

Characterizing Defects in a UiO-AZB Metal–Organic Framework

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S Supporting Information

ABSTRACT: Exploring defect sites in metal-organic framework materials has quickly become an interesting topic of discussion in the literature. With reports of the enhancement of material properties with increasing defect sites, we were interested in probing the defect nature of UiO-AZB (UiO = University of Oslo, AZB = 4,4'-azobenzenedicarboxylate) nanoparticles. In this report, we investigate the use of acetic, formic, and benzoic acids as the modulators to prepare UiO-AZB. The results of ¹H NMR techniques and BET surface area analysis elucidate the extent of defects in our samples and are provided along with detailed discussions of the observed experimental trends. Interestingly, formic acid samples resulted in the most defected structure, reaching 36%. Additionally, for benzoic acid samples, with a 33% defect level, a drastic reduction in the accessible SA from 2682 m^2/g to as low as 903 m^2/g was observed, as the concentration of benzoic acid was increased.



This was attributed to the creation of macropores in the individual crystallites and confirmed by average pore width analysis.

INTRODUCTION

Metal-organic framework (MOF) research has flourished over the past several decades. MOFs are assemblies of metal clusters linked through multidentate organic molecules and have been proposed for a variety of applications from gas storage/separation^{1,2} to toxin sequestration³⁻⁵ and drug delivery.⁶⁻⁸ Many structural motifs have been discovered and extensively characterized over the years; however, the crystalline nature of some MOFs renders them susceptible to bulk crystallographic defects, typically not distinguished with general single crystal diffraction. While defective materials may intuitively be considered undesirable, crystalline defects in MOFs have been shown to increase catalytic activity, 9^{-11} enhance conductivity, 12,13 and improve adsorption 14-16 of the bulk material. These material augmentations have led to increased interest and debate regarding the essence of defects and the best approaches of how to control and quantify them, especially concerning the University of Oslo (UiO) series of MOFs.

UiO materials are specifically attractive for many applications due to the reports of exceptional chemical, thermal, and mechanical stability of UiO-66 (containing the 1,4-benzenedicarboxylate linker, BDC).¹⁷ The use of "modulators" in the synthesis of UiO materials, to form octahedral $Zr_6O_4(OH)_4$ secondary building units (SBUs), renders these materials disposed to increased incidences of crystalline defects. Modulators serve not only to form the SBUs but also to competitively bind with the chosen linker and direct MOF crystal growth. Therefore, in the final bulk material, the modulator may remain attached to the SBU, resulting in missing linkers. Additionally, it has been proposed that OH^- , H_2O , and Cl^- can also occupy missing linker sites.^{10,11,16,18–20}

Several reports in the literature have attempted to describe the quantity of defect sites in bulk materials using various

methods, mostly for UiO-66.^{17,21-26} Structural evidence quantifying missing linkers in UiO-66 came from a report by Zhou et al.,²⁵ where they used neutron diffraction of samples synthesized with varying concentrations of acetic acid modulator. They reported an average of 1 in every 12 linkers to be missing, bringing network connectivity to 11 instead of the 12 expected for an ideal UiO-66 sample. Farha^{10,27} and coworkers identified a maximum of 1.8 missing linkers for UiO-66 (Hf)¹⁰ using titration techniques to evaluate defects in several UiO materials. Thermogravimetric analysis (TGA) is another technique reported to quantify defects in UiO-66,17,22 and using this method, it has been shown that different batches of UiO-66 MOF prepared by a single synthesis can result in materials with drastically different degrees of missing linkers (up to 6 missing linkers per the 12 expected in an ideal UiO- $(66)^{17}$

¹H NMR techniques have also been used to elucidate the quantity of missing linker defects in UiO MOFs.^{21,22} Samples are digested in a deuterated solvent, and the integration corresponding to linker and modulator peaks present in the spectra are compared to find the modulator: linker ratio (discussed further in the results and discussion section). Using, this technique, Lillerud et al.²² have reported ratios ranging from <0.1 to \sim 0.8 for UiO-66 materials synthesized using acetic acid and trifluoroacetic acid, respectively. A value of 0.8 corresponds to an impressive five missing linkers per cluster and supports the assertion that UiO-66 can accommodate high levels of missing linkers. They were also able to demonstrate an increase in this ratio with increasing concentrations of modulator, indicating that higher levels of modulator used,

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resulted in more missing linkers under their synthetic conditions. For example, when formic acid concentrations were increased from 6 to 100 mol equiv (mol modulator: mol Zr^{4+}), their integration ratios ranged from ~0.1 to 0.35.

