Supporting Information

A dual-function all-inorganic intercluster salt comprised of the polycation ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ and polyanion α-$[PMo_{10}V_2O_{40}]^{5-}$ for detoxifying sulfur mustard and soman

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Preparation of the solution containing ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$[s1]: $AlCl_3 \cdot 6H_2O$ (12 g) was dissolved in 200 mL deionized water to prepare 0.25 mol/L $AlCl_3$ solution. NaOH (4.5 g) was dissolved in 450 mL deionized water to prepare 0.25 mol/L NaOH solution. The NaOH solution was added dropwise and slowly (≥ 15 min) into the $AlCl_3$ solution at 80℃ under stirring to obtain the clear solution containing ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (6.0 mmol/L), denoted as Al_{13}^{7+}.

Preparation of crystalline sulfate of Al_{13}, viz., $Na[Al_{13}O_4(OH)_{24}(H_2O)_{12}][SO_4]_4 \cdot xH_2O$ (denoted as Al_{13}-SO_4): A volume of 170 mL of the Al_{13}^{7+} solution from above was slowly added into 125 mL of 0.1 mol/L Na_2SO_4. The mixture was allowed to stand for one day to obtain large amount of precipitate, denoted as Al_{13}-SO_4. IR data (KBr, cm^{-1}): 1129 (w), 981 (w), 640 (m), 540 (s), 491 (w)[s2].

Figure S1. Photographic image of Al_{13}-$PMo_{10}V_2$

Table S1. the selected bond lengths. Al_{13}-$PM_{10}V_2$ (refer to the atom numbering schemes)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
M1	O25	1.837(9)	Al1	O1	1.938(8)
M1	O26	1.839(10)	Al1	O2	1.856(7)
M1	O27	1.627(9)	Al1	O3	1.849(7)
M1	O28	1.979(9)	Al1	O4	2.019(7)
M1	O36[1]	1.946(9)	Al1	O5	1.853(8)
M1	O63[1]	2.375(12)	Al1	O6	1.895(8)
M1	O65	2.456(12)	Al2	O3	1.855(7)
M2	O28	1.842(10)	Al2	O3[2]	1.855(7)
M2	O29	1.858(10)	Al2	O4	2.032(10)
M2	O30	1.625(8)	Al2	O7	1.969(11)
M2	O31	1.925(10)	Al2	O8	1.841(8)
M2	O32	1.926(10)	Al2	O8[2]	1.841(8)
M2	O63[1]	2.413(11)	Al3	O8[2]	1.870(8)
M2	O66[1]	2.447(12)	Al3	O8	1.870(8)
M3	O25[1]	1.946(9)	Al3	O9	1.982(12)
M3	O31	1.867(9)	Al3	O10	1.847(8)
M3)	O33	1.619(8)	Al3	O10[2]	1.847(8)
M3	O34	1.876(9)	Al3	O11	2.013(11)
M3)	O42[1]	1.925(10)	Al4	O10	1.864(9)
M3	O65[1]	2.455(12)	Al4	O11	2.043(8)
M3	O66[1]	2.400(12)	Al4	O12	1.849(7)
M4	O64[1]	2.335(13)	Al4	O13	1.939(9)
M4	O64[1]	2.335(13)	Al4	O14	1.832(9)
M4	O37A	2.045(17)	Al4	O15	1.865(8)
M4	O40A	1.867(16)	Al5	O4	1.815(10)
M5	O63[1]	2.500(12)	Al5	O11	1.806(11)

M5	O64[1]	2.376(12)	Al5	O16	1.817(8)
M5	O64[1]	2.376(12)	Al5	O16[2]	1.817(8)
M5	O37A	2.005(18)	Al6	O14	1.866(9)
M5	O39A	1.845(17)	Al6	O15	1.843(9)
M6	O64[1]	2.408(12)	Al6	O16	2.068(9)
M6	O64[1]	2.408(12)	Al6	O17	1.914(9)
M6	O39A	1.841(18)	Al6	O18	1.865(10)
M6	O40A	1.784(17)	Al6	O19	1.837(9)
P1	O63	1.542(12)	Al7	O16	2.035(9)
P1	O63[1]	1.542(12)	Al7	O18	1.852(10)
P1	O66	1.506(11)	Al7	O21	1.876(10)
P1	O66[1]	1.506(12)	Al7	O22	1.872(9)
P1	O64	1.647(13)	Al7	O23	1.843(9)
P1	O64[1]	1.647(12)	Al7	O24	1.943(11)
P1	O65	1.448(12)	Al8	O5	1.841(8)
P1	O65[1]	1.448(12)	Al8	O6	1.878(9)
Al8	O20	1.948(8)	Al8	O16	1.997(8)
Al8	O21	1.852(9)	Al8	O19	1.855(9)

Symmetry code: [1]-x,1-y,2-z; [2]+x,3/2-y,+z. M stands for Mo (s.o.f. 0.8) + V (s.o.f. 0.2) which share the same site.

