[Supporting Information (SI) to accompany:]

Green Synthesis of MOF-based textile composites for the degradation of a chemical warfare agent simulant

Nelly Couzon[a], Pauline Hardy[a], Manuela Ferreira[b], Nisrine Hammi[a], Jérémy Dhainaut[a], Frédérique Pourpoint[a], Sébastien Royer[a], Thierry Loiseau[a], Christine Campagne[b], Christophe Volkringer*[a]

[a] : Univ. Lille, CNRS, Centrale Lille, UMR 8181 – UCCS – Unité de Catalyse et Chimie du Solide, F-59000 Lille, France

[b] : Univ. Lille, ENSAIT, ULR 2461–GEMTEX–Génie et Matériaux Textiles, F-5900 Lille, France

Table of Contents

Section S1. General procedures, materials, and instrumentations

Materials

$ZrCl_4$ (Alfa Aesar, 99.5+ %), 2-aminoterephthalic acid ($H_2BDC-NH_2$, Sigma Aldrich, 99 %), acetic acid (VWR Chemicals, 99-100 %), formic acid (Honeywell Fluka, 98.0-100%), chitosan (Aldrich, high molecular weight), N-ethylmorpholine (NEM, Alfa Aesar, 98 %), dimethyl 4-nitrophenyl phosphate (also called paraoxon-methyl or DMNP, Sigma Aldrich, < 98 %), and ethanol (Carlo Erba Reagents, 96 %) were all purchased commercially and used without further purification. Cotton, polyester (PE) and polyamide (PA 6,6) textiles were provided by the GEMTEX team of ENSAIT (Roubaix, France).

General protocol for UiO-66-NH_2/chitosan synthesis on textiles

First, the chitosan solution was prepared by mixing 100 mg of high molecular weight chitosan with 16 mL of H_2O and 1 % v/v of acetic acid. After stirring 24h, 50 mg of $ZrCl_4$ was added to the solution and stirred for 1 h. The textile (cotton, polyamide PA or polyester PE, 5*5 cm) was then impregnated in the above solution for 24 h.

A ligand solution composed of 38 mg of BDC-NH_2, 12 mL of EtOH and 3 mL of formic acid was prepared by sonification until total dissolution (~ 30 min). The textile was then removed for the first solution and directly introduced to the ligand solution until the total evaporation of the solutions (24h to 72h). Finally, the sample was removed and washed abundantly by ethanol and sonicated for 2 min. The resulting product was dry at ambient temperature for several hours before characterizations.

Based on Zr reactivity and calculated by ICP analysis, the yields of UiO-66-NH_2 attached at the surface of the composites are 22%, 6% and 9%, for the composite synthesized with cotton, polyester and polyamide, respectively.

Characterization

X-Ray Diffraction (XRD). Powder XRD data was recorded on a Bruker D8 Advance A25 diffractometer with Bragg-Brentano geometry using Cu K_α radiation, from 3 ° to 50 °, with a step size of 0.02 ° and a counting time of 0.5 s/step.

Surface area determination. Due to the low specific surface area of the synthesized composite (i.e MOF + chitosan + textile), the measurement was made using krypton. Kr adsorption isotherms were obtained at 77 K using a Micromeritics ASAP2020 apparatus after outgassing the samples at 120°C under secondary vacuum (5 Pa) for several hours. The specific area was determined using the BET method in the P/P_0 range of 0.065-0.2 for Kr.

Scanning Electron Microscopy. SEM images of composite fibers were obtained using a Hitachi SU5000 with an acceleration voltage of 5 keV. Samples were coated with 300 to 350 Å thickness of metallic chromium. For EDX analysis, samples were coated with 200 to 250 Å thickness of carbon.

Infrared Spectroscopy. IR spectra were acquired on a Perkin-Elmer Spectrum Two spectrometer from 4000 to 400 cm^{-1} using a diamond attenuated total reflectance (ATR).

