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Effective, Facile, and Selective Hydrolysis of the Chemical Warfare Agent VX Using Zr_6-Based Metal–Organic Frameworks

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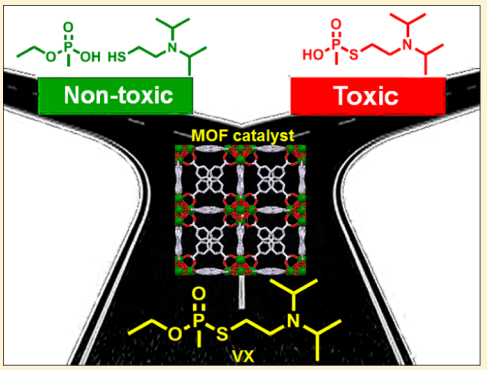
Supporting Information

ABSTRACT: The nerve agent VX is among the most toxic chemicals known to mankind, and robust solutions are needed to rapidly and selectively deactivate it. Herein, we demonstrate that three Zr_6-based metal–organic frameworks (MOFs), namely, UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$, are selective and highly active catalysts for the hydrolysis of VX. Utilizing UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$ in a pH 10 buffered solution of *N*-ethylmorpholine, selective hydrolysis of the P–S bond in VX was observed. In addition, UiO-67-$N(Me)_2$ was found to catalyze VX hydrolysis with an initial half-life of 1.8 min. This half-life is nearly 3 orders of magnitude shorter than that of the only other MOF tested to date for hydrolysis of VX and rivals the activity of the best nonenzymatic materials. Hydrolysis utilizing Zr-based MOFs is also selective and facile in the absence of pH 10 buffer (just water) and for the destruction of the toxic byproduct EA-2192.



INTRODUCTION

Because of the extreme toxicity of chemical warfare agents (CWAs) containing phosphonate linkages, such as Sarin (GB), Soman (GD), and VX (Figure 1), their detoxification has been extensively explored.[1,2] Destruction and decontamination of CWAs have received renewed attention given the recent conflict and subsequent disarmament of Syria's chemical weapons program.[3,4] CWAs containing phosphonothioate and related units (see Figure 1c) are particularly insidious; they effectively inhibit the enzyme acetylcholine esterase, shutting down pulmonary muscle control and causing death by oxygen deprivation within minutes.[5−8] While enzymes such as phosphotriesterase (PTE) are extremely effective at hydrolyzing these agents,[9−12] enzymes often lack the robustness necessary for many practical and nonbiological applications. Therefore, new materials are needed for chemical filtration and detoxification as well as bulk destruction of these agents.[10,13]

Metal–organic frameworks (MOFs) are a rapidly growing class of permanently porous and crystalline solid-state materials.[14−16] MOFs have great potential as adsorbents and catalysts given a high concentration of well-dispersed metal-based nodes, their periodic structures, and their exceptionally large surface areas, permanent porosity, and tunable chemical pores. Given these attributes, MOFs are uniquely suited for the capture and destruction of chemical warfare agents in applications that demand robust solutions.[17−19]

In this regard, we have recently focused on the destruction of CWAs (and their simulants, vide infra) utilizing a class of MOFs built from Zr_6-based nodes and multitopic organic linkers.[20−23] Our studies have been driven by the casual link between the structure of the PTE enzyme active site and the structure of the Zr_6-based nodes.[20,22] Both contain a bimetallic, Lewis acidic moiety linked by a bridging hydroxide that facilitates substrate binding and subsequent phosphorus–oxygen bond hydrolysis.[24,25] In addition, Zr_6-based MOFs have been found to be remarkably robust, showing excellent thermal, mechanical, and chemical stability.[26−32]

Our initial work was focused on identifying Zr_6-based MOFs capable of rapidly hydrolyzing CWA simulants, such as dimethyl 4-nitrophenyl phosphonate [DMNP (Figure 1a)] that can be safely handled in academic laboratories.[20,21] A handful of Zr_6-based MOFs were found to effectively hydrolyze DMNP, some of them with half-lives of <1 min.[23] More recently, we demonstrated that one of these Zr_6-based MOFs, NU-1000, is also capable of cataltyically degrading the G-agent

