

Supporting Information

**Vapor phase catalytic photooxidation of sulfides to sulfoxides: application
to the neutralization of sulfur mustard simulants**

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1) General

Chemicals were purchased from Merck Sigma-Aldrich, Acros Organic, Fluka and Fisher Scientific and used without further purification. Authentic CEESO/CEESO₂ were prepared by previously reported methods and isolated.^[1] CDCl₃ and MeOD were purchased from Eurisotop. ¹H-NMR spectra were recorded in CDCl₃ on a Bruker Avance DPX 400 spectrometer operating at 400 MHz. GC-MS analyses were performed on two distinct apparatus: i) HP 6890 Series gas chromatograph system coupled to a HP 5973 mass selective detector, or ii) ThermoScientific Trace 1300 GC system equipped with a single quadrupole mass spectrometer detector, using the following sequences : i) iso 70 °C (2 min), grad 30 °C min⁻¹ (1 min), grad 50 °C min⁻¹ (4 min), iso 300 °C (2 min); ii) iso 60 °C (3 min), grad 40 °C min⁻¹ (6 min), iso 300 °C (1 min). Calibration curves were measured for 1 μL injections of 1, 2, 3, 4, 5 mM solutions of CEES, HEES, CEESO and CEESO₂ in acetone containing 2.5 mM of 1,3-dichlorobenzene (DCB) as an internal standard. The following retention times were obtained: HEES (R_{T1} = 3.67 min, R_{T2} = 4.64 min), CEES (R_{T1} = 3.71 min, R_{T2} = 4.68 min), DCB (R_{T1} = 4.25 min, R_{T2} = 5.32 min), CEESO (R_{T1} = 5.27 min, R_{T2} = 6.47 min), CEESO₂ (R_{T1} = 5.35 min, R_{T2} = 6.56 min). For the kinetic experiments, 20 μL of the analyte solution (containing 4 μmol CEES-derived products) was diluted in acetone containing DCB (2.5 μmol). White LED wires (Inspire Ledflexi kit, 4000 K, 7.8 W, 1.5 m, 400 lm/m) were purchased from Leroy Merlin.

2) Procedure for the photocatalytic oxidation in the gas phase

A typical procedure is given for the oxidation of 2-chloroethylethylsulfide (CEES): meso-Tetraphenylporphyrin (TPP, 100 μL of a 2 mM solution, 0.2 μmol) in CHCl₃ is deposited on a filter paper (1 × 5 cm) and allowed to dry for 2 min. The paper is then connected to a hook attached to the inner portion of a rubber septum. Neat 2-chloroethylethylsulfide (23.5 μL, 200 μmol) is introduced in a 25 mL round-bottom flask (filled with air) which is closed with the rubber septum (connected to the paper-supported TPP). The vertical position of the paper is adjusted in order to stand 1 cm from the bottom of the RbF. The flask is positioned in a beaker (7 cm diameter) fitted with white LED wires (Fig. S2). The reaction is initiated by switching the LED wire ON, and it is then stopped by switching it OFF after the specified reaction time (usually 1 h). After cooling down for 5 min, the filter paper is removed and the flask and filter paper are washed with CDCl₃, transferred to a tinted NMR tube, and analyzed by ¹H-NMR and by GC. Conversion is determined from NMR analysis of the crude mixture by comparison with authentic CEES, CEESO and CEESO₂ (Fig. S4). For absolute quantification, a solution of dioxane (20 μL, 1 M) was added to the NMR tube to serve as an internal standard.

Experiments under N₂ and O₂ atmosphere were run by pre-purging the RbF with the suitable gas for 5 min. The other sulfides and photosensitisers were tested under similar conditions (200 μmol substrate, 0.1 mol% photocatalyst), except for the phthalocyanine photosensitiser which was deposited as a 1 mM suspension in CHCl₃ (due to solubility issues).

3) Procedure for the photocatalytic oxidation in the liquid phase

meso-Tetraphenylporphyrin (100 μL of a 2 mM solution in CDCl₃, 0.2 μmol) is added to a 25 mL round-bottom flask containing 900 μL CD₃OD and filled with air. 2-Chloroethylethylsulfide (23.5 μL, 200 μmol) is then added and the flask is closed with a rubber septum. The flask is positioned in a beaker and illuminated with white LEDs for 1 h using the same setup as above (no stirring). The product distributions are analyzed directly by ¹H-NMR. For absolute quantification, a solution of dioxane (20 μL, 1 M) was added to the NMR tube to serve as an internal standard.

