

Electronic Supplementary Information (ESI) for

**Fast Degradation of a Nerve Agent Simulant Catalyzed by Two
Isorecticular 6-Connected Zr₆ and Hf₆ Cluster Based Metal-Organic
Frameworks**

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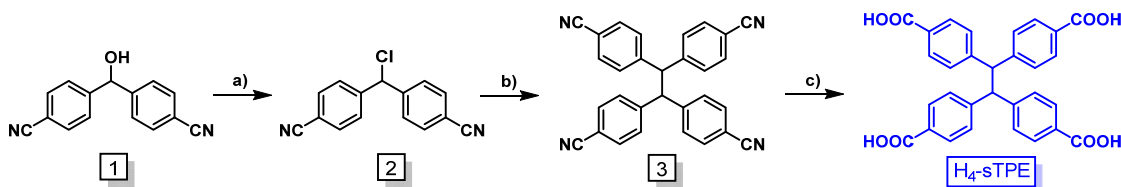
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Materials and Instruments

Unless specifically mentioned, all chemicals are commercially available and were used as received. NMR spectra were taken on a Bruker AV400 at room temperature. The powder X-ray diffraction (PXRD) measurements were taken on a Bruker D8 diffractometer using Cu- K_{α} radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. Low-pressure gas sorption measurements were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with the extra-high pure gases. The infrared spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrometer as KBr pellets. Thermal gravimetric analyses (TGA) were performed on a TA-Q50 thermoanalyzer thermogravimetric analyzer in nitrogen atmosphere from 45 °C to 800 °C at the rate of 10 °C min⁻¹. Deuterated solvents were purchased from Energy Chemical and used without further purification. ZrCl₄ (99.5%, Sigma-Aldrich), TFA (99%, Energy Chemical), HfCl₄ (99.9%, Adamas-beta), DMF (99.5%, General-Reagent), acetic acid (99.5%, Aladdin), trifluoromethanesulfonic acid (99%, Energy Chemical), cotton fibers were ordered from commercial vendors. Before using, cotton fibers were soaked in 6% NaOH solution for 1 h at 90 °C, wash to neutral with deionized water and dried at room temperature.

Synthesis and Characterizations

Synthesis of 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl) tetrabenzoic acid (H₄-sTPE)



Scheme S1. The synthesis of organic linker H₄-sTPE. (a) SOCl₂, piperidine, CH₂Cl₂, 40 °C for 12 h; (b) NaI, acetone, 60 °C for 12 h; (c) CF₃SO₃H, HAc, H₂O, 120 °C for 36 h.

4,4'-(chloromethylene)dibenzonitrile (Compound 2)

Bis(4-Cyanophenyl)methanol (3.00 g, 12.80 mmol) dissolved in dry DCM (30 mL), after ultrasonic dissolution, thionyl chloride (3.80 mL, 53.53 mmol) and piperidine (30 μL, 0.3 mmol) were dropped under nitrogen atmosphere. The reaction mixture was stirred at 40 °C for 12 h, cooled to room temperature, and then stirred with ice water for 15 min. The residue was dissolved in dichloromethane (400 mL), washed with water (300 mL×3), dried over anhydrous Na₂SO₄, filtered and evaporate the solvent under reduced pressure to give 4,4'-(chloromethylene)dibenzonitrile (3.15 g, 97.3%) as a yellow oil, which does not require purification for the next reaction.

4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzonitrile (Compound 3)

4,4'-(chloromethylene)dibenzonitrile (3.00 g, 11.87 mmol) and sodium iodide (5.34 g, 35.6 mmol) dissolved in acetone (30 mL) under nitrogen atmosphere, stirred the reaction mixture at 60 °C for 12 h in the dark. After the raw materials were consumed, the saturated solution of sodium sulfite added and stirred for 15 min, the residue was filtered. Washed the crude product via ethanol (30 mL × 2) and filtered to give 4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzonitrile (2.45 g, 94.8%) as a white powder. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.67 (t, *J* = 6.8 Hz, 16H), 5.65 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 148.36, 133.09, 129.70, 119.04, 109.99, 53.16.

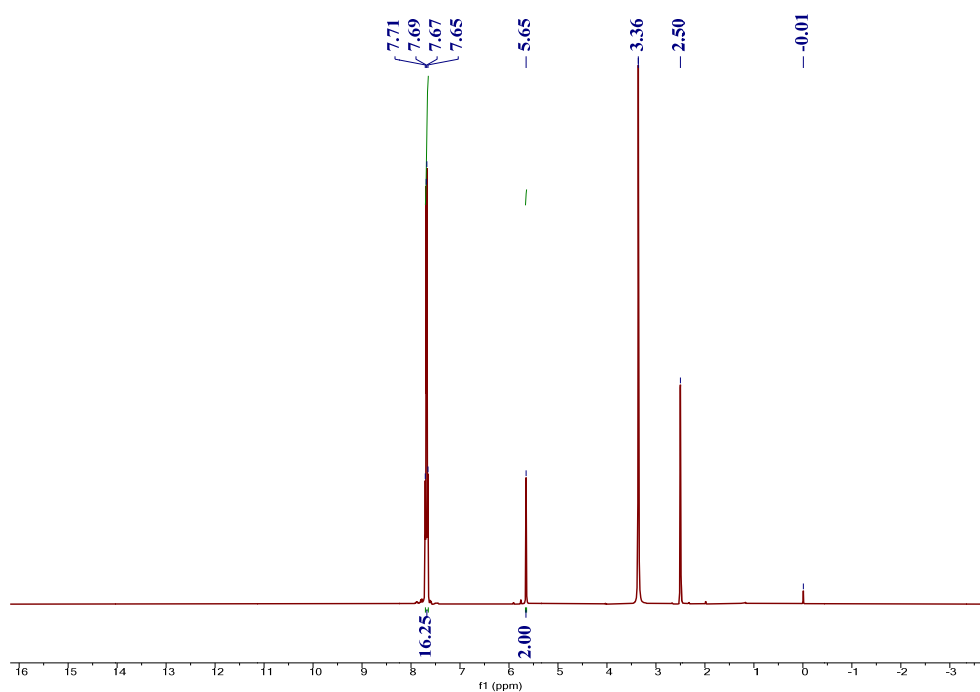


Fig. S1. The ^1H NMR of **Compound 3** (400 MHz, DMSO).