^{13}C Solid state NMR. Solid state NMR experiments were carried out on a Bruker Advance III 9.4 T spectrometer (100.6 MHz ^{13}C) equipped with a 3.2 mm triple resonance probe (used in double resonance) spinning at a frequency of ν_R=10.0 kHz. ^{13}C spectra was recorded using a cross polarization experiment (CPMAS). The first $\pi/2$ ^1H rf-field (radio-frequency) amplitude was 97 kHz. During the contact, a ^{13}C rf-field amplitude of 60 kHz and a linear ramp from 78 to 97 kHz on the ^1H channel were used. The contact time was t_{cp} = 2 ms. A recycling delay of 5 s and a number of scans of 768 for the UiO-66-NH_2 and chitosan and 9984 for the membrane were used leading to an experimental time of 64 min and 14 h 52 min respectively. A SPINAL-64 decoupling sequence of 80 kHz was used during the acquisition.[1] The ^{13}C chemical shifts were referenced externally using the carboxyl group of the glycine at 176.03 ppm.

For ^{13}C solid state NMR, a specific mixture of UiO-66-NH^2 and chitosan was prepared following the protocol above-mentioned, but without fabric.

Abrasion tests. Abrasion resistance of our composite was tested using a Martindale SDL Atlas, following the norm ISO 12947-3:1999. It consists in following the weight loss after a determined number of cycles of abrasion.[1] A 3.8 cm diameter sample was placed against a 14 cm diameter wool abrasive textile, with a pressure of 9 kPa, and underwent a given number (cycle) of circular frictions at a constant speed (52 cycles/min). Cycles up to 1250 has been made on cotton, with the intervals 100, 250, 500, 750 and 1000. Pristine polyamide and polyesters textiles being more resistant to abrasion, additional cycles (2500 and 3750) were tested. We considered a sample stable (not damaged) when the weight loss is lower or equal to 2 % after 1250 cycles for cotton, or 3750 cycles for polyamide and polyester textile.

Artificial ageing. Artificial ageing was carried out in Xenotest 440 (Atlas Material Testing Technology GmbH, Linsengericht Germany) using a xenon-arc radiation. The spectral distribution of sunlight is simulated well in the ultraviolet (UV) and visible wavelength range by the use of appropriate filters (for daylight and daylight behind window glass). The sample holders rotate around the lamp with one side of the holder facing the lamp continuously. The device is equipped with xenon lamps and operated at following conditions: 50 W/m^2 and 44°C black panel temperature.

The room temperature and humidity were maintained respectively at approximately 30 ± 1 °C and 60% throughout the experiment. The tested properties of the samples were evaluated after 24 hours of artificial accelerated ageing.

Air permeability test. Standard test method for air permeability of textile was carried out with an analyzer from Eni Development, following the norm ISO EN 9237:1995 for industrial fabric. Typically, a circular piece of fabric (20 cm^2) is submitted to an air pressure of 200 Pa at 20.4°C with a relative humidity of 64.1%. Each sample (pristine fabric or MOF/chitosan/fabric) was measured four times, the results are presented in table S1.

Degradation of Paraoxon-Methyl (DMNP). The protocol used was similar to the one previously developed by Farha *et al*.

[2] A 1 x 1 cm^2 composite sample was weighed, cut in smaller pieces and dispersed in an aqueous solution of 1 mL of N-ethylmorpholine (NEM) at 0.45 M in a 2 mL vial. After 20 minutes of stirring, 4 µL of DMNP was added to the solution. Conversion of DMNP was

monitored by following the formation p-nitrophenoxide, a DMNP degradation product with a typical absorbance at 407 nm, by using a UV/Visible Shimadzu UV1800 spectrometer. A 10 µL aliquot was taken at determined intervals and diluted in 5 mL of 0.45 M NEM. Concentration of p-nitrophenoxide was then calculated using the Beer-Lambert equation, the molar absorptivity coefficient ε of p-nitrophenoxide being 18330 $M^{-1}.cm^{-1}$.[3]

