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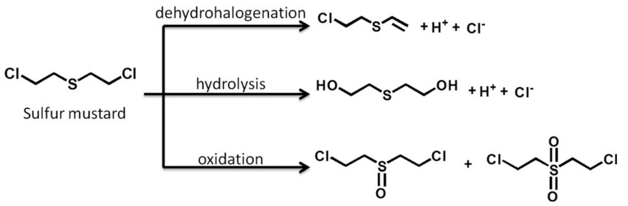
# Selective Photooxidation of a Mustard-Gas Simulant Catalyzed by a Porphyrinic Metal–Organic Framework**

*Yangyang Liu, Ashlee J. Howarth, Joseph T. Hupp,* and Omar K. Farha**

**Abstract:** *The photooxidation of a mustard-gas simulant, 2-chloroethyl ethyl sulfide (CEES), is studied using a porphyrin-based metal–organic framework (MOF) catalyst. At room temperature and neutral pH value, singlet oxygen is generated by PCN-222/MOF-545 using an inexpensive and commercially available light-emitting diode. The singlet oxygen produced by PCN-222/MOF-545 selectively oxidizes CEES to the comparatively nontoxic product 2-chloroethyl ethyl sulfoxide (CEESO) without formation of the highly toxic sulfone product. In comparison to current methods, which utilize hydrogen peroxide as an oxidizing agent, this is a more realistic, convenient, and effective method for mustard-gas detoxification.*

The first large-scale attack involving a chemical warfare agent (CWA) in modern history occurred in Ypres, Belgium during World War I when chlorine gas was used by the German army.[1] After this initial attack, the advancement of chemical weapons became a major focus throughout World War I leading to the development of blood, choking, and blistering agents.[2] The most effective CWA used in World War I was the blistering agent sulfur mustard, also known as mustard gas or HD.[3] Despite the subsequent development of more toxic chemical weapons, including nerve agents, and despite an international ban on its use, sulfur mustard has remained a chemical weapon of choice in modern warfare and is still considered to be one of the most effective chemical weapons when used in modern combat.[4] As a consequence, it is important to develop materials that are capable of catalytically degrading sulfur mustard, not only to prevent human exposure by incorporating materials in gas-mask filtration systems but also to detoxify sulfur mustard stockpiles.[5]



*Scheme 1.* Three pathways of sulfur-mustard detoxification: dehydrohalogenation, hydrolysis, and oxidation.

Sulfur mustard (i.e., bis(2-chloroethyl)sulfide) can be degraded and detoxified by dehydrohalogenation,[6] hydrolysis,[7] or oxidation[8] (Scheme 1). The dehydrohalogenation degradation pathway is too slow to be effective for decontamination applications.[5–6] Detoxification by hydrolysis is also limited by the low solubility of sulfur mustard in water and the formation of intermediate products that slow down the hydrolysis.[9] As a result, partial oxidation of sulfur mustard to bis(2-chloroethyl)sulfoxide has been established to be the most promising detoxification route; however, overoxidation of the sulfoxide to the sulfone produces a blistering agent that is just as toxic as sulfur mustard itself (see Scheme 1, oxidation). It is therefore markedly important to control the oxidation of sulfur mustard such that only bis(2-chloroethyl)sulfoxide is generated. One way to achieve control over product formation is to use a mild oxidant that selectively produces only the partially oxidized sulfoxide.[8f]

Extensive research has been performed on the oxidation of sulfides to sulfoxides and sulfones,[10] with numerous studies focusing on the mild and selective oxidation of sulfides to sulfoxides to the exclusion of sulfones. Prominent among investigated oxidants is singlet oxygen ($^1O_2$).[11] The most common method of producing $^1O_2$ is based on the energy transfer from an excited triplet state of a photosensitizer to ground-state molecular oxygen ($^3O_2$).[12] This process has been studied in great detail; thus there exists an extensive library of dyes for the efficient production of $^1O_2$.[13] Prominent among them are both naturally occurring and artificial porphyrins and porphyrin derivatives.[13a,14] Unfortunately, owing to their lipophilic nature, many porphyrins aggregate in aqueous environments, even at low concentration, thus hindering their practical applications as photosensitizers.[15] One approach to overcoming aggregation and deactivation is to configure porphyrins as linkers in metal–organic frameworks (MOFs). For three-dimensional (3D) MOFs with porous, non-catenated structures, site isolation (dye isolation) is a natural outcome.

