# **Inorganic Chemistry**

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#### Article

## Role of Zr<sub>6</sub> Metal Nodes in Zr-Based Metal–Organic Frameworks for Catalytic Detoxification of Pesticides

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**ABSTRACT:** Pesticides are chemicals widely used for agricultural industry, despite their negative impact on health and environment. Although various methods have been developed for pesticide degradation to remedy such adverse effects, conventional materials often take hours to days for complete decomposition and are difficult to recycle. Here, we demonstrate the rapid degradation of organophosphate pesticides with a Zr-based metal–organic framework (MOF), showing complete degradation within 15 min. MOFs with different active site structures (Zr node connectivity and geometry) were compared, and a porphyrinbased MOF with six-connected Zr nodes showed remarkable



degradation efficiency with half-lives of a few minutes. Such a high efficiency was further confirmed in a simple flow system for several cycles. This study reveals that MOFs can be highly potent heterogeneous catalysts for organophosphate pesticide degradation, suggesting that coordination geometry of the Zr node significantly influences the catalytic activity.

### ■ INTRODUCTION

Although pesticides have contributed significantly to agricultural production worldwide, most of them are toxic, leading to increasing health and environmental concerns for humans and other living organisms.<sup>1-9</sup> A marked toxicity of pesticides can be seen in recent reports showing that acute exposure to pesticides has caused 110,000 fatalities globally each year by self-poisoning.<sup>1,2</sup> Among pesticide types, organophosphatebased pesticides (OPs) are one of the most commercialized classes.<sup>3</sup> The acute toxicity of OPs is originated from the inhibition of acetylcholinesterase, resulting in neurological disorders.<sup>4</sup> Although registered pesticides are verified not to persist in the environment beyond the intended periods, residues of OPs in groundwater have been found to range between ng/L and low  $\mu$ g/L concentrations.<sup>5</sup> Exposure of nontarget ecosystems to OPs has caused serious health and environmental issues, for example, surface water contamination,<sup>6</sup> wildlife poisonings,<sup>3</sup> brain anomalies in children,<sup>7</sup> prenatal exposure,<sup>8</sup> and adverse birth outcomes (Figure 1).<sup>9</sup> Since the adverse effects of OPs are global threats, delivering solutions to evaluate, sense, and detoxify OPs becomes an extremely urgent issue.

An effective pesticide detoxification method is degradation to nontoxic species, advantageous for complete toxicity clearance. Conventional methods to detoxify pesticides include ozonation,<sup>10</sup> Fenton treatment,<sup>11</sup> photocatalysis,<sup>12</sup> and microbial degradation.<sup>13,14</sup> A number of different approaches and materials, for example, oximes,<sup>4</sup> surfactants,<sup>15</sup> metal ox-



Figure 1. Adverse effects of pesticides.

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ides,<sup>16–18</sup> silica nanoparticles,<sup>19</sup> organometallic complexes,<sup>20–22</sup> and enzymes,<sup>23</sup> have been reported for the degradation of OPs. However, conventional physicochemical approaches are not cost-effective and often result in incomplete conversions.<sup>10,11</sup> Nucleophilic species, such as oximes and surfactants, are difficult to recycle.<sup>4,15</sup> Metal oxides often require light sources or result in stoichiometric not catalytic reactions.<sup>11,18</sup> Enzymes are easily inactivated under nonphysiological conditions, and the process is accompanied by high costs and difficulties in recovery. Therefore, heterogeneous catalysts with high catalytic activities and facile recycling are appealing candidates for pesticide degradation.