4) Supplementary figures

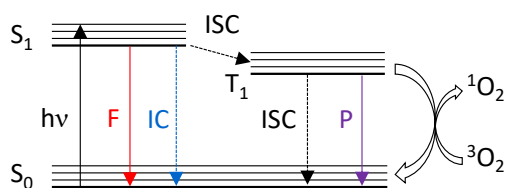


Figure S1 – Jablonski diagram representing singlet oxygen production upon irradiation of a photosensitiser (F = Fluorescence, P = Phosphorescence, IC = Internal Conversion, ISC = Inter-System Conversion, S_0 = singlet ground state, S_1 = singlet excited state, T_1 = triplet excited state).

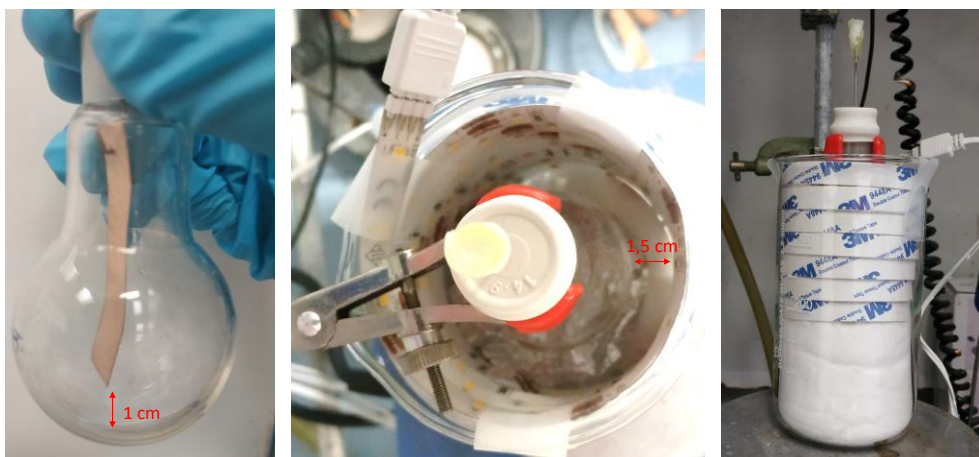


Figure S2 – (left) Positioning of the filter paper in the RbF; (middle and right) Positioning of the RbF in the LED-containing beaker in top and side-view.

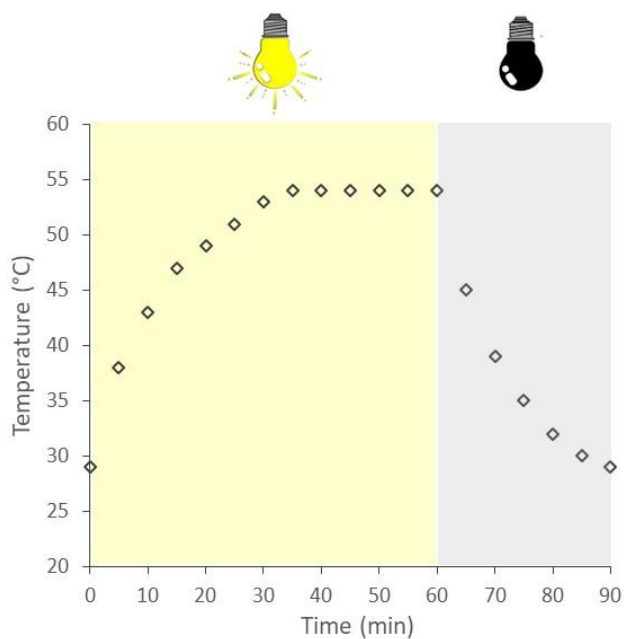


Figure S3 – Temperature monitoring inside the flask (without substrate/catalyst) for the gas-phase oxidation setup: the white LED is switched ON at $t = 0$ min and switched OFF at $t = 60$ min. A thermometer was inserted in the flask and the temperature was read at constant interval. Separate experiments were run and stopped after different illumination times (30, 45, 60, 90 and 120 min).

