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Functionalizing the Defects: Post Synthetic Ligand Exchange in the Metal Organic Framework UiO-66

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ABSTRACT: Herein, we explore the possibility of functionalizing UiO-66 with the monoethanolamine (MEA) moiety. Several unsuccessful routes are discussed before we show that it can be achieved via a 2 stage post synthetic ligand exchange (PSE) reaction with a highly defective UiO-66 sample. The intermediate material is the most porous UiO-66 sample ever reported. We expect that this novel approach will allow many other functional moieties to be introduced.

Due to the near infinite possibilities regarding their structure, porosity, and function, metal-organic frameworks (MOFs) are of great promise for a variety of applications. One popular subset of these materials are "Zr_6 MOFs", whose inorganic units are based on a common foundation of six zirconium (IV) cations arranged in an octahedron. UiO-66 (**$Zr_6(OH)_4O_4(BDC)_6$**, BDC = Benzene-1,4-dicarboxylate), often hailed for its superior stability, was the first Zr_6 MOF to be reported[1] and is (perhaps consequentially) the most widely studied. Despite this popularity, its inherent capabilities in commonly proposed applications (e.g. adsorption and catalysis) are limited; a fact which we attribute to its modest porosity, the relative inertness of its inorganic nodes, and the lack of reactive functional groups on its terephthalate linkers.

Much attention has therefore been given to functionalized and/or extended derivatives of UiO-66 (e.g. UiO-66-NH_2 and UiO-67), which can easily be obtained via reticular synthesis.[2] Under this traditional synthetic regime, functionality is provided to the MOF by synthesizing it in the presence of an organic linker which resembles that of the parent material, but with an additional, pendant functional group (e.g. $-NH_2$) which does not bind to the inorganic nodes. By the same token, the conventional method for enhancing the porosity of a MOF is to synthesize it with a longer version of the organic linker used to obtain the parent material. While very powerful, these established methods rely on the commercial availability of the desired linker(s), which are often prohibitively expensive. For this reason, many groups synthesize their own linkers in house, which can often be challenging, expensive, and time consuming, especially when considering that the linker is essentially an intermediate from which a successful MOF synthesis is not guaranteed. With all of this in mind, it is clear that an alternative method for functionalizing and/or increasing the porosity of UiO-66 is desired.

To this end, we have taken inspiration from our recent study on the defect chemistry of UiO-66 samples synthesized in the presence of monocarboxylic acid "modulators".[3] Therein, we showed that the modulators actually become incorporated into the framework by compensating for missing cluster defects via coordination of their carboxylate group. These defects significantly enhance the porosity of the material, and it soon occurred to us that we may be able to further exploit this chemistry to introduce new functionality to the UiO-66 framework. Namely, we envisioned that "functionalized modulators" (monocarboxylic acids with additional functionality) could be incorporated in the same manner as those previously studied, leaving their pendant functional groups free for chemical interaction. Such chemistry would unlock new opportunities for MOF researchers, who would no longer be restricted to terephthalate derivatives for introducing organic functionality to UiO-66. Moreover, this method of functionalization could improve the commercial viability of the material since monocarboxylic acids are generally cheaper and more widely available than organic linkers.

In this work, we investigate the possibility of introducing the monoethanolamine (MEA) moiety to the UiO-66 framework (see **Figure 1**). The reasons for this aim were twofold; (1) MEA is known for its excellent CO_2 adsorption properties in solution, and (2) MEA has never before been successfully incorporated into a MOF, likely because the moiety is difficult to assimilate into an organic linker. Instead, we hoped that we could achieve our goal with the "functionalized modulator" approach outlined above; specifically by employing the inexpensive amino acid L-Serine (see **Figure 1**) as modulator. However, we soon became aware of L-Serine's scarce solubility in DMF or any other polar aprotic solvent used to synthesize UiO-66. It was therefore of little surprise when L-Serine was not detected in the product obtained by this method. Syntheses in DMF/H_2O mixtures at various reaction temperatures were similarly unsuccessful, making it clear that the "functionalized modulator" approach was not going to provide a satisfactory result and that an alternative synthesis strategy was required.

