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Highly Efficient and Selective Photooxidation of Sulfur Mustard Simulant by a Triazolobenzothiadiazole-Moiety-Functionalized Metal−Organic Framework in Air

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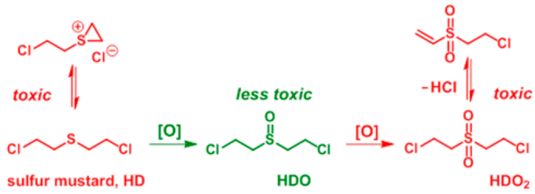
Supporting Information

ABSTRACT: A photoactive triazolobenzothiadiazole (TBTD)-conjugated terphenyldicarboxylate (TPDC) linker was introduced into a porous and robust UiO-68 isoreticular zirconium metal−organic framework (denoted as UiO-68-TBTD) by the de novo synthetic approach of mixed TPDC struts. Under blue-light-emitting-diode irradiation, UiO-68-TBTD can serve as a heterogeneous photocatalyst for the highly efficient and selective oxidation of a sulfur mustard simulant (2-chloroethyl ethyl sulfide) to the corresponding much less toxic sulfoxide product, with a half-life of only 3 min in the open air atmosphere.

Sulfur mustard [bis(2-chloroethyl) sulfide; Scheme 1], also known as HD or mustard gas, is a vesicant and blistering chemical warfare agent (CWA).[1] The partial oxidation of HD to the much less toxic bis(2-chloroethyl) sulfoxide (HDO) but without formation of the quite toxic full-oxidation sulfone derivative (HDO_2; Scheme 1) is regarded as a feasible decontamination route.[2−4] Toward this end, a variety of materials or systems have been developed and evaluated to achieve the catalytic and selective oxidation of HD or its simulants into nontoxic sulfoxide analogues in the past few years,[5−17] such as polyoxometalates,[9] modified mesoporous silica,[10,11] metal oxides,[12] polymer networks,[13,14] and metal−organic frameworks (MOFs).[15−17]

Scheme 1. Oxidation of HD into a Less Toxic Sulfoxide (HDO) and a Highly Toxic Sulfone (HDO_2), Meaning That the Selectivity of Oxidation Is Very Critical for the Safe Degradation of HD



Among these above materials, MOFs as a versatile platform for degrading CWAs are more appealing because of their high porosity and surface area as well as tunable composition, structure, and functionality.[15−20] In particular, Farha, Hupp, and their co-workers have recently made significant strides in developing MOF-based photocatalysts for the oxidative decontamination of sulfur mustard.[21−26] Different photosensitizer moieties, such as porphyrin,[21] fullerene,[24] and boron dipyrromethene (BODIPY),[25] have been incorporated into MOF scaffolds via a straightforward or postsynthetic method. These photoactive moieties in MOFs can be effectively excited under proper irradiation and subsequently transfer the energy to ground-state oxygen ($^3O_2$) with the facile generation of singlet oxygen ($^1O_2$),[27] which is responsible for the highly selective oxidation of sulfide analogues into nontoxic sulfoxide species. Moreover, the ordered 3D structure of the MOF can greatly reduce the aggregation and deactivation of the photosensitizer in the framework and also facilitate diffusion of the substrate toward the active site, thereby accelerating such a photocatalytically oxidative degradation process. For instance, it was observed that the half-life ($t_{1/2}$) for oxidation of the HD simulant 2-chloroethyl ethyl sulfide (CEES) into 2-chloroethyl ethyl sulfoxide (CEESO) by using a BODIPY-functionalized MOF could even be as low as 2 min.[25]

However, it should be noted that these above-reported oxidations of CEES to CEESO have to be conducted in pure molecular O_2 in order to ensure such a fast conversion (Table 1).[21−26] While the same transformation was performed in an air atmosphere, the efficacy would be largely depressed (such as that for a porphyrinic MOF, PCN-222/MOF-545;[21] $t_{1/2}$ = 13 min in O_2 and 21 min in air). Obviously, if the selective photooxidation of CEES could still be accomplished with a high reaction rate by directly using air instead of pure O_2 as the $^1O_2$ source, it would be much more convenient for a practical operation, especially for the case of HD detoxification on site. In this regard, the further development of novel photosensitizer-based organic linkers for MOFs may offer highly promising potential.