Although the point vacancy defects (missing linkers and missing clusters) of UiO-66 have been well documented, there are only a few reports addressing these defects for UiO materials with longer linkers.^{10,28,29} In fact, reports suggest that UiO-67, incorporating 1,4-biphenyldicarboxylate (BPDC), is not as stable as UiO-66,^{30,31} and this is likely due to increases in the defect nature of UiO-67 materials. It is also known that minor changes in the synthetic procedure (i.e., changing the concentration or identity of the modulator) can drastically alter the properties of the final bulk material.^{17,25} Therefore, we were interested in probing the defect nature of UiO-AZB (AZB = 4,4'-azobenzenedicarboxylate, Figure 1).³² We identified three



Figure 1. Representative diagram depicting the general synthetic conditions used. The octahedral cage on the right was generated using single crystal data from ref 30.

different modulators appropriate to produce highly crystalline UiO-AZB materials, acetic (AA), formic (FA), and benzoic acids (BA), and explored a range of concentrations for each modulator, 30–70 molar equivalents (mol equiv) for AA and FA and 10–30 mol equiv for BA. We provide the results of ¹H NMR analysis and N₂ adsorption isotherms to elucidate the extent of missing linkers in all samples generated using our synthetic procedure.

EXPERIMENTAL DETAILS

Materials: The 4-nitrobenzoic acid (98%), sodium hydroxide (\geq 98%), D-glucose (\geq 98%), ZrCl₄ (anhydrous, 99.99%), and benzoic acid (\geq 99.5%) were purchased from Sigma-Aldrich and used without further purification. Glacial acetic acid (certified ACS), formic acid (certified ACS), and dimethylformamide (DMF, Spectrophotometric grade \geq 99.8%) were used as received from Fisher Scientific.

Synthesis of 4,4'-azobenzenedicarboxylic acid (AZB):³³ 4-Nitrobenzoic acid (13 g) and 250 mL of 5 M NaOH were heated to 50 °C in a 500 mL round-bottom flask. An aqueous solution of 3.7 M D-glucose (150 mL) was added slowly (30 mL/min) to the flask with vigorous stirring. The reaction was allowed to stir for 10 min and then cooled to room temperature. The solution was aerated for 12 h, and 5 M (200 mL) aqueous acetic acid was added to precipitate the AZB. The orange solid was collected via vacuum filtration and dried in a 100 °C oven for 18 h (9.6 g, ~91%). ¹H NMR (500 MHz, basic D₂O, δ , ppm) trans: 7.94, 7.92 (d, 2H, *J* = 10 Hz), 7.82, 7.80 (d, 2H, *J* = 10 Hz); cis: 7.68, 7.66 (d, 2H, J = 10 Hz), 6.91, 6.89 (d, 2H, *J* = 10 Hz), (Predicted *m*/*z* = 270.2; M–H– = 269 *m*/*z*).

MOF Synthesis: UiO-AZB materials were made by a procedure previously reported.^{32,34} AA (30–70 equiv), FA (30–70 equiv), and BA (10–30 equiv) as the modulators in the synthesis were explored. The general procedure consisted of adding 0.0233 g of ZrCl₄ (0.1 mmol), 0.0270 g of H₂AZB (0.1 mmol), 5 mL of DMF (20 mL when benzoic acid was the modulator), 10 μ L of H₂O, and the appropriate

equivalents of modulator (*x* mol mod.: 1 mol Zr⁴⁺) to a glass vial. The mixture was sonicated for ~1 min and then placed into a 120 °C oven for 24 h. The resultant powder was collected via centrifugation and washed with DMF. All materials were then flushed of DMF solvent by soaking in EtOH with fresh EtOH replacement every hour, for a total 5 h (5 EtOH soaking cycles). Materials were then evacuated in a vacuum oven at 50 °C for 24 h. Evacuations at temperatures beyond this resulted in loss of crystallinity.