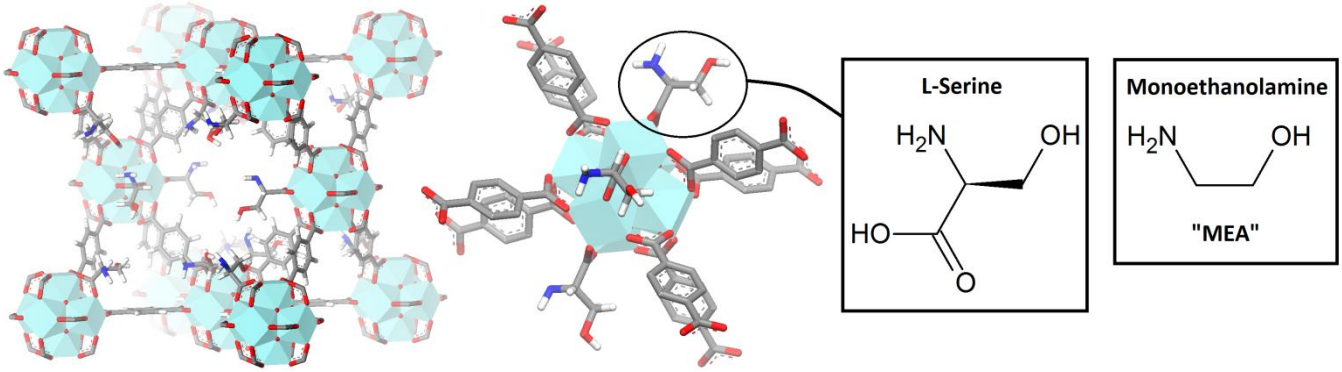

Figure 1. Left: hypothetical structural model in which L-serine ligands compensate for a missing cluster defect in UiO-66. Synthesizing a UiO-66 sample with such defects is the goal of this work. Middle: environment of each Zr_6 cluster in the structure.

For this, we drew encouragement from the plethora of literature on post synthetic methods. In particular, the Cohen group has demonstrated the ease at which UiO-66 can undergo a variety of post synthetic reactions, e.g. post synthetic ligand exchange (PSE).[4] Inspired by their work, we endeavored to introduce the MEA moiety via a PSE reaction between UiO-66 and L-serine. However, we are increasingly aware that not all UiO-66 samples are created equal: almost all synthesis procedures yield a defective material, and the concentration and/or nature of the defects can vary significantly depending on the synthesis conditions.[2, 3, 5] Anticipating that these variations could strongly impact UiO-66's reactivity in PSE reactions, we opted to synthesize it via a method which has previously given the Cohen group success in their work.[4] The stand-out feature of the method is the addition of a 50-fold excess of benzoic acid as modulator, and so we refer to the resulting UiO-66 sample as "50Benz".

From our characterization of 50Benz (see SI, Section **4.1**), it is clear that the sample contains a very high concentration of missing cluster defects – similar to the most defective sample from our previous study.[3] As in said work, we strongly assert that the defects are compensated by deprotonated modulator molecules, in this case benzoate. This assertion is backed up by the detection of a very large amount of benzoate in the dissolution/^{1}H NMR spectrum obtained on the sample (**Figure 2**, black curves). Indeed, the molar ratio between benzoate and BDC $\left(\frac{\mathbf{Benz.}}{\mathbf{BDC}}\mathbf{m}_R\right)$ in the sample is 0.78 (as determined by integration see **Section 3.3** of SI), higher than the equivalent ratios in any of the samples from our previous study.[3]

Our conclusions regarding the defectivity of 50Benz are further validated by **Figure 3**, where one can see that the nitrogen adsorption isotherm obtained on the sample matches rather well with that simulated from Reo-Benz (see **Figure 4**), a hypothetical defective UiO-66 structural model in which benzoate ligands compensate for a very high concentration of missing cluster defects (one defect per unit cell). However, we note that this conclusion is in direct contradiction with our previous study, in which we concluded that the concentration of missing cluster defects systematically increases as the acidity of the modulator is increased.[3] Under such a regime, one would not expect benzoic acid, a rather weak acid (pK_a = 4.20) to produce a material with a high concentration of defects. Nevertheless, we can think of two reasons why such a defective material was indeed produced: (1) solubility effects - benzoic acid is a solid with finite solubility in the MOF synthesis solvent (DMF) while the modulators from the previous study were all liquids with complete miscibility;[3] (2) steric effects - these were not such an issue in the previous study, where the modulator molecules were limited to 1-2 carbon atoms.[3]