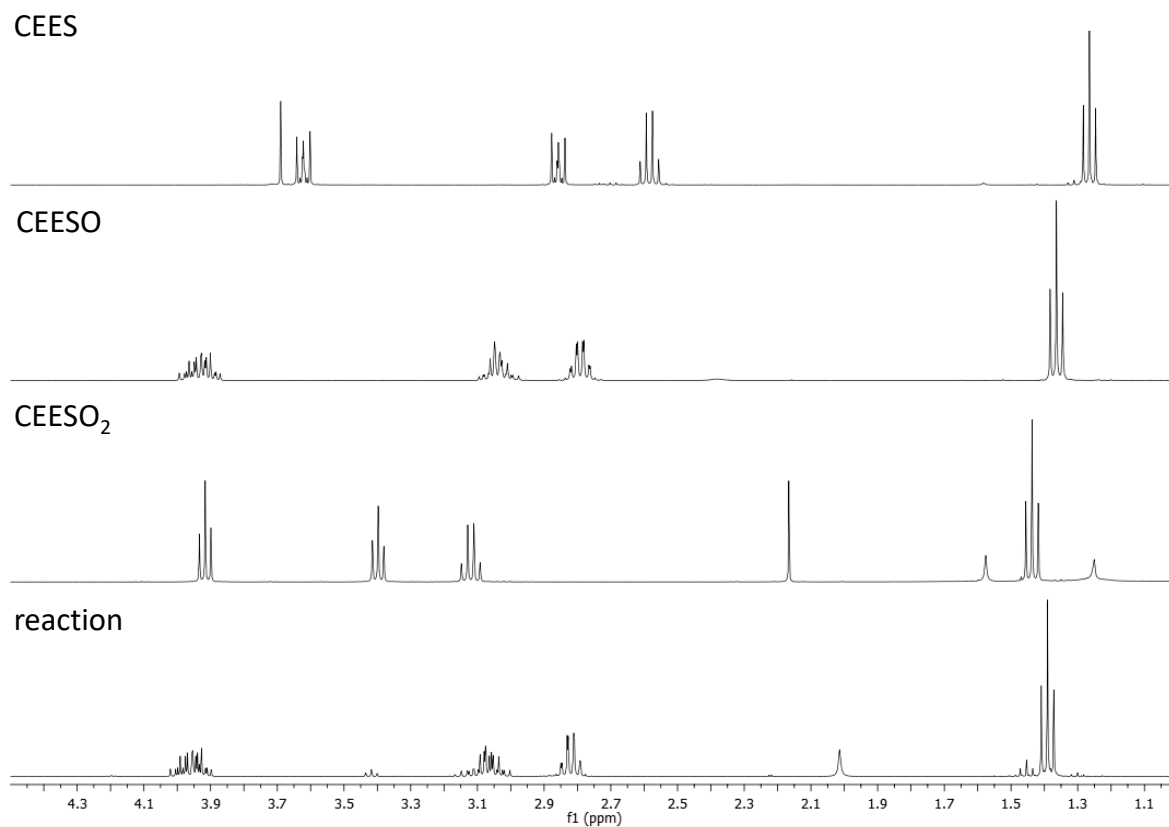


Figure S4 – $^1\text{H-NMR}$ spectra alignment for pure 2-(chloroethyl)ethylsulfide (CEES), 2-(chloroethyl)ethylsulfoxide (CEESO), 2-(chloroethyl)ethylsulfone (CEESO₂) and the reaction mixture recovered after gas-phase photocatalytic oxidation of CEES by TPP/air system for 1 h.

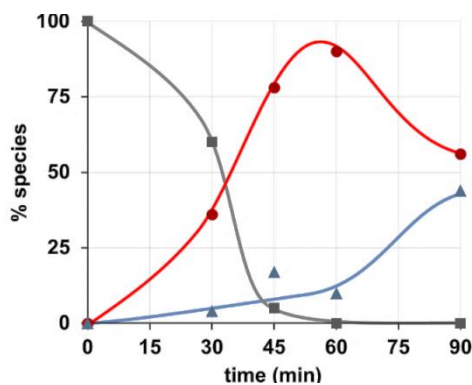


Figure S5 – Evolution of the species distribution over time for the gas-phase photocatalytic oxidation of CEES (200 μmol) in the presence of TPP (0.1 mol%) on the filter paper and under white LED illumination. The % species is determined based on $^1\text{H-NMR}$ integration based on the formula: $I_{\text{species}} / (I_{\text{CEES}} + I_{\text{CEESO}} + I_{\text{CEESO}_2})$ with (■) CEES, (●) CEESO, and (▲) CEESO₂. NB: each species distribution shown corresponds to a distinct experiment.