In general, the 3D structure of MOFs is constructed from organic linkers and metal nodes.[16] The functionality and topology of MOFs can be tuned by changing the geometry

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and functional groups of the organic linkers, and by using different metals ions. Recently, $Zr^{IV}$-based MOFs have been studied extensively for applications in heterogeneous catalysis, mainly owing to their exceptional stability and tunable functionalities.[17] Furthermore, the high surface area[18] and permanent porosity of MOFs can lead to enhanced interactions between a substrate and an active site incorporated into the framework, thus accelerating the catalysis. This behavior is especially important for catalytic processes, including the decontamination of chemical warfare agents such as nerve agents or mustard gas, where degradation time is critical.[19] To this end, the MOF-catalyzed hydrolysis of organophosphate nerve agents and their simulants has been of particular interest to our group.[20] Herein, we present the first example of a MOF used as a heterogeneous catalyst for the oxidative degradation of a mustard-gas simulant.

In view of the porphyrin functionality, high porosity, and exceptional stability of PCN-222/MOF-545 (**1**), we selected this MOF as a heterogeneous catalyst for the photooxidation of the mustard-gas simulant 2-chloroethyl ethyl sulfide (CEES). As shown in Figure 1, free-base PCN-222/MOF-545 (fb-**1**), consisting of tetrakis(4-carboxyphenyl)porphyrin linkers ($TCPP^{4-}$; Figure 1 a) and eightfold connected $Zr_6$ nodes (Figure 1 b), features channels with diameters of 3.7 and 1.6 nm (Figure 1 c, d). MOF fb-**1** is stable over a wide pH range and can be readily synthesized from $ZrCl_4$, $H_4TCPP$, and benzoic acid in DEF (*N,N′*-diethylformamide).[17e] Nitrogen adsorption experiments (Supporting Information, Figures S2 and S3) and powder X-ray diffraction (PXRD, Figure S4) confirmed the activation of fb-**1**.

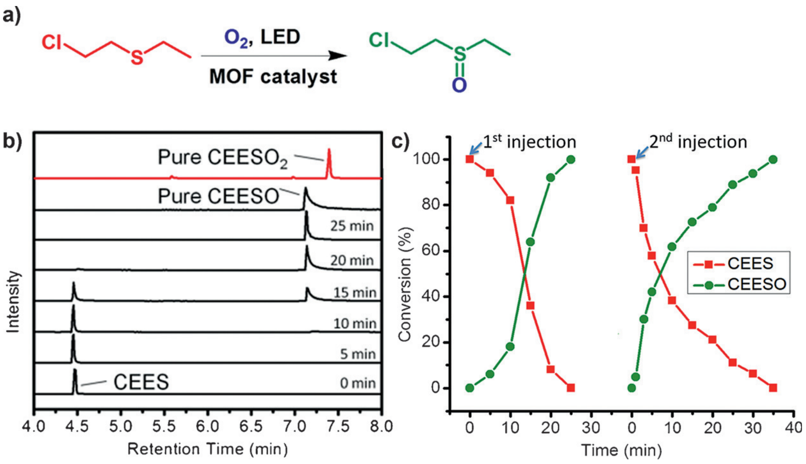

*Figure 2.* a) Photooxidation of CEES under LED irradiation and $O_2$ atmosphere catalyzed by MOF-based catalyst fb-**1**. b) Gas chromatography (GC) signals indicating the progress of the oxidation of CEES (4.45 min) to CEESO (7.14 min) in the presence of fb-**1** (1.2 mg). For comparison, chromatograms of pure CEESO (7.14 min) and pure $CEESO_2$ (7.38 min) were also recorded, confirming that CEESO was the only product. c) Oxidation profile of CEES in the presence of fb-**1** (1.2 mg) while being irradiated with a blue LED with two consecutive injections of CEES (0.2 mmol).

