Inorganic Chemistry

Degradation of Paraoxon and the Chemical Warfare Agents VX, Tabun, and Soman by the Metal–Organic Frameworks UiO-66-NH₂, MOF-808, NU-1000, and PCN-777

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S Supporting Information

ABSTRACT: In recent years, Zr-based metal–organic frameworks (MOFs) have been developed that facilitate catalytic degradation of toxic organophosphate agents, such as chemical warfare agents (CWAs). Because of strict regulations, experiments using live agents are not possible for most laboratories and, as a result, simulants are used in the majority of cases. Reports that employ real CWAs are scarce and do not cover the whole spectrum of agents. We here present a comparative study in which UiO-66-NH₂, NU-1000, MOF-808, and PCN-777 are evaluated for their effectiveness in the degradation of paraoxon and the chemical warfare agents tabun, VX, and soman, in *N*-ethylmorpholine buffer (pH 10) as well as in pure water. All MOFs showed excellent ability to



degrade the agents under basic conditions. It was further disclosed that tabun is degraded by different mechanisms depending on the conditions. The presence of an amine, either as part of the MOF structure $(UiO-66-NH_2)$ or in the agent itself (VX, tabun), is the most important factor governing degradation rates in water. The results show that MOFs have great potential in future protective applications. Although the use of simulants provides valuable information for initial screening and selection of new MOFs, the use of live agents revealed additional mechanisms that should aid the future development of even better catalysts.

■ INTRODUCTION

Metal Organic Frameworks (MOFs) are a relatively new class of crystalline solids with tunable properties such as porosity and pore size.^{1,2} They are built by the formation of coordination bonds between metal-ion or metal-oxide clusters (called secondary building units (SBUs)) and polytopic organic linkers. The $Zr_6(\mu 3-O)_4(\mu 3-OH)_4$ SBU has been used to synthesize a variety of MOFs that catalyze the hydrolysis of organophosphate (OP) agents, including extremely toxic chemical warfare agents (CWAs).^{3,4} These MOFs were accessible by varying the shape, size, and number of carboxylate groups present on the organic linker. As the Zr₆ SBU can accommodate a maximum of 12 carboxylates, the use of different linkers creates MOFs with varying symmetries, structures, and different physical and/or chemical properties. For instance, UiO-66 is composed of terephthalic acid linkers and the resulting structure contains 6 Å octahedral and 9 Å tetrahedral pores with a Langmuir surface area of 1187 m² g^{-1.5} In the defect-free (ideal) structure of UiO-66, all 12 nodes in the SBU are occupied (12-connected). By changing the bitopic linker used in UiO-66 to the tritopic benzene-1,3,5-tricarboxylic acid linker, the 6-connected MOF-808 can be obtained.⁶ In a similar fashion, the use of the tetratopic 1,3,6,8-tetrakis(pbenzoic acid)pyrene (H₄TBAPy) leads to NU-1000, in which 8 of the 12 nodes of the Zr-SBU are occupied.^{7,8} Because of the ability of these types of MOFs to rapidly degrade OP agents,

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they may serve as the key active material in future protective applications, such as canisters,⁹ sensors,¹⁰ coatings,¹¹ and clothing.¹²⁻¹⁴

The data reported so far revealed several factors that influence degradation kinetics. It was found that a higher catalytic activity can be achieved by using 6- or 8-connected Zr-MOFs as those MOFs have more vacant sites (catalytic sites) available on the SBU compared to 12-connected MOFs, such as UiO-66, that rely on structural defects as catalytic sites.^{15,16} Other properties, such as pore size, were also found to be of importance, presumably by providing easier access of the agent to catalytic sites within the framework.¹⁷ The (partial) substitution of linkers with basic amine groups^{17–19} as well as postsynthetic treatment of MOFs with alkoxides,²⁰ as exemplified with UiO-66-NH₂ (and the structurally related UiO-67-NH₂), resulted in higher catalytic activity compared to the unmodified MOFs and enhanced catalytic activity in unbuffered conditions (MQ). The pH of the buffer played a role in the exchange rate of zirconium-bound water molecules for OPs.²¹ The size of the MOF particles was found to have a significant effect on the hydrolysis rates of OPs as more surface/catalytic sites per weight unit of MOF become accessible with smaller particles.²² Finally, degradation products

