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Multiple Functional Groups in UiO-66 Improve Chemical Warfare Agent Simulant Degradation

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A library of 26 mixed ligand UiO-66 analogs were synthesized, characterized, and screened for catalytic degradation of the chemical warfare agent (CWA) simulant dimethyl 4-nitrophenylphosphate (DMNP). The MOFs were screened and compared to physical mixtures of the same single component MOFs, as well as to the most active MOFs in the literature for reference. Several of the MOFs display higher catalytic activity than the parent UiO-66 and other single ligand UiO-66 analogues.

There is a need to develop advanced materials to protect warfighters and civilians against chemical warfare agents (CWAs), such as organophosphorous nerve agents, as worldwide efforts to outlaw their use in conflicts have been unsuccessful.[1] Recently, metal-organic frameworks (MOFs) have emerged as a potential candidate for degradation of CWAs due to their porous nature and density of catalytically active metal centers.[2] MOFs are constructed from multitopic organic ligands that link together inorganic metal nodes known as secondary building units (SBUs) to form highly porous two- and three-dimensional complex frameworks.[3] Some zirconium-based-MOFs have displayed high catalytic activity against CWAs, and this is primarily attributed to the strong Lewis acidity of the metal center.[2]

Theoretical models, such as density functional theory (DFT), suggest the catalytic degradation of the CWAs occurs at open metal sites or defect sites of the MOF SBUs.[4] As such, most attempts to improve MOF catalytic activity against CWAs has focused on experimentally engineering more defect sites at the SBU by optimizing various MOF synthetic conditions such as equivalents of acid modulator, temperature, time, etc.[5] While this approach has been promising, a second approach involving different functional groups on MOF ligands has also promoted more rapid degradation of CWAs and their simulants.[6] These reports have shown MOFs with amine functionalities degrade CWAs and the CWA simulant dimethyl-4-nitrophenyl phosphate (DMNP) at a faster rate than unfunctionalized MOFs.[6b, 6c] These experiments were conducted under highly basic conditions (pH = 10), and this increased activity is attributed to the amine ligand behaving as a Brønsted base.[4c] However, other reports have shown, in the case of UiO-66-NH2 (UiO = University of Oslo), that this increased activity is not observed at more neutral conditions (pH = 8).[7] Current efforts have focused on optimizing MOF catalysis near neutral pH to best emulate field conditions wherein this material would come in contact with CWAs.[6a, 7-8] Recently, we reported a 4-fold increased activity by functionalizing UiO-66 ligands with iodine (i.e., UiO-66-I), and this enhancement in activity was attributed to halogen bonding between iodine atoms and DMNP molecules creating a more electrophilic phosphorus center.[6a] This finding indicates that subtle changes at the organic linkers of UiO-66 can play a significant role in the increased catalytic activity of MOFs against CWAs.

We sought to capitalize on the improvement organic ligands can bring by systematically varying the ligand substituents. Previously, Yaghi et al. reported a series of multivariate (MTV) MOF-5 materials that created heterogenous pore environments by incorporating nine different functionalized ligands into a single MOF.[9] The MTV-MOF-5 materials were examined for gas sorption properties, exhibiting enhancements in storage and selectivity that were greater than the individual ligand systems. The authors attributed this increase in uptake and selectivity to synergistic ligand effects,[9] but the specific effects were not enumerated. Here, we apply this concept for the first time to a catalytic system and observe a similar synergistic enhancement with UiO-66 for a contemporaneous application regarding the degradation of CWA simulants.