Metal–organic frameworks (MOFs), porous materials composed of metal clusters and organic linkers, are one of the leading classes of heterogeneous catalysts due to the tunable catalytic activities of metal clusters, diverse chemical functionalization, and high density of active sites with regular distributions.<sup>24–28</sup> In particular, Zr-based MOFs with high chemical stabilities have shown notable catalytic degradation of organophosphate species, that is, chemical warfare agents.<sup>29–41</sup> Nevertheless, only a few studies have explored MOFs for the degradation of OPs.<sup>42–47</sup> For example, paraoxon (POX) was the only pesticide type studied with Zr-based MOFs.<sup>42</sup>

Here, we report the outstanding OP degradation with Zrbased MOFs. Interestingly, a porphyrin-based MOF, PCN-224, with six-connected Zr nodes reveals striking OP degradation performance without significant activity variation, depending on pesticide types. Furthermore, PCN-224 retained high degradation efficiency for several cycles in a simple continuous flow system. Such a high catalytic activity is attributed to the active site structure: Zr node connectivity and geometry, potential factors governing degradation efficiency. This work represents a significant advance of conventional OP degradation materials to a highly efficient MOF catalyst with recycle capability, suggesting that coordination geometry of the Zr active site is a crucial factor for enhancing the catalytic activity of the Zr-based MOF.

#### EXPERIMENTAL SECTION

**Synthesis of PCN-224.** The PCN-224 sample was synthesized following a reported recipe with some modifications.<sup>48</sup> To a 100 mL vial,  $ZrOCl_2\cdot 8H_2O$  (125 mg), meso-tetra(4-carboxyphenyl)porphine (H<sub>4</sub>TCPP) (25 mg), DMF (50 mL), and acetic acid (12.5 mL) were added. After sonication, the mixture was heated at 65 °C for 72 h in an oven. The resulting powder was washed with DMF (20 mL ×3) for 2 d and acetone (20 mL ×9) for 4 d through centrifugation. After the solvent was decanted, the powder was dried at 90 °C for 12 h. The dried powder of PCN-224 was stored in a desiccator.

Synthesis of MOF-808. The synthesis of MOF-808 was based on a reported method.<sup>49</sup> To a 50 mL vial,  $ZrOCl_2\cdot 8H_2O$  (160 mg), 1,3,5benzenetricarboxylic acid (H<sub>3</sub>BTC) (110 mg), and a mixed solution of DMF (20 mL) and formic acid (20 mL) were added. The sample was heated at 100 °C for 7 d in an oven. The resulting powder was washed with DMF (20 mL ×3) for 2 d and acetone (20 mL ×4) for 2 d through centrifugation. After the solvent was decanted, the powder was dried at 80 °C for 3 h. The dried sample of MOF-808 was stored in a desiccator.

**Synthesis of NU-1000.** The NU-1000 sample was synthesized following a reported recipe.<sup>50</sup> To a 20 mL vial,  $ZrOCl_2.8H_2O$  (97 mg), benzoic acid (2.7 g), and DMF (8 mL) were added. The mixture was heated in an oven at 80 °C for 1 h. After heating, 1,3,6,8-tetrakis(*p*-benzoic acid)pyrene (H<sub>4</sub>TBAPy) (40 mg) was added. Then, the mixture was sonicated for 20 min. The sample was stirred at 100 °C for 24 h on a hot plate. The resulting solid was washed with DMF (10 mL ×3) through centrifugation. After washing, acid

treatment was conducted to remove benzoate in the NU-1000 sample. After the solvent was decanted, a mixed solution of DMF (12 mL) and 8 M HCl (0.5 mL) was added. Then, the sample was heated in an oven at 100 °C. The solid was washed with DMF (10 mL  $\times$ 3) for 2 d and acetone (10 mL  $\times$ 3) for 2 d. The NU-1000 sample was stored in acetone.