Powder X-ray Diffraction (PXRD): For X-ray diffraction analysis, a 600 W Rigaku MiniFlex powder diffractometer operating with a Cu (K α = 0.15418 nm) radiation source was used, with a sweeping range of 3°-50° in continuous scanning mode. Data were collected in 0.1° increments at a scanning rate of 1°/min, and patterns were generated with PDXL software.

Scanning Electron Microscopy (SEM): A Leo (Zeiss) 1550 fieldemission scanning electron microscope, equipped with an in-lens detector and operating at 5.0 kV, was used to collect SEM images. NPs were prepared for SEM imaging by first dispersing them in ethanol (0.1 mg/mL) via sonication. The resulting solution was then deposited via drop casting, with a short stem Pasteur pipet (1 drop), onto precut 5 mm × 5 mm glass slides. After room temperature drying, slides were mounted onto an SEM sample peg using double sided Cu tape and the sides of the slides were painted with conductive carbon paint. A Cressington 208 High Resolution Sputter Coater with a Au/Pd target (80/20) was used to deposit a conductive layer on the surface of the slides in order to allow for imaging. Samples were coated for 60 s.

Thermogravimetric Analysis (TGA): A Q-series TGA from TA Instruments was used to analyze the thermal stability of materials. A 10 mg amount of sample in a high temperature platinum pan was heated under air from 25 °C up to 1000 °C with a heating rate of 10 °C/min.

Gas Sorption Isotherms: The N₂ sorption isotherm measurements were collected on a Quantachrome Autosorb-1 at 77 K. The samples were placed in a 6 mm large bulb sample cell, which was degassed under vacuum for 24 h at room temperature. The surface areas of the materials were determined by fitting the adsorption data within the P/P_0 pressure range appropriate to the BET equation, ensuring that the *y*-intercept of the linear BET plot was positive.

¹H Nuclear Magnetic Resonance: ¹H NMR measurements were made using an Agilent U4-DD2 400 MHz NMR with a 96 sample robot. Samples were prepared for NMR by digesting ~1.0 mg in 600 μ L of 50 mM Na₂HPO₄ in D₂O via sonication for 1 h. 50 μ L of an 8 mM 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TMSP) standard were added to each sample, and the sample was transferred to an NMR tube for analysis.

Theoretical Surface Area Calculation: The geometric accessible surface area calculations were performed using a nitrogen-sized spherical probe that is rolled over the atoms of the structure, according to the method described by Duren et al.³⁵ The diameter of the nitrogen molecule was set to 2^{1/6} times the Lennard–Jones σ parameter, with a σ value of 3.32 Å used, based on the TraPPE force field.

RESULTS AND DISCUSSION

Three different monocarboxylate modulators (AA, FA, and BA) of varying concentrations were investigated for the synthesis of UiO-AZB. The concentration ranges studied were 30–70 equiv for AA and FA and 10–30 equiv for BA. Varying the concentration of the modulator has been shown to control particle sizes,^{30,36} where an increase in modulator concentration typically results in larger particles. This is explained by faster MOF nucleation at lower concentrations of modulator, therefore, reducing crystal growth and resulting in smaller particles. Indeed, upon increasing the modulator concentration, particle sizes increased as evidenced by SEM (Figure 2, and Figure S1). We originally attempted to synthesize UiO-AZB without adding a modulator but were not able to obtain a crystalline product, evidenced by broadened amorphous features in the powder X-ray diffraction (PXRD) patterns of



Increasing concentration

Figure 2. Particle sizes determined from SEM images of materials synthesized using AA (top, scale bars are 200 nm), FA (middle, scale bars are 1 μ m), and BA (bottom, scale bars are 1 μ m except for 10 equiv BA whose scale bar is 200 nm).

these syntheses (Figure S2). The PXRD patterns obtained for all modulated samples matched single crystal data reported in the literature^{30,34} (Figure S3), confirming that the modulators used produced bulk materials isostructural with the reported UiO-AZB.