Herein, we have designed and synthesized a triazolobenzothiadiazole (TBTD)-conjugated terphenyldicarboxylate

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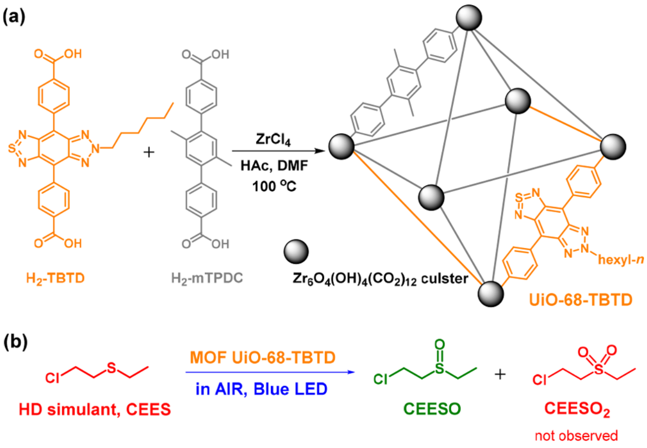
Table 1. Comparison of $t_{1/2}$ Values for CEES Oxidation by Using Various MOF-Based Photocatalysts[a]

MOF photocatalyst	effective photosensitizer	mol %[b]	atmosphere	LED (mW cm^{-2})	$t_{1/2}$ (min)	ref
PCN-57-S	benzothiadiazole	0.1	pure O_2	UV (865)	7.5	26
PCN-57-Se	benzoselenadiazole	0.1	pure O_2	purple (865)	3.5	26
NU-1000	pyrene	1	pure O_2	UV (450)	6.2	23
NU-1000-PCBA	pyrene and C_{60}	1	pure O_2	UV (450)	3.5	24
PCN-222	porphyrin	0.5	pure O_2	blue (325)	13	21
PCN-222	porphyrin	0.5	air	blue (325)	21	21
Br-BDP@NU-1000	BODIPY	0.2	pure O_2	green (325)	2.5	25
UiO-68-TBTD	TBTD	0.2	air	blue (100)	3	this study

[a] All of the reactions were performed in a methanol solvent at room temperature. No overoxidized product $CEESO_2$ was observed in all cases, which should be attributed to the high selectivity of the mild $^1O_2$ oxidant. [b] The molar ratio of the catalyst loading was calculated based on the moles of effective photosensitizers in MOF photocatalysts.

(TPDC) linker (denoted as H_2-TBTD; Scheme 2a), in which the benzothiadiazole (BTD) part was annelated with a benzotriazole (BTz) moiety to give birth to an efficient $^1O_2$ photosensitizer. Subsequently, the ligand was readily integrated into the UiO-68 isoreticular zirconium MOF by the mixed TPDC struts[28−33] (H_2-TBTD and H_2-mTPDC; Scheme 2a). In the open air atmosphere and under blue-light-emitting-diode (LED) irradiation, the photoactive TBTD-functionalized MOF UiO-68-TBTD can work as a heterogeneous photocatalyst for the highly efficient and selective oxidation of the HD simulant CEES into CEESO (Scheme 2b).

Scheme 2. (a) Synthetic Route for the MOF UiO-68-TBTD with Mixed TPDC Linkers of H_2-TBTD and H_2-mTPDC and (b) Selective Photooxidation of a HD Simulant, CEES, Catalyzed by UiO-68-TBTD under Blue-LED Irradiation in an Air Atmosphere