Pesticide Degradation Experiments. Degradation profiles of organophosphate pesticides (OPs) were obtained by in situ<sup>31</sup>P NMR measurement at room temperature. PCN-224, MOF-808, and NU-1000 samples were activated under vacuum at 100 °C for 12 h, 150 °C for 24 h, and 120°C for 12 h, respectively. The activated MOF samples (0.75 µmol Zr<sub>6</sub>) of PCN-224 (1.6 mg), MOF-808 (1.1 mg), and NU-1000 (1.7 mg) were dispersed in a buffer solution (1 mL) of H<sub>2</sub>O (0.9 mL), D<sub>2</sub>O (0.1 mL), and 4-ethylmorpholine (50  $\mu$ L) through sonication for 1 min. Separately, 25  $\mu$ mol OP [5.4  $\mu$ L for POX, 3.9  $\mu$ L for dichlorvos (DDVP), and 4.9  $\mu$ L for naled] was mixed with acetonitrile (0.1 mL). Caution: OPs are highly toxic. Experiments should be conducted with appropriate safety procedures. After the OP solution (0.1 mL) was added to the dispersed MOF sample, the mixture was shaken for 10 s and moved to an NMR tube. Then, the immediate <sup>31</sup>P NMR measurement was conducted. The NMR spectra were collected every minute for 30 min. The first spectrum was obtained at around 2.5 min after the OP solution was added to the MOF sample.

**DDVP Degradation with PCN-224 in a Simple Continuous Flow System.** A buffer solution of  $H_2O$  (10 mL) and 4ethylmorpholine (0.5 mL) was prepared. PCN-224 (16.4 mg, 7.5  $\mu$ mol Zr<sub>6</sub>) was homogeneously dispersed in the buffer solution (3 mL) through sonication for 1 min. The mixture was filtered through a syringe filter (PTFE with 0.2  $\mu$ m pore size; 13 mm diameter) so that PCN-224 was loaded on the filter. The syringe filter was washed with a new syringe containing the buffer solution (1 mL) on a syringe pump (0.1 mL/min). Separately, DDVP solution for five injections was prepared by mixing the buffer solution (5 mL), DDVP (9.75  $\mu$ L, 62.5  $\mu$ mol), and acetonitrile (0.5 mL). The DDVP solution (1 mL) was injected through the MOF filter using the syringe pump (0.1 mL/ min). With the same MOF filter, five injections continuously proceeded. For each injection, the filtrate was mixed with D<sub>2</sub>O (0.1 mL) and then analyzed with <sup>31</sup>P NMR spectroscopy.

#### RESULTS AND DISCUSSION

We targeted three commercial pesticides, POX, DDVP, and naled. POX has been extensively studied for its acute toxicity to mammals.<sup>51</sup> DDVP is one of the most widely used indoor pesticides, but there are concerns about indoor air pollution and toxicity to nontarget organisms, such as fish.<sup>52,53</sup> Naled, used for mosquito control, has adverse effects following prenatal exposure.<sup>54</sup> Regarding MOF candidates for efficient OP degradation, we compared the structures of Zr-based MOFs with high chemical stabilities, PCN-224,48 MOF-808,49 NU-1000,<sup>55</sup> and UiO-66 (Figure 2).<sup>56</sup> These MOFs have Zr<sub>6</sub> clusters with different connectivities (12 for UiO-66, 8 for NU-1000, and 6 for MOF-808 and PCN-224), derived from their different organic linkers. Sites unoccupied by linkers typically have solvents, H<sub>2</sub>O/OH, or monocarboxylate species, which can be replaced with substrates. Hence, the lower connectivity of the Zr<sub>6</sub> node yields a larger number of potential catalytic active sites. A previous study by Farha, Hupp, and co-workers on organophosphate nerve agent hydrolysis has revealed that Zr-based MOFs with lower node connectivities displayed higher degradation efficiencies.<sup>38</sup> A possible explanation is that the Zr-OH<sub>2</sub> bond strength becomes weaker with decreasing connectivity, thus facilitating the replacement of water with substrates.<sup>57,58</sup> While MOF-808 has the lowest node connectivity among the most investigated Zr-based MOFs for nerve agent hydrolysis, we hypothesized that PCN-224, also with six-node connectivity, could be a highly active OP



Figure 2. Framework structures,  $Zr_6$  node connectivities, and simplified node geometries of PCN-224, MOF-808, NU-1000, and UiO-66.

degradation catalyst. Therefore, PCN-224, MOF-808, and NU-1000 were prepared and their OP degradation efficiencies were compared.