With confirmation of crystalline samples, the focus became quantification of the defect nature of the materials. ¹H NMR spectra and N_2 adsorption isotherms were used in order to elucidate the extent of missing linker defects in the UiO-AZB materials. TGA analysis was ineffective to evaluate defects in UiO-AZB due to a consistent and gradual loss in the TGA curve below ~440 °C (Figure S4). In the absence of a clear plateau in this region, determination of defects had a large degree of associated error. This specific complication with TGA defect analysis was highlighted by Farha and co-workers.¹⁰

¹H Nuclear Magnetic Resonance (¹H NMR). UiO MOFs are unstable in highly basic environments, and so, can be digested in these conditions for ¹H NMR analysis. This is a powerful tool for the quantitative investigation of missing linkers. Not only can it provide a precise concentration of linkers in solution when a known amount of sample is digested, it can also be used to deem whether missing linkers are replaced by modulator species. In the ¹H NMR spectra, the integration of signals is proportional to the number of protons responsible for the signal. When multiple species are present in solution (e.g., linker and modulator) the integrations of signals assigned to each species can be used to determine the relative amounts of the various components. Furthermore, the addition of a ¹H NMR standard allows for the determination of exact concentrations of compounds in solution. This technique has been utilized in the literature to investigate and quantify missing linker defects for UiO-66.15,22

The technique reported by Lillerud²² et al. using ¹H NMR to investigate missing linkers was followed herein. By using the relative integrations of each component, we are able to calculate the modulator to AZB ratio (mod/AZB) using eq 1,

$$\left(\frac{I_{\text{MOD}}}{H_{\text{MOD}}}\right) \times \left(\frac{H_{\text{AZB}}}{I_{\text{AZB}}}\right) = \frac{\text{Mod}}{\text{AZB}} \text{ ratio}$$
(1)

where $I_{\rm MOD}$ is the summed integration of all the signals due to the modulator, $H_{\rm MOD}$ is the number of protons attributed to the modulator in solution, $H_{\rm AZB}$ is the number of protons corresponding to AZB (16 due to 8 for each isomer), and $I_{\rm AZB}$ is the summed integration of all signals due to AZB. This ratio can be used to quantify the extent of modulator that remains bound to the structure after synthesis, washing, and evacuation. For example, a ratio value of 1.0 would mean there are equal concentrations of modulator and AZB linker, signifying that 33% of the linkers are missing per cluster (or 4 of the expected 12).

To obtain samples for ¹H NMR analysis, the MOFs were digested in a 50 mM Na_2HPO_4 solution in D_2O (see Supporting Information for detailed digestion procedure). Figure 3 shows example ¹H NMR spectra for BA, AA, and



Figure 3. (Top) Example spectrum of digested samples synthesized with BA. (Middle) Example spectrum of digested samples synthesized with AA. (Bottom) Example spectrum of digested samples synthesized with FA.

FA samples. Signals due to the linker are found in all spectra. Two doublets corresponding to the protons of trans-AZB are found at 8.05 and 7.93 ppm, while the doublets due to protons of the cis isomer are found at 7.77 and 7.02 ppm. Spectra of the digested samples synthesized using BA displayed a doublet at 7.88 ppm, representative of the two protons located on BA ortho to the carboxy group. There are also two triplets in the BA sample spectra at 7.56 and 7.48 ppm, corresponding to protons located meta and para to the carboxy group, respectively. The spectra of digested samples synthesized using AA display a singlet due to the three protons of the acetyl group at 1.92 ppm. Spectra of the samples synthesized using FA display the AZB peaks as well as the formate proton peak at 8.46 ppm.