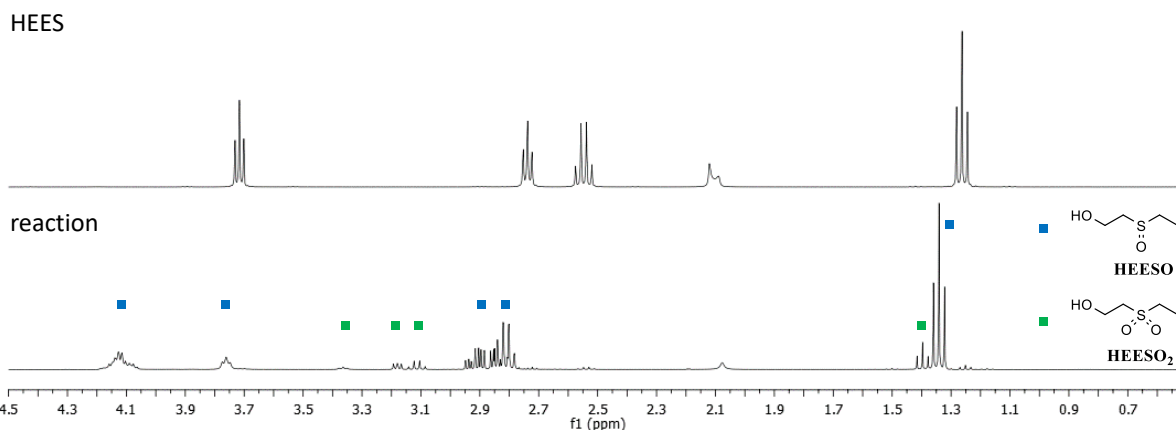


Figure S6 – $^1\text{H-NMR}$ spectra alignment for pure 2-hydroxyethylethylsulfide (HEES) and the reaction mixture recovered after gas-phase photocatalytic oxidation for 8 h. The peak assignment for 2-hydroxyethylethylsulfoxide (HEESO) and 2-hydroxyethylethylsulfone (HEESO₂) is consistent with a previous report.^[2]

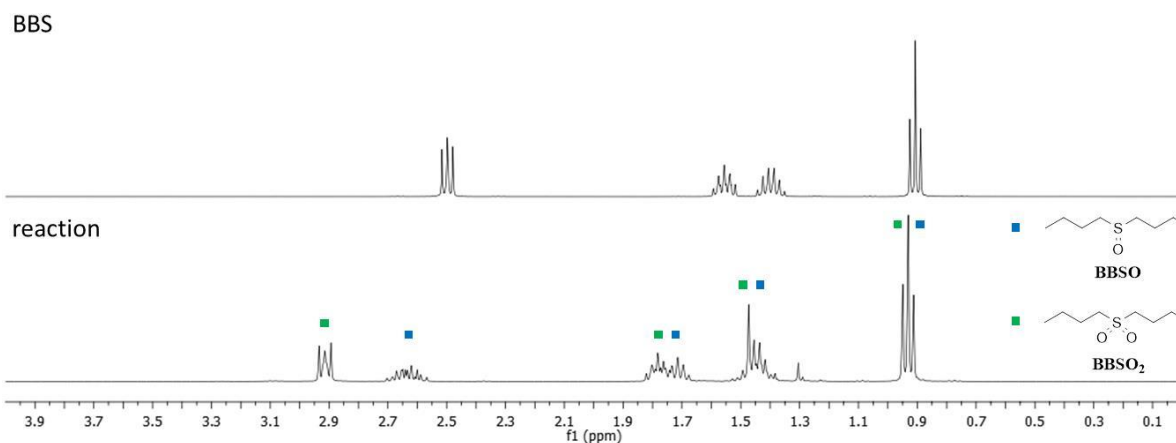


Figure S7 – $^1\text{H-NMR}$ spectra alignment for pure di-*n*-butylsulfide (BBS) and the reaction mixture recovered after gas-phase photocatalytic oxidation for 2 h. The peak assignment for di-*n*-butylsulfoxide (BBSO) and di-*n*-butylsulfone (BBSO₂) is consistent with a previous report.^[3]