Section S2. Supplementary characterizations

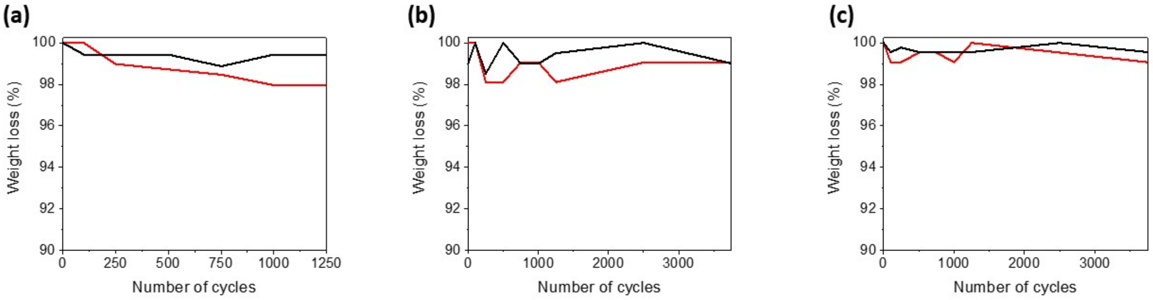

Figure S1. Abrasion resistance tests of UiO-66-NH_2/chitosan deposited on cotton (a), polyamide (b) or polyester (c). Black line corresponds to pristine textiles (cotton, PA or PE) and red lines are the composites.