Due to the acid/base hydrolysis of DMF, formic acid and dimethylamine are formed at elevated temperatures and during the sample digestion procedure. Therefore, a peak corresponding to the formate proton is visible in all spectra (8.46 ppm). Numerous washing cycles (up to 5) did not result in loss of the formate peak, indicating either trapped solvent or additional node interactions. To account for the presence of formate in the BA and AA samples, we calculated the mod/AZB ratio under two separate assumptions: (1) that the formate present is binding to the structure (Figure 4A) such that its integration



Figure 4. Modulator to AZB ratio as a function of modulator concentration for samples synthesized using AA (black squares), FA (red circles), and BA (blue triangles) as the modulator. Plot A assumes formic acid present in the BA and AA samples is binding to the structure, while plot B assumes FA is not binding.

must be included in the consideration of the mod/AZB ratio or (2) that it is not bound (Figure 4B) and is the result of trapped FA and, therefore, not included in the calculation. From the comparison of these two mathematical treatments, we see that the assumption of bound DMF hydrolysis products results in mod/AZB ratios that are slightly higher for the AA and BA samples. In the case of FA samples, similar mathematical treatments are not possible and, therefore, we assume that the calculated FA/AZB ratio will be a slight overestimation when compared to the other data in Figure 4B. Despite these obstacles, the overall trends are clear.

To assess the total modulator to AZB ratio for all samples, the mod/AZB ratio was plotted as a function of modulator concentration. First, there seems to be no significant increase in the ratio with increasing concentrations of modulator for all samples, except in the case of 10 equiv of BA, whose value was lower at ~ 0.3 compared to the remainder of the BA samples. BA samples overall gave the highest ratios, up to ~0.6 for samples synthesized beyond 10 equiv of BA. A ratio of 0.6 (3 BA unit per 5 AZB units) corresponds to 23% of linkers missing or 2.8 of the 12 expected per cluster. The samples synthesized with AA display ratios at \sim 0.2, indicating 1 unit of modulator per 5 units of AZB or ~9% of modulator remaining (1 missing linker per cluster). The samples synthesized with FA show ratios of \sim 0.3, but again, we expected the FA ratios to be artificially high. A ratio of 0.3 corresponds to 15% or roughly 1.8 missing linkers per cluster.

The issue of trapped vs bound modulator (including FA formed via DMF decomposition) was circumvented by the addition of a 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TMPS) standard to the samples. This allows us to calculate the AZB concentration in solution, independent of the presence of varying modulators. Knowing the concentration of the standard, the integration of standard signals and the integration of AZB signals can be used to calculate the concentration of AZB in solution, using eq 2. This gives an

experimental value of AZB, and by calculating the theoretical value of AZB based on the amount of sample digested, we can calculate a "% recovery" of AZB based on how much we expected from an "ideal" material with no missing linkers according to eqs 3 and 4. In eq 2, [AZB] is the experimental concentration of AZB in solution, I_{AZB} is the summed integration from the signals attributed to both *trans-* and *cis*-AZB, [S] is the concentration of the standard, and I_S is the integration of the signal from the standard (normalized to 9 in the case of TMPS).

$$[AZB] = \frac{I_{AZB} \times [S]}{I_{S}}$$
(2)

In eq 3, mg_{UiOAZB} is the mass of material digested, mol_{AZB-ideal} is the moles of AZB present in an ideal sample (6 mol AZB/1 mol UiOAZB), MW_{UiOAZB} is the molecular weight of ideal UiO-AZB = 2287.34 g/mol, V is the total volume of solution analyzed (650 μ L in our case), and Theo_{AZB} is the theoretical concentration of AZB expected for the sample assuming no missing linkers. We can relate this % recovery to a % defects via eq 5, which corrects the percent recovery for the difference in molecular weight between an ideal sample and the defected sample (derivation shown in the Supporting Information).

$$\frac{(\mathrm{mg}_{\mathrm{UiOAZB}})(\mathrm{mol}_{\mathrm{AZB-ideal}})}{(\mathrm{MW}_{\mathrm{UiOAZB}})(V)} = \mathrm{Theo}_{\mathrm{AZB}}$$
(3)

$$\frac{[AZB]}{Theo_{AZB}} \times 100\% = \% \text{ recovery}$$
(4)