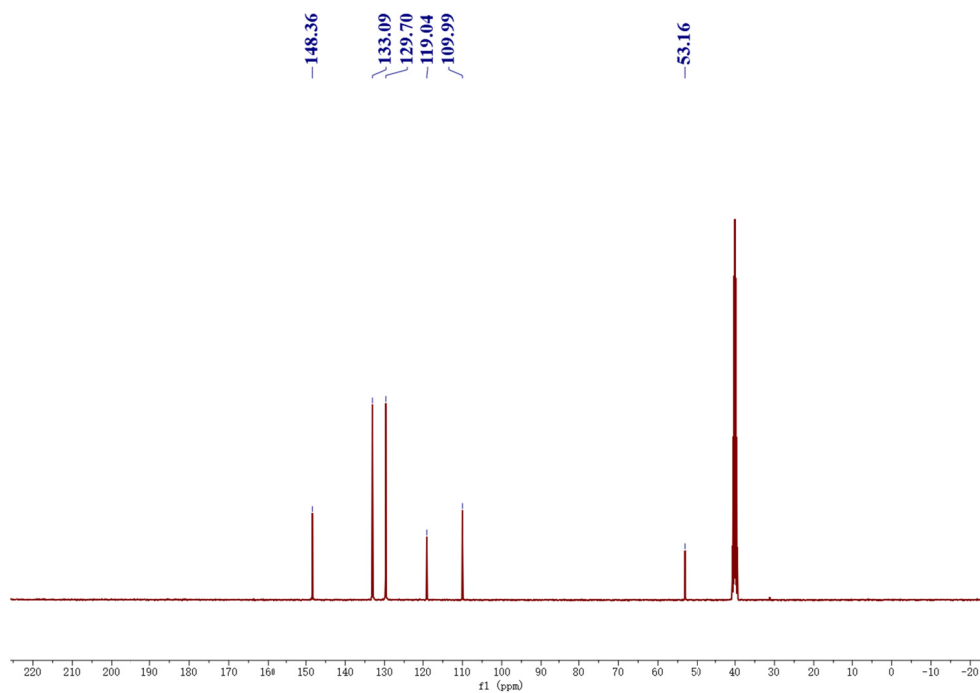


Fig. S2. The ^{13}C NMR of **Compound 3** (101 MHz, DMSO).

4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzoic acid (**H₄-sTPE**)

4,4',4'',4'''-(ethane-1,1,2,2-tetrayl)tetrabenzonitrile (1.00 g, 2.3 mmol) dissolved in trifluoromethanesulfonic acid (2 mL), acetic acid (2 mL) and deionized water (1 mL) under an ice bath, after ultrasonic dissolution, the reaction mixture was stirred at 120 °C for 36 h. Cooling down to room temperature, 30 mL deionized water was added to precipitate the product, stirred for 20 min. The mixture was filtered and washed with water (15 mL × 3). The solid was dried in an oven at 50 °C for 1 h to obtain white powder (0.9 g, 98%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.75 (s, 4H), 7.70 (d, *J* = 7.9 Hz, 8H), 7.63 (d, *J* = 8.2 Hz, 8H), 5.52 (s, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 167.53, 148.67, 129.93, 129.22, 128.96, 53.91. ESI-HR MS: *m/z* calcd for C₃₀H₂₂O₈: 510.1315, found: 510.1279 [M]⁺.

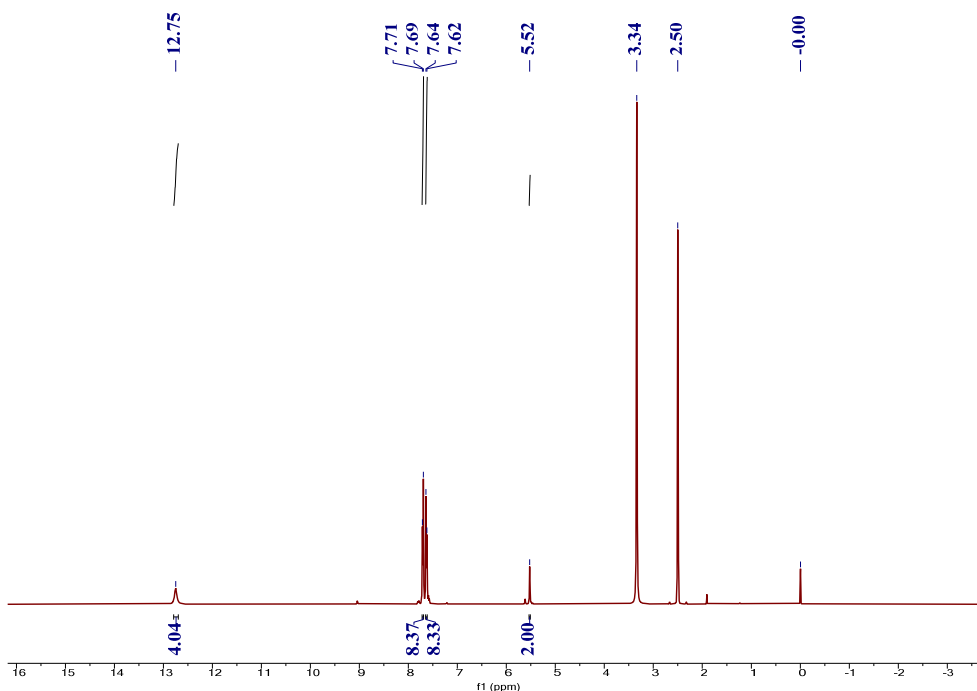


Fig. S3. The ¹H NMR of **H₄-sTPE** (400 MHz, DMSO).

