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# Microwave-Assisted Cyanation of an Aryl Bromide Directly on a Metal−Organic Framework

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A microwave-assisted postsynthetic modification (PSM) reaction on a metal−organic framework (MOF) has been realized. Cyanation of the $Zr^{4+}$-based UiO-66-Br was achieved with CuCN and microwave irradiation to produce UiO-66-CN. This protocol represents a notable example of PSM on an aryl halide MOF producing a cyano-functionalized MOF.

Metal−organic frameworks (MOFs) are porous materials that are constructed from inorganic metal ion clusters and tunable organic linkers.[1] An immense range of MOF materials have been developed to date, mostly under solvothermal reaction conditions.[2] In the past decade, MOFs have emerged as an exciting area in inorganic and materials chemistry for use in gas adsorption, separation, catalysis, and drug delivery.[3]

Recently, we[4−7] and others[8−15] have described postsynthetic modification (PSM) as a method for manipulating the organic linkers in MOFs. PSM is versatile with regard to the scope of MOF substrates to which it can be applied, and new physical and chemical properties can be realized in MOFs via this approach.[7,16] Despite significant advances, the majority of PSM reactions have been confined to MOFs bearing a limited variety of functional group “handles” including amines, aldehydes, alkynes, and a few others.[17,18] For example, amino-containing MOFs have been converted to amides,[4] iso(thio)cyanates,[6] ureas,[19] imines,[10,11] and azides.[13] Novel PSM reactions, which originate from alternative functional group handles, are of great value for advancing the utility of PSM and creating MOF materials that are otherwise inaccessible by conventional synthetic approaches.

Described herein is the establishment of a new PSM route using aryl bromide functionalized MOFs. Aryl bromides are well-known for undergoing a wide variety of chemical transformations.[20] Aryl bromide containing MOFs have been known for some time, at least since the description of isoreticular metal−organic framework-2 (IRMOF-2) in 2002.[2] IRMOF-2 is comprised of octahedral $Zn_4O$ clusters linked by 2-bromo-1,4-benzenedicarboxylate (Br-BDC) ligands. However, most transformations described with aryl bromides require reaction conditions or reagents (base) that would undermine the limited chemical stability of IRMOFs.[21] Therefore, to achieve PSM on MOFs containing the Br-BDC ligand, more stable MOF compositions are required.

Among the more chemically robust MOFs that have been reported, the $Zr^{4+}$-based MOFs developed by Lillerud (so-called UiO materials) have attracted increasing attention.[22] UiOs, based on $Zr_6O_6$ clusters and linear dicarboxylate ligands (such as 1,4-benzenedicarboxylate, BDC), exhibit significant chemical and thermal stability, and we and others recently reported that the synthesis of UiO-66 analogues

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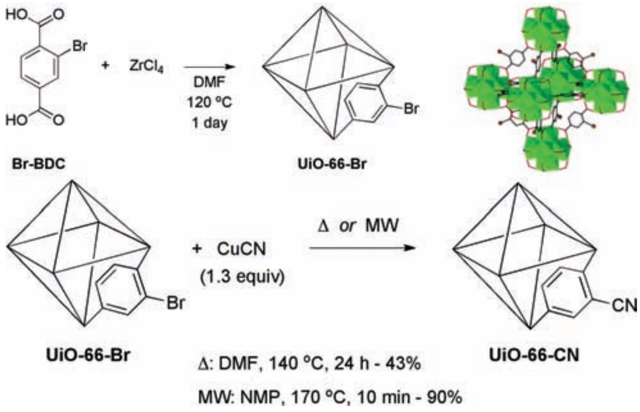
**Scheme 1.** Synthesis of UiO-66-Br (top) and PSM Cyanation to UiO-66-CN (bottom)[a]



[a] A representation of the UiO-66 framework is shown (top right) with the $Zr_6O_6$ cuboctahedron SBUs highlighted in green.