% recovery =
$$(1 - \% \text{ defects}) \times \frac{\text{MW}_{\text{UiOAZB-ideal}}}{\text{MW}_{\text{UiOAZB-defected}}}$$
 (5)

Again, for all of the modulators (excluding 10 equiv of BA), there did not seem to be a distinct difference in the average % defects when the concentration of the modulators was increased (Figure 5A). Therefore, we averaged all the % defect



Figure 5. (A) The % defects calculated from ${}^{1}\text{H}$ NMR spectra according to eqs 2–5) as a function of modulator equivalents for samples synthesized using AA (black squares), FA (red circles), and BA (blue triangles). (B) Average % defects of each modulator.

values obtained for each modulator regardless of the concentration (Figure 5B). For BA, we omitted the % defects from the samples made with 10 equiv. When comparing the modulators to each other (Figure 5, B), it is clear that AA is on average less defected, 29% defects, when compared to BA and FA, 33% and 36% defected, respectively. The BA samples made with 10 equiv resulted in ~23% defects. Interestingly, the trend is distinctively different from that found from the Mod/AZB ratio and follows what would be expected from the acid strength of the modulator, i.e. the pK_a 's of the acids increase FA

(3.75) < BA (4.20) < AA (4.75). Such a trend was previously observed by Lillerud in the study of defects in UiO-66 with AA, FA, difluoroacetic acid, and trifluoroacetic acid.²² Given the agreement of the % defect calculation with literature precedent, the hypothesis that stronger acids result in more defected structures is applied throughout the rest of the discussion.

The differences between the Mod/AZB ratio method and the % defect calculation indicate a key finding in regards to defect analysis in various MOF structures. Differentiating between trapped modulator and bound modulator is critical to an accurate picture of MOF defects. The difference in trend between the two methods (AA < BA < FA; % defects vs AA < FA < BA; Mod/AZB ratio) indicate that the benzoic acid/AZB ratio overestimates defects, if it is assumed all benzoic acid present in the ¹H NMR spectrum is bound to nodes. Therefore, to rectify the differences between the two values, trapped benzoic acid must be present. Such a discrepancy is not qualitatively seen with either AA or FA. However, this can be expected, as AA and FA are liquid modulators and, thus, more easily removed from the pores during traditional activation procedures as compared to the solid modulator, benzoic acid. This clearly provides support for the calculation of % defects in comparison to a standard as opposed to the ratio method when solid modulators are used in the synthetic procedure. It is also important to note that neither method clearly identifies the nature of all defects, which may include missing linkers replaced by modulator, hydroxide, or water and/or missing nodes and more importantly the orientation of defects to each other as will be discussed below.

N₂ Adsorption Isotherms. Gas sorption isotherms have been extensively used throughout MOF literature as a benchmark to provide insights into the porosity of frameworks. N₂ isotherms for all of the samples were measured, and BET theory was applied to the appropriate pressure ranges governed by the criteria outlined in the literature.^{35,37,38} Several reports indicate that increases in the modulator concentration result in an increase in gas uptake and thus the SA of UiO-66.^{22,25} This experimental evidence supports the logical hypothesis that increased modulator concentrations result in more defects that open more surface area for gas sorption. Of the samples investigated in this study, this trend was not observed. In the case of UiO-66, there have only been two main types of defects suggested and evidenced in the literature: missing linker defects and missing clusters. In fact, drastic increases in SAs of UiO-66 as more modulator is added have been attributed mainly to missing cluster defects, which is evidenced by broad peaks below $\sim 5^{\circ}$ in the PXRD pattern.^{22,28} Based on the PXRD patterns for the materials studied, similar evidence of missing clusters was not present. Given the larger unit cell or UiO-AZB, it is possible that missing linker defects would appear in the XRD pattern below 3° (the detection limit of our instrument). That said, previous reports only address the "point-like" vacancy defects characteristic of crystalline materials. During crystal growth, other crystal defects are possible including line and planar imperfections. For example, Siperstein²⁴ and coworkers show that decreasing CO₂ uptake can be attributed to pore blockage defects in $Cu_3(BTC)_2$ (BTC = 1,3,5-benzenetricarboxylate). These types of defects may arise from pockets of trapped solvent or as a result of crystal growth around synthetic byproducts (such as ZrO2 in the case of UiO materials). The same MOF has also been shown to contain plane slipping defects³⁹ and crystal fractures⁴⁰ that can result from postsynthetic activation treatments. Furthermore, systematic experimental SA analyses, and how SA changes as more modulator is added, have not been conducted for UiO materials with longer linkers than UiO-66, which incorporates BDC.