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may give rise to catalyst poisoning and lowered turnover.^{13,23} All of the above was concluded from separate studies, and although comparable conditions were used (0.45 M *N*ethylmorpholine (NEM) buffer), direct cross-comparisons of MOF potency are difficult to make as a result of inevitable interlaboratory differences or differences in batches of synthesized materials. More importantly, examples of the use of live agents with these MOFs are relatively scarce,^{3,20} because of the restrictions that apply to most laboratories with the use of such dangerous agents. Consequently, most of these MOFs have been tested with CWA surrogates (usually dimethyl methylphosphate (DMMP), or dimethyl 4-nitrophenyl-phosphate (DMNP)).

We therefore decided to compare, under identical conditions, the catalytic activity of UiO-66-NH₂, NU-1000, and MOF-808 in the hydrolysis of several chemical warfare agents (Figure 1)



Figure 1. Structures of chemical warfare agents used in this study.

of different chemical nature (VX (P-S), GD (soman, P-F), GA (tabun, P-CN) and POX (paraoxon, P-O). In addition, we decided to include PCN-777 in this selection. PCN-777 is a 6-connected MOF, built from 4-4'-4''-s-triazine-2,4,6-triyl-tribenzoic acid linkers, and has the same topology as MOF-808, but with larger pore sizes.²⁴ This MOF was not previously evaluated as a catalyst in the hydrolysis of OP agents. The degradation reactions were carried out by monitoring (³¹P NMR) the conversion of agent when mixed in excess with a MOF either in a basic solution (0.4 M *N*-ethylmorpholine (NEM), adopted from previous reports) or in unbuffered conditions (pure water). We here report the results of these experiments. First of all, the degradation studies complement

those already reported for simulants as data of the hydrolysis of a broad range of live agents is currently lacking for the majority of MOFs reported.³ In this respect, it is worth noting that tabun has not previously been used in such experiments. Second, the results led to a better understanding of the key features that govern the effectiveness in the degradation of various CWAs under different circumstances. Finally, we report that the different chemical structures of CWAs gave rise to agentspecific interactions with the MOFs and differences in the mechanisms of degradation for some CWAs.

EXPERIMENTAL SECTION

MOF Syntheses. UiO-66-NH₂,²⁵ NU-1000,⁷ MOF-808,⁶ and PCN-777²⁴ were synthesized according to reported solvothermal methods. Briefly, this method entails the heating of a mixture of a Zr(IV) source (usually ZrOCl₂, or ZrCl₄) and the requisite linker in a solvent (e.g., dimethylformamide) in a closed dram vial. In a number of cases, a modulator is added in the form of a monodentate carboxylic acid. These modulators (e.g., formic acid, trifluoroacetic acid, or benzoic acid) occupy nonconnecting sites on the nodes and/or influence the nucleation in the synthesis process. Activation of synthesized materials (removal of solvents from the pores) was accomplished by solvent-exchange, followed by application of heat under vacuum.

Degradation Experiments. Caution! CWAs (GA, VX, GD) are extremely toxic compounds and experiments should only be conducted by trained personnel in a laboratory that is permitted to use such agents.

The hydrolysis reactions were monitored by ³¹P NMR (64 scans, 2 s relaxation delay) at 25–27 °C. The 0.92 mM MOF suspensions were made by mixing 1–2 mg of MOF (0.83 μ mol, MW NU-1000 = 2180.78, MOF-808 = 1353.71, PCN-777 = 3184.05, UiO-66-NH₂ = 1754.15 g·mol⁻¹) in a variable amount of 10% D₂O/H₂O or 0.4 M N-ethylmorpholine buffer (in 10% D₂O/H₂O) via sonication for 5–10 min. To 450 μ L of the MOF suspension (0.92 μ M) was added 50 μ L of GA/GD/VX or diethyl *p*-nitrophenyl phosphate solution (50 mM in dry acetonitrile), resulting in a 0.83 mM MOF/5 mM agent suspension (ratio 1:6). The mixture was vigorously shaken for 10 s. A sample (340 μ L) of the suspension was transferred to an NMR tube (5 mm) and fitted with a trimethylphosphate containing insert. The progress of the reaction was monitored with 3 min increments for 40 min. To measure conversion at 30 s, a reaction mixture was prepared

