Supporting Information

Enhancing the quantum yield of singlet oxygen: Photocatalytic degradation of mustard gas simulant 2-chloroethyl ethyl sulfide catalyzed by a hybrid of polyhydroxyl aluminum cations and porphyrin anions

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1. Preparation of ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ [1]: $AlCl_3 \cdot 6H_2O$ (6 g, 25 mmol) was dissolved in 100 mL deionized water to obtain a 0.25 mol/L $AlCl_3$ solution. A 0.25 mol/L NaOH solution was obtained by dissolving NaOH (2.25 g, 56.25 mmol) in 225 mL deionized water. The $AlCl_3$ solution was stirred at 80 °C and the prepared NaOH solution was slowly dripped into the $AlCl_3$ solution (the time was longer than 15 min). At the end of the reaction, the ε-$[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ (6 mmol/L) clarification solution, referred to as Al_{13}^{7+} solution, was obtained.

2. Preparation of Al_{13}-SO_4 [1]: The 100 mL of the above Al_{13}^{7+} solution was slowly added to the 75 mL of a Na_2SO_4 solution (0.1 mol/L), and a large amount of white precipitation was formed after 1 day, which was recorded as Al_{13}-SO_4. The FTIR data (KBr, cm^{-1}): 1130 (w), 975 (w), 648 (m), 542 (s), 491 (w).

3. Preparation of the CEES standard curve

The standard curve of CEES was drawn according to Frank's method [2]: 5 μL of CEES was dissolved in 5 mL of methanol and mix well to obtain a 1 μL/mL CEES stock solution. Then, 0, 20, 40, 60, 80, and 100 μL of CEES stock solution was added into six different centrifuge tubes, followed by the addition of 100, 80, 60, 40, 20, and 0 μL of absolute ethanol to each of these tubes, respectively. Then, 100 μL of absolute ethanol and 200 μL of blue reagent (blue reagent is prepared by dissolving 0.04 g NaOH and 0.24 g thymolphthalein in a mixed solution of 2.5 mL H_2O and 17.5 mL absolute ethanol) were added to each of the tubes. The above standard solution was placed in a water bath at 80 °C for 15 min. After cooling to room temperature, 0.6 mol/L acetic acid solution (5 μL, 353 μL HAc + 647 μL distilled water) and 3 mL of 95% ethanol solution were added. At this time, the CEES standard solutions with different concentration gradients were prepared, and the absorbance at 445 nm was recorded. The absorbance and the concentration of the CEES standard solution were plotted and fitted to obtain the linear relationship of the standard curve.

The UV absorption and standard curve of CEES is shown in Figure S1. The relationship between the absorbance and concentration agrees with Eq. S1:

$$A = 00773\ C + 0.0065\ (R^2 = 0.9993) \quad \text{(S1)}$$

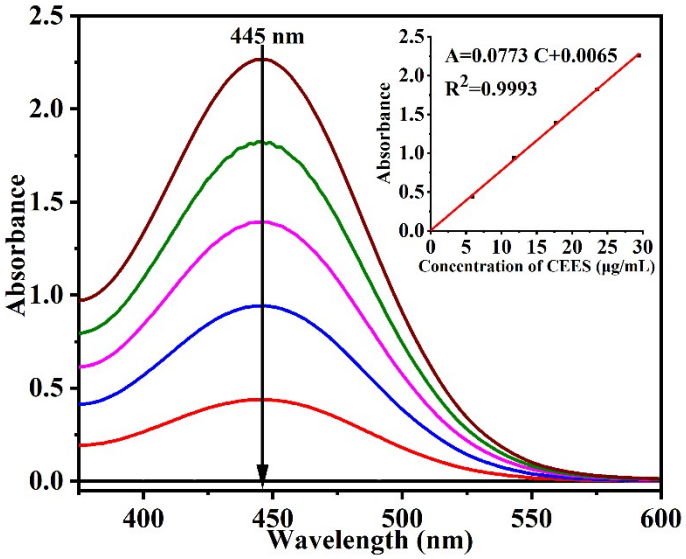

Fig. S1 UV-visible absorbance of the CEES standard solution (Inset: the linear fitting relationship between UV-visible absorbance at the maximum absorption wavelength of 445 nm and CEES concentration). Concentrations of CEES relating to the lines from bottom to top are as follows: 0, 5.874, 11.748, 17.621, 23.495, 29.369 μg/mL.