The photoactive organic linker H_2-TBTD can be conveniently obtained starting from our recently reported precursor compound of the diamino-BTD derivative after a three-step reaction.[32] As depicted in Scheme S1, the precursor dimethyl 4,4′-(5,6-diaminobenzo[*c*][1,2,5]-thiadiazole-4,7-diyl)-dibenzoate (**1**) was cyclized with $NaNO_2$ under acidic conditions to give compound **2** with formation of a BTz moiety, which was further reacted with 1-bromohexane in the presence of triethylamine to afford N-alkylated compound **3**. Then, the ester **3** was hydrolyzed to generate the target linker H_2-TBTD with a high overall yield. Here an *n*-hexyl group was introduced with the purpose of increasing the linker solubility, whereas such a long tail fragment would possibly block the pores or channels in the MOF architecture. To overcome this drawback, a de novo mixed-strut approach was thus employed to incorporate the ligand H_2-TBTD with a small percentage into the UiO-68 analogue MOF because of the well-known high porosity and chemical and thermal stability of the UiO series zirconium MOFs.[28,33] Specifically, a mixture of H_2-TBTD and H_2-mTPDC linkers (in a 1:3 molar ratio) with matching ligand lengths was reacted with $ZrCl_4$ in *N*,*N*′-dimethylformamide at 100 °C for 2 days to produce the target MOF UiO-68-TBTD (for details, see the Supporting Information). This mix-and-match synthetic approach will guarantee formation of the UiO-68 framework as well as maintain the pore opening. As expected, a powder X-ray diffraction (PXRD) investigation of UiO-68-TBTD confirmed that its framework is isostructural with the parental MOF UiO-68 along with a highly crystalline architecture (Figures 1a and S1). Additionally, N_2 sorption at 77 K was performed to reveal its porosity. As shown in Figure 1b, a typical type I reversible isotherm with a sharp increase prior to a plateau was observed, indicative of a microporous feature. Also, the Brunauer−Emmett−Teller surface area and pore-size distribution by

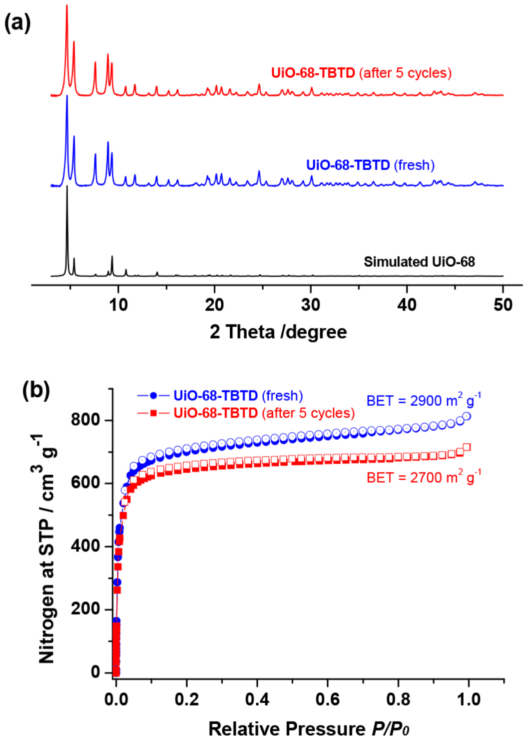


Figure 1. PXRD patterns (a) and N_2 sorption isotherm at 77 K (b) for UiO-68-TBTD (fresh and after five successive CEES oxidation cycles).

nonlocal density functional theory were estimated to be ~2900 $m^2\,g^{-1}$ and ~1.6 nm (Figure S8), respectively. This high porosity and large open channel of UiO-68-TBTD will aid in the diffusion of substrate and product in and out of the framework, thus facilitating an enhanced performance for heterogeneous catalysis.

We first investigated organic linker H_2-TBTD for the photocatalytic oxidation of the HD simulant CEES in a homogeneous system[34] because it has been demonstrated that the featured structure of a BTD/BTz hybrid can function as an excellent sensitizer moiety for $^1O_2$ generation.[35] Because the linker has an absorption band in the visible-light range of 425−500 nm (Figure S10), commercially available blue-LEDs with λ_{max} = 450 nm were employed to excite the TBTD chromophore in the photocatalytic reaction (power density = 100 mW cm^{-2}). After 20 min of irradiation in the open air atmosphere at room temperature, the full conversion of CEES to CEESO was observed in the presence of 0.2 mol % H_2-TBTD as the photocatalyst (Figures 2 and S12), in which the half-life ($t_{1/2}$) was calculated to 6.5 min. No overoxidized product of 2-chloroethyl ethyl sulfone ($CEESO_2$) was detected, which should be attributed to the highly selective nature of $^1O_2$ working as an oxidant.

