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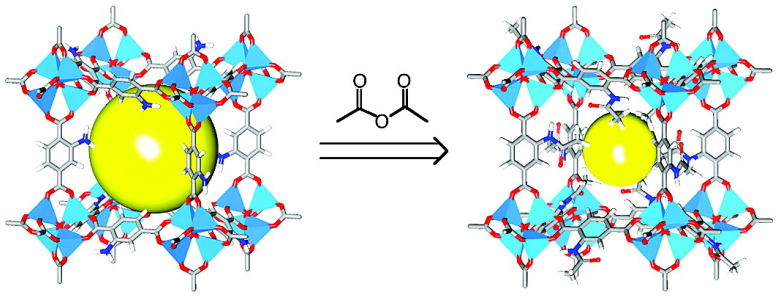

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Postsynthetic Covalent Modification of a Neutral Metal−Organic Framework

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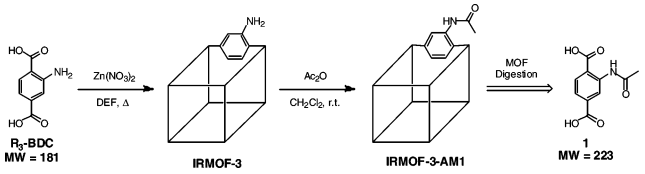
Metal−organic frameworks (MOFs) are a rapidly growing class of materials, composed of metal ions or metal ion clusters as nodes and organic ligands as linkers.[1,2] These materials have been shown to be thermally robust and in many cases highly porous. For these reasons, MOFs have been proposed to have several potential applications in the areas of catalysis, sensors, and gas storage.[3] A large number of the most robust, porous MOFs that have been studied to date are synthesized by solvothermal complexation of metal ions and organic linkers in sealed vessels. Consequently, any functional sites present in MOFs must be either incorporated into the organic linker prior to MOF synthesis[4,5] or generated as a consequence of the MOF structure (e.g., unsaturated metal centers).[6,7] A limitation of solvothermal synthesis is that only functional groups that are compatible with the reaction conditions (e.g., thermally stable, non-coordinating) can be utilized. While there is precedence for the chemical modification of nanomaterials,[5,8−14] to our knowledge, only one example of a crystalline MOF changed by direct covalent modification on the assembled lattice has been reported.[15]

The presence of organic ligands as a constituent of the inorganic−organic hybrid MOF structure makes these solid-state materials more attractive targets for manipulation by organic reactions than other inorganic materials (e.g., zeolites). By targeting the organic linking component of the MOF, one can exploit the vast array of organic reactions available to transform the starting MOF into a new MOF with altered functional groups and thus different physical and chemical properties. By analogy to the concept of "posttranslational" modification of proteins,[16] we propose that the "postsynthetic" modification of MOFs could be a valuable method of generating MOFs of unprecedented structure and function. Herein, we report the postsynthetic modification of a known MOF as a simple proof of concept.

Yaghi's isoreticular metal−organic framework-3 (IRMOF-3) is a known MOF with a cubic topology prepared from $Zn(NO_3)_2 \cdot 4H_2O$ and 2-amino-1,4-benzene dicarboxylic acid (R_3-BDC).[17] The 2-amino group of the R_3-BDC ligand does not participate in coordination to the tetranuclear Zn_4O nodes that link the structure together and are potentially available for undergoing a variety of organic transformations (Scheme 1). Therefore, IRMOF-3 represents a good model system for a postsynthetic covalent modification study. Bulk samples of IRMOF-3 were prepared following the reported procedure[18] and were activated by guest exchange with $CHCl_3$, followed by vacuum drying prior to further treatment. In a typical postsynthetic modification reaction, crystals of IRMOF-3 suspended in CH_2Cl_2 (or $CHCl_3$) were treated with ca. 2 equiv of acetic anhydride at room temperature for a period of hours to days. The reaction was then stopped by repeated washing of the solid material with fresh CH_2Cl_2, followed by soaking in CH_2Cl_2 for ∼2 to 3 days before drying under vacuum (see Supporting Information).

Initial evidence for the reaction between acetic anhydride and IRMOF-3 (to produce the modified framework IRMOF-3-AM1) was obtained by electrospray ionization mass spectrometry (ESI-MS) and nuclear magnetic resonance (NMR). Samples of IRMOF-3-AM1 were digested using dilute acid and DMSO and analyzed by ESI-MS. The negative mode mass spectra obtained clearly showed a base peak at m/z 222 (Figure S1, $[\mathbf{1}\text{-H}]^-$), which corresponds to the modified ligand (compound **1**, Scheme 1). Similarly, dried samples of IRMOF-3-AM1 digested and dissolved in dilute DCl/D_2O and DMSO-d_6 solution examined by ^{1}H NMR showed new resonances at 2.10, 7.60, 8.05, and 9.07 ppm **(**Figure 1**)** confirming the formation of **1** due to the reaction of IRMOF-3 with acetic anhydride. The ^{1}H NMR spectrum also showed a resonance due to acetic acid, which is largely attributed to the partial hydrolysis of **1** under the acidic conditions used to digest IRMOF-3-AM1,[19] as the extensive washing, soaking, and drying processes performed on IRMOF-3-AM1 are expected to remove most of the reaction byproducts.[18] Nevertheless, ignoring the effect of hydrolysis during sample digestion, the percent conversion (acetylation) of IRMOF-3 is >80% after 5 days, as estimated by integration of the ^{1}H NMR spectra.