The proton NMR (^{1}H NMR) spectrum of H_4TCPP and the solid-state NMR map of ^{27}Al in Al_{13}-TCPP are shown in Figure S2. Two hydrogen protons on the central nitrogen atom of the porphyrin ring at the -2.93 ppm chemical shift, hydrogen protons from four carboxyl groups at the 13.31 ppm chemical shift, 8 hydrogen on the pyrrole ring at the 8.86 ppm chemical shift, and 16 hydrogen on the benzene ring in the 8.33 ~ 8.40 ppm range can be seen in the 8.86 ppm chemical shift, which is consistent with the reported literature [3].

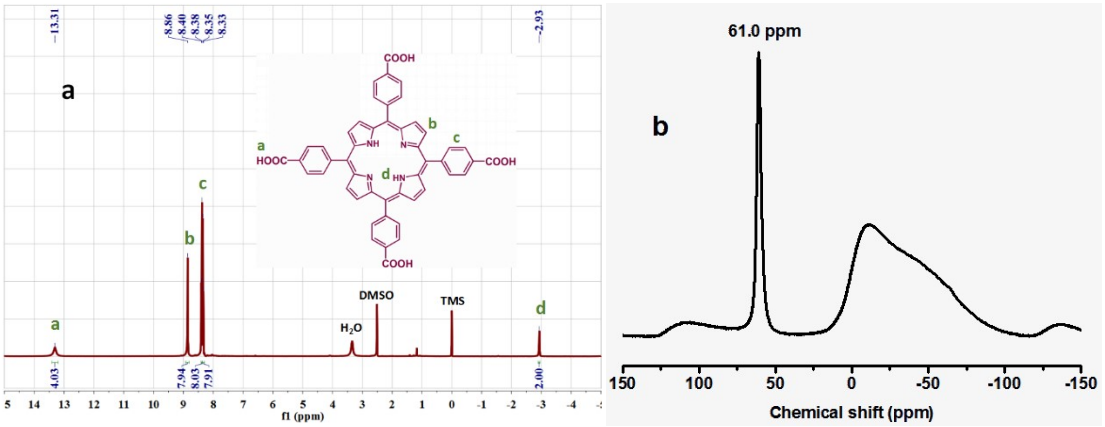

Fig. S2 ^{1}H NMR spectrum of H_4TCPP recorded in DMSO-d_6 at room temperature (a) and solid-state ^{27}Al NMR spectrum of Al_{13}-TCPP (b).

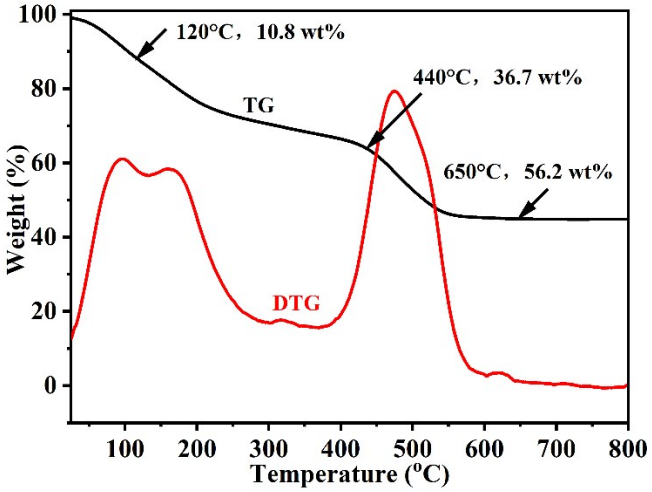

Fig. S3 TG-DTG curves of Al_{13}-TCPP.