All samples resulted in type II isotherms, and example isotherms for AA and BA are shown in Figure 6 (A and B



Figure 6. (A) N_2 isotherms for materials synthesized with 30 equiv (black), 40 equiv (red), 50 equiv (blue), 60 equiv (orange), 70 equiv (green) of AA. (B) N_2 isotherms for materials synthesized with 10 equiv (black), 15 equiv (red), 20 equiv (blue), 25 equiv (orange), 30 equiv (green) of BA. (C) BET SA of materials synthesized with varying concentrations of AA (black squares), FA (red circles), and BA (blue triangles). (D) Pore width for AA (black squares), FA (red circles), and BA (blue triangles) as a function of modulator concentration.

respectively). Figure 6C displays the BET SA of all samples. Overall, AA samples gave the highest SAs. Several trials of BET analysis of AA samples were used to evaluate the batch variation of AA over the concentration range. Given the standard deviation of the surface area (~10%), for all AA samples the SA was the same (within error). Therefore, the averaged SA for AA materials was $2687 \pm 218 \text{ m}^2/\text{g}$. FA resulted in SAs that increased from $2559 \text{ m}^2/\text{g}$ at 30 equiv of FA to $2769 \text{ m}^2/\text{g}$ with 40 equiv; however, above 40 equiv, the SA dropped as low as $1985 \text{ m}^2/\text{g}$ with 70 equiv of FA. When the lowest amount of BA was used, we observed an SA of $2682 \text{ m}^2/\text{g}$, which consistently fell to 903 m²/g when the BA concentration was increased from 10 to 30 equiv.

Type II isotherms are indicative of mesoporous (2-50 nm pore widths) and macroporous (>50 nm) materials. In the low pressure region of the isotherm, the formation of a monolayer of N₂ occurs on the adsorption sites at the framework "walls". At higher pressures, once the monolayer has formed, adsorption becomes dominated by pore filling and the sharp rise in the isotherm at relative pressures near unity indicates unrestricted adsorption where saturation of the pores is taking place.⁴¹ In the case of a sample with large mesopores or macropores, the surface area decreases compared to a microporous (<2 nm) sample of the same framework, because the "walls" for gas sorption are absent in these large cavities and, therefore, have less adsorption sites.^{42,43} The introduction of macroporosity in our samples explains why we observe lower surface areas than the theoretical SA of the fully intact structure, which was found to be $3352 \text{ m}^2/\text{g}$ (see Supporting Information for calculation parameters). Average pore width analysis for all samples is displayed in Figure 6D.

For the FA samples, the pore width decreased as the concentration of FA increases. If no other factors are playing a role, the SA should therefore increase. However, we observe a decrease in the SA above 40 equiv of FA, indicating that other aspects of the defectivity should be considered other than the pore width. From the ¹H NMR analysis, it is clear that, in the case of FA, the concentration of modulator does not affect the mod/AZB ratio and, therefore, does not serve to introduce the occurrence of more defects. However, we see that increasing the FA concentration does affect the porosity of UiO-AZB, evidenced by a decrease in the SA and pore width. This leads to the conclusion that, at higher concentrations of FA, the total void volume decreases due to increasing pore blockage defects. In this case, pore blockage is not due to trapped solvent, because the amount of solvent in the ¹H NMR spectra are not significantly different as the concentration of modulator is increased. However, the pores could be blocked through ZrO₂ production at higher concentrations of FA, resulting in crystal growth around these contaminants. Alternatively, samples could contain inseparable byproduct (ZrO2 or otherwise), resulting in decreased SA due to an averaging effect. However, SEM analysis does not indicate that an inseparable byproduct is present.