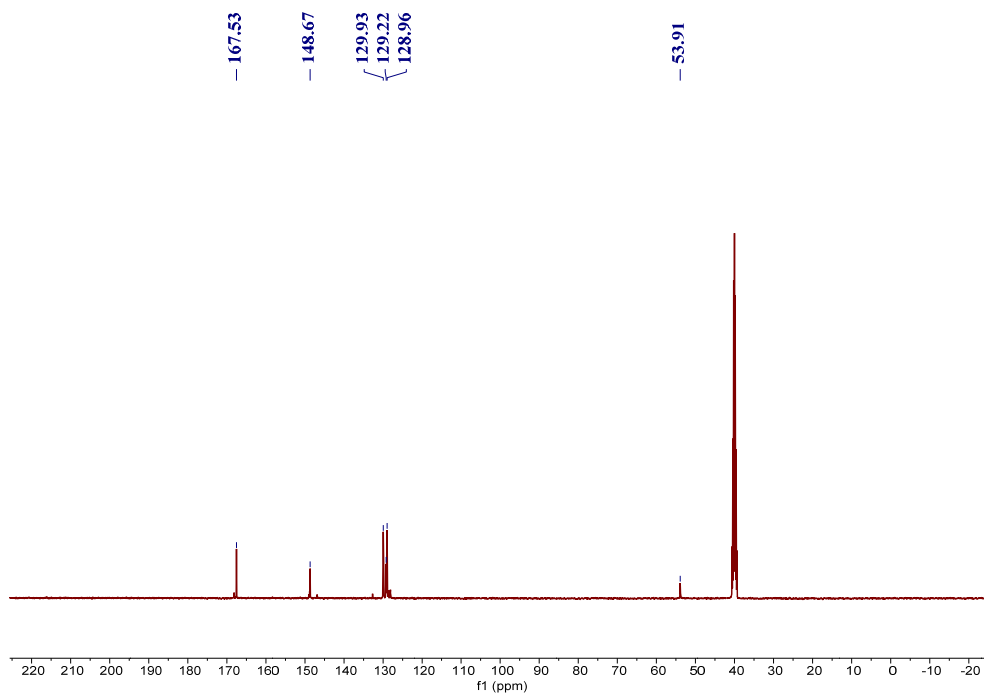


Fig. S4. The ^{13}C NMR of $\text{H}_4\text{-sTPE}$ (101 MHz, DMSO).

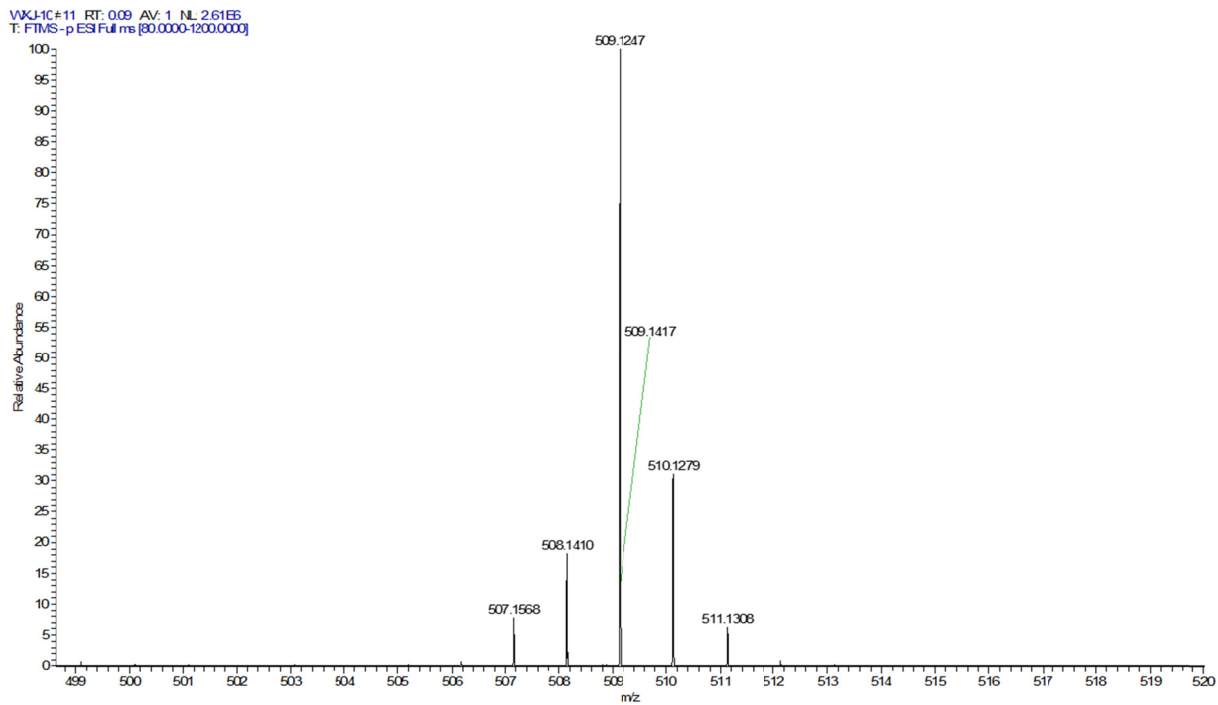


Fig. S5. ESI-HR MS of $\text{H}_4\text{-sTPE}$.