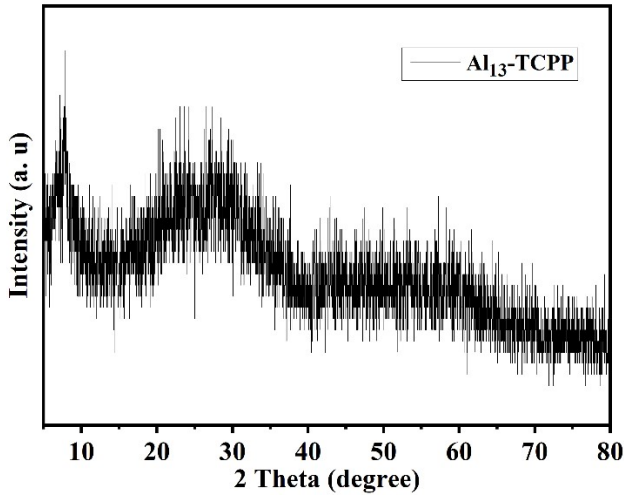

Fig. S4 Powder XRD pattern of Al_{13}-TCPP.

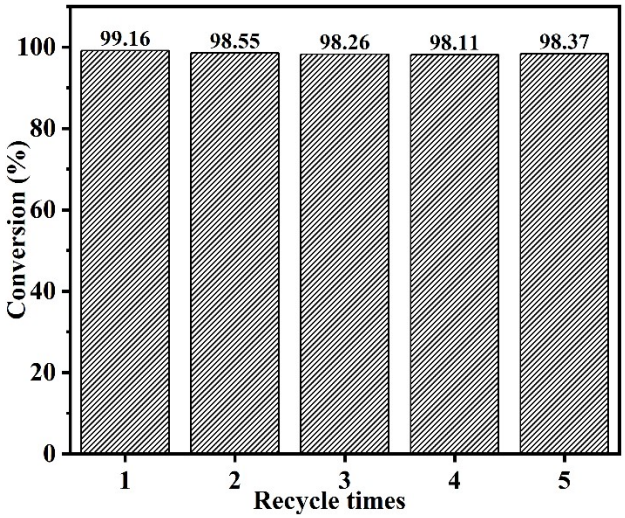

Fig. S5 The reusability of the degradation of CEES by Al_{13}-TCPP in methanol-water solvent mixture. Degradation conditions: 500 W xenon lamp ($\lambda > 400$ nm), reaction time 90 min, catalyst dosage: 5 mg Al_{13}-TCPP, 5 μL CEES.