Herein, a library of 26 mixed ligand UiO-66 derivatives, using various combinations of five different ligands (Figure 1), were synthesized and screened for catalytic degradation of DMNP via a high-throughput screening (HTS) method. The mixed ligand

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derivatives display superior ability for DMNP degradation (at pH = 8) than physical mixtures of the various MOFs. This result underscores the significance of the HTS methodology as the ability to rapidly assess catalytic behavior of materials is no longer a barrier to evaluating catalytic MTV-MOFs. To confirm this was indeed a ligand-based effect, MOF defect sites were quantified via thermogravimetric analysis (TGA) and the results indicate no correlation with catalytic activity. These findings suggest that multiple ligand functional groups in the same active site pocket can play a synergistic role in increasing the catalytic activity against DMNP.
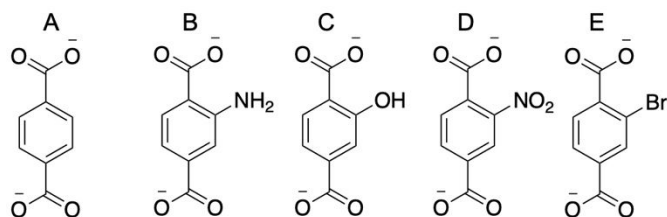

Figure 1. Ligands used for MTV-UiO-66 mixed ligand synthesis.

All MOFs in this study were synthesized using an acetic acid modulated synthesis procedure (see Supporting Information).[10] For mixed ligand synthesis of UiO-66, five ligands were selected; 1,4-benzendicarboxylate (bdc^{2-}) and four derivatives (Figure 1): two with electron donating functional groups (NH_2-bdc^{2-}, OH-bdc^{2-}) and two with electron withdrawing groups (NO_2-bdc^{2-} and Br-bdc^{2-}). Using these ligands, we synthesized all possible ligand combinations (e.g., one, two, three, four and five ligands in a single MOF) leading to a library of 26 different mixed ligand UiO-66 derivatives termed multivariate UiO-66 (MTV-UiO-66). MOFs were named according to which ligands they are composed of; for example, MTV-UiO-66-AB contains a 1:1 mixture of bdc^{2-} and NH_2-bdc^{2-} ligands whereas MTV-UiO-66-BCE contains a 1:1:1 mixture of NH_2-bdc^{2-}, OH-bdc^{2-}, and Br-bdc^{2-}.

MTV-UiO-66 MOFs were characterized via powder X-ray diffraction (PXRD) to determine MOF formation. MOF samples were also digested in dilute acid and characterized via ^{1}H NMR to determine the percent incorporation of each ligand (Figure 2, Figures S1-S31, Table S1). To quantify the ligand incorporation in each MOF, characteristic peaks of each ligands ^{1}H NMR spectra were identified and used to quantify the components in the MTV-UiO-66 MOFs (Figure 2). The library of MOFs was screened for their ability to degrade the CWA simulant DMNP using a previously validated HTS method (Figure 3).[8] DMNP has been utilized as a safer alternative to CWAs while most effectively mimicking the phosphoester bond. Cleavage of the DMNP phosphoester linkage is monitored by UV-Vis spectroscopy by tracking the appearance of a colorimetric product, p-nitrophenoxide, which absorbs strongly at 407 nm. Rates were calculated to account for varying molar mass of MOFs so a more direct comparison could be made between the materials using a previously reported analysis.[6a]

The MTV-UiO-66 MOFs display significantly higher activity than MOFs with only one type of ligand; no correlation as a function of electron donating or withdrawing group was observed. For example,