Table S2. Selected bond angles for Al_{13}-$PM_{10}V_2$ (refer to the atom numbering schemes).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O25	M1	O26	92.8(4)	O14	Al4	O15	77.7(4)
O25	M1	O28	158.9(4)	O15	Al4	O11	93.8(3)
O25	M1	O36[1]	87.6(4)	O15	Al4	O13	92.5(4)
O25	M1	O63[1]	97.0(4)	O4	Al5	O16	109.0(3)
O25	M1	O65	65.5(4)	O4	Al5	O16[2]	109.0(3)
O26	M1	O28	88.3(4)	O11	Al5	O4	108.4(5)

O26	M1	O36[1]	157.9(4)	O11	Al5	O16	111.1(3)
O26	M1	O63[1]	67.2(4)	O11	Al5	O16[2]	111.1(3)
O26	M1	O65	93.0(5)	O16[2]	Al5	O16	108.1(6)
O27	M1	O25	101.5(5)	O14	Al6	O16	94.8(4)
O27	M1	O26	101.4(5)	O14	Al6	O17	93.5(4)
O27	M1	O28	98.9(5)	O15	Al6	O14	77.5(4)
O27	M1	O36[1]	100.1(5)	O15	Al6	O16	95.0(4)
O27	M1	O63[1]	158.8(5)	O15	Al6	O17	92.3(4)
O27	M1	O65	161.2(5)	O15	Al6	O18	169.8(4)
O28	M1	O63[1]	64.1(4)	O17	Al6	O16	169.9(4)
O28	M1	O65	93.4(4)	O18	Al6	O14	93.8(4)
O36[1]	M1	O28	83.6(4)	O18	Al6	O16	80.3(4)
O36[1]	M1	O63[1]	90.8(4)	O18	Al6	O17	93.5(4)
O36[1]	M1	O65	67.1(4)	O19	Al6	O14	171.8(4)
O63[1]	M1	O65	39.6(4)	O19	Al6	O15	95.7(4)
O28	M2	O29	90.9(5)	O19	Al6	O16	81.0(4)
O28	M2	O31	160.3(4)	O19	Al6	O17	91.4(4)
O28	M2	O32	88.5(4)	O19	Al6	O18	92.5(4)
O28	M2	O63[1]	65.0(4)	O18	Al7	O16	81.5(4)
O29	M2	O31	88.6(4)	O18	Al7	O21	93.4(5)
O29	M2	O32	157.0(5)	O18	Al7	O22	170.8(5)
O29	M2	O63[1]	93.7(5)	O18	Al7	O24	90.7(5)
O30	M2	O28	99.9(5)	O21	Al7	O16	81.6(4)
O30	M2	O29	100.4(5)	O21	Al7	O24	89.8(5)
O30	M2	O31	99.6(5)	O22	Al7	O16	93.5(5)
O30	M2	O32	102.4(5)	O22	Al7	O21	93.6(4)
O30	M2	O63[1]	159.6(4)	O22	Al7	O24	95.3(5)
O31	M2	O32	84.3(4)	O23	Al7	O16	95.2(5)
O31	M2	O63[1]	95.4(4)	O23	Al7	O18	94.3(5)

O32	M2	O63[1]	65.3(4)	O23	Al7	O21	171.1(5)
O25[1]	M3	O65[1]	64.2(4)	O23	Al7	O22	78.3(5)
O31	M3	O25[1]	158.2(5)	O23	Al7	O24	94.6(5)
O31	M3	O34	92.2(4)	O24	Al7	O16	168.0(5)
O31	M3	O42[1]	87.5(4)	O5	Al8	O6	80.0(3)
O31	M3	O65[1]	95.3(4)	O5	Al8	O16	96.2(3)
O33	M3	O25[1]	100.8(4)	O5	Al8	O19	94.2(4)
O33	M3	O31	100.7(5)	O5	Al8	O20	89.6(4)
O33	M3	O34	102.0(5)	O5	Al8	O21	173.7(4)
O33	M3	O42[1]	100.1(5)	O6	Al8	O16	92.5(3)
O33	M3	O65[1]	161.6(5)	O6	Al8	O20	92.8(4)
O34	M3	O25[1]	87.1(4)	O19	Al8	O6	172.0(4)
O34	M3	O42[1]	157.6(5)	O19	Al8	O16	82.5(4)
O34	M3	O65[1]	68.1(4)	O19	Al8	O20	92.7(4)
O42[1]	M3	O25[1]	85.0(4)	O20	Al8	O16	172.8(4)
O42[1]	M3	O65[1]	89.6(5)	O21	Al8	O6	93.7(4)
O34	M4	O37	79.6(6)	O21	Al8	O16	83.2(4)
O34	M4	O40	167.0(6)	O21	Al8	O19	91.9(4)
O34	M4	O64[1]	94.5(4)	O21	Al8	O20	91.5(4)
O35	M4	O34	100.5(4)	O1	Al1	O4	172.9(4)
O35	M4	O36	101.3(5)	O2	Al1	O1	91.3(3)
O35	M4	O37	112.6(7)	O2	Al1	O4	84.0(3)
O35	M4	O40	90.0(6)	O2	Al1	O6	93.3(4)
O35	M4	O64[1]	157.1(5)	O3	Al1	O1	92.7(3)
O36	M4	O34	88.1(4)	O3	Al1	O2	93.7(4)
O36	M4	O37	145.5(7)	O3	Al1	O4	82.4(4)
O36	M4	O40	97.5(6)	O3	Al1	O5	93.5(3)
O36	M4	O64[1]	96.5(4)	O3	Al1	O6	170.4(4)
O37	M4	O40	89.3(7)	O5	Al1	O1	90.4(3)