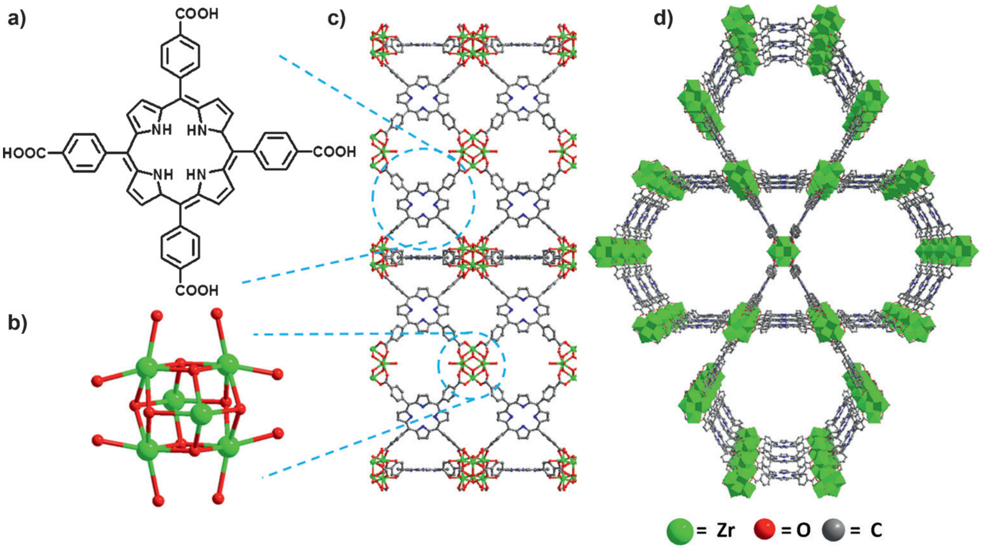

*Figure 1.* Structure of free-base PCN-222/MOF-545 (fb-**1**). a) Tetrakis(4-carboxyphenyl)porphyrin linker, $H_4TCPP$. b) $[Zr_6(\mu_3\text{-}O)_8(O)_8]^{8-}$ node. c) MOF fb-**1**, viewed along the *a* axis. d) 3D structure of fb-**1**, viewed along the *c* axis. Hydrogen atoms are not shown in the structure for clarity.

Previous research has shown that CEES is an effective simulant for sulfur mustard.[21] In most studies, either hydrogen peroxide or *tert*-butyl hydroperoxide have been used as oxidizing agents. However, owing to the strongly oxidizing nature of these reagents, two oxidation products are often observed: 2-chloroethyl ethyl sulfoxide (CEESO) and 2-chloroethyl ethyl sulfone ($CEESO_2$).[22] Given that $CEESO_2$ itself is toxic, we set out to selectively oxidize CEES to CEESO, without formation of $CEESO_2$, by using a mild photooxidation method. In this approach, fb-**1** is used as a photosensitizer to produce singlet oxygen under LED irradiation. Figure 2 shows the oxidation of CEES in the presence of fb-**1** under 1 atm $O_2$ while being irradiated with a blue LED (see Figure S1 for details on the irradiation wavelength). To perform the oxidation, fb-**1** (0.5 mol %) was dispersed in methanol and sealed in a glass microwave tube before the mixture was purged with $O_2$ and irradiated for 20 min. CEES was then added to the mixture, and the reaction was monitored by GC-MS. CEESO was the only product observed, with full conversion at 25 min under these conditions (Figure 2 b). The GC-MS spectrum for pure $CEESO_2$ is also shown in Figure 2 b for comparison, confirming the product selectivity of the reaction. Fig-

