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## Removal of chlorine gas by an amine functionalized metal-organic framework via electrophilic aromatic substitution

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Jared B. DeCoste,<sup>\*a</sup> Matthew A. Browe,<sup>b</sup> George W. Wagner,<sup>b</sup> Joseph A. Rossin,<sup>c</sup> and Gregory W. Peterson<sup>\*c</sup>

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**Here we report the removal of chlorine gas from air via a reaction with an amine functionalized metal-organic framework (MOF). It is found that UiO-66-NH<sub>2</sub> has the ability to remove 1.24 g of Cl<sub>2</sub>/g of MOF via an electrophilic aromatic substitution reaction producing HCl, which is subsequently neutralized by the MOF.**

Since its use as the first modern chemical warfare agent (CWA) during the Second Battle of Ypres in World War I, chlorine gas has been a threat to military personnel.<sup>1</sup> While many more toxic threats, such as sarin (GB), soman (GD), and VX, have been weaponized on a large scale as CWAs, toxic industrial chemicals (TICs) remain a major threat due to their widespread production and availability. This ubiquitous industrial use, coupled with its most recent weaponized implementation in Iraq and Syria, make protection against chlorine once again a priority. Thus, having materials that can efficiently remove chlorine from airstreams is of utmost importance. Moreover, the same chemistries that are applied to the removal of chlorine from gas-streams could conceivably be used in the removal of chlorine from drinking and/or waste water-streams.

Current gas mask technologies typically use an activated carbon impregnated with metal salts, acids, and amines for the filtration of a broad range of toxic chemicals.<sup>2, 3</sup> One shortcoming of impregnated, activated carbons is that over time the various impregnants have a tendency to react with one another, rendering them ineffective against the chemical threats for which they were designed to protect.<sup>4</sup> Thus, nanomaterials with bound functional groups are ideal for the removal of chemical threats avoiding deleterious effects.

Metal-organic frameworks (MOFs) are hybrid materials composed of inorganic metal nodes, known as secondary

building units (SBUs), linked together by polydentate organic ligands to form a reticulated network. MOFs have demonstrated the capability to be utilized in gas storage,<sup>5-10</sup> gas separations,<sup>11, 12</sup> and molecular sensing,<sup>13-15</sup> among other applications; furthermore, MOFs have been researched extensively for their ability to be used for the adsorption of TICs and the degradation of CWAs.<sup>16-18</sup> Both the SBU and the organic linker have been shown to have the ability to affect the adsorption properties of the MOF. When the correct combination of SBU and linker is used, a MOF can adsorb or react with chemicals from various families or that require more complex interactions for removal.

The UiO family of MOFs has gained much interest due to its unprecedented chemical and physical stability.<sup>19-21</sup> More recently, UiO MOFs have shown the ability to perform catalytic hydrolysis,<sup>22,23</sup> as well as photocatalytic degradation.<sup>24</sup> The simplest member of the UiO family, UiO-66, is composed of Zr<sub>6</sub>O<sub>6</sub> SBUs each connected to 12 bidentate terephthalic acid ligands as shown in Figure 1. UiO-66-NH<sub>2</sub> has 2-amino terephthalic ligands, and has been shown to enhance the removal of various toxic gases over the parent MOF,<sup>25, 26</sup> as well as lower the band gap of the MOF.<sup>24</sup> Here we show the enhanced chlorine removal of UiO-66-NH<sub>2</sub>, over the parent UiO-

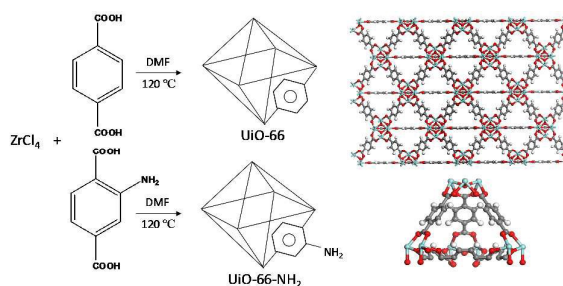


Figure 1. Reaction schemes showing the formation of UiO-66 (left, top) and UiO-66-NH<sub>2</sub> (left, bottom) and the UiO-66 structure showing the octahedral cages with a diameter  $\approx$  1.6 nm (right, top) and the tetrahedral cages with a vertical window opening  $\approx$  1.0 nm and 0.6 nm between each benzene ring (right, bottom).