O37	M4	O64[1]	53.2(6)	O5	Al1	O2	172.5(4)
O40	M4	O64[1]	73.2(6)	O5	Al1	O4	95.0(3)
O26	M5	O39	90.4(6)	O5	Al1	O6	79.3(3)
O26	M5	O63[1]	63.1(4)	O6	Al1	O1	93.6(3)
O26	M5	O64[1]	96.4(4)	O6	Al1	O4	91.9(4)
O32	M5	O26	87.4(4)	O3[2]	Al2	O3	94.7(5)
O32	M5	O39	167.8(6)	O3	Al2	O4	81.8(3)
O32	M5	O63[1]	64.5(4)	O3[2]	Al2	O4	81.8(3)
O32	M5	O64[1]	97.5(4)	O3	Al2	O7	90.4(3)
O37	M5	O26	148.4(7)	O3[2]	Al2	O7	90.4(3)
O37	M5	O32	86.3(7)	O7	Al2	O4	168.5(5)
O37	M5	O39	89.3(7)	O8	Al2	O3[2]	171.5(4)
O37	M5	O63[1]	86.3(8)	O8	Al2	O3	92.8(3)
O37	M5	O64[1]	53.9(7)	O8[2]	Al2	O3	171.5(4)
O38	M5	O26	98.1(4)	O8[2]	Al2	O3[2]	92.8(3)
O38	M5	O32	100.1(4)	O8[2]	Al2	O4	95.3(3)
O38	M5	O37	113.5(7)	O8	Al2	O4	95.3(3)
O38	M5	O39	92.2(6)	O8[2]	Al2	O7	93.5(4)
O38	M5	O63[1]	154.9(4)	O8	Al2	O7	93.5(4)
O38	M5	O64[1]	157.6(4)	O8	Al2	O8[2]	79.5(5)
O39	M5	O63[1]	103.8(6)	O8	Al3	O8[2]	78.0(5)
O39	M5	O64[1]	70.7(6)	O8[2]	Al3	O9	92.7(4)
O64[1]	M5	O63[1]	47.3(4)	O8	Al3	O9	92.7(4)
O29[1]	M6	O39	163.8(6)	O8	Al3	O11	95.1(3)
O29[1]	M6	O40	89.4(6)	O8[2]	Al3	O11	95.1(3)
O29[1]	M6	O64[1]	92.9(5)	O9	Al3	O11	169.9(5)
O39	M6	O40	81.4(7)	O10	Al3	O8[2]	172.0(4)
O39	M6	O64[1]	71.5(6)	O10	Al3	O8	94.3(3)
O40	M6	O64[1]	70.1(6)	O10[2]	Al3	O8	171.9(4)

O41	M6	O29[1]	100.8(4)	O10[2]	Al3	O8[2]	94.3(3)
O41	M6	O39	92.6(6)	O10[2]	Al3	O9	89.8(4)
O41	M6	O40	90.4(6)	O10	Al3	O9	89.8(4)
O41	M6	O42	102.2(4)	O10	Al3	O10[2]	93.4(5)
O41	M6	O64[1]	156.1(4)	O10	Al3	O11	83.3(4)
O42	M6	O29[1]	87.0(5)	O10[2]	Al3	O11	83.3(4)
O42	M6	O39	99.2(6)	O10	Al4	O11	82.1(4)
O42	M6	O40	167.4(6)	O10	Al4	O13	88.9(4)
O42	M6	O64[1]	98.0(5)	O10	Al4	O15	94.3(4)
O63	P1	O63[1]	180.0(8)	O12	Al4	O10	93.1(5)
O63	P1	O64[1]	104.3(6)	O12	Al4	O11	82.0(3)
O63	P1	O64	75.7(6)	O12	Al4	O13	92.9(4)
O66	P1	O64	105.2(6)	O12	Al4	O15	170.9(5)
O66[1]	P1	O64	74.8(6)	O13	Al4	O11	169.3(5)
O64[1]	P1	O64	180.0	O14	Al4	O10	171.5(4)
O65[1]	P1	O63	66.4(6)	O14	Al4	O11	95.2(4)
O65[1]	P1	O63[1]	113.6(6)	O14	Al4	O12	94.5(5)
O65	P1	O66[1]	114.4(7)	O14	Al4	O13	94.5(4)
O65[1]	P1	O66[1]	65.6(7)	O65[1]	P1	O64[1]	72.2(6)