MOF-808 and NU-1000 samples were synthesized and activated following previously reported procedures, 49,50 while a modified method was used to obtain the pure phase of PCN-224. The structural integrity of the activated MOF samples was confirmed with powder X-ray diffraction patterns (Figure 3a).  $N_2$  adsorption analysis at 77 K at  $P/P_0 = 1.0$  revealed uptake amounts of 840, 580, and 970 cm<sup>3</sup>/g for PCN-224, MOF-808, and NU-1000, respectively (Figure 3b). The pore size distribution data of PCN-224 and MOF-808 showed pore sizes of 19 and 18 Å, respectively (Figure S1), while 12 and 29 Å pores were observed for NU-1000. The gas sorption results corresponded to reported values for  $N_2$  uptake and pore size distribution.<sup>48,49,55</sup> The particle sizes of the as-synthesized samples were confirmed by scanning electron microscopy (Figure 3c). Particle sizes of ~2.5, ~10, and ~2  $\mu$ m were observed for PCN-224, MOF-808, and NU-1000, respectively. The characterization results revealed successful sample preparation for OP degradation experiments.

Before degradation analysis, the formula weights of the activated MOFs were determined from the <sup>1</sup>H NMR spectra of the digested MOF samples (Figures S2–S4). The activated MOF sample (3 mol %, 0.75  $\mu$ mol Zr<sub>6</sub>) was dispersed in water buffered with *N*-ethylmorpholine. After the pesticide solution in acetonitrile was added, hydrolysis progress was monitored by <sup>31</sup>P NMR spectroscopy. As the reaction proceeded, the intensity of the peaks at approximately –6.8, –3.3, and –3.0 ppm for POX (Figures S5–S7), DDVP (Figures S8–S10), and naled (Figures S11–S13), respectively, decreased in all the MOF samples. During the POX degradation, a peak at ~0.5

ppm, corresponding to diethyl phosphate (DEP), appeared. During the degradation of DDVP and naled, peaks corresponding to dimethyl phosphate (DMP), at 2.8 ppm, were observed. The formation of DEP and DMP indicates that the pesticides are hydrolyzed by the cleavage of P-O-C bonds, a well-known mechanism for the degradation of nerve agent simulants.<sup>35,59</sup> Based on the NMR results, simple hydrolysis schemes are shown in Scheme 1.

We compared the degradation efficiencies of PCN-224, MOF-808, and NU-1000 for the three OPs (Figure 4). Pesticide conversions were calculated from the integrated peak ratios. Initial reaction rates and half-lives were calculated with a first-order kinetic equation (Table 1 and Figures S14-S21).<sup>60</sup> Interestingly, PCN-224 demonstrated rapid hydrolysis of all the pesticides, while MOF-808 and NU-1000 showed relatively slower degradation (Figure 4a-c). The initial half-lives of degradation by PCN-224 were 2.1, <1, and 1.1 min for POX, DDVP, and naled, respectively. However, MOF-808 and NU-1000 showed half-lives of <5 min for only one pesticide. In particular, the conversion of POX, DDVP, and naled by PCN-224 reached almost 100% within 15 min, and the hydrolysis rate of the respective pesticide did not vary significantly (Figure 4a). In contrast, 68 and 38% conversions were observed for DDVP and naled by MOF-808, respectively (Figure 4b). NU-1000 showed conversions of 65% for DDVP and 40% for POX (Figure 4c). When we rearranged the degradation plots in terms of pesticide, PCN-224 showed the highest activity for the three pesticides (Figure 4d-f). In the case of DDVP, the degradation efficiency of PCN-224 was notably greater than those of MOF-808 and NU-1000 (Figure 4e). As control experiments, we filtered MOF catalysts 1 min after injection of pesticides. The filtrate samples were analyzed with <sup>31</sup>P NMR. POX, DDVP, and naled were not degraded in a short time without MOF catalysts (Figure S22). We also compared crystallinity of PCN-224, MOF-808, and NU-1000 after pesticide degradation (Figure S23). Powder X-ray diffraction patterns of those MOFs showed that crystallinity was retained after the catalytic reactions. Through an overall comparison of the three MOFs, we confirmed that PCN-224 has a high catalytic activity for OP degradation, which is less pesticide-type-dependent than those of MOF-808 and NU-1000.