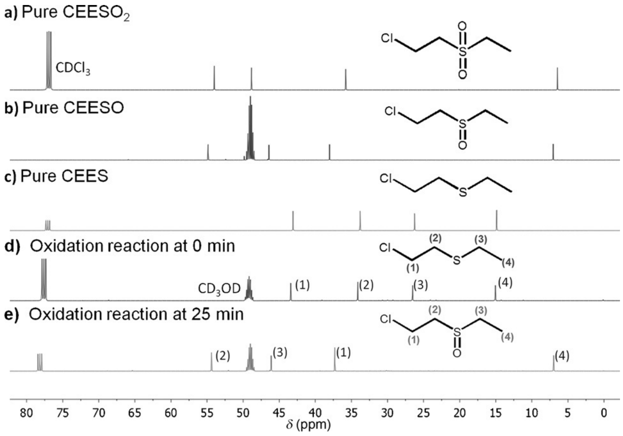

***Figure 3.*** $^{13}$C NMR spectra of a) pure CEESO$_2$ in CDCl$_3$, b) pure CEESO in CD$_3$OD, c) pure CEES in CDCl$_3$, and d) spectrum taken at 0 min before the oxidation of CEES in the presence of fb-**1** (1.2 mg). The reaction was performed at room temperature in CD$_3$OD, and the NMR sample was dissolved in CDCl$_3$. e) $^{13}$C NMR spectrum measured 25 min after oxidation started in CDCl$_3$, indicating that the oxidation was complete and only one oxidation product, CEESO, was obtained.

ure 3c illustrates the kinetics of the oxidation reaction, with two consecutive injections of 0.2 mmol CEES. The full conversion of the second aliquot indicates the reusability of the catalyst. Additional experiments, entailing four consecutive injections of substrate into the catalyst-containing suspension, revealed no loss of catalytic activity (Figure S6).

$^1$H NMR and $^{13}$C NMR spectroscopy were also used to monitor the reaction and identify the product. To eliminate solvent signals in the $^1$H NMR spectrum, CD$_3$OD was used as the reaction solvent instead of MeOH. $^1$H NMR (Figure S8) and $^{13}$C NMR (Figure 3) spectra were recorded at 0 and 25 min after the addition of CEES (Figure 3d,e). For comparison, the $^{13}$C NMR spectra of pure CEESO$_2$, CEESO, and CEES were also recorded (Figure 3a–c).

At 0 min, $^{13}$C NMR peaks at 42.9, 33.7, 26.1, and 14.6 ppm indicate the presence of the simulant CEES (Figure 3d). After 25 min, these peaks had disappeared, and new peaks were observed at 53.4, 45.1, 36.3, and 6.0 ppm, which confirmed the full conversion of CEES into CEESO after 25 min (Figure 3e). Furthermore, the $^{13}$C NMR spectrum of the reaction solution at 25 min is identical to that of CEESO (Figure 3b,e), corroborating that CEESO is the only product. This result demonstrates that singlet oxygen generated by fb-**1** upon irradiation with an inexpensive, commercially available LED is a very selective oxidant for CEES oxidation.

To study the effects of irradiation wavelength and power on the rate and selectivity of CEES oxidation, we also conducted the photooxidation reaction using inexpensive and commercially available white and red LEDs (see Figure S1 for irradiation wavelengths and power-density details). Whereas blue light leads to excitation into the Soret band of TCPP, red light excites TCPP to the Q band, and white light excites into all bands of the porphyrin visible-region absorption spectrum.[23] Regardless of the excitation wavelength, the oxidation of CEES by singlet oxygen produced from fb-**1** proved to be highly selective (Figure 4a). Under these conditions, excitation using the higher-power blue LED gives the fastest reaction time with half-lives of 13 and 7 min for the first and second injections, respectively (Figure 2c). Importantly, this selective photooxidation of CEES also worked when air was used instead of pure oxygen as the $^1$O$_2$ source with a reaction half-life of 21 min (Figure S7).

Powder X-ray diffraction (PXRD) measurements demonstrated that fb-**1** retained its structure and crystallinity after catalysis (Figure 4b). Moreover, no Zr was detected by inductively coupled plasma optical emission spectroscopy (ICP-OES, detection limit ca. 5 ppb) in the filtered solution after oxidation (Table S1). Porphyrin compounds were also not observed in the NMR spectra of the reaction solution (Figures 3 and S15–S18). Control experiments without fb-**1** revealed zero conversion of CEES (Figure S5). We can therefore conclude that the reaction is indeed heterogeneous, catalyzed by solid fb-**1**, and not by free and solubilized porphyrin molecules.