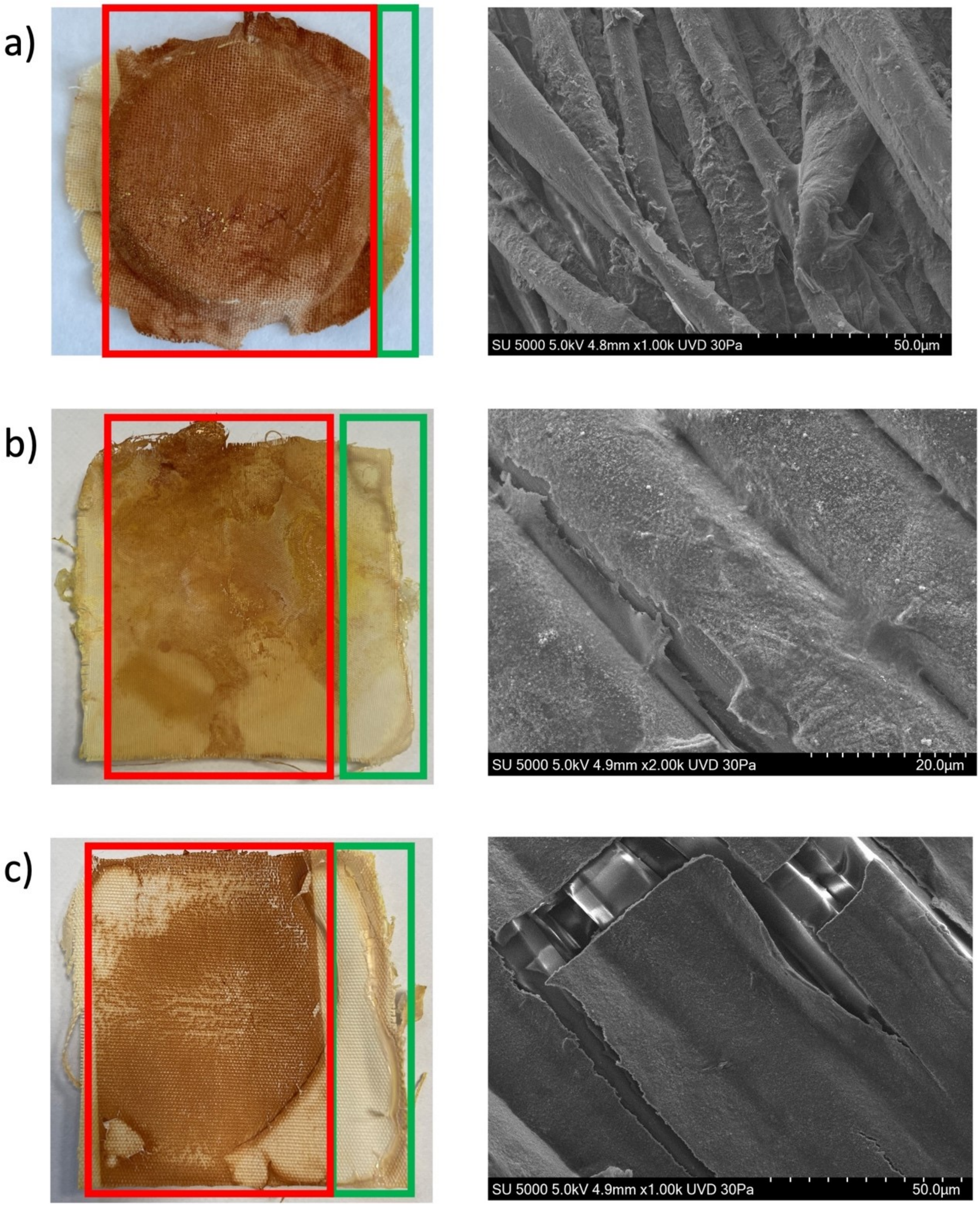

Figure S2. Optical (left) and SEM picture of the composites (UiO-66-NH_2/Chitosan/Fabric) after exposition in the irradiation chamber at 30°C with moisture. Composite with cotton (a), polyamide (b) and polyester (c). The irradiated and the non-irradiated area are delimited by a red and green square, respectively.