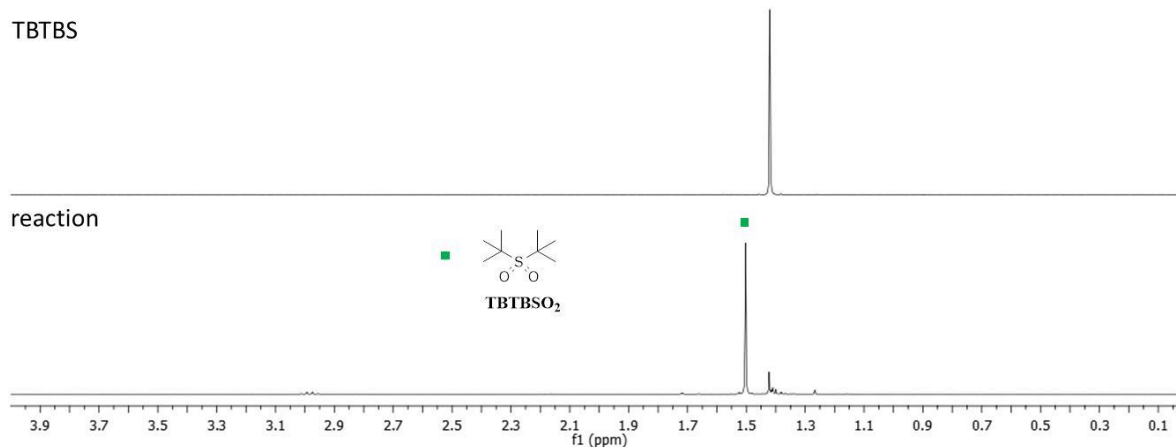


Figure S8 – $^1\text{H-NMR}$ spectra alignment for pure di-*tert*-butylsulfide (TBTBS) and the reaction mixture recovered after gas-phase photocatalytic oxidation for 8 h. The peak assignment for di-*tert*-butylsulfone (TBTBSO₂) is consistent with the literature.^[4,5] The absence of the signal at 1.33 ppm indicates the absence of di-*tert*-butylsulfoxide (TBTBSO).^[6,7]

EES

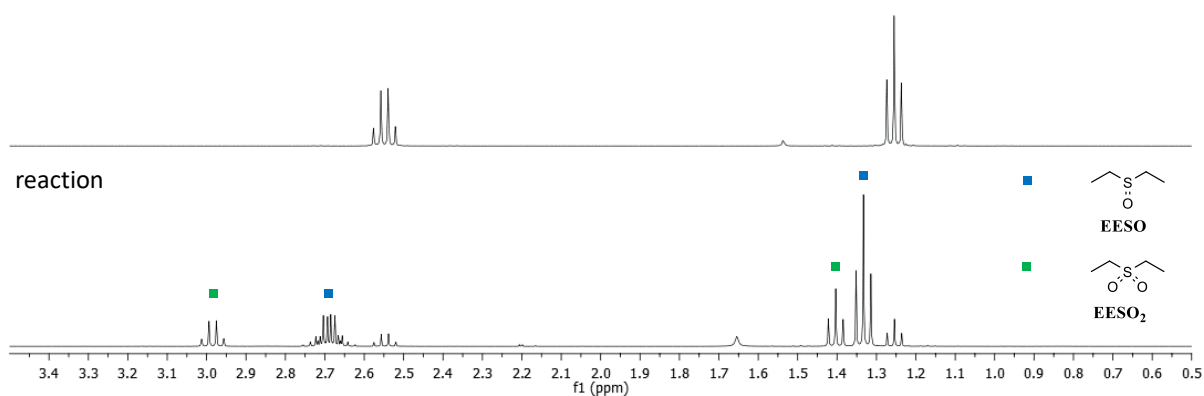


Figure S9 – ¹H-NMR spectra alignment for pure diethylsulfide (EES) and the reaction mixture recovered after gas-phase photocatalytic oxidation for 8 h. The peak assignment for diethylsulfoxide (EESO) and diethylsulfone (EESO₂) is consistent with previous reports.^[8,9]