MOF synthesis

Zr-sTPE

ZrCl₄ (18 mg), H₄-sTPE (6 mg), and TFA (250 μL) were mixed in 3 mL of DMF in a 10 mL dram vial and ultrasonically for 30 min at room temperature. The white mixture was placed in a preheated oven at 120 °C for 48 h. After cooling down to room temperature, white polycrystalline MOFs were collected by centrifugation (3 min, 6000 rpm) and solvent exchanged with fresh DMF three times. The powder was dried at 60 °C overnight to obtain a Zr-sTPE MOF (54%).

Hf-sTPE

HfCl₄ (28 mg), H₄-sTPE (6 mg), and TFA (250 μL) were mixed in 3 mL of DMF in a 10 mL dram vial and ultrasonically for 30 min at room temperature. The white mixture was placed in a preheated oven at 120 °C for 48 h. After cooling down to room temperature, white polycrystalline MOFs were collected by centrifugation (3 min, 6000 rpm) and solvent exchanged with fresh DMF three times. The powder was dried at 60 °C overnight to obtain a Hf-sTPE MOF (58%).

Procedure for Preparation of MOF Zr-sTPE and Hf-sTPE coating on cotton fabrics

ZrCl₄ (36 mg)/HfCl₄ (56 mg), H₄-sTPE (12 mg), and TFA (250 μL) were ultrasonically dissolved in 3 mL of DMF in 10 mL glass vials at room temperature. Then the pretreated cotton fiber (1 cm × 1 cm) was mixed thoroughly with the MOF precursor solution, and ultrasonic treatment for 10 minutes. Subsequently, the vial was placed in a box furnace and heated to 120 °C for 48 h. After the solvothermal synthesis, the MOF-coated cotton fibers were washed twice with 50 mL of DMF. After the DMF wash, the MOF-coated cotton fibers underwent further solvent exchanged in anhydrous ethanol, with the solvent being replaced every 12 hours for a total of three times. Finally, the MOF-coated cotton fibers were dried at 60 °C overnight. The MOF mass loading was calculated to be 58% for Zr-sTPE and 55% for Hf-sTPE.

Catalytic Degradation of Dimethyl 4-Nitrophenyl Phosphate (DMNP)

The kinetics of catalytic degradation of DMNP was characterized using a procedure similar to the methods described in previous reports¹ and the completion of the reaction in the simulated solution was confirmed by ³¹P NMR. MOF powder sample (Zr-sTPE 2 mg; Hf-sTPE 3 mg, 6 mol%) was first dispersed in 1.5 mL of N-ethylmorpholine aqueous solution (0.45 M, pH = 10) in a 5 mL Centrifuge tube. The resulting dispersion was vigorously sonicated for 5 min and stirred at 1100 rpm for 5 min. Then, 4 μ L of DMNP was then added to the MOF suspension and the stirring was kept at 1100 rpm. A 20 μ L aliquot was taken from the reaction mixture at a specific time and diluted with 5 mL of deionized water for UV-visible absorbance spectroscopy. The reaction progress was evaluated by monitoring the *p*-nitrophenoxide (degraded product from DMNP) absorbance at 407 nm. The concentration of *p*-nitrophenoxide was calculated based on Lambert-Beer Law. The percent conversion of DMNP was calculated from the concentration ratio of degraded DMNP to the initial DMNP. In the cycle test, we collected the MOF powder by centrifugation, washed with anhydrous ethanol (5 mL \times 3) and dried at room temperature for 10 h for the next cycle of DMNP test.

As for calculating half-life time ($t_{1/2}$) of DMNP hydrolysis, the reaction was assumed to follow first-order kinetics in the early stage. The rate constant (k) was determined by fitting the plot of $\ln[\text{DMNP}]$ against time. The half-life ($t_{1/2}$) was then calculated using the formula $t_{1/2} = \ln(2)/k$.

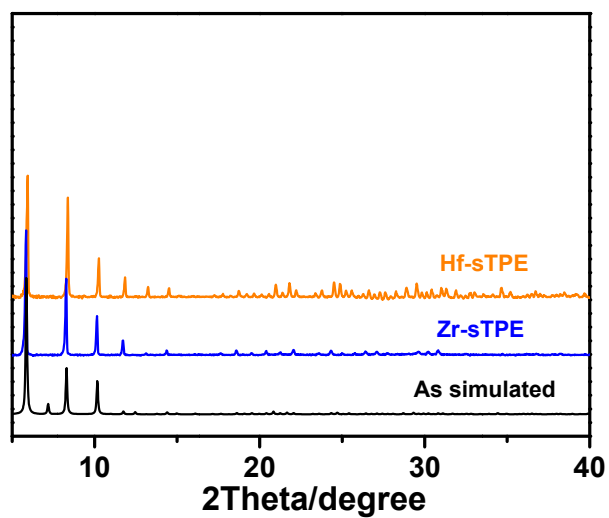


Fig. S6. PXRD patterns of as-synthesized Zr/Hf-sTPE and simulated PXRD pattern for MOF Zr-TCPE, indicative of they share isosubstructural frameworks.