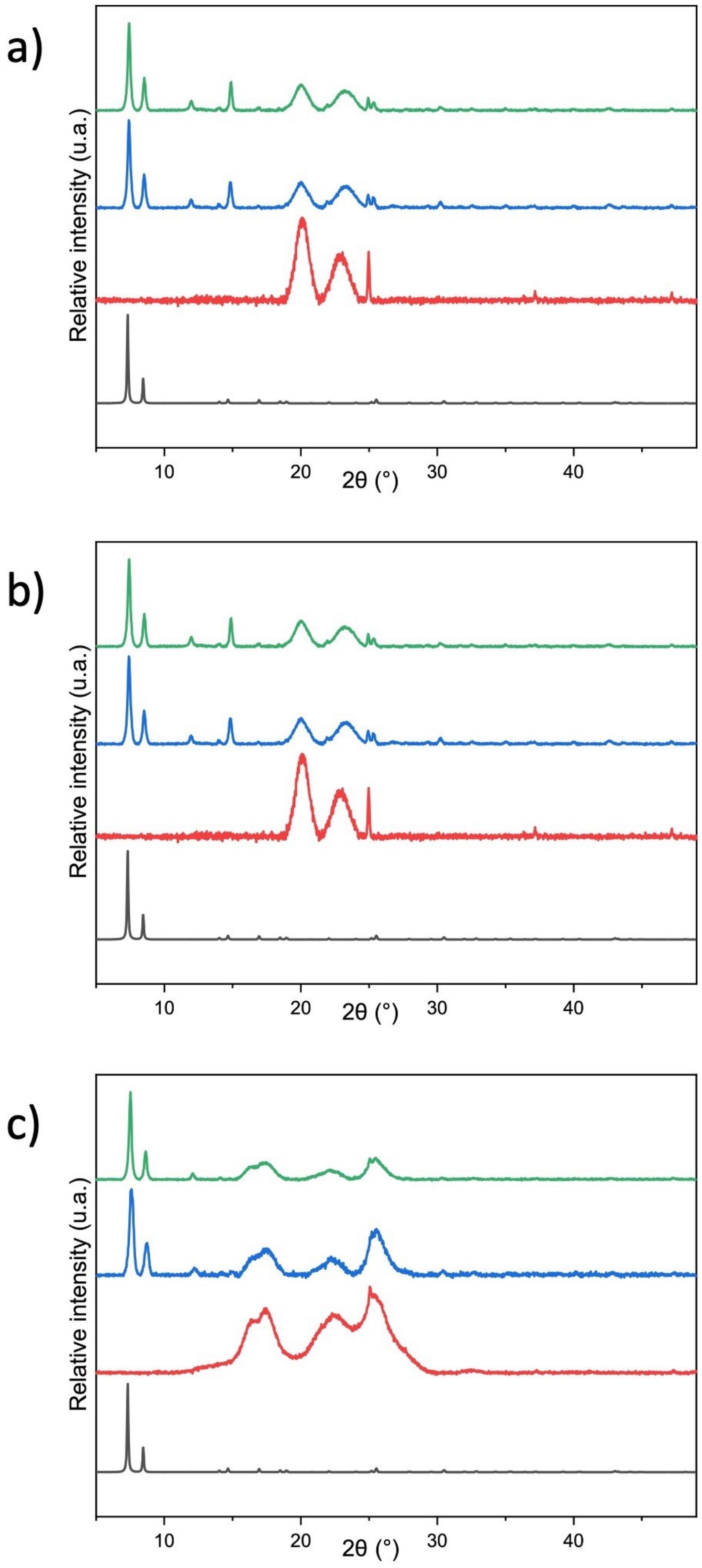

Figure S3. PRXD diagrams comparing pristine UiO-66-NH2 (black), the pristine fabric (red), the fabric/chitosan/MOF composite before (blue) and after exposition to the irradiation chamber. Composite with cotton (a), polyamide (b) and polyester (c).

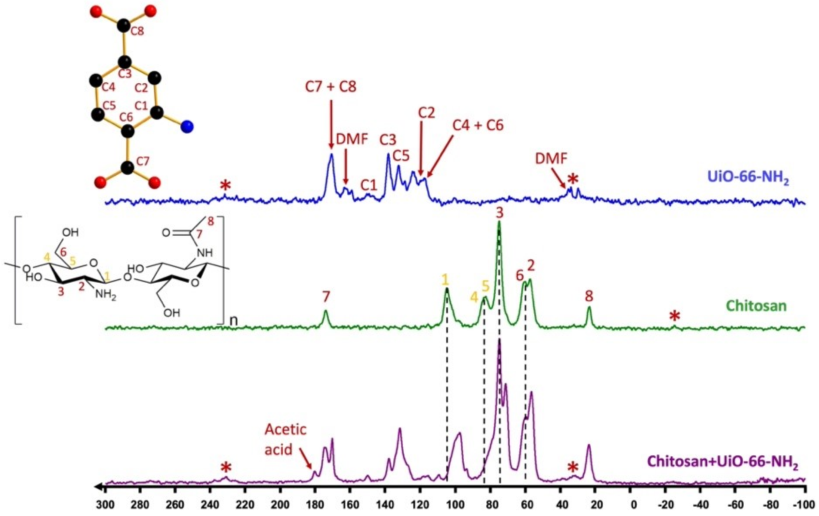

Figure S4. ^{13}C solid-state CPMAS NMR spectra of UiO-66-NH2, chitosan and a mixture of chitosan and UiO-66-NH_2. Chitosan[4] and UiO-66-NH_2[5] assignments are based on reference 4and 5, respectively.