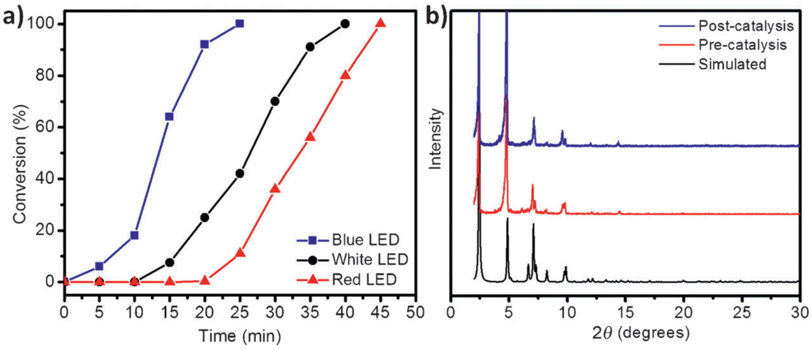

***Figure 4.*** a) Oxidation profile of CEES in the presence of fb-**1** (1.2 mg) using differently colored LEDs for irradiation: blue (blue squares), white (black dots), or red LEDs (red triangles). With all three LEDs, CEESO was observed as the only product. b) PXRD patterns of fb-**1**, pre- and post-catalysis and simulated.

Singlet oxygen sensor green (SOSG) was used to confirm the generation of $^1$O$_2$ by fb-**1** in MeOH and to determine the rate of $^1$O$_2$ production under the reaction conditions used for CEES oxidation. MOF fb-**1** was irradiated using the red LED (Figure S1) in the presence of SOSG in MeOH, and the emission from SOSG was monitored as a function of irradiation time (Figure S20a). SOSG is known to produce green fluorescence emission centered at 524 nm when it reacts with $^1$O$_2$.[24] The curve obtained by plotting the SOSG emission intensity versus the irradiation time (Figure S20b) can be fit using Eq. (1),[25] (where $I_F$ = fluorescence intensity, $t$ = irradiation time, $k$ = $^1$O$_2$ generation rate constant, and $A$ = a constant proportional to the amount of $^1$O$_2$ generated) to give a $^1$O$_2$ generation rate constant for fb-**1** of $1.5 \times 10^{-3}$ s$^{-1}$ under these conditions. This rate constant is similar to that observed with a MOF used in experiments related to photodynamic therapy.[25]

$$I_{\mathrm{F}} = A(1-e^{-kt}) \qquad (1)$$

In conclusion, the porphyrin-containing MOF fb-**1**, in which porphyrin moieties are isolated by the porous, three-dimensional nature of the framework, was used as a photosensitizer to generate $^1O_2$ using inexpensive and commercially available LEDs. Singlet oxygen generated by fb-**1** was found to selectively oxidize the sulfur-mustard simulant CEES with a half-life of only 13 min to the relatively non-toxic sulfoxide without producing the highly toxic sulfone. Selective oxidation under mild conditions is an important consideration for sulfur-mustard decontamination applications, for example, in gas-mask filtration systems and for the bulk removal of sulfur-mustard stockpiles. Aside from $^1O_2$ generation, the high surface areas and permanent porosities of MOFs can enhance the adsorption of toxic chemical agents and accelerate the catalytic process, rendering MOFs compelling heterogeneous catalysts for the detoxification of chemical warfare agents.

## Experimental Section

All reagents were purchased from commercial sources and used without further purification. PCN-222/MOF-545 (free base) was synthesized as reported previously.[17e]

Photooxidation experiments: For catalytic tests, PCN-222/MOF-545 (free base) was dispersed in 1 mL methanol, and the reaction mixture was sealed in a glass microwave tube. After purging with $O_2$ for 20 min and irradiating with an LED (white, red, or blue) for 20 min, 2-chloroethyl ethyl sulfide (CEES; 23 μL, 0.2 mmol) and an internal standard (1-bromo-3,5-difluorobenzene; 5 μL, 0.04 mmol) were added to the microwave tube with a syringe, and irradiation was continued. The reaction was monitored by GC and NMR spectroscopy ($CD_3OD$ was used instead of MeOH for the NMR studies). For more experimental details, see the Supporting Information, Section S3.

**Keywords:** chemical warfare agents · heterogeneous catalysis · metal–organic frameworks · photooxidation · singlet oxygen

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