MTV-UiO-66-B MOF and the MTV-UiO-66-E MOF display about 3-fold poorer activity than when these ligands are both incorporated into the MTV-UiO-66-BE. Interestingly, seven of the top eight MTV-UiO-66 MOFs contain the NH_2-bdc^{2-} linker while the single ligand MTV-UiO-66-B is one of the poorest performing MOFs. This result indicates there is a synergistic ligand effect occurring when multiple functional groups are incorporated into a single MOF. MOF particle size was analysed via scanning electron microscopy (SEM) and the results indicate no basis in the DMNP activity as a function of particle size (Figure S32). The surface area of the MOFs was analysed via N_2 gas sorption and show no correlation with the DMNP catalysis data, hence enhanced catalysis is not a result of higher BET surface area (Figure S33-S43). To further study these MOFs, thermogravimetric analysis (TGA) was conducted to quantify ligand defects using a procedure previously published by Lillerud et al.[5a] The results indicate nearly all MOFs have identical ligand defects and no correlation between activity and ligand defect sites (Figure S44-S50, Table S2).
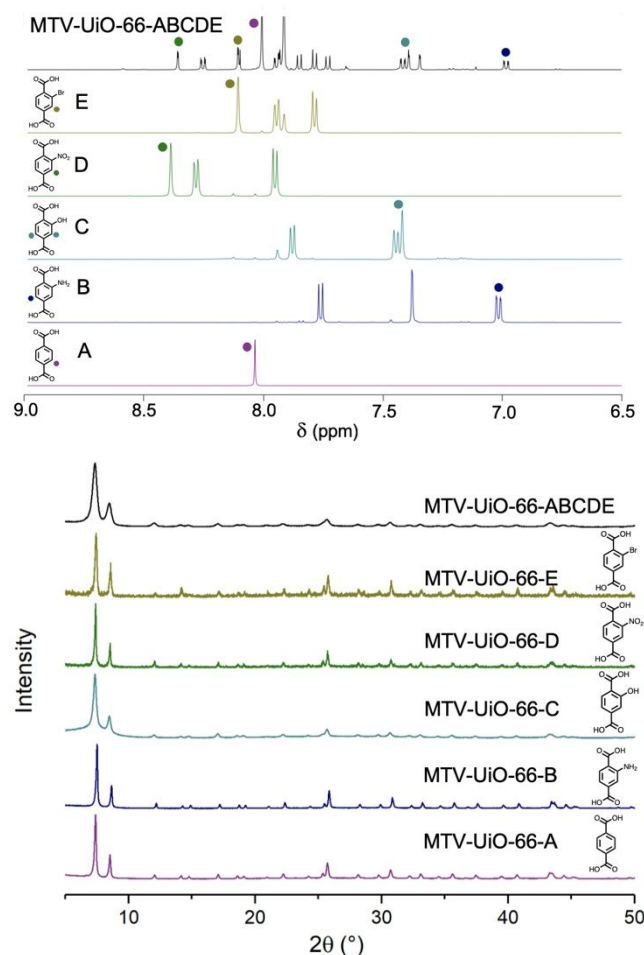

Figure 2. *Top*: ^{1}H NMR of digested single ligand MOFs and MTV-UiO-66-ABCDE highlighting peak labels used to quantify ligand incorporation. *Bottom*: PXRD of single ligand MOFs and MTV-UiO-66-ABCDE.

To further verify the synergistic effects of multiple ligand functional groups, single ligand MOFs were physically mixed using the same ratios as those present in the MTV-UiO-66 and screened for DMNP degradation (Figure 4). For example, a 1:1 mixture of MTV-

UiO-66-B and MTV-UiO-66-E were compared against MTV-UiO-66-BE. These results indicate that ligand incorporation within the MTV-UiO-66 significantly increases the catalytic degradation of DMNP when compared to physical mixtures of MOFs. Mixtures of single component MOFs with differing functional groups perform essentially the same as the individual MOFs. For example, the UiO-66 derivative containing ~33% 1,4-benzenedicarboxylic acid (bdc^{2-}), ~33% Br-bdc^{2-} and ~33% NH_2-bdc displays over 3-fold better activity than a physical mixture combining 33% UiO-66, 33% UiO-66-NH_2, and 33% UiO-66-Br. These results further indicate a synergistic ligand effect contributing to the degradation of DMNP in the mixed ligand systems.