<sup>a</sup> Leidos, Inc., PO Box 68, Gunpowder, MD 21010, USA E-mail: jared.b.decoste2.ctr@mail.mil

<sup>b</sup> Edgewood Chemical Biological Center, 5183 Blackhawk Rd. Aberdeen Proving Ground, MD 21010, USA E-mail: Gregory.w.peterson.civ@mail.mil

<sup>c</sup> Guild Associates, Inc., 5750 Shier Rings Rd., Dublin, OH, 43016, USA

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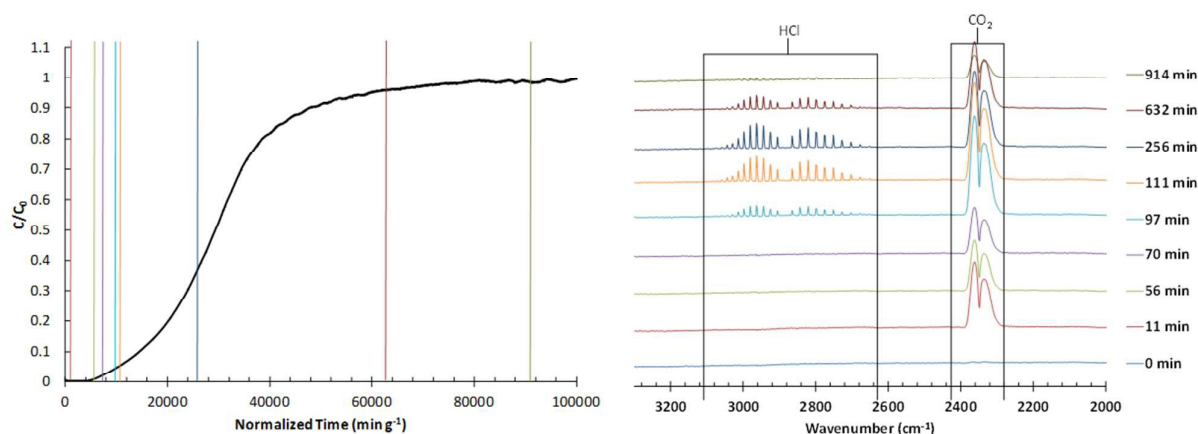


Figure 2.  $\text{Cl}_2$  microbreakthrough plot vs. normalized time for UiO-66- $\text{NH}_2$  (left) with colored vertical lines representing the time resolved FTIR spectra of the effluent showing the evolution of  $\text{CO}_2$  and HCl (right).

66, through a unique two-step removal mechanism that utilizes the organic ligand to initiate electrophilic chlorination and the inorganic SBU to react with the HCl byproduct in tandem.

To date, the only known study of chlorine gas on MOFs was performed by Britt et al.<sup>27</sup> In this study, four MOFs were examined for their chlorine capacities; however, no deeper analyses on the reaction mechanisms of these MOFs were performed. The authors concluded that the electron rich amine groups of IRMOF-3 contributed to the removal of chlorine through the formation of an ammonium chloride adduct. In our study, various MOFs were screened for their chlorine removal capacities using microbreakthrough experiments. Here we present an in depth analysis of the effect of the  $-\text{NH}_2$  functional group on the removal of  $\text{Cl}_2$  from contaminated air streams.