Symmetry code: [1]-x,1-y,2-z; [2]+x,3/2-y,+z. M stands for Mo (s.o.f. 0.8) + V (s.o.f. 0.2) which share the same site.

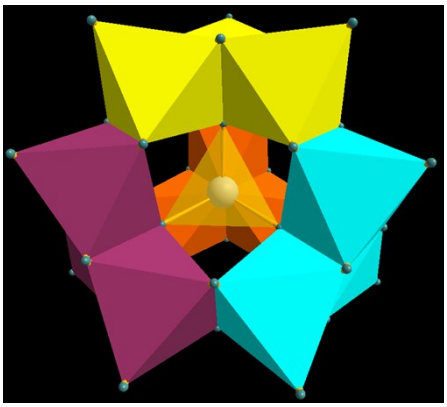

Figure S2. Polyhedral representation of ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ composed of four three-Al subclusters (one three-Al subcluster is shown in cyan, one in yellow, one in purple, and the forth in orange) surrounding a AlO_4 tetralhedron (shown in gold color) wide hexagon-shaped faces and four small triangle-shaped faces, which are composed of the edge-sharing OH ligands and terminal H_2O ligands. (H atoms of bridging OH and of aqua ligand are not shown for clarity).

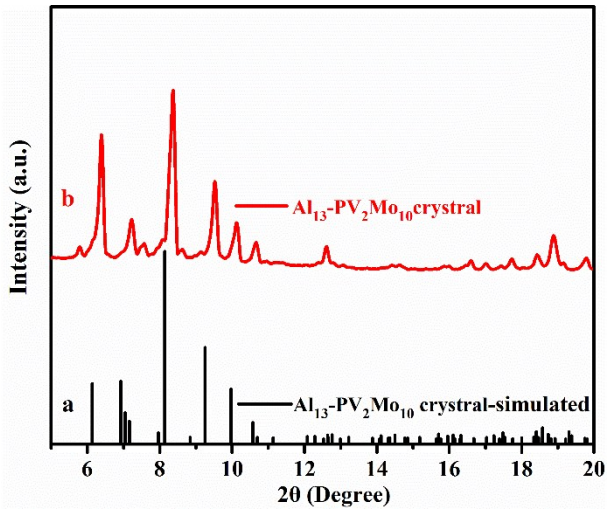

Figure S3. The simulated P-XRD patterns of Al_{13}-$PMo_{10}V_2$ crystal (a) and the experimental P-XRD patterns of Al_{13}-$PMo_{10}V_2$ crystal (b).

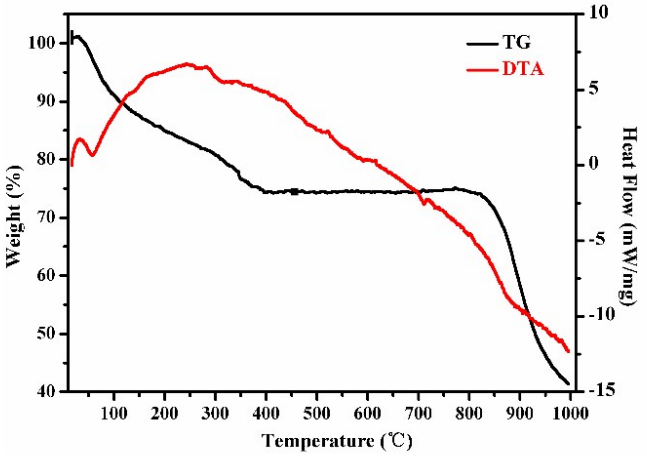

Figure S4. TG-DTA curve of Al_{13}-$PMo_{10}V_2$.