VES

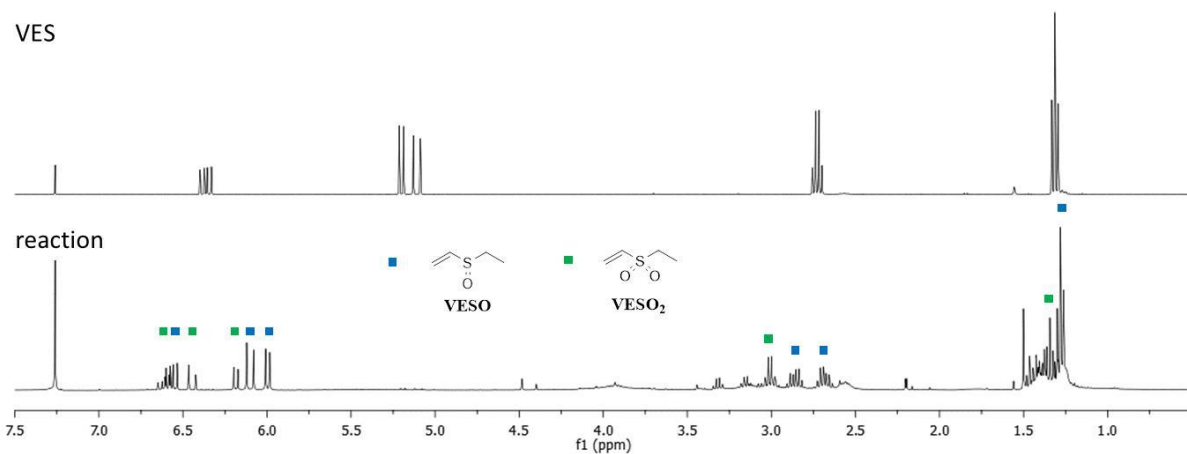


Figure S10 – ¹H-NMR spectra alignment for pure vinyl ethyl sulfide (VES) and the reaction mixture recovered after gas-phase photocatalytic oxidation for 2 h. The peak assignment for vinyl ethyl sulfoxide (VESO) and vinyl ethyl sulfone (VESO₂) is consistent with previous reports.^[10,11]