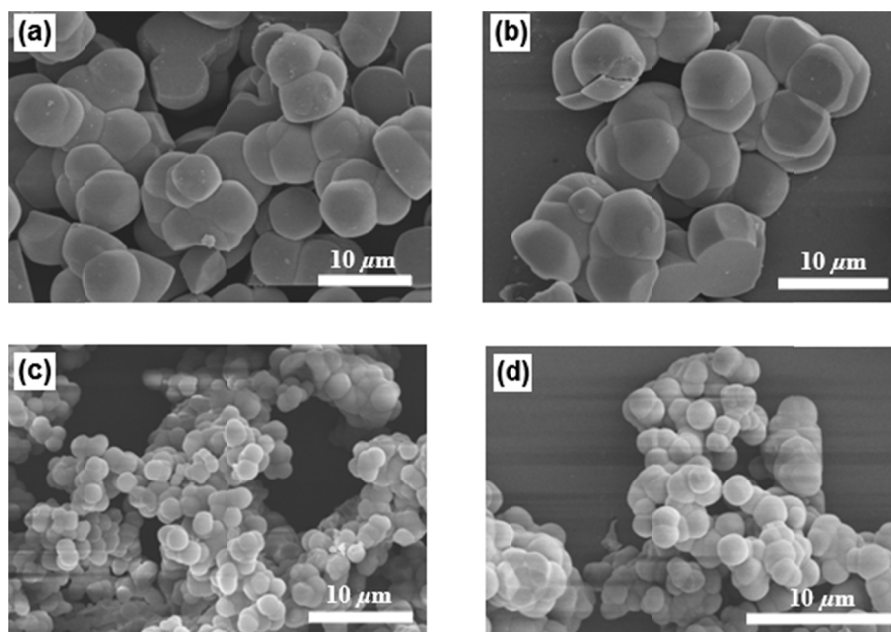


Fig. S7. SEM images of Zr-sTPE (a, b), Hf-sTPE (c, d) before degradation (a, c) and after DMNP degradation (b, d).

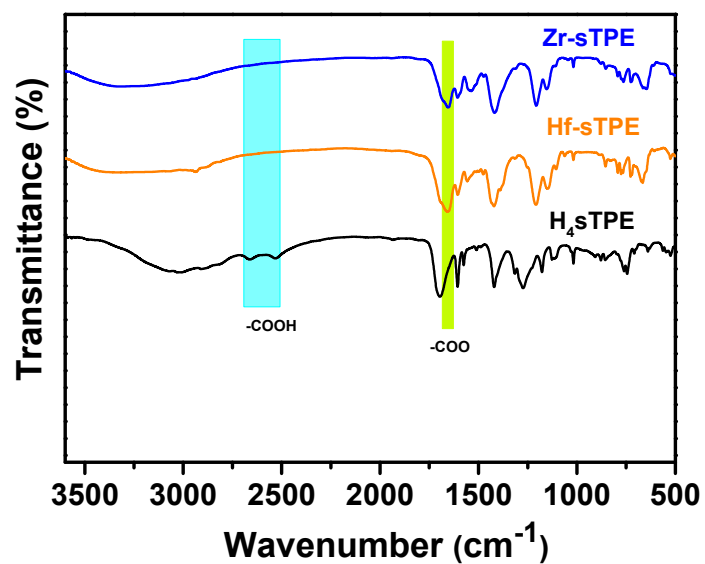


Fig. S8. The FT-IR comparison of H₄-sTPE, Zr-sTPE and Hf-sTPE, the disappearance of peak of COOH at 2667 and 2533 cm⁻¹ indicative of the coordination of carboxylic acid with Zr⁴⁺ and Hf⁴⁺.

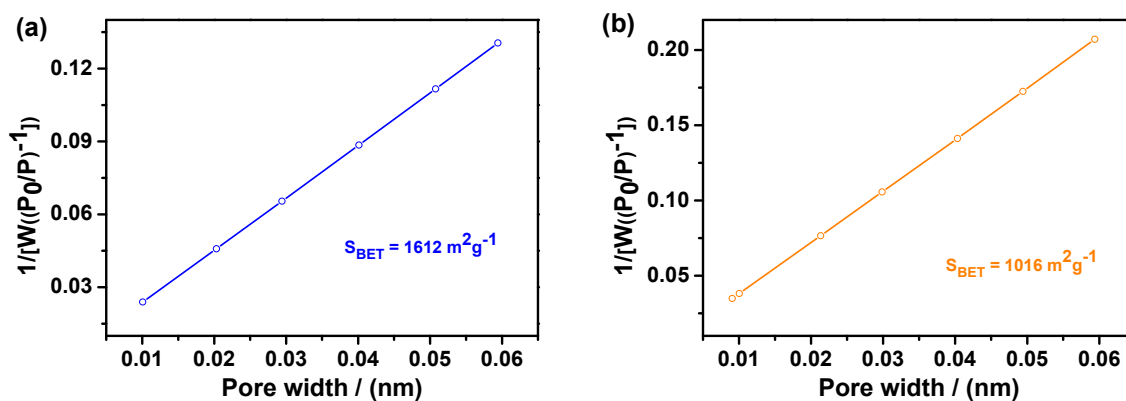


Fig. S9. BET plots of Zr-sTPE (a) and Hf-sTPE (b).

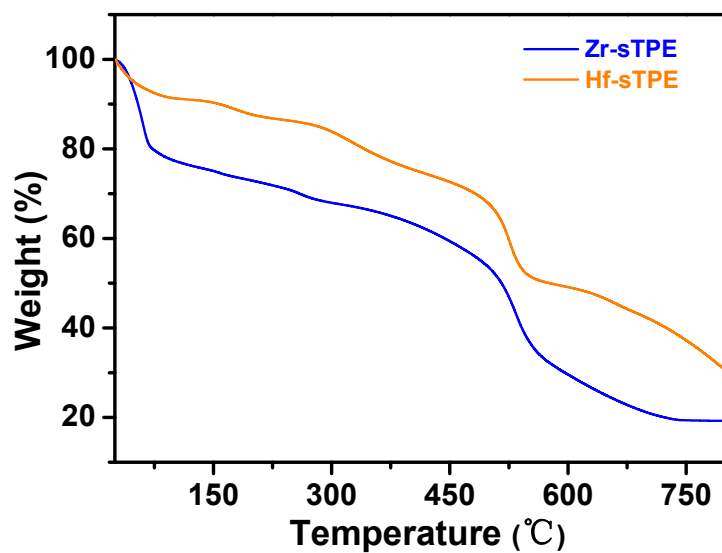


Fig. S10. TGA of Zr-sTPE and Hf-sTPE under N₂ atmosphere with a heating rate of 10 °C/min, suggesting they can be stable as high as ~450 °C.