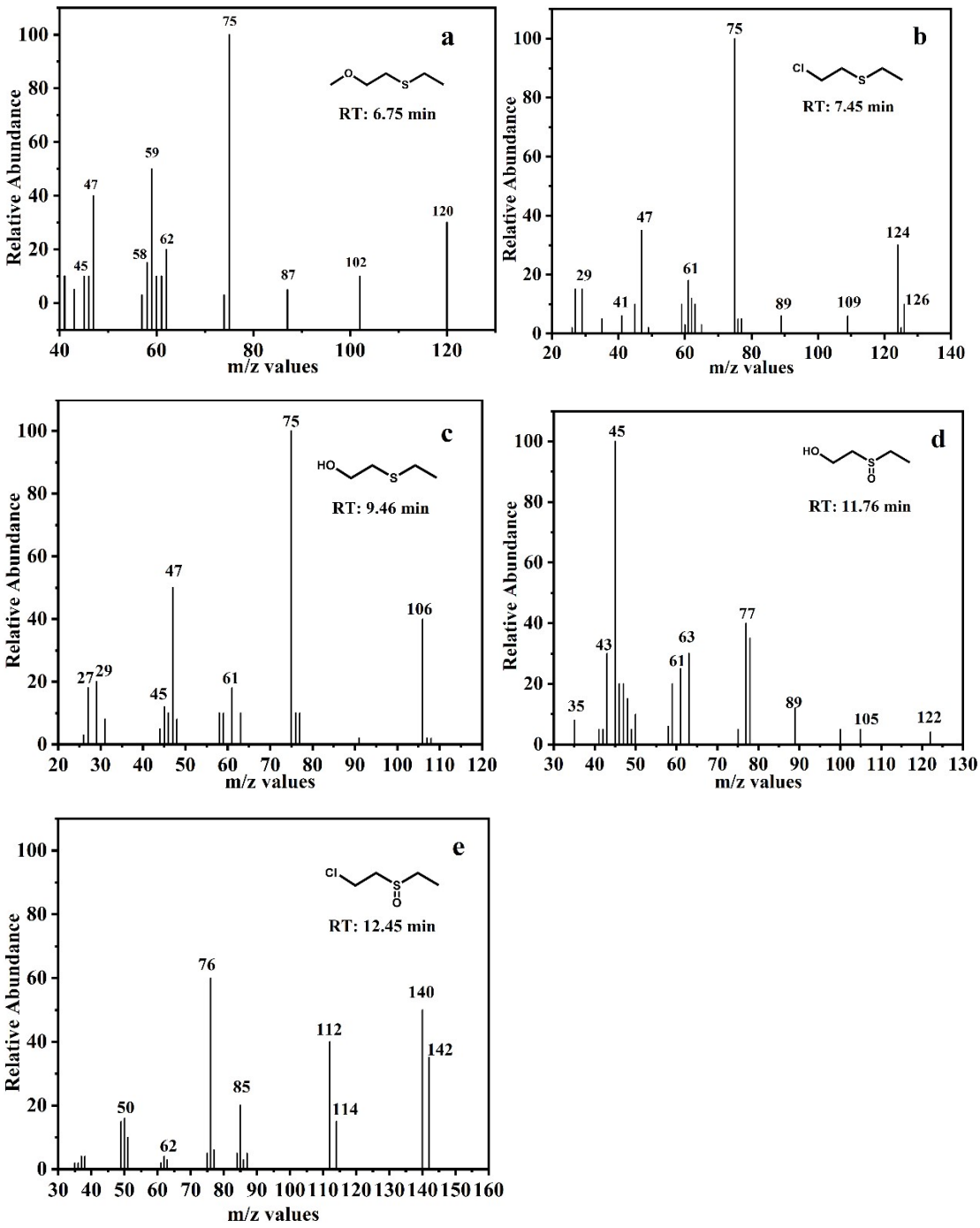

Fig. S6 MS spectra of the degradation products of CEES appearing at different retention time (RT). Degradation conditions: 500 W xenon lamp (λ > 400 nm), reaction time 180 min, solvent: 5 mL methanol, catalyst dosage: 5 mg Al_{13}-TCPP, 5 μL CEES.

Fig. S7 MS spectra of the degradation products of CEES at different retention time (RT). Degradation conditions: 500 W xenon lamp (λ > 400 nm), reaction time 90 min, solvent: 5 mL methanol-water mixed solvent (v/v = 1:1), catalyst dosage: 5 mg Al_{13}-TCPP, 5 μL CEES.

Table S1. The performance of different catalysts for the photocatalytic degradation of CEES by singlet oxygen

catalyst	Catalyst loading (compared to CEES)	oxidant	half-life (min)	light source (wavelength)	reference
PCN-222	4mol%	O_2	12 min	blue LED (470nm)	[4]

NU-1000	1mol%	O_2	6 min	UV (390-400 nm)	5
NU-400	1mol%	O_2	15 min	UV (390-400 nm)	6
Ag_{12}TPyP	1mol%	O_2 Air	1.5min 6min	white LED (450-460nm)	7
MOF-545	1mol%	O_2	6 min	blue LED (450nm)	8
UMCM-313	1mol%	O_2	4 min	blue LED (450nm)	8
Al_{13}-TCPP	0.0375mol%	Air	14.7 min	xenon lamp (>400nm)	this work

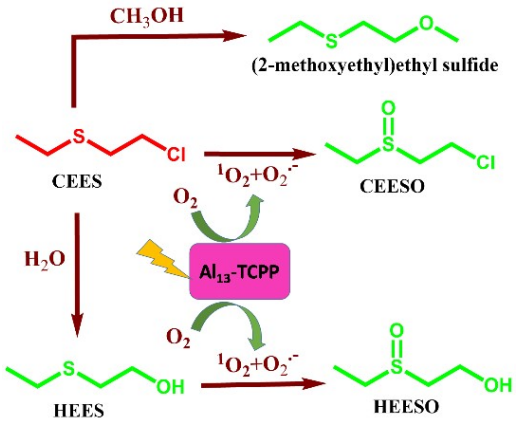

Fig. S8 The products of the catalytic degradation of CEES by Al_{13}-TCPP in methanol and methanol-water solvent mixture.

References

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