The remarkable OP degradation efficiency of PCN-224 motivated us to determine the factors influencing its high activity. We first compared modulator amount in Zr<sub>6</sub> nodes of PCN-224, MOF-808, and NU-1000 because the number of modulator ligands has a significant impact on node accessibility, according to a recent report by Hupp, Lu, and co-workers.<sup>41</sup> <sup>1</sup>H NMR spectra of activated PCN-224, MOF-808, and NU-1000 samples showed 5.6 acetate, 3.0 formate, and 2.9 formate per Zr<sub>6</sub> node, respectively, while maximum potential active sites are 6, 6, and 4 for the MOFs (Figures S24-S26). PCN-224 has the most modulator ligands among the analyzed MOFs, thus meaning initially more blocked active sites. We also identified that most of the acetate and formate ligands were removed when the MOF samples were soaked in N-ethylmorpholine solution following the OP degradation experimental condition. Hence, the high catalytic activity of PCN-224 is not simply explained with the effects of the modulator ligand. Assuming that all Zr<sub>6</sub> node active sites are fully accessible by pesticide molecules, we focused on node connectivity and geometry. For the degradation of the nerve agent, less Zr node connectivity leads to higher degradation

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Figure 3. Characterizations of Zr-based MOFs to be used for pesticide degradation. (a) Simulated and experimental powder X-ray diffraction patterns, (b)  $N_2$  isotherms at 77 K, and (c) scanning electron microscopy images of PCN-224, MOF-808, and NU-1000. Scale bars indicate 5  $\mu$ m.

Scheme 1. Simple Degradation Schemes for the OPs, POX, DDVP, and Naled



efficiency, possibly due to the increased number of active site and the lower bond strength between Zr and coordinated  $H_2O$ , as described in the first paragraph of this section. While PCN-224 and MOF-808 have the same six-node connectivity, significantly different catalytic activities in OP degradation suggest that other factors are involved in the efficiency. Recently, Snurr and co-workers reported computational studies on the effects of node connectivity and topology on the binding of nerve agents.<sup>58</sup> In the study, the binding energy of coordinated H<sub>2</sub>O varies with node topology as well as connectivity. For example, the binding energy of H<sub>2</sub>O within the small pore is stronger than that within the large pore in NU-1000. This indicates that node geometry is important for water displacement, one of the potential rate-limiting steps. Therefore, we compared the node topologies of PCN-224 and MOF-808 (Figure 5). The  $Zr_6$  node of PCN-224 has six equatorial linker-binding sites (Figure 5a). The remaining six active sites are at the axial positions. In contrast, the node of MOF-808 has six active sites at the equatorial positions and six axial linker-binding sites (Figure 5b). We speculate that such distinct node geometries lead to different free energies of water displacement, the binding of the organophosphate, and the displacement of the degraded product, which are three potential rate-determining steps, as suggested in the computational works.<sup>58</sup> Although quantitatively evaluating the degradation efficiency of MOFs remains challenging, we suggest that calculating the free energy differences of the PCN-224 model for these steps will provide meaningful qualitative insights into how Zr<sub>6</sub> node geometry affects catalytic activity.



Figure 4. Degradation profiles of OPs. The conversion of POX, DDVP, and naled in the presence of (a) PCN-224, (b) MOF-808, and (c) NU-1000. The rearranged graphs for comparing catalytic activities of PCN-224, MOF-808, and NU-1000 for (d) POX, (e) DDVP, and (f) naled.

