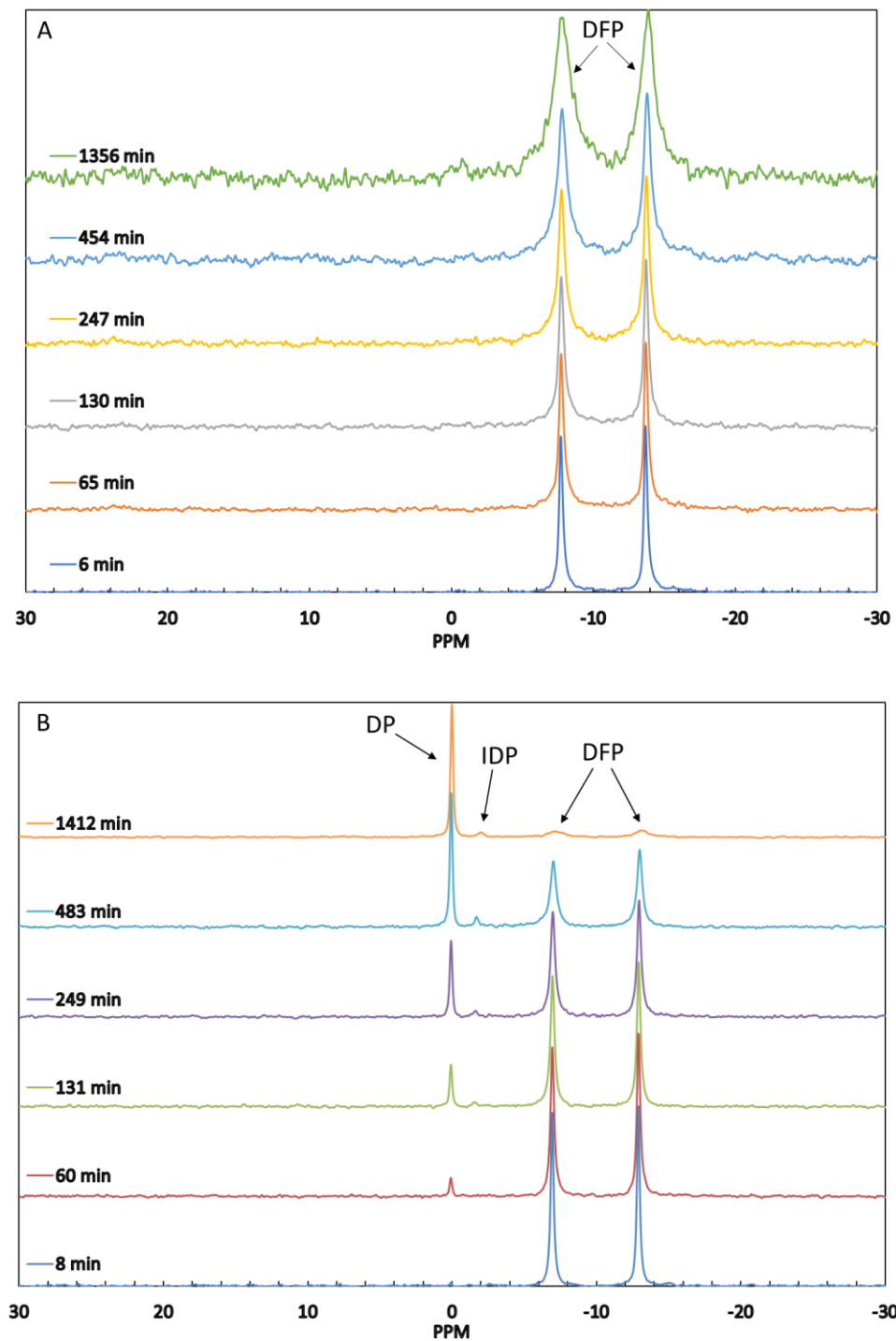**Figure S3.** Percent conversion of DMNP for PVDF/Ti(OH)₄/UiO-66, PVDF/Ti(OH)₄/UiO-66/TEA, PVDF/TEA composites and TEA performed in distilled water.
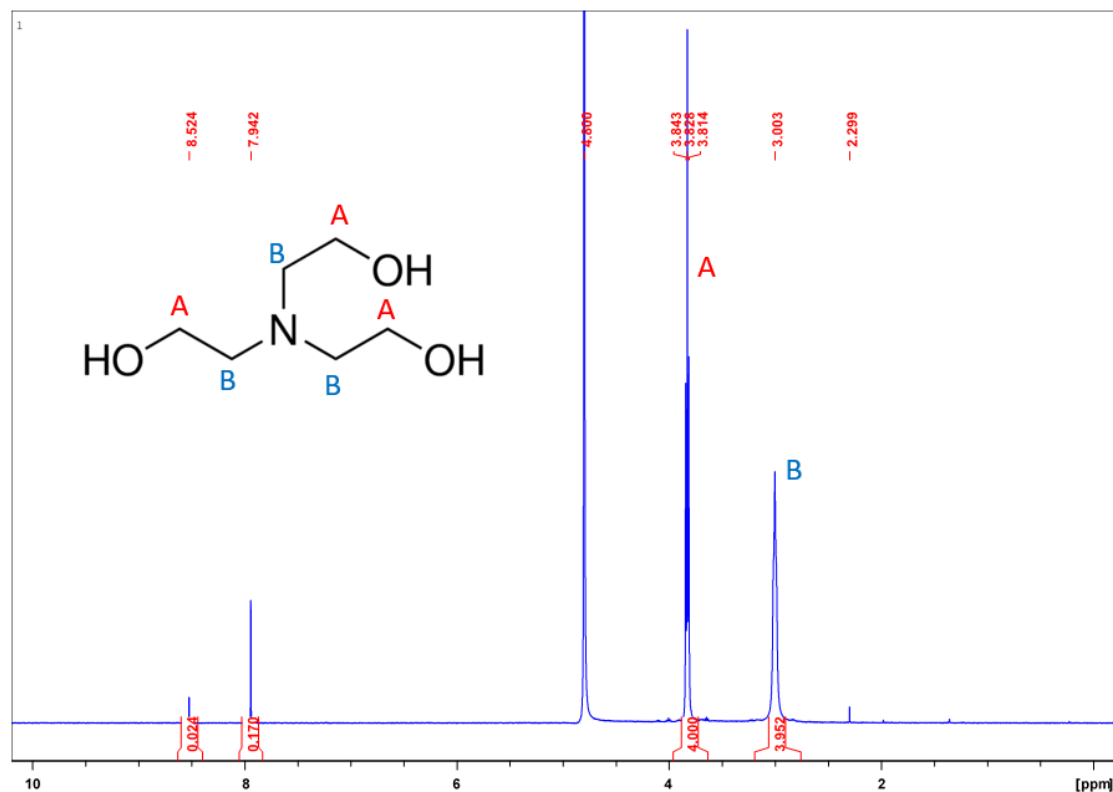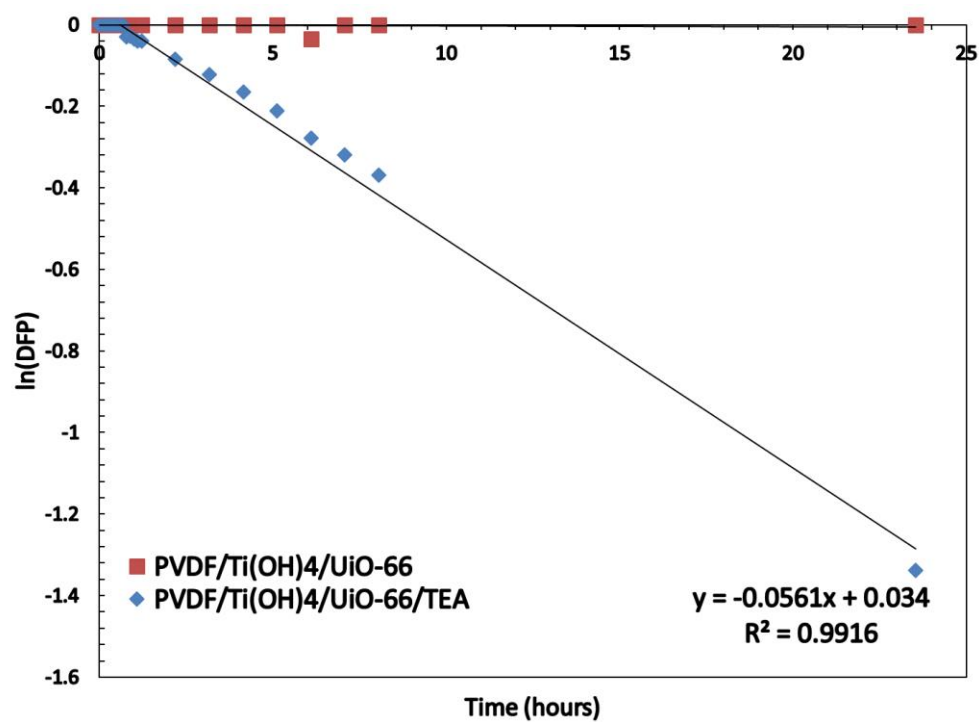