Microbreakthrough experiments (described in depth in the SI) were performed on approximately 10-15 mg samples of various materials, and the results can be seen in Figure S1.<sup>28, 29</sup> The capacity for each MOF and BPL-Cu-3T (a bituminous coal-based activated carbon impregnated with copper and 3% triethylenediamine, used as a representative material for current activated carbon filters) was calculated and can be seen in Table 1. The variety of UiO MOFs studied allows one to see the effect the  $-\text{NH}_2$  group has on the  $\text{Cl}_2$  removal capacity versus the presence of other functional groups. Furthermore, the three MOFs (UiO-66- $\text{NH}_2$ , MIL-53- $\text{NH}_2$  (Al), and ZIF-8) with capacities far higher than the others each have nitrogen atoms in their respective organic linker molecule (pendant  $-\text{NH}_2$  groups or aromatic nitrogen atoms). It should be noted that the lone pair of electrons on the nitrogen atoms in ZIF-8 are coordinated to the metal ions. These capacities correspond to 5.0, 0.7, and 1.700  $\text{Cl}_2$  molecules per nitrogen atom of UiO-66- $\text{NH}_2$ , ZIF-8, and MIL-53- $\text{NH}_2$  (Al), respectively. These capacities are evident that the removal mechanism is more complex than the formation of ammonium chloride adducts for MOFs with pendant amine groups, as proposed by Britt et al.<sup>27</sup> Additionally, the breakthrough profiles (Figure S1) immediately baseline upon purging of the feed with dry air, suggesting the occurrence of a chemical reaction and not physisorption.

Based on its extremely high chlorine removal capacity and the enhanced structural and chemical stability of UiO MOFs, UiO-66- $\text{NH}_2$  is a prime candidate for use in respiratory protection.

Table 1. Chlorine Capacities for Various Materials

	BET Surface Area ( $\text{m}^2 \text{g}^{-1}$ )	Capacity ( $\text{mol kg}^{-1}$ )	Capacity ( $\text{g g}^{-1}$ )
BPL-Cu-3T	760	1.9	0.13
UiO-66	1100	0.4	0.03
UiO-66-OH	950	0.7	0.05
UiO-66- $\text{NH}_2$	1070	17.5	1.24
MIL-53	1290	0.1	0.01
MIL-53- $\text{NH}_2$ (Al)	720	8.0	0.56
Cu-BTC	1700	0.1	0.01
ZIF-8	1800	6.1	0.43

Upon exposure to ambient moisture conditions and various chemicals, UiO-66 and UiO-66- $\text{NH}_2$  have shown the ability to maintain their crystalline structure.<sup>20, 21, 30</sup> Upon exposure to  $\text{Cl}_2$ , however, the structural integrity of UiO-66- $\text{NH}_2$  is compromised, as seen in the X-ray diffraction (XRD) pattern (Figure S2.). In contrast, the parent UiO-66 material maintained its structural integrity upon exposure to  $\text{Cl}_2$  (Figure S3). MOF degradation typically is initiated with the coordinate covalent bonds between the carboxylate groups of the organic linker and the metal ions of the SBU;<sup>31</sup> thus, UiO-66 and UiO-66- $\text{NH}_2$  are typically stable toward the same types of chemical species. The fact that UiO-66- $\text{NH}_2$  degrades in the presence of  $\text{Cl}_2$ , while UiO-66 does not, leads to the hypothesis that other species are being produced during the removal of  $\text{Cl}_2$  by UiO-66- $\text{NH}_2$ , leading to the degradation of the MOF structure.

Products created by the reaction of  $\text{Cl}_2$  with UiO-66- $\text{NH}_2$ , were monitored in the effluent of the microbreakthrough reaction using a Fourier transform infrared spectrometer (FTIR), and time-resolved analyses were performed. As  $\text{Cl}_2$  cannot be monitored via FTIR, the breakthrough time must be estimated from the previous microbreakthrough experiments, where  $\text{Cl}_2$  was monitored by a photoionization detector, as detailed in Figure 2. The 56 minute scan is where  $\text{Cl}_2$  breakthrough initially occurs, albeit less than 10% breaks

through until the 111 minute scan. Breakthrough is nearly complete at the final scan of 914 minutes. Throughout the experiment it can be seen that the evolution of CO<sub>2</sub> (doublet center at 2350 cm<sup>-1</sup>) increases for the first 111 minutes of the experiment, and then decreases as the experiment continues. The other notable species is the appearance of HCl (series of bands centered at 2880 cm<sup>-1</sup>) at 97 min that increases until 256 min where it then begins to decrease. The HCl species is nearly gone by the final FTIR spectrum at 914 minutes, when Cl<sub>2</sub> breakthrough is complete and presumably not reacting with the MOF to produce additional HCl.