Table 1. Summary of Kinetic Data and Maximum Conversions (after 40 min) Obtained in the Degradation Reactions of POX, GD, VX, and GA in NEM Buffer (pH 10) and Water, by the MOFs NU-1000, MOF-808, PCN-777, and UiO-66-NH₂ (pH 2.8–4.4)

conditions		NEM			MQ		
agent	MOF	k, min ⁻¹	$t_{1/2}$, min	conv ^a , %	k, min ⁻¹	$t_{1/2}, \min$	conv ^a , %
POX	NU-1000	0.27	2.6	100	n.d.	n.d.	n.d.
	MOF-808	0.19	3.6	100	n.d.	n.d.	n.d.
	PCN-777	0.19	3.6	100	n.d.	n.d.	n.d.
	UiO-66-NH ₂	0.02	35	75 ^a	0.007	99	21
GD	NU-1000 ⁸	n.d.	<1	100	n.d.	n.d.	<2
	MOF-808	n.d.	<1	100	n.d.	n.d.	<2
	PCN-777	n.d.	<1	100	n.d.	n.d.	<2
	UiO-66-NH ₂	n.d.	<1	100	n.d.	n.d.	<2
VX	NU-1000	0.13	5.3	100	0.081	8.7	77
	MOF-808	n.d.	<0.5	100	0.11	6.3	73
	PCN-777	n.d.	<0.5	100	0.040	17.3	34
	UiO-66-NH ₂	0.32	2.2	100	0.14	5.0	85
GA	NU-1000	n.d.	<1	100	0.0072	97	23
	MOF-808	n.d.	<1	100	0.0074	94	24
	PCN-777	n.d.	<1	100	0.019	37	37
	UiO-66-NH ₂	n.d.	<1	100	0.018	39	33

^aConversion within the experimental time frame.

under identical conditions and filtered using a 0.2 μM HPLV filter after 30 s.

Control experiments were conducted in an identical manner, but in the absence of MOF material (background hydrolysis of agent).

Data Analysis. The percentage hydrolysis at each time point was determined by dividing the ³¹P NMR integral(s) of the signal(s) of the hydrolysis products by the sum of all ³¹P integrals (and multiplying with 100). The time point values were defined as the time of measurement start plus 1.5 min (total measurement time per time point was 3 min). Initial hydrolysis rates were determined by plotting the natural log of the averaged agent concentrations (of duplicate or triplicate measurements) vs time and taking the slope (-k) of the fitted straight line to calculate the half-life using the equation $t_{1/2} = \ln t_{1/2}$ 2/k. In some cases, curves could not be fitted due to half-lives (much) lower than the time required for measurements. In those cases, halflives were estimated by assuming that at least 6 half-lives had passed (<2% remaining agent) at the first time point. In other cases, attenuated hydrolysis rates at later time points were observed (resulting in biphasic curves and sometimes reduced final conversion percentages). In those cases, the initial hydrolysis rates (k) and associated half-lives were estimated by fitting the first couple of time points only.

RESULTS AND DISCUSSION

The results of the degradation experiments are presented per agent and are displayed in separate graphs for reactions in NEM buffer and in water. Table 1 summarizes the initial hydrolysis rates (k, \min^{-1}) , the half-lives $(t_{1/2}, \min)$, and the maximum conversion percentages. Data that repeats previously reported work is marked with a reference.

The results of the hydrolysis of paraoxon (POX) in the presence of the MOF catalysts are depicted in Figure 2. In NEM buffer (Figure 2a), NU-1000, MOF-808, and PCN-777 showed comparable activity (with half-lives ranging between 2 and 4 min). UiO-66-NH₂ gave much slower hydrolysis rates ($t_{1/2} \approx 35$ min) of POX. In contrast, UiO-66-NH₂ was the only MOF to display some hydrolytic activity toward POX in MQ (Figure 2b). The hydrolysis rates of POX into diethylphosphate



Figure 2. Degradation rates of ethyl-paraoxon in the presence of several MOFs in (a) NEM buffer and (b) in water.

were generally slower than those reported previously for the structurally similar agent dimethyl-4-nitrophenylphosphate (DMNP).^{8,15,17,18} POX, which is larger than DMNP, may experience more difficulty accessing pores and reaching catalytic sites. Differences could also be invoked by small differences in UiO-66-NH₂ batches reflected in structural defects (catalytic sites) and particle size or by the use of a slightly different protocol.