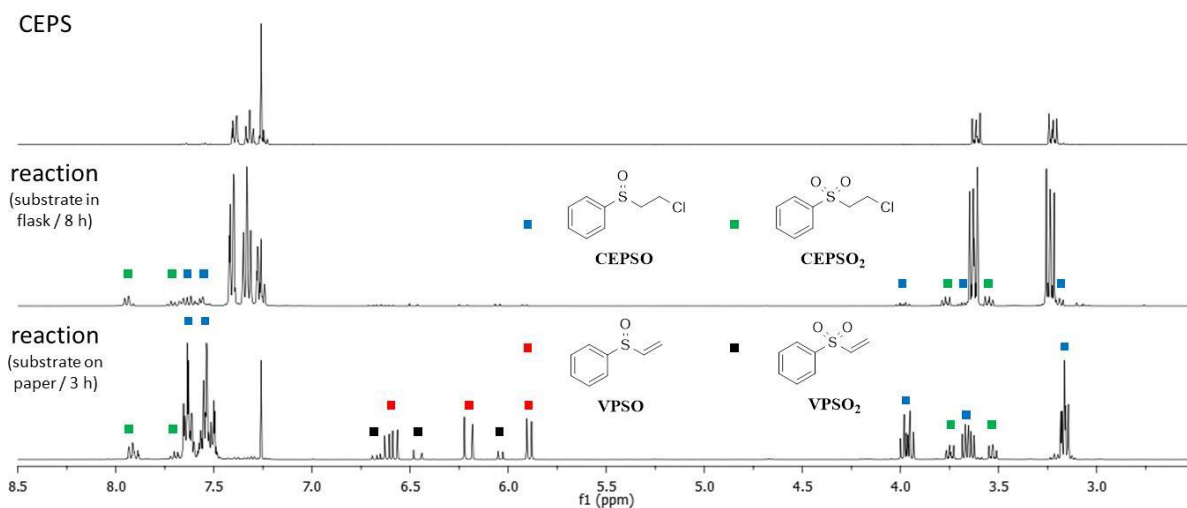


Figure S11 – ¹H-NMR spectra alignment for pure chloroethylphenylsulfide (CEPS) and the reaction mixtures recovered after gas-phase photocatalytic oxidation of CEPS run in the flask (8 h) or on the paper (3 h). The peak assignment for chloroethylphenylsulfoxide (CEPSO), chloroethylphenylsulfone (CEPSO₂), vinylphenylsulfoxide (VPSO), and vinylphenylsulfone (VPSO₂) is consistent with previous reports.^[12,13,14]

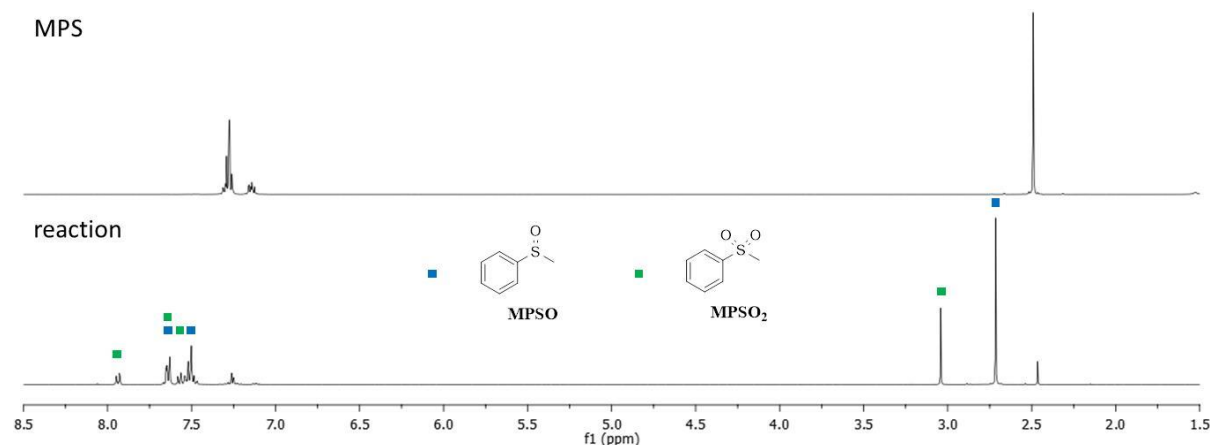


Figure S12 – ¹H-NMR spectra alignment for pure methylphenylsulfide (MPS) and the reaction mixture recovered after gas-phase photocatalytic oxidation of MPS by TPP/air system for 3 h. Assignment of the peaks for methylphenylsulfoxide (MPSO) and methylphenylsulfone (MPSO₂) is consistent with previous reports.^[8,10]

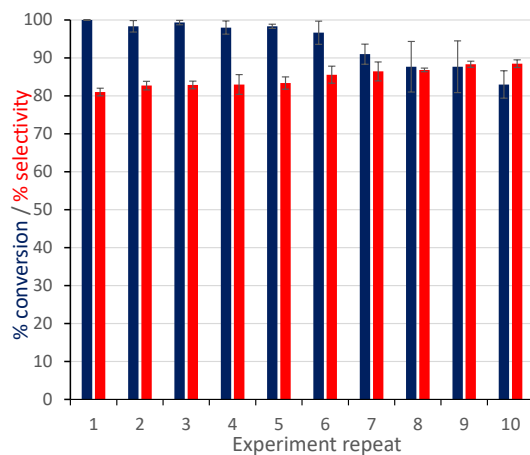


Figure S13 – Histograms representing the % of conversion (■) and % of selectivity to sulfoxide (■) for successive CEES oxidation experiments in the gas-phase re-using the same piece of paper embedded with the TPP photocatalyst (0.1 mol%). Experiments were performed in triplicate and the error bars represent the standard deviation.