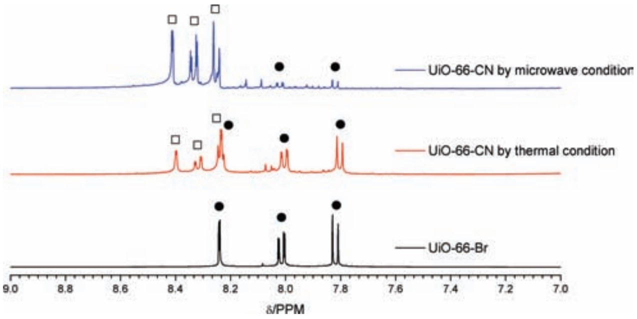


**Figure 1.** $^1$H NMR spectra of UiO-66-CN produced by thermal and microwave procedures (spectra obtained by digestion in HF and $CD_3OD$). Filled circles indicate Br-BDC, and open squares indicate CN-BDC. A spectrum of unmodified UiO-66-Br is shown for reference.

based on functionalized BDC ligands was quite straightforward.[23,24] Furthermore, amino-containing UiO-66-$NH_2$ was readily modified by PSM in a manner similar to that used on other MOF systems.[23,24] Herein, we show that the bromo-containing UiO-66-Br can undergo an unparalleled PSM transformation that has not been described for any other MOF, producing a new class of nitrile-bearing crystalline, porous solids.

UiO-66-Br was synthesized by the combination of $ZrCl_4$ with Br-BDC, as previously described (Scheme 1).[23] The chemical stability of UiO-66-Br is quite similar to those of other UiO-66 derivatives, including a high tolerance to polar solvents like alcohols, DMSO, and even aqueous solutions. In an attempt to realize novel PSM reactions, UiO-66-Br was subjected to cyanation. The nitrile group is an important precursor for various other functional groups, such as carboxylic acids, aliphatic amines, and heterocyclic compounds.[24] Established named reactions, such as the Rosenmund−von Braun reaction[25] and Sandmeyer[26] reaction, are generally used for the preparation of aryl nitriles.

Our first attempts at PSM on UiO-66-Br utilized CuCN (1.3 equiv) in a *N*,*N*-dimethylformamide (DMF) suspension of UiO-66-Br for 24 h at 140 °C (Scheme 1).[27] After removal of the excess copper (Table S1, Supporting Information) by washing with DMF, an aqueous KCN solution, and methanol, the bromo groups of UiO-66-Br were found to be ca. 43% converted to nitrile groups. The percent conversion from bromo to nitrile was determined by $^1$H NMR upon digestion of the MOF in HF in $CD_3OD$,[23] a method now commonly used for the characterization of PSM on MOFs. In the $^1$H NMR spectra, the 2-cyano-1,4-benzenedicarboxylate (CN-BDC) resonances generated from the UiO-66-CN product (Figure 1, Figure S1) are shifted downfield relative to the Br-BDC starting material.

Encouraged by these preliminary results, we sought to improve the cyanation PSM reaction conditions. The high chemical and thermal stability of UiO-66-Br led us to attempt microwave-assisted cyanation.[28] UiO-66-Br was suspended in *N*-methyl-2-pyrrolidone (NMP) and subjected to microwave irradiation (170 °C, 10 min), producing UiO-66-CN in ca. 90% yield (as determined by $^1$H NMR analysis; Figure 1, Figure S2). Electrospray ionization mass spectrometry (ESI-MS) and infrared spectroscopy (ATR-FTIR) also confirmed conversion to the modified CN-BDC ligand (Figures S3 and S4). To the best of our knowledge, this is the first time microwave irradiation has been utilized in the PSM of a MOF. Importantly, microwave irradiation resulted in a much faster and higher yielding PSM reaction when compared to standard thermal conditions.