X-ray photoelectron spectroscopy (XPS) was performed on UiO-66 and UiO-66-NH<sub>2</sub> pre and post exposure to Cl<sub>2</sub>. It can be seen from the deconvolution of the Cl 2p spectrum in Figure S5, that there are two distinct chlorine species produced upon exposure of UiO-66-NH<sub>2</sub> to Cl<sub>2</sub>. The chlorine species at a binding energy of 198.8 eV is consistent with the 2p<sub>3/2</sub> peak of a zirconium-chlorine bond,<sup>32</sup> while the species at 200.7 eV is consistent with the 2p<sub>3/2</sub> peak of an aryl carbon-chlorine bond.<sup>32, 33</sup> It is also interesting to note that there is no evidence of any Cl atoms on the UiO-66 exposed to Cl<sub>2</sub>. These results paired together suggest that the organic 2-aminoterephthalate ligand works in tandem with the inorganic Zr<sub>6</sub>O<sub>6</sub> SBU to react Cl<sub>2</sub>. The carbon 1s XPS spectra shown in Figure S6 exhibit the loss of a shoulder peak at approximately 288.4 eV, corresponding to a carboxylate group coordinated to a metal atom.<sup>34</sup> The loss of a carboxylate group is consistent with the appearance of CO<sub>2</sub> in the FTIR experiment, and the destruction of the MOF structure as seen in XRD.

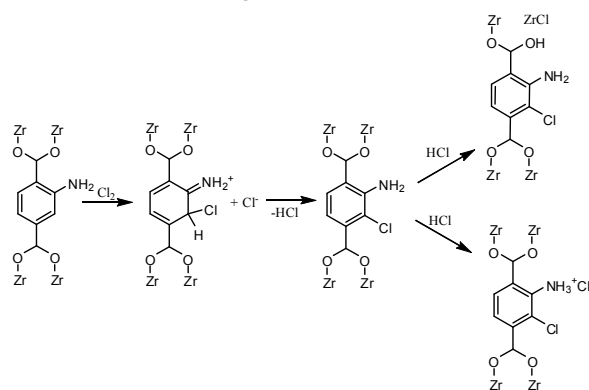
Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra were collected on the pre- and post-Cl<sub>2</sub> exposed UiO-66 and UiO-66-NH<sub>2</sub> (Figures S6 and S7). There were minimal changes in the UiO-66 spectrum; however, there is a general broadening of the FTIR bands seen for UiO-66-NH<sub>2</sub> upon exposure to Cl<sub>2</sub>. This broadening is indicative of structural breakdown and potential perturbation of the structure.<sup>20</sup> It is also important to note the appearance of FTIR bands at 1605 and 1404 cm<sup>-1</sup>, which are indicative of ZrOCl<sub>x</sub>-type species, supporting the XPS results.

To further elucidate the reaction of Cl<sub>2</sub> with UiO-66-NH<sub>2</sub>, the Cl<sub>2</sub>-exposed MOF was digested and <sup>1</sup>H nuclear magnetic resonance (NMR) was performed, as seen in Figure S9. While there is still a small amount of unreacted 2-aminoterephthalic acid (ATA, the UiO-66-NH<sub>2</sub> linker) left in the MOF as indicated by δ ≈ 7.73 (dd), 7.85 (d), and 8.00 (d) ppm, the major products are perturbed versions of the linker, as indicated by singlets in the aromatic region at δ ≈ 7.43, 7.58, and 7.73 ppm. The chemical shifts being exclusively singlets in varying ratios indicate aromatic rings that are substituted to varying degrees with chlorine atoms in place of the hydrogen atoms on the unperturbed 2-aminoterephthalic acid linker. Another interesting feature in the <sup>1</sup>H NMR is the presence of a 1:1:1 triplet at δ ≈ 7.06 ppm, which is indicative of an ammonium ion present in the solution likely due to degradation of the linker at the amine site. As this feature is not present in the pre Cl<sub>2</sub> exposed UiO-66-NH<sub>2</sub> spectrum, it appears as though

this degradation of the linker occurs during Cl<sub>2</sub> exposure, and not from degradation during the digestion process.