Figure S4: H-NMR of D₂O after soaking with PVDF/Ti(OH)₄/UiO-66/TEA composite showing evidence of TEA leaching from composite.
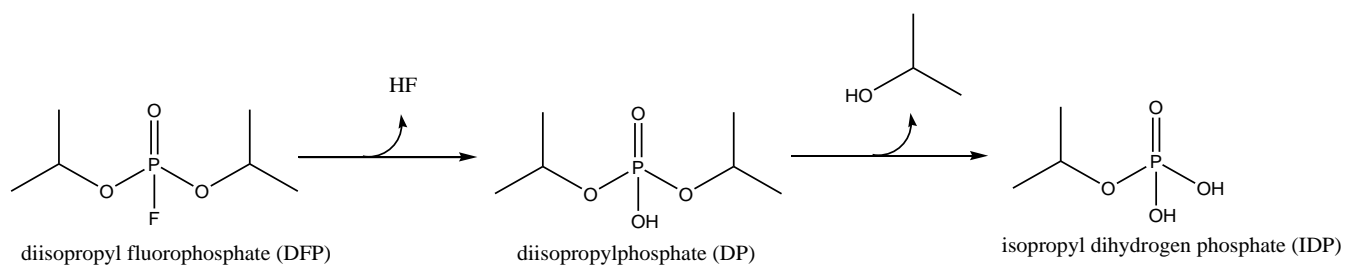
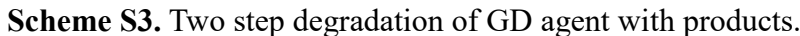**Figure S5.** Solid state ^{31}P HR MAS NMR of DFP degradation with PVDF/Ti(OH)$_4$/UiO-66 (A) and PVDF/Ti(OH)$_4$/UiO-66/TEA (B) composite fibers.