Several studies on the microwave-assisted synthesis of MOFs have been described.[15,29,30] In light of these reports, we attempted the microwave synthesis of UiO-66-Br and UiO-66-CN from $ZrCl_4$ with Br-BDC or CN-BDC, respectively. Using the same microwave heating conditions used in the PSM cyanation (in either DMF or NMP), neither UiO-66-Br nor UiO-66-CN was produced. These experiments strongly suggest that the microwave PSM reaction conditions used here are truly a heterogeneous transformation of the UiO-66-Br framework, not involving a series of dissolution, modification, and reformation steps.

Complete characterization on UiO-66-CN confirmed that it is a stable, microporous material. Powder X-ray diffraction (PXRD) shows that the crystallinity of UiO-66-CN is retained (Figure 2). Thermogravimetric analysis (TGA) indicated that UiO-66-CN possesses good thermal stability comparable to the other UiO-66 derivatives (Figure S5). Scanning electron microscopy (SEM) images showed that the crystallites were identical in appearance before and after the PSM reaction (Figure S6). Finally, the surface area of UiO-66-CN was measured by dinitrogen gas sorption (77 K), which gave a Brunauer−Emmett−Teller (BET) surface area of 661 ± 53 $m^2/g$ (three independent samples). This is comparable to that of the parent UiO-66-Br (~851 $m^2/g$),[23] indicating that the material remains microporous even after the microwave modification procedure.

Fundamentally, the introduction of labile and reactive functional groups on an organic ligand not intended for constructing a framework can complicate the solvothermal

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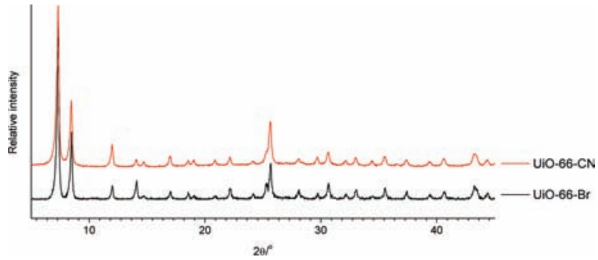

**Figure 2.** PXRD patterns of UiO-66-Br and UiO-66-CN. The UiO-66-CN sample was produced under microwave irradiation reaction conditions.

synthesis of MOFs. The ability of nitrile groups to bind metal ions, as well as their susceptibility to hydrolysis under forcing conditions, prompted us to explore whether UiO-66-CN could be prepared directly from CN-BDC under solvothermal conditions. The CN-BDC ligand was prepared starting from Br-BDC in three steps (Scheme S1). The use of CN-BDC with $ZrCl_4$ in DMF under standard solvothermal conditions (120 °C, 24 h) for preparing UiO-66 failed to generate UiO-66-CN. After testing a number of reaction conditions (Table S2), UiO-66-CN was eventually obtained directly from CN-BDC by lowering the reaction temperature (85 °C, Figure S7). These control experiments clearly illustrate the utility of PSM in MOF functionalization. Even in a MOF system highly tolerant of ligand derivatization, CN-BDC did not produce UiO-66-CN under the same reaction conditions as used for UiO-66 and many UiO-66 derivatives.[23] More importantly, the synthesis of UiO-66-CN directly from CN-BDC requires four steps, including the synthesis of the MOF, giving an overall yield of 31% and requiring ~98 h. However, by using PSM, the same MOF can be prepared in only two steps, in ~24 h and in 90% yield. Therefore, it is clear that for UiO-66-CN, PSM is a more efficient and higher-yielding route to obtain the desired MOF.

In conclusion, we have reported the first PSM reaction using an aryl halide chemical handle within a MOF. Furthermore, for the first time, microwave irradiation was used to obtain rapid and clean PSM, which performed better than standard thermal conditions. The use of both aryl halides and microwave irradiation opens up new tools and hence new possibilities for tuning the pore environment in MOFs.

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**Supporting Information Available:** Experimental details, Scheme S1, Tables S1 and S2, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.