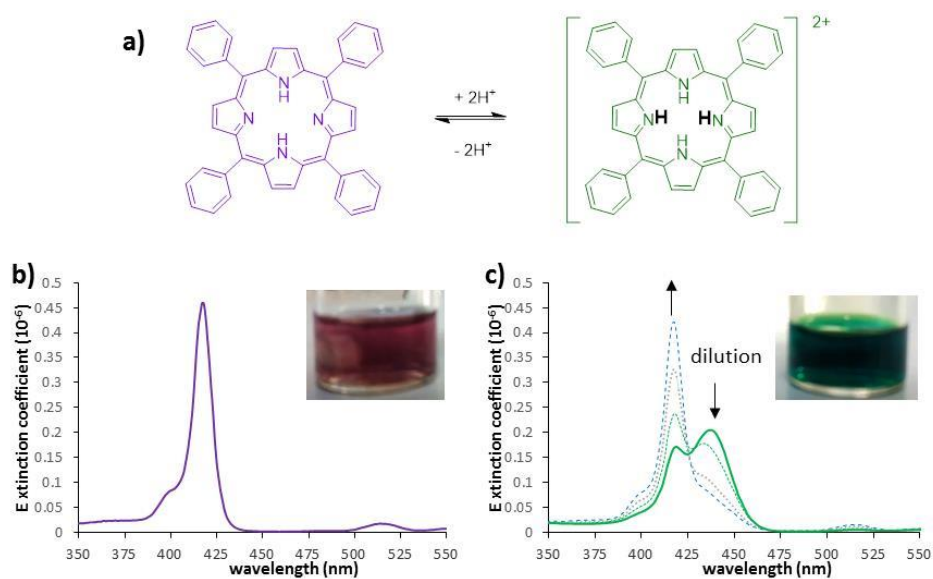
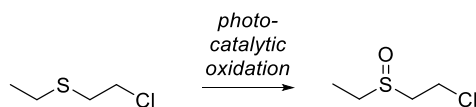


Figure S14 – a) Representation of TPP and $[TPPH_2]^{2+}$; b) UV-vis spectra recorded for the reaction mixture before the addition of CEES diluted 200-folds (Inset is the picture of the undiluted reaction mixture before CEES addition); c) UV-vis spectra recorded for the reaction mixture after CEES addition and 1.5 h illumination diluted either 200 (---), 100 (···), 50 (- - -), 25-fold (—) (Inset is the picture of the undiluted reaction mixture after CEES addition and 1.5 h illumination).

5) Supplementary table

Table S1. Performances of selected systems in the selective photocatalytic oxidation of the sulfur mustard simulant 2-(chloroethyl)ethylsulfide.



Photocatalyst	Conditions	Medium	Loading (mol%)	Time (min)	Conv./Sel. (%)	Reference
Tetraphenyl porphyrin	white LED Air	Gas phase	0.1	60	100/92	This work
Acetylated riboflavin	450 nm O ₂	CH ₃ CN/H ₂ O	2	10	100/82	<i>Adv. Synth. Catal.</i> 2016, 358 , 1654
Porphyrin-based Zr-MOF	blue LED O ₂	Ethylmorpholine/ MeOH	4	60	95/ -	<i>ACS Nano</i> 2015, 9 , 12358
Methylene Blue	610 nm 9 bar O ₂ or air Flow reactor	EtOH	0.06	4	99/98	<i>Green Chem.</i> , 2020, 22 , 4105
BODIPY	blue LED O ₂ atm	MeOH	0.8	30	Quant/ -	<i>ACS Appl. Mater. Interf.</i> 2018, 10 , 18771
[Y(H ₉ TPPA)(H ₂ O) _x]Cl ₂ ·yH ₂ O	blue LED O ₂	MeOH	2	28	Quant/-	<i>ACS Appl. Nano Mater.</i> 2019, 2 , 465
Pyrene-based MOF	UV LED O ₂	MeOH	1	15	Quant/99	<i>J. Mater. Chem. A</i> , 2016, 4 , 13809
TPP	tungsten lamp O ₂	CDCl ₃	2	3.5	64/87	<i>Tetrahedron Lett.</i> 1999, 40 , 6519
Zinc phthalocyanine	halogen lamp air	neat	0.5	1440	- 40/ -	<i>ACS Appl. Mater. Interf.</i> 2013, 5 , 10191

6) References

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