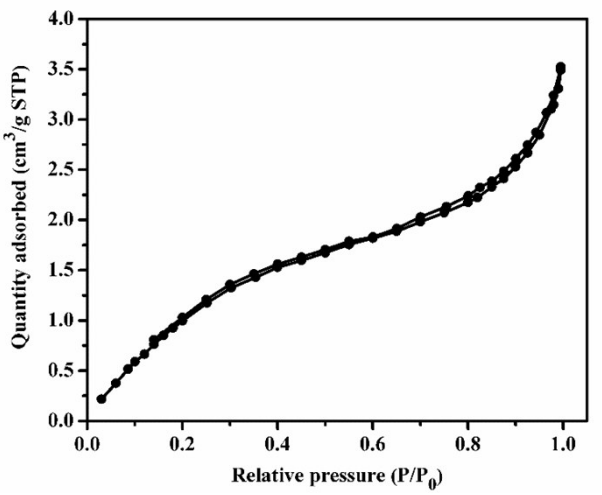

Figure S5. The N_2 adsorption/desorption isotherm plot of Al_{13}-$PMo_{10}V_2$ at 77K.

Establishment of the HD Standard Curve

The HD standard curve was established according to the Frank's method[3]. First, 5 μL of HD was dissolved in 1 mL of petroleum ether. After mixing, 200 μL of the solution was removed and added to 800 μL of petroleum ether to obtain a 1 mg/mL HD stock solution. Then, 0, 20, 40, 60, 80, and 100 μL of HD stock, and 100, 80, 60, 40, 20, and 0 μL of petroleum ether, were added into six individual centrifuge tubes, respectively. Subsequently, 100 μL of anhydrous ethanol and 200 μL of Blue reagent were added into each tube to obtain six HD standard solutions at different concentrations. The standard solutions were incubated in an 80°C water bath for 15 min, cooled to room temperature. Then, 5 μL of 0.6 mol/L acetic acid solution and 3 mL of 95% ethanol solution were added into each tube to obtain diluted standard solutions (Figure S6). UV absorbance of the standard solution was measured at the maximum absorption wavelength of λ_{max}= 445 nm (Figure S7). The absorption values were plotted against the concentration of the standard solutions. After linear fitting, the HD standard curve was obtained as $Y = 0.07718X + 0.02558$（$R^2 = 0.998$）(Eq. s1), where Y stands for absorbance λ_{max}= 445 nm and X stands for HD concentration (μg/mL).

After degradation of HD with various decontaminants, the UV absorption of the reaction solution at the maximum absorption wavelength was measured, and the residual HD concentration was calculated according to Eq. s1. Subsequently, the decontamination efficiency η of HD by various decontaminants was obtained using the equation $\eta = \left(\frac{C0 - CA}{C0}\right) \times 100\%$ (Eq. s2), where C_0 is the initial HD concentration, C_A is the remaining HD concentration after decontamination.

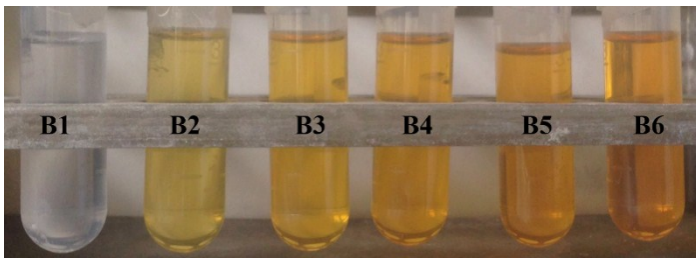

Figure S6. Image of the HD standard solutions at various concentration (B1-B6).

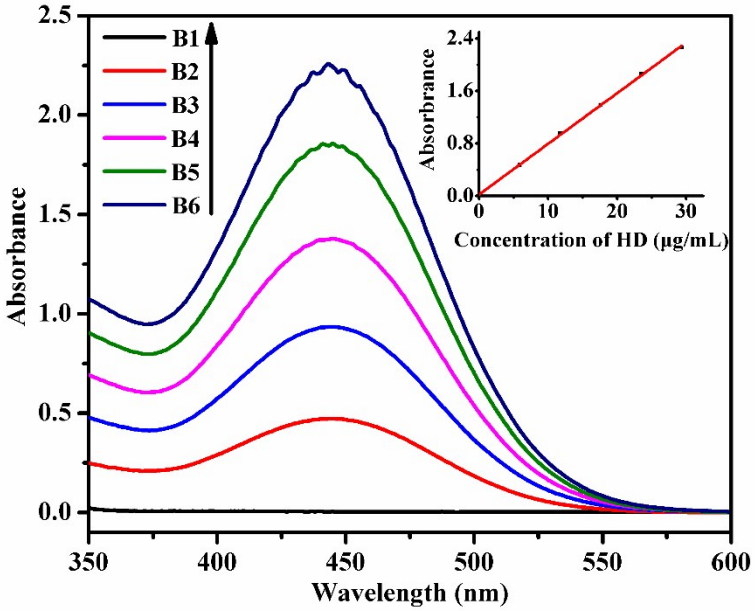

Figure S7. UV absorption spectra of the HD standard solutions. Inset: linear relationship between UV absorption and HD concentration at the maximum absorption wavelength. B1-B6: HD standard solutions with the concentration of 0, 5.874, 11.748, 17.621, 23.495, 29.369 μg/mL, respectively. Solvent: 95% ethanol.

