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Postsynthetic Modification of a Metal−Organic Framework for Stabilization of a Hemiaminal and Ammonia Uptake

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S *Supporting Information*

ABSTRACT: In our study, we show by solid-state ^{15}N NMR measurements that an important zirconium metal−organic framework (UiO-66) with amino-functionalized links is composed of a mixture of amino and $-NH_3^+Cl^-$ salt functionalities rather than all amino functionality to give a composition of $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_4(BDC\text{-}NH_3^+Cl^-)_2$ (UiO-66-A). UiO-66-A was postsynthetically modified to form a mixture of three functionalities, where the hemiaminal functionality is the majority species in UiO-66-B and aziridine is the majority functionality in UiO-66-C. UiO-66-A−C are all porous with surface areas ranging from 780 to 820 m^2/g and have chemical stability, as evidenced by reversible ammonia uptake and release showing capacities ranging from 134 to 193 cm^3/g.

Postsynthetic modification of porous metal−organic frameworks (MOFs) has allowed organic,[1] metal-coordination,[2] and organometallic reactions[3] to be carried out on covalently linked organic functionalities within the pores. Challenges arise during attempts to characterize the starting points, intermediates, and products of these reactions. These challenges can be met by digesting the MOF in strong acid or base and measuring its solution NMR spectrum.[4] Although digestion is useful for examination of products that are insensitive to acid, it is not applicable for the detection of reactive species that may be present along the reaction pathway. The use of solid-state ^{13}C NMR to address the problem is not always informative because of the lack of the needed sensitivity to definitively characterize closely related organic species. In our study, we illustrate the use of solid-state ^{15}N NMR in elucidating the true chemical nature of what was presumed to be an amino-functionalized MOF. Specifically, UiO-66 is a zirconium MOF, [$Zr_6O_4(OH)_4(BDC)_6$, where BDC = 1,4-benzenedicarboxylate], that was recently reported to have exceptional chemical stability, and the amino-functionalized UiO-66-NH_2 (hereafter UiO-66-A) derivative was also prepared and found to have the same topology.[5,6] Here, we show that the amino-functionalized MOF, UiO-66-A, is comprised of a mixture of functionalities (66% amino and 33% ammonium chloride) to give $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_4(BDC\text{-}NH_3^+Cl^-)_2$ (Scheme 1A). Reaction of the amino-functionalized links in UiO-66-A with acetaldehyde yields the hemiaminal product (UiO-66-B, Scheme 1B), which is found to exist in thermal equilibrium with the aziridine product (UiO-66-C, Scheme 1C). Indeed, solid-state ^{15}N NMR has been instrumental in uncovering the presence of mixed functionalities within the structures of the MOF starting material and products. We further show the differing affinities of these functionalities for ammonia uptake and the resiliency of the MOF material, as evidenced by maintenance of its crystallinity and porosity throughout all of the organic transformations and the reversible storage of ammonia.

UiO-66-A is constructed from a face-centered arrangement of cube octahedral $Zr_6(OH)_4O_4(-CO_2)_{12}$ units that are connected by aminoterephthalate to form large porous tetrahedral and octahedral units with the amino functionalities pointing into the pores (Figure 1).[7]

In our study, UiO-66-A was synthesized by adding solution mixtures of zirconium tetrachloride (0.233 g, 1.00 mmol) in 10 mL of *N*,*N*-dimethylformamide (DMF) and $H_2BDC\text{-}NH_2$ (0.543 g, 3.00 mmol) in 30 mL of DMF. Each of the mixtures was heated to 85 °C and sonicated to dissolve the respective components. The solutions were then combined in a 60 mL scintillation vial and heated to 120 °C for 24 h. The resulting white crystalline powder was collected by filtration.[8] All guest molecules were removed from the pores of UiO-66-A so that its structure and permanent porosity could be examined. Activation was achieved by washing samples of UiO-66-A with DMF (3 × 30 mL) over a 30-min period, followed by immersing the material in MeOH (30 mL). After 24 h, the solvent was decanted and replaced with neat MeOH. The solvent-exchange procedure was repeated over a 5-day period. Finally, heating the material at 120 °C at 30 mTorr for 48 h activated the pores of UiO-66-A. Powder X-ray diffraction (PXRD) analyses were performed on samples of UiO-66-A to ascertain its crystallinity (Figure 2A). Close analysis of the peak positions and relative intensities indicated that it is structurally analogous to its BDC counterpart (UiO-66).[8]

UiO-66-A was further characterized by cross-polarization magic-angle-spinning (CP/MAS) ^{13}C and ^{15}N NMR spectra. Experiments performed on the activated material showed the expected resonances at 170 ppm for the carbonyl carbon atoms and 148, 136, 129, and 115 ppm for the aromatic carbon atoms of the phenylene links.[9] Solid-state ^{15}N NMR spectra were analyzed for UiO-66-A that had been synthesized from ^{15}N-enriched $H_2BDC\text{-}NH_2$.[8] The ^{15}N NMR spectrum showed two resonances at 56 and 137 ppm; these features can be attributed to the free aromatic amine resonance and the protonated amine salt