Table 1. Initial Half-Lives (min) for OP Degradation by PCN-224, MOF-808, and NU-1000



**Figure 5.**  $Zr_6$  node topologies of PCN-224 and MOF-808. The structure and simplified model of the  $Zr_6$  node with peripheral linker phenyl groups in (a) PCN-224 and (b) MOF-808, respectively. The potential active sites are depicted with red rods on the respective node of PCN-224 and MOF-808.

To further assess the high catalytic activity of PCN-224, degradation of DDVP was investigated using a simple continuous flow system (Figure 6). The activated powder of PCN-224 was dispersed in a buffer solution, loaded onto a syringe filter by filtration, and washed with the buffer solution. DDVP solution (1 mL) was then injected through the PCN-

![](_page_4_Figure_6.jpeg)

Figure 6. Degradation of DDVP with PCN-224 in a simple continuous flow system. For each injection, the conversion of the filtrate was confirmed with  $^{31}$ P NMR spectroscopy.

224-loaded filter using a syringe pump (0.1 mL/min). The next injection proceeded with a new DDVP solution. After each respective injection, the filtrate was collected and analyzed using <sup>31</sup>P NMR spectroscopy. Almost 100% conversion was observed after the first run, slightly decreasing to 95% after 5 injections. During the flow system experiment, the purple color of the filtrate was observed, indicating leaching of tetrakis(4-carboxyphenyl)porphyrin (TCPP). The amount of TCPP in the filtrate samples from MOF loading,

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washing, and following five injection steps was identified using UV-vis spectroscopy (Figure S27 and Table S1). After the washing step, leaching of 2 mol % was observed, while <1 mol	Seonghoon Kim – Department of Chemisi Institute of Science and Technology, Ulsan Korea	try, Ulsan National 44919, Republic of
% was found after the other steps (Figure S28). From the second injection onward the leaching amount of TCPP was	Eunji Jin – Department of Chemistry, Ulsan of Science and Technology Illsan 44919	n National Institute Republic of Korea
only $\sim$ 0.2 mol %. Based on these results, the high catalytic activity of PCN-224 for DDVP degradation was confirmed in the flow system, with reusability for several cycles.	Chang Yeon Lee – Department of Energy Engineering/Innovation Center for Chem Incheon National University, Incheon 220 Korea; • orcid.org/0000-0002-1131-90	and Chemical ical Engineering, 012, Republic of 71
	Complete contact information is available a	t:
In this work, we showed catalytic degradation of OPs, widely used pesticides toxic to humans and other organisms. For three	https://pubs.acs.org/10.1021/acs.inorgchem	ı.1c00653
commercial OPs, POX, DDVP, and naled, we investigated	Notes	
degradation efficiencies of Zr-based MOFs, PCN-224, MOF- 808. and NU-1000. with different active site structures.	The authors declare no competing financial	interest.
Compared to other MOFs, PCN-224 exhibited remarkable	ACKNOWLEDGMENTS	
conversion rates with POX, DDVP, and naled, showing half-	This work was supported by the Karee Env	ironmont Industry

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lives of a few minutes. Moreover, degradation efficiencies of

PCN-224 were not significantly varied depending on pesticide

types. The high activity of PCN-224 was further explored in a

simple continuous flow system, showing conversions of >95%

for several cycles. By comparing node connectivity and

geometry in Zr-based MOFs, we attribute the high activity

of PCN-224 to node coordination geometry, determined by the positions of linker-binding sites. This work demonstrates

that Zr-based MOFs can be utilized as extremely efficient

heterogeneous catalysts for OP degradation, suggesting node

geometry as a critical factor governing organophosphate

The Supporting Information is available free of charge at

Experimental details, pore size distribution and <sup>1</sup>H NMR

spectra of PCN-224, MOF-808, and NU-1000, <sup>31</sup>P

NMR spectra of pesticides in the presence of MOFs, <sup>1</sup>H

NMR spectra for identifying modulator amount, and

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UV-vis analysis for TCPP leaching (PDF)

degradation efficiency.

ASSOCIATED CONTENT

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