Establishment of the GD Standard Curve

The following method was used to prepare the GD stand curve[s3]. GD (5 μL) was dissolved in 1 mL of isopropanol. After mixing, 200 μL of the solution was added to 800 μL of isopropanol to obtain a 1 mg/mL GD stock solution. GD stock solution of 0, 20, 40, 60, 80, and 100 μL were added to 100, 80, 60, 40, 20, and 0 μL of isopropanol, respectively. Subsequently, 100 μL of 0.2% (w/w) benzidine and 100 μL of 1% (w/w) sodium perborate were added to each tube to obtain GD standard solutions at different concentrations. The standard solutions were incubated in a 37°C water bath for 15 min, cooled to room temperature, and 3 mL of isopropanol were added into each tube to obtain the diluted standard solutions (Figure S8). UV absorbance was measured at 425 nm

(Figure S9). The ultraviolet absorption values were plotted against the concentration of the standard solutions. After the linear fitting, the GD standard curve was obtained as Y = 0.1368 + 0.03221X（R^2 = 0.998）(Eq. s3), where Y stands for absorbance at λ_{max}= 425 nm and X stands for GD concentration (μg/mL).

After degradation of GD with various decontaminants, the UV absorption of the reaction solution at the maximum absorption wavelength was measured, and the residual GD concentration was calculated according to Eq. s3. Subsequently, the decontamination efficiency η of GD by various decontaminants was obtained using the equation $\eta = \left(\frac{C0 - CA}{C0}\right) \times 100\%$ (eq. s4), where C_0 is the initial GD concentration, C_A is the remaining GD concentration after decontamination.

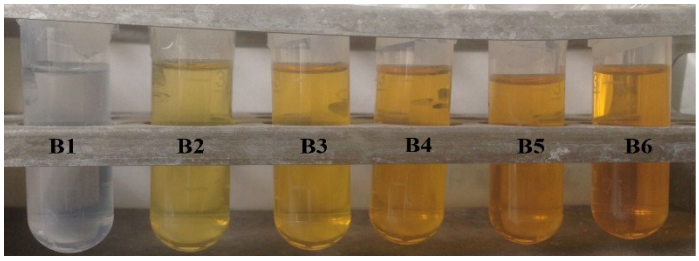

Figure S8. Image of the GD standard solutions at various concentration (B1-B6).

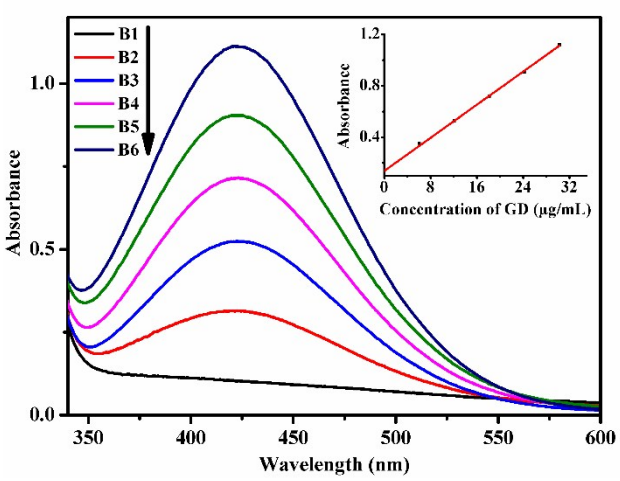

Figure S9. UV absorption spectra of the GD standard solutions. Inset: linear relationship between UV absorption and GD concentration at the maximum absorption wavelength. B1-B6: GD standard solutions with the concentration of 0, 6.061, 12.12, 18.18, 24.24, 30.31 μg/mL. Solvent: isopropanol.

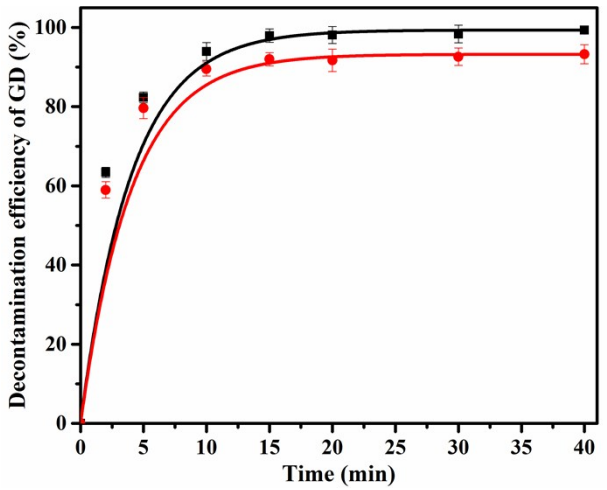

Figure S10. Comparison of the degradation efficiency of Al_{13}-$PMo_{10}V_2$ (black) and MOF-808 (red). Degradation condition: 25°C, 40 min. Degradation agent dosage: 50 mg. GD solution: 4 μL of GD dissolved in 40 μL of isopropanol solution.