As previously mentioned, Yaghi et al., utilized multiple functional groups to enhance the gas sorption properties in MOF-5. These studies showed that through incorporation of multiple ligands in a MTV-MOF-5, the H_2 gas sorption capacity more than doubled. Further, using other combinations of ligands in MTV-MOF-5, specific combinations gave a four-fold increase in selectivity for CO_2 over CO. These enhancements in the gas sorption properties of MTV-MOF-5 were significant, but the origin of these effects remains unknown. Similarly, in this report we have shown a 3-fold increase in the catalytic degradation of DMNP by MTV-UiO-66-BE, and we attribute this to a synergistic ligand effect; however, the precise origin of this effect is unclear at this time. Nevertheless, we show that numerous derivatives of MOFs can be screened, and trends rapidly established across many materials using our HTS methodology.
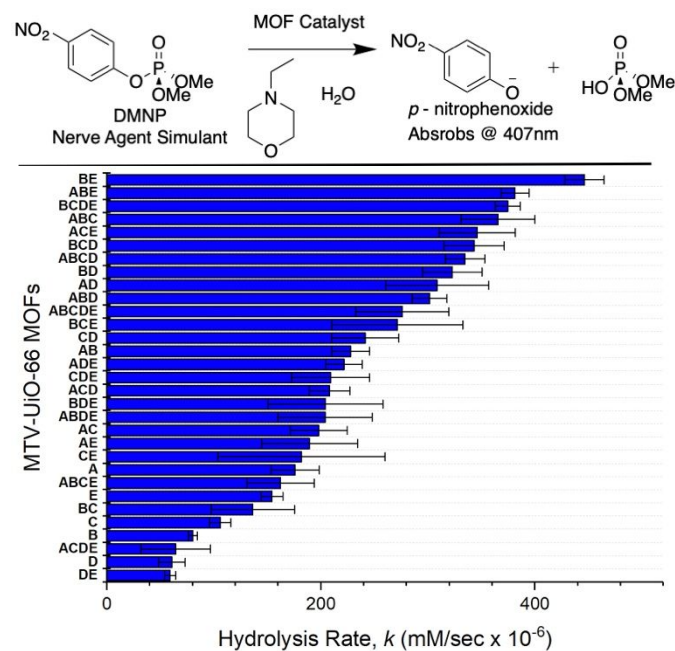

Figure 3. *Top:* Scheme of DMNP assay conditions. *Bottom:* Rate of catalytic degradation of DMNP by all MTV-UiO-66 MOFs.

In conclusion, a library of 31 mixed ligand UiO-66 MOFs was synthesized and screened for the catalytic degradation of the CWA simulant DMNP. The top performer in our library is MTV-UiO-66-BE which consists of NH_2-bdc and Br-bdc linkers. This MOF is over three times more active than either the single ligand MTV-UiO-66-B (UiO-66-NH_2) and MTV-UiO-66-E (UiO-66-Br) or a physical mixture of these two MOFs. Full

characterization and defect quantification were conducted that indicate no correlation or increased activity as a result of defects. As such, this increased activity in the MTV-UiO-66 series originates from a synergistic ligand effect enabling more rapid degradation of DMNP. These results further underscore the significance of functional groups on MOF ligands in the degradation of CWAs and their simulants and the nature of the synergy observed in mixed ligand MOFs is currently the subject of ongoing studies.
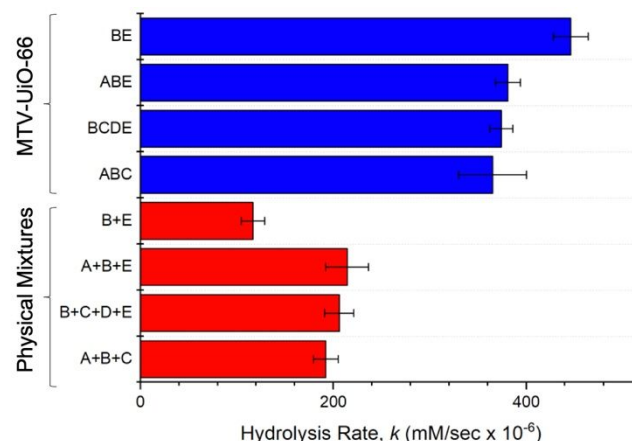

Figure 4. Rate of catalytic degradation of DMNP by top MTV-UiO-66 MOFs (*blue*) compared to their physical MOF mixtures (*red*).

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