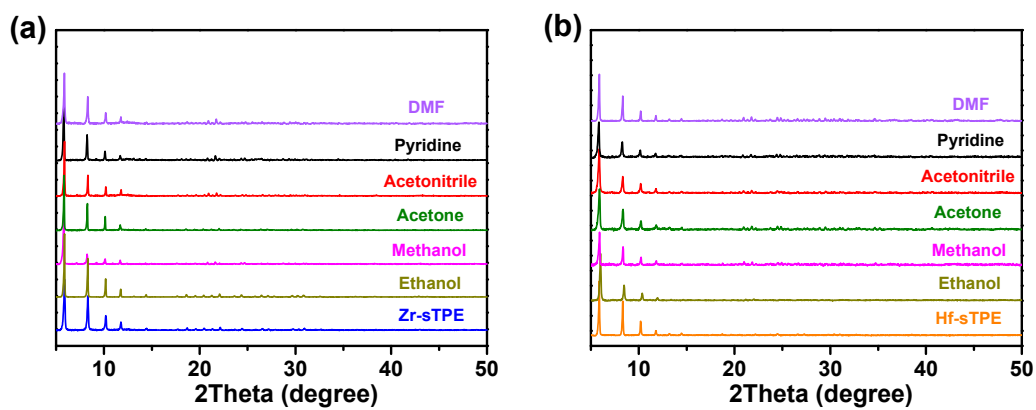


Fig. S11. PXRD patterns of Zr-sTPE (a) and Hf-sTPE (b) after the treatment for 24 h in different organic solvents. The PXRD patterns of all treated Zr-sTPE and Hf-sTPE remain intact, indicating that they maintained their crystallinity in common organic solvents.

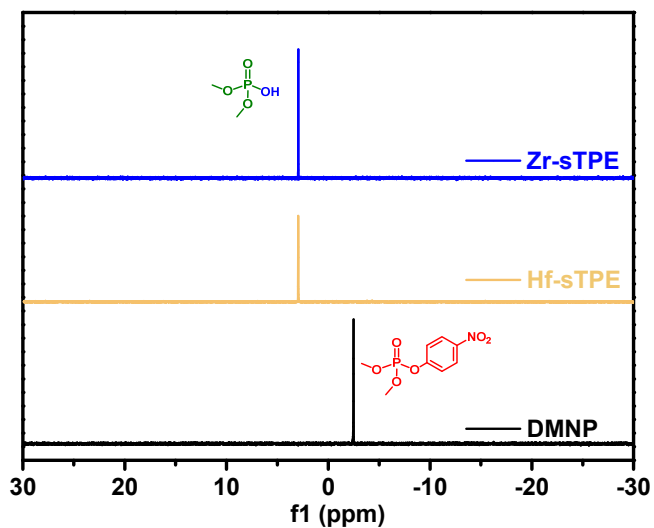


Fig. S12. ^{31}P NMR spectra of the hydrolysis of DMNP (-4.4 ppm) to the product of dimethoxy phosphate (2.8 ppm), after catalysis by Zr-sTPE and Hf-sTPE.

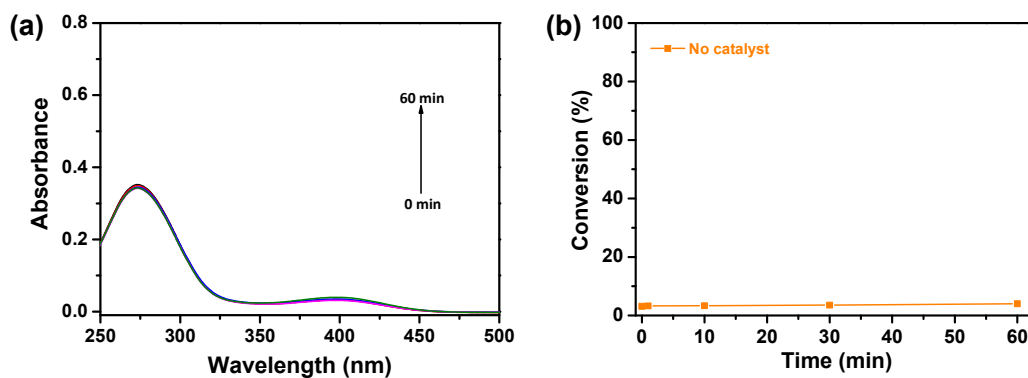


Fig. S13. Time-dependent UV-vis spectra for monitoring DMNP hydrolysis in the absence of the MOF catalyst (a) and percentage conversion of DMNP versus time (b).