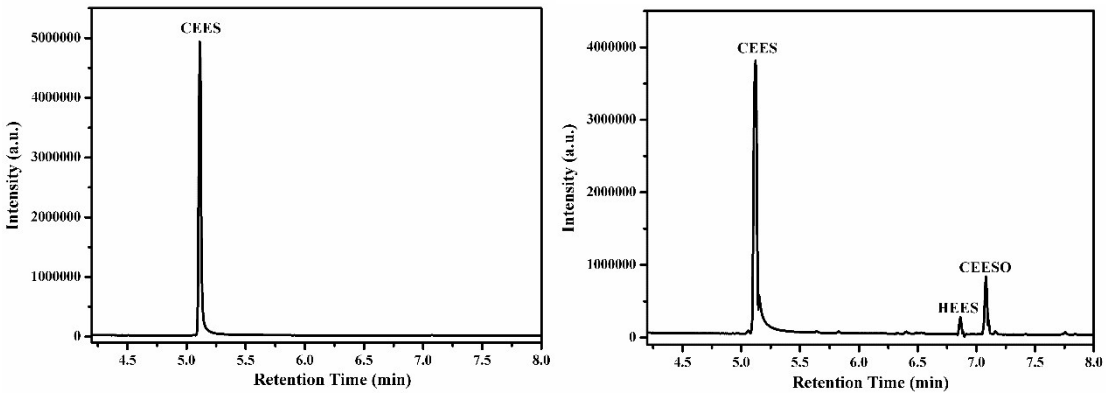

Figure S11. The GC chromatograms of pure CEES and degradation products of CEES after degradation with Al_{13}-$PMo_{10}V_2$.

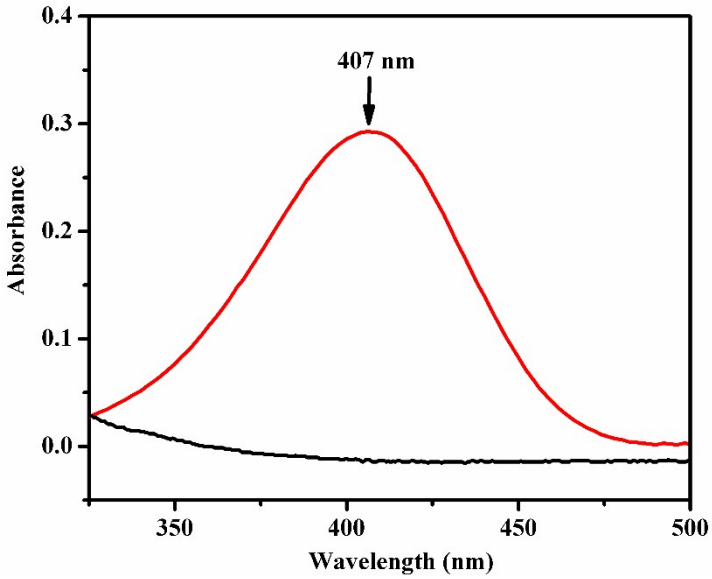

Figure S12. The UV absorption spectra of pristine DMNP (black) solution and the DMNP

solution after degradation by Al_{13}-$PMo_{10}V_2$ (red). Degradation condition: 25°C. Dosage of Al_{13}-$PMo_{10}V_2$: 50 mg. 0.5 mL of DMNP in a solution of acetone and water (9:1 v/v). Degradation time: 1 h.

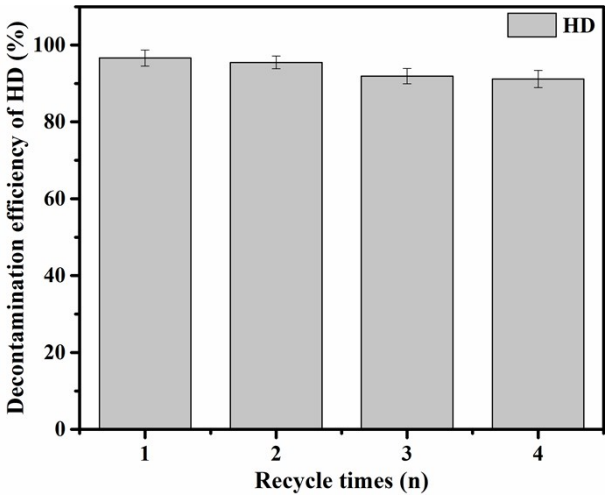

Figure S13. The reusability of Al_{13}-$PMo_{10}V_2$ for degrading HD. Degradation condition: 25°C. HD solution: 4 μL of HD dissolved in 40 μL of petroleum ether solution. Reaction time: 120 min.