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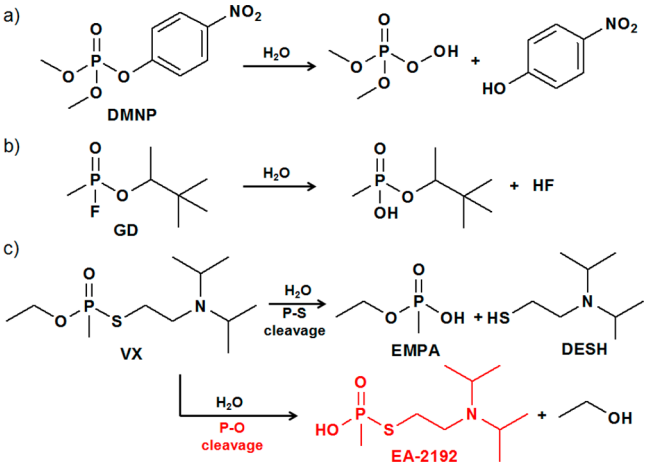

Figure 1. Stoichiometric hydrolysis reactions of representative phosphonate-based simulants and nerve agents: (a) dimethyl 4-nitrophenyl phosphonate (DMNP, simulant), (b) *O*-pinacolyl methylphosphonofluoridate (GD, G-agent), and (c) *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate (VX, V-agent).

O-pinacolyl methylphosphonofluoridate [GD (Figure 1b)] with remarkable speed and efficacy (Figure 1b). In addition, density functional theory (DFT) calculations indicated that the Zr_6 clusters of NU-1000 were also favored to selectively hydrolyze *O*-ethyl *S*-[2-(diisopropylamino)ethyl] methylphosphonothioate [VX (Figure 1c)] to the nontoxic products EMPA (ethyl methylphosphonic acid) and DESH [2-(diisopropylamino)ethanethiol] by cleavage of the P−S bond.[22]

The hydrolysis of VX under mild conditions is particularly challenging. This is in large part a selectivity issue; the P−O, P−S, and C−O bonds can all be hydrolyzed,[10] which is due to the number of potential modes of binding of VX to the catalyst active site.[33] Exacerbating this problem, hydrolysis of the P−O bond produces the toxic byproduct EA-2192 [*S*-2-(diisopropylamino)ethyl *O*-hydrogen methylphosphonothioate]. Instead, hydrolysis of the P−S bond is desired as the resultant products, EMPA and DESH, are much less toxic. While many materials have been examined for the degradation of VX,[1,2] some of the most facile and selective materials developed to date include metal oxides and hydroxides [e.g., TiO_2 and $Zr(OH)_4$][34] as well as fluoride ion-exchange resins.[35,36] Unfortunately, these materials are often tested stoichiometrically (or substoichiometrically) and/or have inhibitively slow degradation kinetics that have limited their real-world implementation.[37] Thus, there is still a compelling need to develop new materials, particularly catalysts, that can selectively and rapidly hydrolyze VX (and other CWAs) under mild conditions.[10]

We sought to determine if a series of Zr_6-based MOFs, namely, UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$ (Figure 2), are capable of selectively and actively hydrolyzing VX. Earlier DFT calculations based on Zr_6 node-bound VX indicated a significant thermodynamic preference for hydrolyzing the P−S bond (−123 kJ mol^{-1}) of VX versus the P−O bond (−79 kJ mol^{-1}). Our selection of Zr_6-based MOFs was further motivated by their high activity toward the DMNP simulant[20,21,38] but also based on the ease of synthesis as well as their known stability in H_2O.[39] We speculated that the biphenyl dicarboxylate (BPDC) linker in UiO-67 prevents steric crowding about the Zr_6-based node and facilitates hydrolysis in comparison to Zr_6-based MOFs with shorter linkers such as

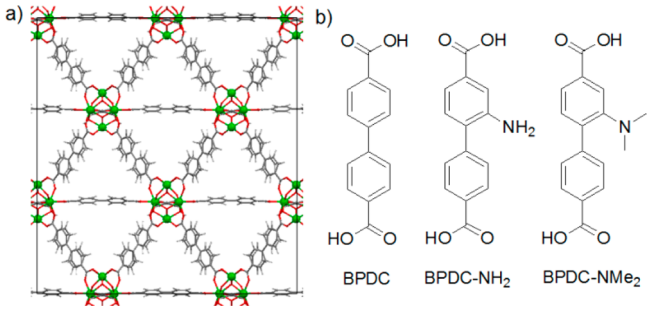

Figure 2. (a) Crystalline topology of UiO-67 (Zr, green; O, red; C, gray; H, white) and (b) chemical structures of ligands for UiO-67 and its derivatives used in this study.