The background hydrolysis rate of soman (GD) in NEM buffer (without MOF) proceeded with a half-life between 12 and 15 min (see the SI). However, in the presence of any of the MOFs tested, extremely fast hydrolysis into pinacolyl methylphosphonate was observed, resulting in 100% conversion after the first time point (see the SI). In sharp contrast, when the reactions were carried out in MQ, no degradation of GD was recorded. Even UiO-66-NH₂ did not show any catalytic activity in this case, which may seem unexpected given the observed hydrolysis of POX (albeit slow) and the slightly more labile P-F bond compared to a P-O bond. Perhaps the differences are invoked by different energies associated with coordinative- and/or hydrogen bond based binding of the agents to the Zr-nodes as was recently demonstrated, using computational methods, for DMNP and GD/VX analogues in combination with NU-1000.8 The results further clearly illustrate the necessity of the presence of an adjuvant in the case of GD hydrolysis, for instance, in the form of a basic buffer.

The hydrolysis of VX was greatly enhanced by the presence of all MOF catalysts in NEM buffer (Figure 3a). In this case,



Figure 3. Degradation rates of VX in the presence of several MOFs in (a) NEM buffer and (b) in water.

the presence of MOF-808 and PCN-777 resulted in extremely fast hydrolysis rates which led to complete degradation of VX into ethyl methylphosphonate (EMPA) within the first time point (5.5 min). Attempts were made to obtain data for earlier time points by filtering off the MOF after 30 s of reaction time; however, due to the rapid reaction and the relatively long time required (when compared to 30 s!) to conduct the filtration step, the experimental error is rather high. Nevertheless, for MOF-808 and PCN-777, the half-lives were estimated to be less than half a minute. The high rates observed may be partly explained by the higher availability of catalytic zirconium sites (lower connectivity) in MOF-808 and PCN-777 compared to NU-1000 and UiO-66-NH₂ as well as their increased accessibility because of the larger pore sizes in both MOF-808 and PCN-777. Any influence of the differences in pore size between MOF-808 and PCN-777 could not be established because of the inability to distinguish between the hydrolysis rates of these two MOFs with the method used. UiO-66-NH2 and NU-1000 showed very fast hydrolysis rates in NEM buffer too, with half-lives of 2.2 and 5.5 min, respectively. Although NU-1000 has more and better accessible catalytic sites compared to UiO-66-NH₂, the latter clearly benefits from the presence of the amine.

A striking observation was that, when the reactions were carried out in MQ, all MOFs were able to mediate VX hydrolysis with half-lives varying between approximately 9 and 17 min (Figure 3b). This is in sharp contrast with the results obtained with GD and POX in MQ, in which only UiO-66-NH₂ showed some activity when reacted with POX. Also, in the case of VX, UiO-66-NH₂ stands out as the best performing MOF tested in MQ with a half-life of only 5 min. Further, it was found that PCN-777 performed worse than MOF-808 in MQ, which was unexpected as PCN-777 has a larger pore size than the isoreticular MOF-808, thus providing even more opportunity for enhanced diffusion rates of agent in the pores or accessibility of Zr-nodes. This result may stem from a somewhat lower quality MOF obtained as a result of using heat-vacuum activation instead of scCO2-activation²⁶ (which required equipment that was not available), leading to a reduced BET surface area measured for PCN-777 as compared to reported values of PCN-777 and MOF-808 (see the SI). Another factor that may have contributed to the lower activity of PCN-777 is its slightly larger particle size $(2-6 \mu M)$ compared to MOF-808 ($\sim 1 \mu M$).