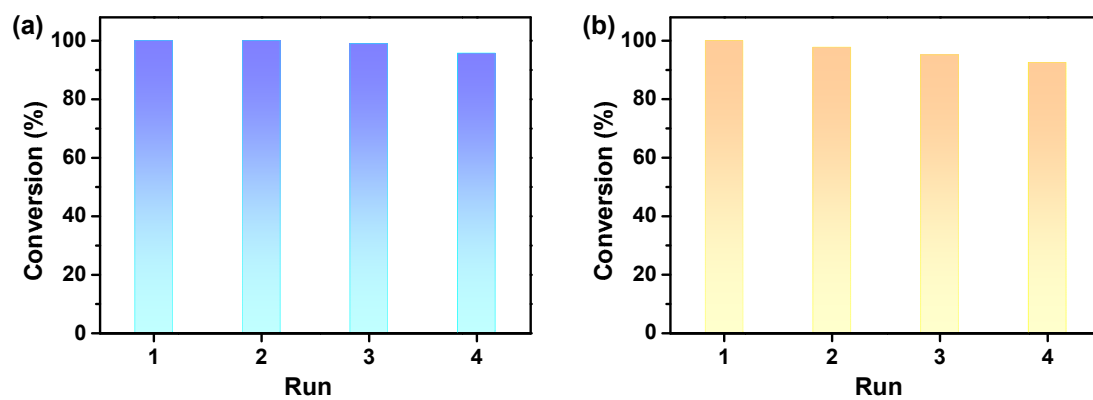


Fig. S14. The reusability of the **Zr-sTPE** (a) and **Hf-sTPE** (b) for DMNP degradation.

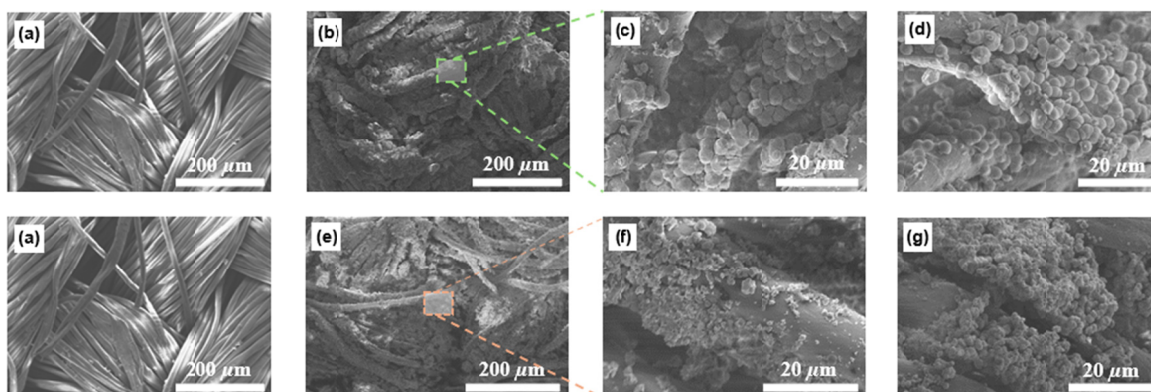


Fig. S15. SEM images of cotton fabric (a); Zr-sTPE (b, c), Hf-sTPE (e, f) coated cotton fibers before catalysis; Zr-sTPE@ cotton (d), Hf-sTPE@ cotton (g) after degradation.

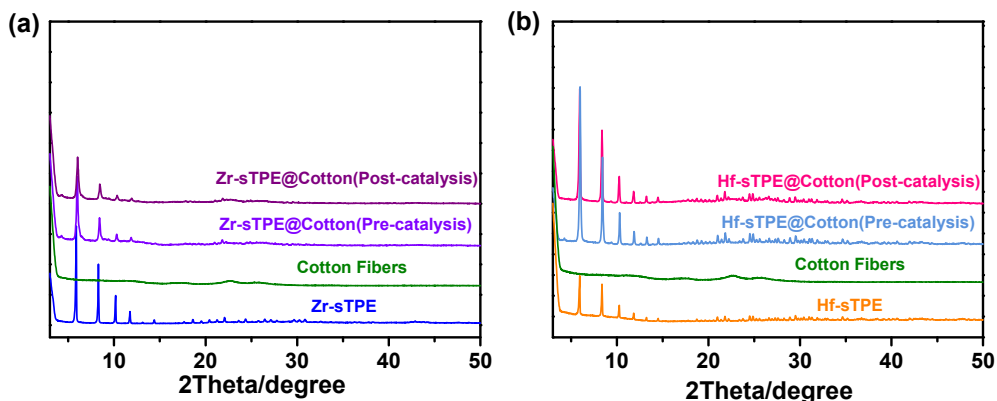


Fig. S16. PXRD patterns of Zr-sTPE@cotton (a) and Hf-sTPE@cotton (b) before and after degradation. The PXRD revealed that Zr-sTPE@cotton and Hf-sTPE@cotton are consistent with those of parent materials Zr-sTPE and Hf-sTPE, indicated the well-maintained crystallinity and phase purity of post-MOF coating on cotton fibers.

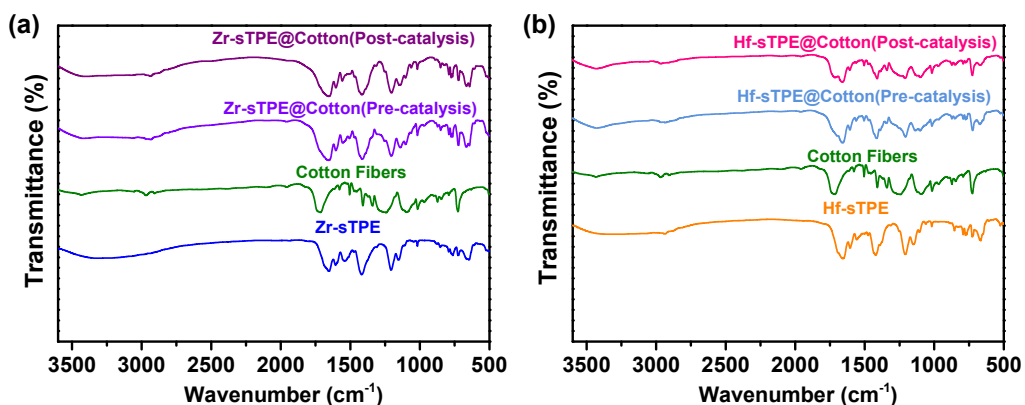


Fig. S17. FT-IR spectra of Zr-sTPE@cotton (a) and Hf-sTPE@cotton (b) before and after degradation. FT-IR indicated that the peaks at 3427 cm^{-1} , 2908 cm^{-1} associated with the stretching vibration of $-\text{CH}_3$ and $-\text{OH}$ in cotton fibers, Zr-sTPE@cotton and Hf-sTPE@cotton still retained the characteristic peaks of cotton fibers.