UiO-66.[21] Herein we report that UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$ are selective and highly active catalysts for the destruction of the CWA VX. The selectivity and activity are present not only in a buffered solution but also in pure water. These Zr_6-based MOFs are also active for the hydrolysis of the highly toxic byproduct, EA-2192.

EXPERIMENTAL SECTION

Synthesis of the Zr-MOF Catalyst. All reagents were purchased from commercial sources and used without further purification. UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$ were synthesized according to literature procedures.[39] An 8-dram vial was loaded with $ZrCl_4$ (67 mg, 0.29 mmol), DMF (5 mL), and concentrated HCl (0.5 mL) before being sonicated for 20 min until the solids were fully dissolved. The ligand (107 mg, 0.38 mmol) and DMF (10 mL) were then added, and the mixture was sonicated for an additional 20 min before being heated at 80 °C overnight. The resulting solid was washed first with DMF (2 × 30 mL) and then with EtOH (2 × 30 mL). UiO-67, UiO-67-$N(Me)_2$, and UiO-67-NH_2 were desolvated and activated by supercritical CO_2.[40−42]

Monitoring the Hydrolysis of VX in Buffer or Water. To a 5 mm NMR tube was added 2.5 mg (1.1 μmol of Zr_6-based nodes) catalyst [formula weights, UiO-67, 2120.8; UiO-67-NH_2, 2210.8; UiO-67-$N(Me)_2$, 2373.2] followed by 47 μL of *N*-ethylmorpholine and 0.7 mL of water [0.5 M *N*-ethylmorpholine (pH 10)] for buffered experiments. For nonbuffered experiments, 0.75 mL of water was used (no *N*-ethylmorpholine); 3.9 μL (14.7 μmol) of VX was then added and the tube capped, and the tube was vigorously shaken before being placed in the NMR magnet for monitoring by ^{31}P NMR. Initial reaction half-lives ($t_{1/2}$) were extracted by plotting the natural log of the concentration versus time; for a pseudo-first-order process, the slope ($m = -k$) is related to the half-life by the equation $t_{1/2} = \ln 2/k$.

Monitoring the Hydrolysis of the VX/EA-2192 Mixture in Buffer or Water. VX (3.9 μL, 14.7 μmol) was added to a 5 mm NMR tube followed by 47 μL of *N*-ethylmorpholine and 0.7 mL of water [0.5 M *N*-ethylmorpholine (pH 10)] for buffered experiments. After 6 days, 2.5 mg (1.1 μmol) of catalyst was added to a NMR tube and vigorously shaken before the tube was placed in the NMR magnet for monitoring by ^{31}P NMR. For nonbuffered experiments, 0.75 mL of water was used (no *N*-ethylmorpholine). After 7 days, 2.5 mg of catalyst was added to a NMR tube and vigorously shaken before the tube was placed in the NMR magnet for monitoring by ^{31}P NMR. Initial reaction half-lives ($t_{1/2}$) were extracted by plotting the natural log of the concentration versus time; for a pseudo-first-order process, the slope ($m = -k$) is related to the half-life by the equation $t_{1/2} = \ln 2/k$.

RESULTS AND DISCUSSION

The hydrolysis of VX was conducted under conditions similar to those previously reported for the DMNP simulant as well as GD (see the Experimental Section for additional details).[20,22] The reactions were conducted in the presence of *N*-

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ethylmorpholine to buffer the reaction solution at pH 10. The hydrolysis of VX was monitored by ^{31}P NMR spectroscopy, an example of which is shown in Figure 3a (see Figure S2 of the

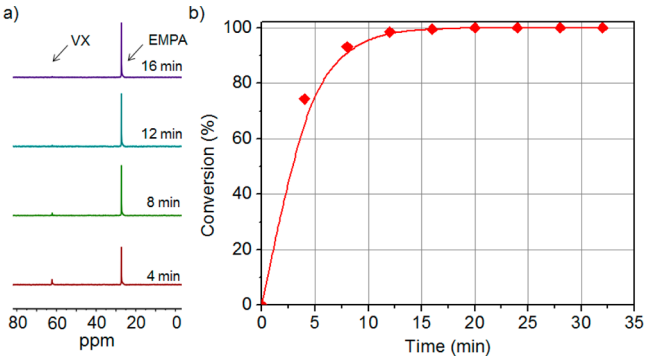

Figure 3. (a) ^{31}P NMR spectra indicating the progress of selective hydrolysis of 14.7 μmol of VX (62.5 ppm) to the nontoxic EMP (27.5 ppm) in the presence of 1.1 μmol of UiO-67-NMe$_2$ in a buffer solution and a 0.5 M 4-ethylmorpholine solution (pH 10) at room temperature. (b) Hydrolysis profile, calculated by comparing the integrated ^{31}P peaks, of VX to EMP in the presence of UiO-67-NMe$_2$ in a buffer solution based on ^{31}P NMR spectra.