Scheme 1. Scheme for the Postsynthetic Modification of IRMOF-3



To further interrogate the modification process, the acetylation of IRMOF-3 was monitored over time by ^{1}H NMR. The reaction was carried out on crystalline IRMOF-3 in $CDCl_3$ and the relative ratio of the reactant (acetic anhydride) to byproduct (acetic acid) was monitored over a period of 3 days. As illustrated in Figure 2, the generation of acetic acid is apparent within 2 h and the reaction approaches completion after ∼2 to 3 days at ambient conditions. No appreciable amount of R_3-BDC or **1** was detected in solution, corroborating the structural integrity of IRMOF-3 and indicating that the observed reactivity is via a heterogeneous reaction mechanism. Furthermore, the crystallinity of the modified product, IRMOF-3-AM1 was examined by powder X-ray diffraction (PXRD) and as shown in Figure 3, the cubic lattice of IRMOF-3 is well-retained even after covalent modification with the acetyl groups. The PXRD data was also confirmed with a preliminary single-crystal X-ray analysis (see Supporting Information). Thermal gravimetric analysis (TGA) of IRMOF-3-AM1 showed comparable thermal stability to IRMOF-3 (Figure S2).

Control experiments, identical to that shown in Figure 2 but employing IRMOF-1 (which lacks the 2-amino group),[17] showed essentially no conversion of acetic anhydride over the same time period (Figure S4). Similarly, reaction of R_3-BDC with acetic anhydride in $CDCl_3$ (in which R_3-BDC is only sparingly soluble) showed neglible conversion (Figure S5), further corroborating the

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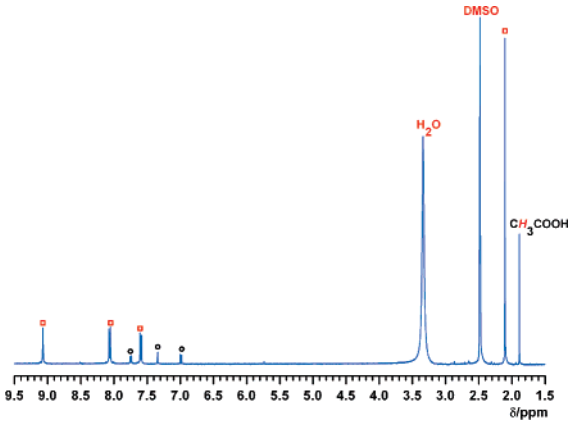

Figure 1. ^{1}H NMR spectrum of DCl/D_2O digested IRMOF-3-AM1 in DMSO-d_6 solution. Red squares and black circles represent signals of **1** and R_3-BDC, respectively.

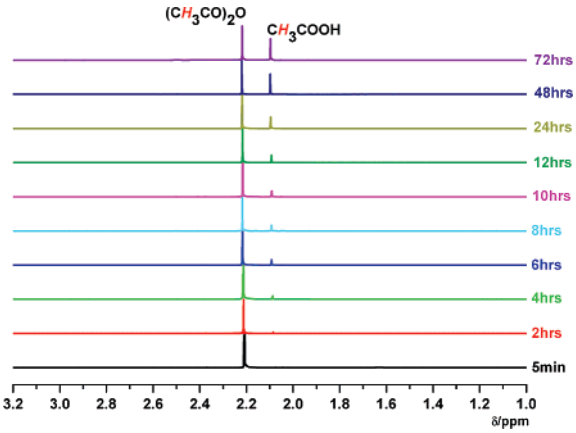

Figure 2. ^{1}H NMR spectra of the reaction solution collected between 5 min and 72 h. Each spectrum is normalized to the acetic anhydride peak. Reaction conditions: room temp, $CDCl_3$ (1.00 mL), dry IRMOF-3 crystals (0.10 mmol equiv of -NH_2), and acetic anhydride (0.21 mmol).

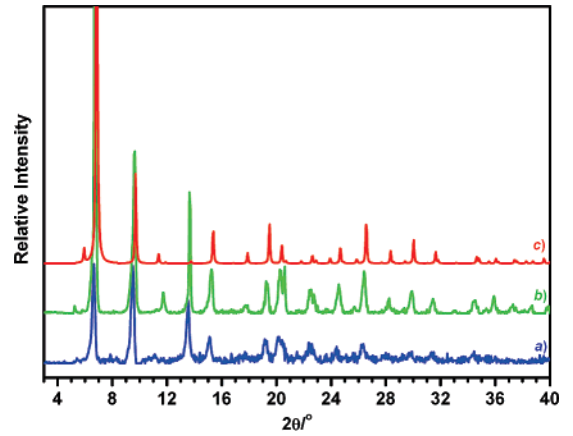

Figure 3. X-ray powder diffraction patterns (background corrected) of (a) modified IRMOF-3 (IRMOF-3-AM1); (b) as-synthesized IRMOF-3; and (c) simulated IRMOF-3.[17]

argument that IRMOF-3 is undergoing a heterogeneous reaction. Interestingly, preliminary results with acetic anhydride in other solvents (e.g., acetone-d_6, where R_3-BDC is more soluble) suggest that the heterogeneous IRMOF-3 transformation still proceeds at a rate comparable to, if not faster than, that of the homogeneous reaction involving R_3-BDC (Figure S6, S7).

In summary, we have demonstrated that it is possible to covalently modify a MOF in a postsynthetic manner. Such a unique modification strategy is expected to facilitate the generation of functional properties not directly accessible from conventional MOF synthetic schemes. The ability to directly modify a MOF using organic reagents may prove to be an efficient means of systematically modifying the cavities of porous MOFs. Furthermore, postsynthetic modification of MOFs may prove to be an important method for the solubilization and stabilization of certain structures such as MOF nanoparticles.[20,21] Given the large number of robust MOFs reported in the literature and the wide variety of organic reagents available, we anticipate the postsynthetic modification of MOFs will be a general approach; efforts to demonstrate this are underway.

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Supporting Information Available: Detailed experimental conditions, Figures S1−S9, Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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