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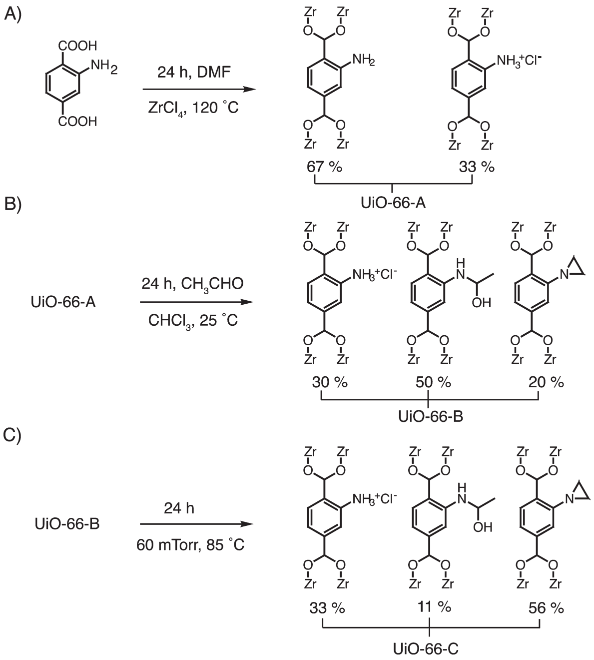
Scheme 1. Synthesis and Postmodification of UiO-66-A



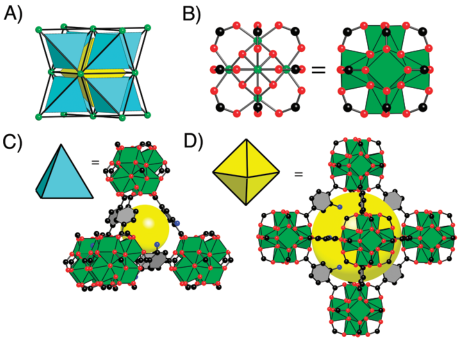


Figure 1. Crystal structure of UiO-66-A. (A) Tiling of the **fcu** unit showing the division of space into tetrahedra (green) and octahedra (yellow). Each yellow sphere and line represents the zirconium oxide unit and the organic linker, respectively. (B) Cube octahedral unit $Zr_6(OH)_4O_4(-CO_2)_{12}$ of UiO-66-A. (C) Tetrahedral unit from the **fcu** net. (D) Octahedral unit from the **fcu** net. Pores in the evacuated crystalline frameworks are illustrated by yellow spheres that contact the van der Waals radii of the framework atoms. Atom colors: zirconium, green polyhedra; carbon, black; nitrogen, dark blue; oxygen, red.

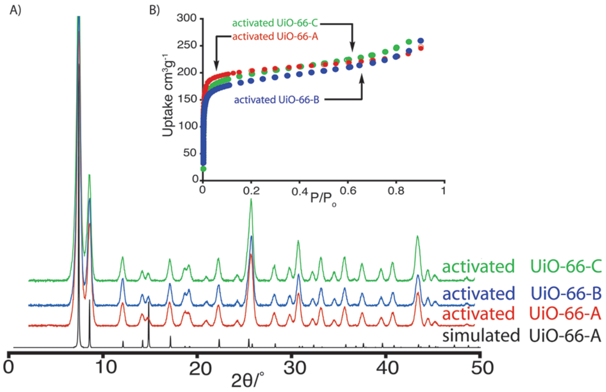


Figure 2. (A) PXRD patterns of UiO-66-A and postmodified compounds (UiO-66-B and -C): simulated UiO-66-A (black), UiO-66-A (red), UiO-66-B (blue), and UiO-66-C (green). (B) N_2 isotherm at 77 K of UiO-66-A and postmodified compounds: UiO-66-A (red), UiO-66-B (blue), and UiO-66-C (green).

$-NH_3^+Cl^-$, respectively.[10] Given that hydrolysis of $ZrCl_4$ produces HCl, it is anticipated that the $NH_3^+Cl^-$ BDC salt moiety is produced during MOF formation. The spectral assignment was supported by solution ^{15}N NMR experiments performed on an equimolar mixture of H_2BDC-$NH_2$and HCl.[7] Integration of direct-excitation NMR with a relaxation time of 45 s gives approximate yields of 2:1 (1.94:1) of the amine. Furthermore, the partial formation of the salt is consistent with elemental analysis, confirming that the structure of UiO-66-A contains both the amino functionality and the $-NH_3^+Cl^-$ salt moiety [i.e., $Zr_6O_4(OH)_4(BDC\text{-}NH_2)_4(BDC\text{-}NH_3^+Cl^-)_2$].[11] Prior to carrying out reactions on UiO-66-A, its porosity was assessed by measuring the N_2 gas adsorption isotherm at 77 K, which clearly showed a type I behavior indicative of permanent porosity (Figure 2B). Brunauer−Emmett−Teller (BET) analysis gave a surface area of 820 m^2/g.