Supporting Information for additional ^{31}P NMR spectra with UiO-67 and UiO-67-NH$_2$ as the catalyst). Importantly, the ^{31}P NMR spectra reveal that UiO-67, UiO-67-NH$_2$, and UiO-67-N(Me)$_2$ all selectively hydrolyze the P−S bond in VX (δ 62.5) to the nontoxic ethyl methylphosphonate (EMP) anion (δ 27.5) and DESH. Notably, the toxic byproduct EA-2192 (cleavage at the P−O bond, δ 43.1) was not observed. These results are consistent with the DFT-derived estimates of bond-specific hydrolysis energies mentioned above.[22]

The percent conversion, calculated by comparing the integrated ^{31}P peaks for VX (δ 62.5) to that of EMP (δ 27.5), for UiO-67-N(Me)$_2$, is shown in Figure 3b. Conversion of VX to EMP is complete within 15 min [for UiO-67-N(Me)$_2$] to approximately 50 min (for UiO-67 and UiO-67-NH$_2$) (Figure S6). The initial $t_{1/2}$ values[43] are 1.8 min [UiO-67-N(Me)$_2$], 6.0 min (UiO-67-NH$_2$), and 7.9 min (UiO-67) (Figures S8−S10). Notably, the background reaction in the absence of a catalyst is negligible over the same time period in buffered solutions (Figure S15). Albeit under different reaction conditions, the half-life with UiO-67-N(Me)$_2$ represents an ∼970-fold enhancement over that for the only other MOF shown to be capable of hydrolyzing VX (HKUST-1; $t_{1/2}$ = 29 h).[44] Notably, the 1.8 min half-life is similar to that yielded by the most active abiotic catalysts described to date.[34,45−47] It is plausible that the enhanced catalytic activity of UiO-67-NH$_2$ and UiO-67-N(Me)$_2$ relative to UiO-67 is due to the ability of the amino moieties to act as a base or proton-transfer agent. The tertiary amine on UiO-67-N(Me)$_2$ is more basic than the primary amine on UiO-67-NH$_2$.[9,21,48] Underivatized UiO-66 also displays selective hydrolysis of VX, albeit at a significantly slower rate [i.e., a 90 min half-life (see Figure S12 and Table S1)] than with underivatized UiO-67, consistent with the prevention of steric crowding about the Zr$_6$ cluster of the UiO-67 series. Turnover frequencies (TOFs) based on the half-life of the VX substrate (per Zr$_6$ cluster) were calculated on the basis of the assumption that all catalyst sites were accessible and, alternatively, that only sites on the exterior of the MOF surfaces were accessible, and are included in Table S1.

Next, we sought to see if the UiO-67 derivatives could hydrolyze VX in the absence of buffer. [It is known that VX slowly hydrolyzes in the absence of buffer; however, the rate is extremely slow. The $t_{1/2}$ is 4.8 days in a dilute aqueous solution,[49] and the reaction is not selective, forming a mixture of EMPA and EA-2192 (Figure S5 and S15).][8] Building off our VX results in buffered pH 10 solution, we placed UiO-67-N(Me)$_2$ in water (no buffer, pH 4.5) and added VX (see the Experimental Section for details). Again, monitoring the reaction via ^{31}P NMR spectroscopy revealed that UiO-67-N(Me)$_2$ was quantitatively selective for P−S bond cleavage (Figure 4a and Figure S7), while no evidence of the presence of