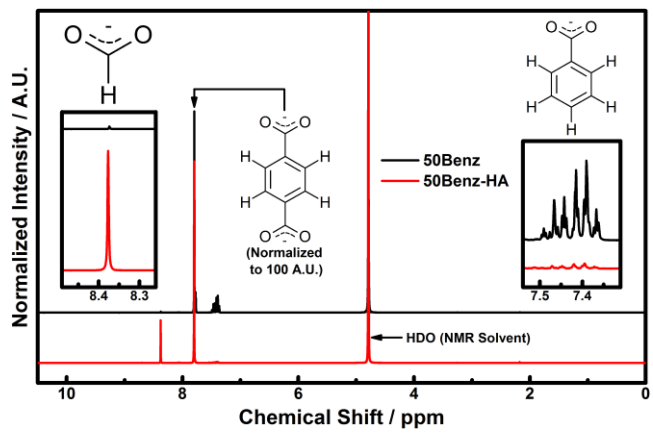

Figure 2. Dissolution/^{1}H NMR spectra obtained on 50Benz before (black) and after (red) HCl activation.

Convinced with our analysis of 50Benz, we attempted to react it with L-Serine, hoping that the benzoate ligands would be exchanged for L-Serine, yielding a UiO-66 product whose defects resemble that presented in **Figure 1**. Similar chemistry has recently been tentatively explored by Gutov et al.[6] However, only a tiny amount of L-serine was incorporated into 50Benz after PSE, as evidenced by dissolution/^{1}H NMR spectroscopy (see **Figure S28**). A control experiment on a near defect free UiO-66 sample (also shown in **Figure S28**) yielded a similar result.

While we were initially surprised by the poor reactivity of 50Benz, we soon envisioned that the bulkiness of its benzoate ligands could be to blame. We then took inspiration from Farha and coworkers, who have repeatedly demonstrated that benzoate ligands can be removed from NU-1000 (another Zr_6 MOF) via post synthetic treatment in a DMF/8M HCl mixture.[7] After applying this "HCl activation" procedure to 50Benz, yielding "50Benz-HA", we were delighted to find very little benzoate $\left(\frac{\mathbf{Benz.}}{\mathbf{BDC}}\mathbf{m}_R = \mathbf{0.04}\right)$ in its dissolution/^{1}H NMR spectrum (red curves in **Figure 2**). Further analysis unveiled a fascinating and unexpected result - benzoate was replaced by formate in near 1:1 stoichiometric proportions (see **Section 4.2.1.** of the SI). This ligand exchange is qualitatively

evident in the spectra presented in **Figure 2**. Since the formate ligands were not added as reagents, they must have instead originated from DMF hydrolysis, a reaction which is catalyzed by strong acids (e.g. the 8M HCl used in the HCl activation process), producing formic acid. Interestingly, formate/benzoate ligand exchange was not observed in the aforementioned work on NU-1000, where it was instead concluded that benzoate is replaced by terminal –OH groups on the clusters.[7] We do not find any evidence for hydroxide substitution in this work (see ATR-IR results in **Section 4.2.4** of the SI).

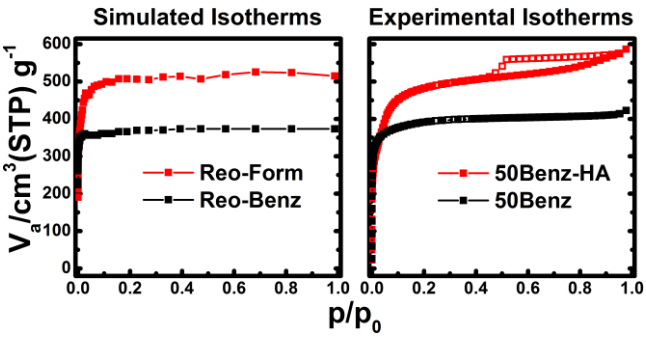

Figure 3. Comparison of simulated and experimentally obtained N_2 sorption isotherms (77K). Simulated isotherms were obtained from the structural models shown in **Figure 4**.