The mechanism was further elucidated by bubbling Cl<sub>2</sub> through an acetonitrile solution of 2-aminoterephthalic acid (the UiO-66-NH<sub>2</sub> linker), and the major products were identified from <sup>1</sup>H NMR (Figure S10) along with gas chromatography-mass spectrometry (Table S2) to be 2-amino-3-chloroterephthalic acid and 2-amino-5-chloroterephthalic acid.<sup>35</sup> These products suggest that Cl<sub>2</sub> is reactive with the MOF linker in the absence of a catalyst, due to the strong activating characteristics of the amine group; consequently, only the ortho and para isomers are observed, while the meta isomer is not. It is also interesting that only monochlorinated species were observed, and no further chlorination occurs, indicating that the MOF structure aids in the subsequent chlorination of the linker in a way that the linker alone cannot.

A proposed mechanism for Cl<sub>2</sub> removal by UiO-66-NH<sub>2</sub> through electrophilic aromatic substitution is shown in Scheme 1. The initial chlorination of the aromatic ring produces a chlorine substitution likely at the position ortho or para to the amine group, as observed in the reaction of just the linker with Cl<sub>2</sub>, and 1 equivalent of HCl. HCl can either be neutralized by the amine group as an ammonium chloride adduct or react with the zirconium-carboxylate bond between the organic linker and the SBU, eventually leading to the structural degradation of the MOF.<sup>20</sup> Subsequent chlorination reactions will consume the other ortho/para position on the aromatic ring, while the strong activating -NH<sub>2</sub> group is intact on the aromatic ring; however, it should be noted that -NH<sub>3</sub><sup>+</sup> is a strong deactivating group, and would allow for chlorination at the meta position to occur. Furthermore, eventually all of the sites where HCl can react are consumed, leading to the observation of HCl eluting from the MOF in the time-resolved



FTIR experiment.

Scheme 1. Proposed reaction mechanism for the removal of Cl<sub>2</sub> by UiO-66-NH<sub>2</sub>.

As indicated by the XRD pattern, the reaction with Cl<sub>2</sub> gas eventually degrades the MOF structure, likely collapsing and blocking pores, causing many potential nucleophilic sites not react. However, the 12-coordinated SBU of UiO MOFs likely delays the structural collapse of the MOF when compared to other 2-aminoterephthalic acid containing MOFs, such as IRMOF-3 and MIL-53-NH<sub>2</sub> (Al). Furthermore, it was shown by

Kim et al. that when 2-amino-3-chloroterephthalic acid or 2-amino-5-chloroterephthalic acid is incorporated into the structure, the pores are still accessible to small molecules such as N<sub>2</sub>.<sup>35</sup> This along with the high removal capacity shows that the pores of UiO-66-NH<sub>2</sub> are still accessible after chlorination.

We reported here on unprecedented removal capacities of 1.24 g of Cl gas per g of UiO-66-NH<sub>2</sub> through an electrophilic aromatic substitution reaction mechanism by the MOF linker, followed by the reaction of HCl with the SBU and/or the formation of an ammonium chloride adduct. The presence of an organic and an inorganic component in MOFs has been hypothesized to be a useful characteristic, but it has rarely been utilized in a tandem reaction mechanism as shown here. Furthermore, the use of the aromatic ring of the MOF to act as a nucleophile in an electrophilic aromatic substitution reaction has not previously been reported. The use of the aromatic ring in UiO-66-NH<sub>2</sub>, or other MOFs with an aryl amine linker, opens the door to many potential reactions not only in air purification, but as to use MOFs as nucleophiles in a variety of organic reactions.

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