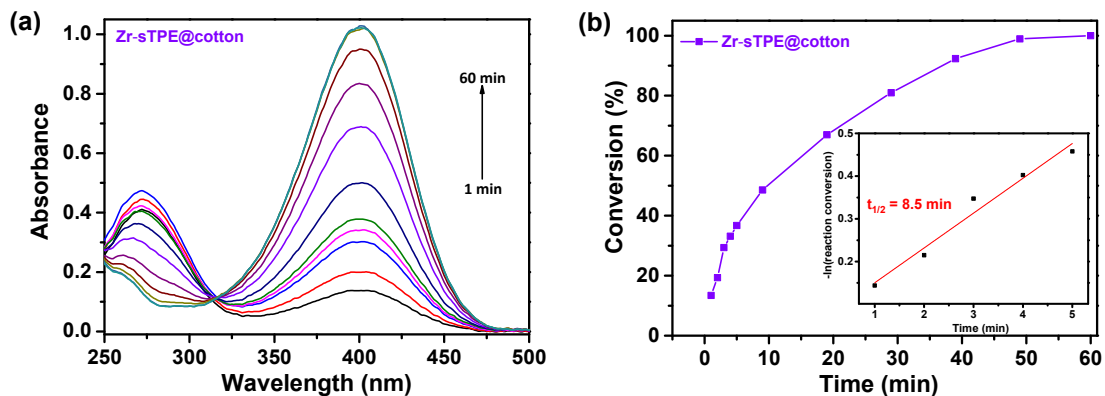


Fig. S18. Ultraviolet-visible monitoring for the formation of *p*-nitrophenoxide after adding Zr-sTPE@cotton (a) and percentage conversion to *p*-nitrophenoxide versus time (b).

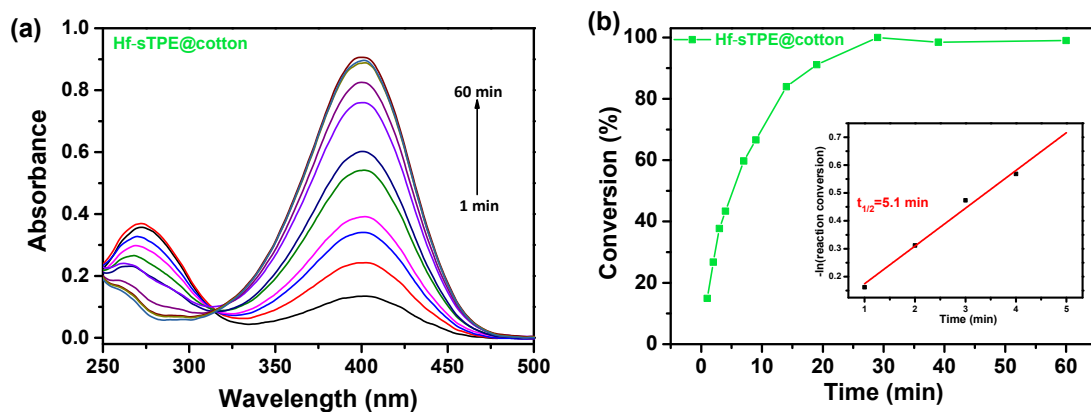


Fig. S19. Ultraviolet-visible monitoring for the formation of *p*-nitrophenoxide after adding Hf-sTPE@cotton (a) and percentage conversion to *p*-nitrophenoxide versus time (b).

Table S1. Comparison of the hydrolysis rate ($t_{1/2}$) of DMNP with various MOFs.

MOFs (connectivity of the metal nodes)	Metal node	Half-lives of DMNP (min) ^a	Ref.
Zr-sTPE (6-connected)	Zr ₆	4.9	This work
Hf-sTPE (6-connected)	Hf ₆	3.5	This work
UiO-66 (12-connected)	Zr ₆	35	1
UiO-66-NO ₂ (12-connected)	Zr ₆	45	
UiO-66-NH ₂ (12-connected)	Zr ₆	1	2
UiO-66-(OH) ₂ (12-connected)	Zr ₆	60	
UiO-67 (12-connected)	Zr ₆	17	3
NU-1000 (8-connected))	Zr ₆	15	4
NU-912 ^b (8-connected))	Zr ₆	11	5
PCN-222/MOF-545 ^c (8-connected)	Zr ₆	8	6
MOF-808 (6-connected))	Zr ₆	< 0.5	7
Ce-BDC	Ce ₆	8	8
Ti-MFU-41	Zn _x Ti _{5-x}	2	9
NU-1012-NDC	Zr ₆ Ti ₄	4.6	

MIL-125	Ti ₈	160	
Ni-MFU-41	Zn _x Ni _{5-x}	44	
Cu-MFU-41	Zn _x Cu _{5-x}	2	10
Co-MFU-41	Zn _x Co _{5-x}	116	

^aConditions: 6 mol % catalyst, 0.4 M EM , pH 10-10.5. ^b3 mol % catalyst, ^c4 mol % catalyst

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