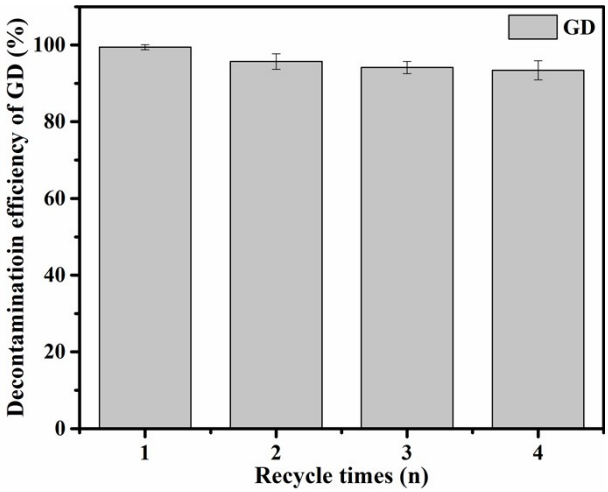

Figure S14. The reusability of Al_{13}-$PMo_{10}V_2$ for degrading GD. Degradation condition: 25°C, 40 min. GD solution: 4 μL of GD dissolved in 40 μL of isopropanol solution.

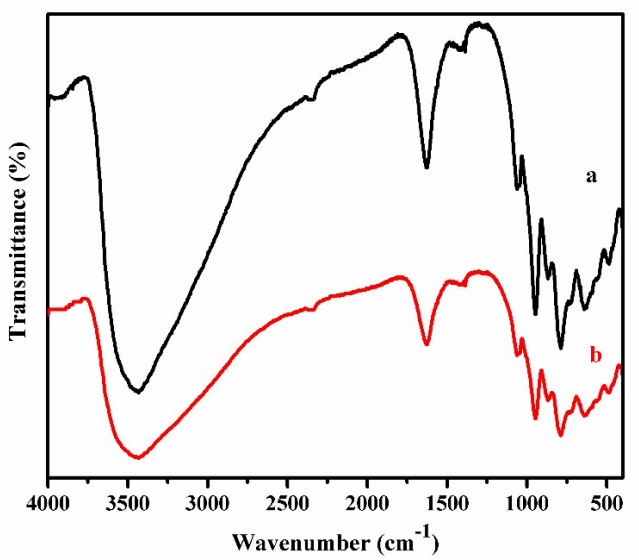

Figure S15. Infrared spectra of Al_{13}-$PMo_{10}V_2$ before (a) and after (b) degradation of HD/GD.

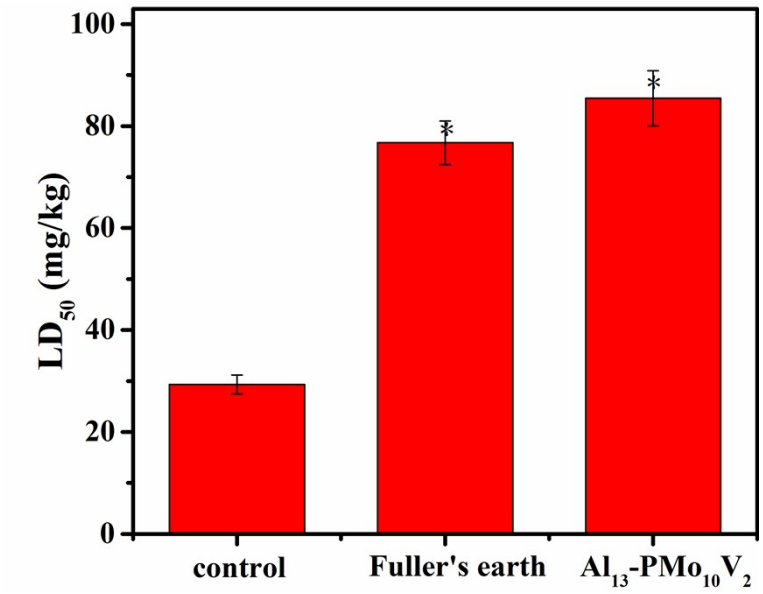

Figure S16. Median lethal dose (LD50) values for the decontamination products in mice model. Error bars = 95% confidence interval (CI). The number of animals used per treatment group was 50. All animals were challenged with neat soman (GD).

References

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