Importantly, the integrity of the structure and the high concentration of missing cluster defects are preserved after HCl activation, as shown by the characterization results presented in **Section 4.2** of the SI. However, the most remarkable feature of 50Benz-HA is its porosity, which is significantly higher than 50Benz (see nitrogen sorption isotherms in **Figure 3**). In fact, 50Benz-HA is the most porous UiO-66 sample ever to be reported - its BET surface area is 1903 m^2g^{-1}, which is over 50% higher than the theoretical value for defect-free UiO-66 (1241 m^2g^{-1}, see our previous study[3]) and narrowly surpasses the previous record recently reported by Wang et al.[8] Moreover, its isotherm features a H4 type hysteresis loop, implying the presence of mesopores. The incredible porosity of 50Benz-HA is due to a combination of 2 factors: (1) the very high concentration of missing cluster defects in the sample, and (2) The lightweight formate ligands which compensate for its defects. Therein is the reason that 50Benz is not nearly as porous (BET S.A. = 1515 m^2g^{-1}) – its defect compensating ligands (benzoate) are much heavier (and bulkier). We assert that it is likely impossible to attain a UiO-66 sample as defective and porous as 50Benz-HA by directly employing formic acid as a modulator in the synthesis, a point which is discussed more thoroughly in **Section 4.3** of the SI.

As a final word on 50Benz-HA, we note that its N_2 adsorption isotherm matches closely with that simulated from Reo-Form (see **Figure 3** for isotherms and **Figure 4** for the model**),** a hypothetical defective UiO-66 structural model derived from Reo-Benz by replacing all of its benzoate ligands with formate ligands (see **Figure 4**). This is perhaps the ultimate validation of our interpretation of the HCl activation process, visually depicted in **Figure 4**.

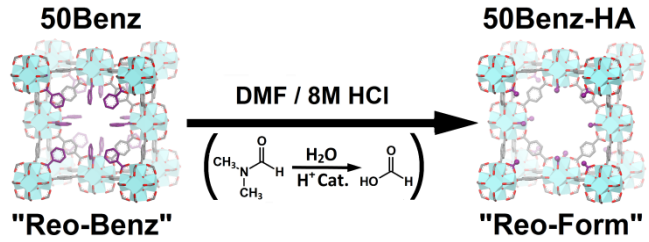

Figure 4. Visual depiction of the HCl activation Process. Exchanged ligands are highlighted in purple.

Finally satisfied, we proceeded to attempt small scale PSE reactions between 50Benz-HA and aqueous (pH = 7) L-serine solutions of varying concentrations at 85 °C. To our delight, significant amounts of L-serine were clearly observed in the dissolution/^{1}H NMR spectra obtained on the products (see **Figure S26**). Entertaining the possibility that L-Serine was simply occluded in the pores, we performed a control PSE reaction at room temperature, and detected a much smaller amount of L-Serine in the material (see **Figure S27**). This strongly implies that a reaction is indeed taking place at 85 °C and that L-serine is actually incorporated into the framework.

With this known, four of the PSE reactions were scaled up so that further characterization and CO_2 adsorption measurements could be performed. The samples named 0M-, 1.5M-, and 3M-Ser were respectively obtained by reacting 50Benz-HA with 0M, 1.5M, and 3M aqueous (pH = 7) L-serine solutions. The fourth sample, 3M-Ser-x2, was obtained by subjecting 50Benz-HA to 2 PSE cycles with the 3M L-serine solution. The dissolution/^{1}H NMR spectra obtained on the samples are shown in **Figure 5**, where it can be seen that the intensity of L-serine's signal systematically increases in the order one would expect. Integration revealed that the L-Serine to BDC molar ratios in the samples are significant: $\frac{\mathbf{Ser.}}{\mathbf{BDC}}\mathbf{m}_R$ = 0.11, 0.16, and 0.23 in 1.5M-Ser, 3M-Ser, and 3M-Ser-x2, respectively (see **Section 3.3** of the SI for method). Moreover, the intensity of the formate signal exhibits the opposite behavior to that of L-Serine, suggesting that L-serine exchanges with 50Benz-HA's formate ligands. However, the exchange is not quantitative; significantly more formate is consumed than L-serine is gained (see SI, **Section 4.5.1**). This means that much of the formate is lost by a different mechanism, possibly hydrolysis. Indeed, some formate is lost even when the PSE reaction is performed in pure water (0M-Ser, red curve in **Figure 5**).