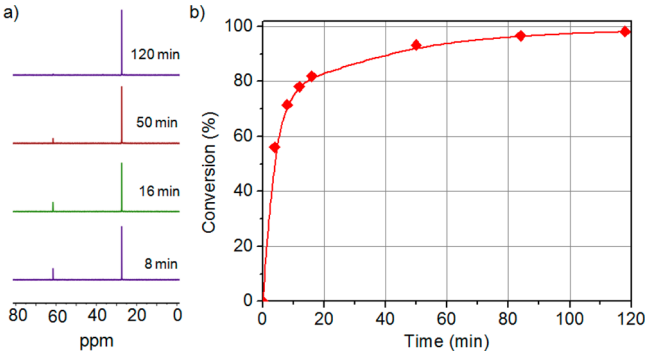

Figure 4. ^{31}P NMR spectra in the absence of buffer indicating (a) the progress of hydrolysis of 14.7 μmol of VX (62.5 ppm) to EMPA (27.5 ppm) with 1.1 μmol of UiO-67-NMe$_2$ at room temperature and (b) the percent conversion of VX to EMPA in the presence of UiO-67-NMe$_2$ in water.

EA-2192 could be detected (Figure S3). The initial $t_{1/2}$ was again extracted and found to be about 7 min in the absence of added buffer (Figure 5), while the background reaction was negligible over the same period (Figures S11 and S15).

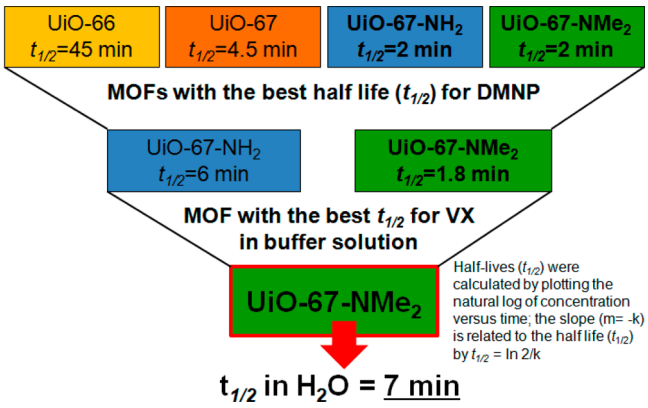

Figure 5. Screening of catalysts for highly selective and active hydrolysis of nerve agent simulants and VX in water.

Because of the persistence and toxicity of EA-2192, we also wanted to see if the series of UiO-67-based MOFs was capable of hydrolyzing EA-2192. EA-2192 is often present in ammunition stockpiles and can persist in the environment after agent deployment because of the nonselective hydrolytic instability of VX.[50] A mixture of VX and EA-2192 (as well as EMPA due to nonselective hydrolysis) was prepared via aging VX in a 0.5 M *N*-ethylmorpholine buffer solution for 6 days (Figure S4a; see the Experimental Section for details).

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Decomposition of VX and EA-2192 was followed simultaneously via ^{31}P NMR spectroscopy in the presence of UiO-67. In pH 10 buffer, initial $t_{1/2}$ values for decomposition of the mixture were found to be ∼11 and ∼29 min for VX and EA-2192, respectively (Figures S16 and S17). Complete hydrolysis of VX was observed after 30 min, while the more persistent EA-2192 was completely hydrolyzed to MPA and DESH after 22 h in the buffered solution (Figures S1, S4b, and S14a). Initial follow-up experiments also suggest that this mixture can be hydrolyzed in the absence of buffer (Figures S5 and S14b).

■ CONCLUSION

In conclusion, a series of Zr_6-based MOFs, including UiO-67, UiO-67-NH_2, and UiO-67-$N(Me)_2$, is capable of hydrolyzing the CWA VX. Importantly, the P−S bond (and not the P−O bond) is selectively hydrolyzed producing the preferred, low-toxicity products EMPA and DESH. One of the MOFs, UiO-67-$N(Me)_2$, hydrolyzes VX in a pH 10 buffered solution with remarkable efficiency (initial $t_{1/2}$ of 1.8 min that rivals those of the best known abiotic materials). Intriguingly, the catalytic hydrolysis also works in the absence of buffer and also destroys the toxic product EA-2192. We look forward to discovering why these Zr_6-based MOFs are so potent for the destruction of phosphonate linkages, and those results will be reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01813.

Hydrolysis mechanisms, conversion versus time data, natural logarithm plots, NMR spectra for hydrolysis, and dynamic light scattering data (PDF)

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Notes

The authors declare no competing financial interest.

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(37) While very impressive half-lives of approximately 1 min have been observed for the degradation of VX using $Zr(OH)_4$, the reaction is not catalytic with respect to the total amount of Zr present. Excess

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$Zr(OH)_4$ (0.234 g, 1.5 mmol) was used for the decontamination of VX (0.02 mL, 0.075 mmol) (ref 34).
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