The intriguingly facile hydrolysis of VX in MQ, compared to the other agents, may in part be explained by the previously computed thermodynamic preference for hydrolyzing the P-S (-123 kJ/mol) bond over the P-O bond (-79 kJ/mol) and P–F bond (-83 kJ/mol) upon coordinative binding of the agents to the Zr_6 -nodes.^{8,19} However, we hypothesized that the hydrolysis rate of VX was also enhanced by the presence of a basic amine (p $K_a \sim 8.5$) in the VX structure itself and/or in the second breakdown product 2-(diisopropylamino)ethanethiol (DESH). The involvement of this amine moiety was evidenced by the observation that VX-Me, which is the nonbasic, Nalkylated derivative of VX, was not hydrolyzed by NU-1000 in MQ (Figure 4, closed circles). As a control, VX-Me was also treated with NU-1000 in the basic NEM buffer, which led to rapid hydrolysis, as expected (Figure 4, open circles). As each VX molecule carries only 1 basic amine, the hydrolysis rates of VX by NU-1000 (and all other MOFs) in MQ were quite remarkable. This efficiency may be explained by the close proximity of this amine to the catalytic site upon binding of intact VX in the MOF. Indeed, the addition of 1 equiv of diisopropylethylamine (DiPEA), representing the basic part of DESH, to a mixture of NU-1000 and VX-Me in MQ enhanced the hydrolysis rate of VX-Me (Figure 4, squares), but not as high as with VX itself (Figure 4, triangles). The added DiPEA acts by intermolecular assistance which is expected to be less effective than the intramolecular assistance (or at least close-



Figure 4. Probing the role of the amine group in VX in the degradation reaction. Comparison of the degradation rates of VX, a VX-Me in the presence of NU-1000 under various conditions. The data of VX-Me in the presence of DiPEA were corrected for spontaneous hydrolysis of VX-Me.

proximity driven assistance) of the amine moiety of VX when bound to NU-1000. The same mechanism is probably also involved in the previously reported hydrolysis of the VX-related compound EA-2192 by UiO-67.¹⁹

In this respect, it is of importance to note that the very toxic EA-2192 (a.k.a. des-ethyl VX or V27a, obtained when the OEt group in the VX structure is replaced with an OH group) could not be detected in the degradation experiments with ³¹P NMR. Thus, VX hydrolysis exclusively led to the formation of the relatively nontoxic ethyl methylphosphonate (EMPA) in all cases, which is in line with earlier findings.¹⁹

The reaction of tabun (GA) in NEM buffer in the presence of each of the MOFs gave similar results as with GD. Thus, the degradation of GA is greatly accelerated by the MOFs in NEM buffer, with respect to the background reaction ($t_{1/2} \approx 35$ min), leading to complete disappearance of tabun at the first time point in all cases (see the SI). In all of these reactions, a single product with a resonance at 11 ppm (³¹P NMR) was formed. LC tandem HR-MS/MS analysis of the filtered reaction mixture revealed that this product was dimethylphosphoramidic acid monoethylester (Figure 5).

O ∥ ₽ CN EtO	O ^{a)} ∥ Me₂N / P EtO	O a,b) II HO ^{-P} OH EtO	O II HO ⁻ P-CN EtO
δ -7.8 ppm	pH 10: δ 11 ppm pH 4: δ 3.7 ppm	pH 10: δ 3.6 ppm pH 4: δ 0.4 ppm	δ -20 ppm

Figure 5. Structures of tabun and the observed hydrolysis products of tabun in the reaction with MOFs. (a) Identified using LC-HR-MS/MS. (b) Identity confirmed by spiking with an authentic sample. (c) Reference 27.

When the experiments were performed in MQ₄ tabun was degraded by all MOFs (Figure 6), similarly but more slowly as observed with VX in MQ. The integral measurements in these ³¹P NMR experiments were slightly less accurate because multiple hydrolysis products were formed simultaneously which led to lower signal-to-noise ratios. Following a similar reasoning as with VX in MQ, the slow, but apparent, hydrolysis of tabun in the MQ experiments can be ascribed to assistance of the dimethylamine function in tabun or by released dimethylamine in solution. UiO-66-NH₂ and NU-1000 mediated reactions led to the formation of predominantly ethyl phosphate (0.4 ppm, Figure 5), while MOF-808 gave a mixture of products with resonances at 0.4 ppm (minor) and 3.7 ppm (major). The



Figure 6. Degradation rates of tabun in the presence of several MOFs in water.