A common reaction in molecular organic chemistry is the condensation reaction of an aldehyde and an amine to form an imine moiety. Recent studies have shown that analogous chemistry can be carried out in the pores of MOF and ZIF materials.[12] Notably, in addition to the expected imine product, the highly reactive hemiaminal reaction intermediate has been crystallographically observed in the pores of an extended framework.[13] UiO-66-B was synthesized by adding CH_3CHO (0.1 mL) to UiO-66-A (0.2 g) in 10 mL of $CHCl_3$. The reactants were left undisturbed for 2 days at room temperature, after which the solvent was decanted and washed with fresh $CHCl_3$ (20 mL × 5) followed by evacuation at 25 °C and 30 mTorr for 24 h to yield a solvent-free framework UiO-66-B.

The solid-state ^{15}N NMR spectrum of UiO-66-B did not show the expected imine resonances, but instead two new resonances at 93 and 71 ppm were observed. The peak at 93 ppm is attributable to a hemiaminal nitrogen.[14] The MAS ^{13}C NMR spectrum of UiO-66-B synthesized from isotopically labeled $^{13}CH_3{}^{13}CHO$ supports the assignment, displaying resonance peaks at 85 and 49 ppm due to the secondary and primary carbon atoms of the hemiaminal, respectively.[14] The additional peak at 71 ppm in the ^{15}N NMR spectrum is consistent with the presence of an aziridine ring, which is also supported by the isotopically enriched ^{13}C MAS NMR spectrum in the resonance at 20 ppm.[15] Integration of a direct-excitation NMR spectrum with a relaxation time of 45 s gives approximate yields of each reaction with 3:5:2 (1:1.74:0.72) of the protonated amine, hemiaminal, and aziridine, respectively.[8]

The putative mixture of functional groups led us to hypothesize that both the kinetic (hemiaminal) and the thermodynamic (aziridine) products were present within the pores of UiO-66-C. Thus, we heated samples of UiO-66-B to 100 °C for 12 h (or kept the samples at room temperature for 2 weeks) to ascertain whether the yield of the thermodynamic product could be increased. Indeed, after heating, samples of UiO-66-B changed from yellow to bright green. ^{15}N NMR spectra obtained from a sample of thermally treated UiO-66-C showed a decrease in the intensity of the hemiaminal product peak at 93 ppm and an increased intensity of the aziridine peak at 71 ppm. The isotopically

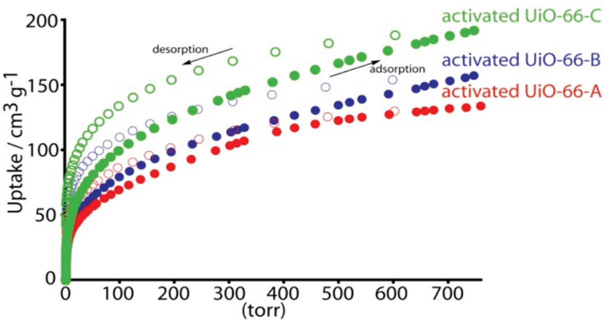


Figure 3. NH_3 isotherm at 298 K of UiO-66-A and postmodified compounds: UiO-66-A (red), UiO-66-B (blue), and UiO-66-C (green).

enriched ^{13}C NMR spectrum showed an analogous relationship between the hemiaminal and aziridine resonances, further confirming the ^{15}N assignments. Again, to quantify the transformation, direct excitation of the ^{15}N NMR spectrum showed a ratio of 3:1:5 (1:0.28:1.68) for the protonated amine/hemiaminal/aziridine.[8]

To confirm that the structure was maintained during the postsynthetic modification reactions, PXRD peaks were examined: both UiO-66-B and UiO-66-C maintained their crystallinity and structure (Figure 2A). Furthermore, the N_2 adsorption isotherm at 77 K demonstrated that UiO-66-B and UiO-66-C retained porosity with BET surface areas of 780 and 800 m^2/g, respectively (Figure 2B).

The exceptional stability and unique functionality of these frameworks provide excellent opportunities to explore the adsorption chemistry of gas molecules such as NH_3, previously considered to be too reactive for MOFs.[16] Ammonia isotherms were measured at 298 K for the three compounds (Figure 3) and found to have significant uptake capacities at 760 Torr (134 cm^3/g, UiO-66-A; 159 cm^3/g, UiO-66-B; 193 cm^3/g, UiO-66-C). Although this value is lower than the uptake observed for MOF-5 (270 cm^3/g at 760 Torr), the stability of UiO-66-A−C materials, as evidenced by maintenance of the analogous structure (NMR) and crystallinity (PXRD), following adsorption and desorption provides important advantages.[8]

The ^{15}N NMR spectrum shows that the terephthalate links of UiO-66-A exist as a mixture of amino and ammonium chloride functionalities rather than having only the amino functionality. Furthermore, the reaction of UiO-66-A with acetaldehyde stabilizes a highly reactive hemiaminal within the pore cavities, which was transformed into an aziridine upon heating. The exceptional chemical stability of UiO-66-A−C was evident from the reversible uptake of ammonia in each framework where, remarkably, both crystallinity and porosity were retained.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Full synthetic and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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