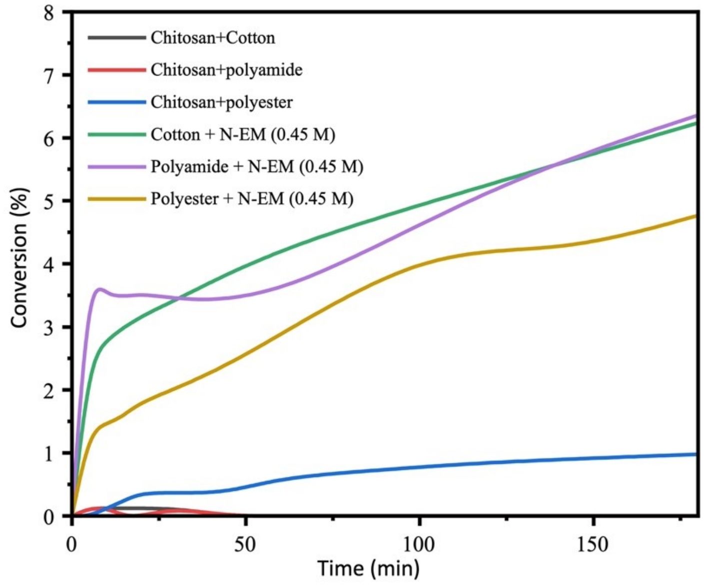

Figure S5. Kinetic of catalytic degradation of DMNP to nitrophenoxide using organic chitosan-based composite (without MOF) in aqueous solution (without NEM) (black: cotton, red:

polyamide, blue: polyester) or fabric in NEM buffer (NEM 0,45 M) (green: cotton, red: polyamide, blue polyester).

Table S1. Air permeability test of the textile fabrics and composites used in this study. The values are expressed as the flow rate (L/s) per area unit (m^2) ($L/m^2/s$).

	Cotton	**Cotton composite**	**PE**	**PE composite**	**PA**	**PA composite**	**PA composite** *(without formic acid in the synthesis)*
Measure 1	671.00	599	9	7	61	10	19
Measure 2	676.00	637	9	9	65	3	13
Measure 3	746.00	654	10	7	65	0	18
Measure 4	730.00	606	10	7	62	0	12
Averaged flow	**705.75**	**624**	**9.5**	**7.5**	**63.25**	**3.25**	**15.5**

References

(1) Fung, B. M.; Khitrin, A. K.; Ermolaev, K. An improved broadband decoupling sequence for liquid crystals and solids. *J. Magn. Reson.* **2000**, *142* (1), 97-101. DOI: 10.1006/jmre.1999.1896.

(2) Katz, M. J.; Mondloch, J. E.; Totten, R. K.; Park, J. K.; Nguyen, S. T.; Farha, O. K.; Hupp, J. T. Simple and Compelling Biomimetic Metal-Organic Framework Catalyst for the Degradation of Nerve Agent Simulants. *Angew. Chem. Int. Ed.* **2014**, *53* (2), 497-501. DOI: 10.1002/anie.201307520.

(3) Zhao, J. J.; Lee, D. T.; Yaga, R. W.; Hall, M. G.; Barton, H. F.; Woodward, I. R.; Oldham, C. J.; Walls, H. J.; Peterson, G. W.; Parsons, G. N. Ultra-Fast Degradation of Chemical Warfare Agents Using MOF-Nanofiber Kebabs. *Angew. Chem. Int. Ed.* **2016**, *55* (42), 13224-13228. DOI: 10.1002/anie.201606656.

(4) Saber-Samandari, S.; Yilmaz, O.; Yilmaz, E. Photoinduced Graft Copolymerization onto Chitosan Under Heterogeneous Conditions. *J.Macromol. Sci.* **2012**, *49* (7), 591-598. DOI: 10.1080/10601325.2012.687970.

(5) Devautour-Vinot, S.; Maurin, G.; Serre, C.; Horcajada, P.; da Cunha, D. P.; Guillerm, V.; Costa, E. D.; Taulelle, F.; Martineau, C. Structure and Dynamics of the Functionalized MOF Type UiO-66(Zr): NMR and Dielectric Relaxation Spectroscopies Coupled with DFT Calculations. *Chem. Mater.* **2012**, *24* (11), 2168-2177. DOI: 10.1021/cm300863c.