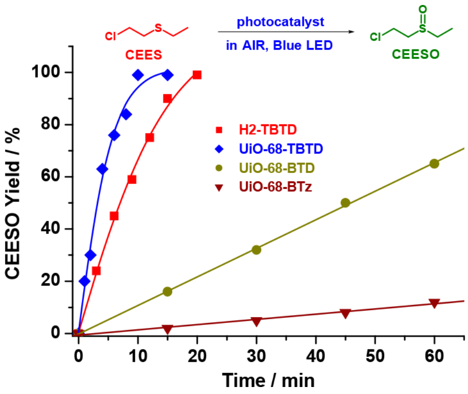


Figure 2. Oxidation of CEES to CEESO over time with different photocatalysts under blue-LED irradiation (100 mW cm^{-2}; 0.2 mmol of CEES in 1 mL of methanol) in the open air atmosphere.

With the desired success of CEES selective oxidation by our synthesized organic linker in a homogeneous system, the photocatalytic performance of a TBTD-functionalized MOF in a heterogeneous system was next studied to estimate its potential application in the oxidative decontamination of sulfur mustard. To our delight, it was observed that CEES can be completely transformed into CEESO without the formation of $CEESO_2$ within 10 min under the same conditions when 0.2 mol % UiO-68-TBTD (mol % based on the TBTD moiety in the MOF) was used as a heterogeneous photosensitizer for $^1O_2$ production (Figures 2 and S13), revealing an improved catalytic activity in comparison to that of its homogeneous counterpart. The corresponding $t_{1/2}$ value was further calculated to be 3 min, which was lower than that of most reported MOFs in 1 atm of O_2 atmosphere, such as PCN-57-Se (or S)[26] and PCN-222[21] (Table 1). Also, it is even comparable to the reported lowest one (2.5 min) by the BODIPY-functionalized MOF Br-BDP@NU-1000.[25] In contrast, our system can be efficiently performed in open air instead of pure O_2, offering a more convenient practical operation. Besides, the MOF UiO-68-TBTD can be easily recycled and reused at least in five successive cycles without any obvious loss of the original catalytic activity and selectivity (Figure S15), indicating the high photostability of the TBTD moiety. Additionally, PXRD and N_2 sorption after five reaction cycles confirmed the highly robust framework of UiO-68-TBTD (Figure 1).

In order to validate the critical role of the featured TBTD moiety on the highly efficient oxidation of CEES, two control MOFs, UiO-68-BTD and UiO-68-BTz containing only the half of the TBTD, were further prepared (for details, see the Supporting Information). As shown in Figure 2, the conversion of CEES to CEESO by UiO-68-BTD exhibited a much slower rate with a long $t_{1/2}$ of 43 min under the same conditions. As for the case of UiO-68-BTz, only 12% conversion of CEES was observed after 60 min of blue-LED irradiation ($t_{1/2}$ = 6.5 h), suggesting negligible catalytic activity. These observations confirmed the need for the TBTD moiety (i.e., the hybrid of BTD/BTz) functioning as an active photocatalytic center to highly drive the selective oxidation of CEES.

In summary, a photoactive TBTD-conjugated TPDC derivative linker has been rationally developed and subsequently integrated into a porous and robust UiO-type isoreticular zirconium MOF UiO-68-TBTD with mixed dicarboxylate struts. In the open air atmosphere, the MOF can efficiently and selectively photocatalyze CEES into CEESO without the formation of $CEESO_2$ under blue-LED irradiation, along with a half-life of as low as 3 min. In comparison to the reported MOF-based analogue photocatalysts, which should utilize pure O_2 as a $^1O_2$ source to ensure rapid oxidation, this study may provide a much more convenient and practical detoxification method for mustard-related agents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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Experimental procedure and additional synthesis and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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