Figure S6. Kinetic analysis of DFP degradation with PVDF/Ti(OH)$_4$/UiO-66 and

PVDF/Ti(OH)$_4$/UiO-66/TEA composite fibers.

diisopropyl fluorophosphate (DFP)   diisopropylphosphate (DP)   isopropyl dihydrogen phosphate (IDP)

Scheme S2. Degradation steps and by-product(s) of DFP.

Scheme S3. Two step degradation of GD agent with products.

Figure S7. Structures of DFP simulant and GD agent showing electron donating groups.

Table S2. GD half-lives achieved with PVDF composites samples along with half-lives of other published works.

Sample	$t_{1/2}$(mins)	ref
PVDF/Ti(OH)$_4$/UiO-66	35	this work
PVDF/Ti(OH)$_4$/UiO-66/TEA	47	this work
20PS-25U-DMF/THF	95	Peterson et al.[6]
10PS-25U-DMF	98	Peterson et al.[6]
MOFabric-33%	131	Lu et al.[5]
20PS-25U-DMF	144	Peterson et al.[6]
10PS-25U-DMF/THF	154	Peterson et al.[6]
MOFabric-19%	161	Lu et al.[5]
PVDF/Ti(OH)$_4$	277	this work
PVDF/UiO-66	365	this work
MOFabric-13%	1155	Lu et al.[5]
MOFabric-7%	1616	Lu et al.[5]

Table S3. Static contact angle measurements of PVDF composite samples with distilled water.

Sample	Contact Angle	Image
PVDF	138	
PVDF/Ti(OH)$_4$	0	
PVDF/UiO-66	139	
PVDF/Ti(OH)$_4$/UiO-66	0	

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