latter product was identical to the one obtained in NEM buffer, but the ³¹P resonance was shifted because of the difference in pH between the two types of samples (pH 10 vs pH 4), which was confirmed by diluting an aliquot of the MQ sample in NEM buffer, resulting in shifting of the 3.7 ppm peak to 11 ppm (and the ethylphosphate resonance from 0.4 to 3.4 ppm; see the SI). The simultaneous formation of several products in the hydrolysis of tabun can in part be explained by the various leaving groups that tabun possesses. On the other hand, the selectivity of hydrolysis may result from subtle differences in pH in the individual (unbuffered) experiments. The latter was concluded by the observation that the use of PCN-777 led to a mixture of products at 0.4 ppm (ethylphosphate) and -20 ppm, which could be assigned²⁷ as phosphorocyanidic acid monoethyl ester. The unexpected difference in selectivity of hydrolyzation of tabun with this MOF may have been invoked by the more acidic conditions (pH 2.8) observed in the reaction with PCN-777 compared to the other MOFs (pH 3.9-4.4, measured after 1 h of reaction time).

A fair comparison of MOF potency is difficult to make, as the results show that several mechanisms are running in parallel, depending on the type of MOF used and the reaction conditions employed. In addition, the hydrolysis of tabun into ethylphosphate required 2 consecutive hydrolysis reactions, further complicating kinetic analyses.

CONCLUSIONS

The degradation rates of the chemically diverse range of organophosphate based chemical warfare agents VX, tabun, soman, and ethyl-paraoxon were measured in the presence of four Zr-based metal-organic frameworks under identical conditions. Three of the four MOF catalysts employed (UiO-66-NH₂, MOF-808, and NU-1000) were previously reported to degrade OP agents, while the use of PCN-777 as a catalyst is reported here for the first time. The degradation rates were measured in an alkaline-buffered system (0.4 M N-ethylmorpholine, pH 10) or in water in order to compare the potential of the MOFs in the degradation reactions under different circumstances and to further uncover the features and mechanisms that govern these detoxification reactions. The experimental data showed that all Zr-based MOFs had great potential for the destruction of the various agents in an alkalinebuffered system. For some agents (GD, GA), conversion rates were so high that differences between MOFs could not be distinguished. In those cases, altered conditions should be considered, such as the use of higher agent/MOF ratios. In cases where differences in potency could be measured (POX, VX), it seems that MOFs with lower connectivity (higher amount of available catalytic sites) have the advantage. The

larger pore size of PCN-777 compared to MOF-808, while having the same topology and connectivity, played no significant role for catalytic degradation. Probably, the pore size of MOF-808 was already sufficient, allowing efficient entry of the organophosphates into both frameworks.

When executed in MQ, organophosphate hydrolysis was slower or even absent, and often incomplete. The incomplete degradation can be ascribed to catalyst poisoning, in which the CWA degradation products occupy catalytic sites.^{13,20,23} UiO-66-NH₂ was the best performing MOF in MQ. Although the small particle size of this MOF (which was about 10 times smaller than that of the other MOFs) presumably contributed to its enhanced catalytic activity,²² it is likely that the presence of the amine function is a major contributor¹⁷⁻²⁰ and that the presence of a basic function is more important than a higher number of catalytic sites in the other MOFs. The latter observation was further exemplified by the previously undiscovered notion that a basic function in the agent (VX. and to a lesser extent, tabun) also had a beneficial effect on hydrolysis rate of the agents. The degradation of VX by all MOFs in MQ proceeded via a close-proximity driven¹⁸ or intramolecular involvement of the amine group in the VX structure.

POX, GD, and VX showed selective hydrolysis (if any) of the respective P–OAr, P–F, and P–S bonds, giving the corresponding phosphoric (in the case of POX) and phosphonic (in the case of GD, VX) acids, in both NEM buffer and MQ. While the P–CN bond in tabun was selectively hydrolyzed in NEM buffer, multiple simultaneous hydrolysis routes were recorded in MQ (cleavage of P–CN, P–NMe₂, or both) and is probably dependent on the pH.

While the use of simulants in the evaluation of the catalytic activity of MOFs remains highly useful for initial screening and selection of MOF catalysts, the results presented here show that evaluation with live agents of different chemical nature provides additional insights into the mechanisms involved in the degradation of specific agents, which should prove useful in the future engineering of MOFs in protective applications.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01809.

Synthesis and characterization of MOFs (BET surface areas, particle sizes, SEM images), hydrolysis curves of all MOF/agent/condition combinations and corresponding kinetic plots, and selected ³¹P NMR spectra and mass spectra used to identify tabun hydrolysis products (PDF)

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Notes

The authors declare no competing financial interest.

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