For BA samples, the total uptake of N₂ increased with increased amounts of BA up to 25 equiv (dotted circle Figure 6B), which pointed to increased porosity. Average pore width analysis indicated that when the concentration of BA is raised, the pore width drastically increases up to ~ 60 Å at 25 equiv. Therefore, it is likely that the drop in the BET SA is a result of the blockage of micropores and/or the formation of larger meso-/macropores in the BA samples as the concentration of BA is raised. From ¹H NMR analysis, it is clear that excess benzoic acid is present in the structure. However, this does not appear to change as a function of added modulator and, therefore, cannot fully explain the decrease in surface area. In a report by Thornton and co-workers,²⁸ where they model several possible defect scenarios and simulate the CO₂ uptake of the resulting "three-site model" (assumed to be three linked clusters that possess the defect of interest), they point out that two missing linkers on a UiO SBU cluster can be either linear or not (i.e., adjacent or not). The orientation of missing linkers that are replaced by modulator species becomes more complex as the number of missing linkers per cluster is increased. For example, imagine a fully decorated cluster (Figure 7, top). If four missing linkers are placed the furthest apart from one another (Figure 7, bottom left), then crystal growth can proceed in all directions. However, if the four missing linkers are all coplanar (Figure 7, bottom right), a whole face of the cluster is restricted from crystal growth. This restriction allows for nanoregions of crystal growth inhibition and results in the formation of large vacant pockets in the final material. Due to $\pi-\pi$ stacking and known dimer formation of BA,⁴⁴ increasing the concentration of BA could result in more prevalent coplanar vacancies and, therefore, increase the average pore spaces in the bulk BA samples, resulting in lower SAs.

In the case of AA, the pore width showed a general decrease, but the large standard deviations indicate that the values were within error. When all AA samples were averaged, the pore width was determined to be 30 ± 12 nm.

CONCLUSIONS/OUTLOOK

UiO-AZB powders were studied in order to investigate the defect nature of the MOFs. The modulators used in the



Figure 7. Diagram of missing linkers on a UiO-AZB cluster. (Top) Fully decorated cluster. (Bottom left) Four missing clusters oriented 90° from the others. (Bottom right) Four missing clusters that are all coplanar. The colors represent: O (red), C (gray), N (blue), Zr (green), and H (white).

synthesis remain attached to the Zr_6 clusters, resulting in various defect levels depending on modulator identity. Use of AA as the modulator was found to result in ~30% defected structure. However, increased AA concentration had no effect on the porosity of the samples. In the case of FA, with an ~40% defected structure, the average pore width and SA decrease as the concentration of FA is raised. This suggests that increasing the FA concentration results in either pore blockage defects or more inseparable byproducts that contaminate the samples, thus, lowering the SA. When BA is increased beyond 10 equiv, the % defects reached 33%, and increased BA concentration further results in larger meso- or macropores that serve to decrease the SA.

Although more work is needed to investigate the chemical nature of defects in MOFs, there are quick techniques that give generalized information about the degree and structural nature of defects in bulk samples. Several factors are responsible for introducing defect sites into framework structures. Previous studies have shown an increase in the SA of UiO-66 when the concentration of modulator was raised due to more missing cluster defects. However, the results presented here confirm that defects are linker dependent and specific SA trends for a single MOF should not be extended to other materials, even if isostructural. Additionally, the results presented indicate that different types of defects are observed within one MOF structure depending on modulator identity. In fact, we show that FA results in pore blockage defects, AA results in the commonly observed missing linker point defects, and BA results in clustered defects and macroporosity. Ultimately, it appears that defect analysis should be conducted on each MOF and each potential modulator. Only after this information is gathered can the crystal properties desired (low defect material, larger porosity) be designed into the material.

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.7b01801.

All instrumentation used along with more detailed experimental procedures are provided. Also, PXRD, TGA, and a ¹H NMR of an FA sample (PDF)

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