Further characterization results obtained on the four PSE products can be found (with accompanying discussion) in **Section 4.5.** of the SI, where we come to the following conclusions regarding the effects of the PSE reactions: (1) the integrity of the structure is maintained; (2) the defectivity of the framework is unchanged; (3) the porosity of the material systematically decreases as increasing amounts of L-serine are incorporated. This decrease in porosity is actually expected based on the proposed ligand exchange chemistry, as shown by our simulated nitrogen adsorption isotherms (**Section 4.5.4.** of SI).

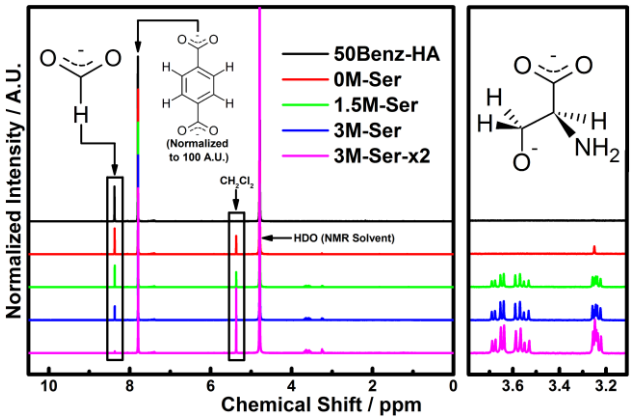

Figure 5. Dissolution/^{1}H NMR spectra obtained on the L-serine PSE products. The spectrum obtained on 50Benz-HA, the starting material, is included for comparison.

All of these findings strongly suggest that we were finally successful in introducing the MEA moiety to the UiO-66 framework in the same manner as that depicted in **Figure 1**. The priority was then to test the CO_2 capture performance of the materials. In particular, we wanted to compare their CO_2/N_2 selectivities under conditions similar to that of a post-combustion flue gas from coal fueled power plants. To this end, we obtained low pressure (0 - 1.1 bar) CO_2 and N_2 adsorption isotherms on each sample at 40 °C. The CO_2/N_2 selectivity of each sample was then calculated via Ideal Adsorbed Solution Theory (IAST, see **Section 3.5** of SI). Moreover, a second CO_2 adsorption isotherm (25 °C) was obtained on each sample so that the isosteric heat of CO_2 adsorption ($\mathbf{Q_{iso}}$) could be calculated. All relevant isotherms are presented in **Section 4.6** of the SI, while a summary of the results is provided in **Table S14** therein. Within said table, one can see that the CO_2/N_2 selectivity of the material improves systematically as the extent of L-serine functionalization increases. The CO_2/N_2 selectivity of the sample with the highest L-serine loading (3M-Ser-x2) is 92 % higher than its 50Benz-HA precursor, but the value is still rather modest (20.7). Moreover, the CO_2 adsorption capacities (at 1.1 bar and 25 °C) and $\mathbf{Q_{iso}}$ values vary very little amongst the samples. The CO_2 capture performance of the MEA functionalized materials is thus not as good as was hoped.

Nevertheless, this study has demonstrated that the reactivity of UiO-66 is highly dependent on not only the presence of defects, but also on the identity of the compensating ligands. Exchanging bulky benzoate ligands with formate afforded a much more reactive (and porous) material (50Benz-HA), allowing the previously elusive MEA moiety to be incorporated via PSE with L-serine. We envision that many other interesting functional moieties could be incorporated in a similar manner. Investigations are currently underway in our lab.

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ASSOCIATED CONTENT

Supporting Information

Details of synthesis and data analysis methods, results (PXRD, TGA-DSC, dissolution/^{1}H NMR, ATR-IR, EDX, SEM, sorption) and discussion thereof. This material is available free of charge at http://pubs.acs.org.

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