Supporting Information

Solid-state degradation and Visual detection of nerve agent GB by SA@UiO-66-NH₂@PAMAM hydrogel

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1.1 Instruments and materials

N,N-dimethylformamide (DMF), hydrochloric acid (HCl), Zirconium chloride (ZrCl₄), 2-amino-terephthalic acid (H₂BDC-NH₂), sodium nitrite (NaNO₂), ethanol (EtOH) and ultrapure water was used in the experiments. Hydrochloric acid and ethanol were obtained from Beijing Lanyi Chemical Products Co. Ltd. (Beijing, China). polyamide-amine 1.0 G (PAMAM) was obtained from jk chemical.

Ultraviolet-visible (UV) absorption spectra were obtained by a UV-2600 spectrometer (Techcomp, China). X-Ray Powder Diffraction data (XRD) were obtained with Ultima IV multipurpose X-ray diffraction system (Japan). Fourier transforms infrared (FTIR) spectra were recorded in the region of 440-4000 cm⁻¹ with an FTIR-8400s Fourier Transform Infrared Spectrometer (Shimadzu). The scanning electron microscope (SEM) was Ultra-High Resolution Scanning Electron Microscope SU8010.

1.2 Synthesis of dimethyl-(4-nitrophenyl)-phosphate (DMNP)



40 ml THF was added to a 100 ml single-mouth flask followed by titanium tetrachloride (16 μ L, 148.3 μ mol) and 4-nitrophenol (1.14 g, 8.2 mmol, 1.1 eq) in nitrogen atmosphere. Finally, triethylamine (2.1 mL, 14.8 mmol, 2.0 eq) was added to the solution for 1 hour, then quenched with water, extracted with ethyl acetate, and

purify by silica gel column chromatography (elution =EtOAc / hexane =1:3 V/V) to obtain the product [1]. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 3.9 (d, J = 11.4 Hz, 6H), 7.39 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 9.2 Hz, 2H)

1.3 Synthesis of UiO-66-NH₂

UiO-66-NH₂ was synthesized according to methods reported in the literature [2]. 0.277 g ZrCl₄ (1.1 mmol) and 0.215 g ligand 2-aminoterephthalic acid (1.19 mmol) were first dissolved in 13 mL of DMF (1.780 mol) and 17 mL of glacial acetic acid (296.7 mmol) and sonicated for 30 min until complete dissolution and dispersion, then pour the mixed solution in the beaker into a 200 mL reaction kettle, set the parameters and time of the oven control platform, and keep the reaction at 120 °C for 24 hours. After the reaction was completed and cooled to room temperature, the obtained yellow precipitate was washed three times with DMF, centrifuged three times, and then washed three times with absolute ethanol and centrifuged three times. The washed and purified powder was dried at 100 °C overnight.

1.4 Synthesis of P-NSE



Tert-butyldimethylsilamine (80 mg, 0.6 mmol) was added to 4-nitrophenol (64 mg, 0.5 mmol) and stirred at room temperature for 30 minutes. The TLC purified crude reaction mixture was prepared with n-hexane/ethyl acetate 90:10 (V/V) [3]. ¹H NMR (400 MHz, CDCl₃): δ (ppm): 8.17 (d, J 9.0 Hz, 2H), 6.92 (d, J = 9.0 Hz, 2H), 1.01 (s, 9H), 0.28 (s, 6H,)

1.5 Determination of UiO-66-NH₂ by ICP

The composite materials SA@UiO-66-NH2@PAMAM and SA@UiO-66-

NH₂@PAMAM@Cotton were tested by inductively coupled plasma luminescence spectrometer. The samples to be tested were digested with nitric acid for 4-5 h, then the residue was filtered out with a filter, and diluted with ultrapure water to a suitable concentration for measurement. The test element was Zr, and the peak seeking wavelength was 343.823 nm.

Fig. S1. Structure of nerve agents.



Fig. S2. The ¹H NMR spectrum of DMNP.



Fig. S3. The ¹H NMR spectrum of P-NSE.



Fig. S4. FTIR spectra of SA gel and SA@UiO-66-NH₂@PAMAM composite gel.



Fig. S5. XRD patterns of UiO-66-NH₂ stimulated, UiO-66-NH₂, and SA@UiO-66-NH₂@PAMAM.



Fig. S6. (a) N₂ adsorption and desorption isotherms of UiO-66 and SA@UiO-66-NH₂@PAMAM at 195.8 °C (b) Pore width of UiO-66 and SA@UiO-66-NH₂@PAMAM.



Fig. S7 ³¹P NMR spectroscopy of SA@UiO-66-NH₂@PAMAM in solid-state degradation of DMNP. Reaction time:0 - 66 min.

66 min	-1:
60 min	-11
54 min	-10
48 min	-9
42 min	-8
36 min	-7
30 min	-6
24 min	-5
18 min	-4
12 min	-3
6 min	-2
0 min	-1

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm) Fig. S8 ³¹P NMR spectra of solid-state degraded DMNP with SA@UiO-66-NH₂@PAMAM stored for ten days. Response time: 0-66 minutes.

66 min	-12
60 min	-11
54 min	-10
48 min	-9
42 min	-8
36 min	-7
30 min	-6
24 min	-5
18 min	-4
12 min	-3
6 min	-2
0 min	-1

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm) Fig. S9 ³¹P NMR spectra of solid-state degraded DMNP with regenerated SA@UiO-66-NH₂@PAMAM. Response time: 0-66 minutes.

66 min	-12
60 min	-11
54 min	-10
48 min	-9
42 min	-8
36 min	-7
30 min	-6
24 min	*5
18 min	-4
12 min	-3
6 min	*2
0 min	-1

^{130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230} f1 (ppm)

Fig. S10 ³¹P NMR spectra of solid-state degraded DMNP with SA@UiO-66-NH₂@PAMAM@Cotton. Response time: 0-66 minutes.

66 min	-12
60 min	-11
54 min	-10
48 min	-9
42 min	-8
36 min	-7
30 min	-6
24 min	-5
18 min	-4
12 min	-3
6 min	-2
0 min	-1
	_

130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 f1 (ppm)

Fig. S11 Reversed-phase HPLC chromatograms (with absorption at 254 nm). (a) DMNP alone. (b) Filtrate of damaged cotton cloth after wiping iron plate.



Fig. S12. UV spectra of P-NSE at different pH.



References

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