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Metal–Organic Frameworks

Tandem Modification of Metal–Organic Frameworks by a Postsynthetic Approach**

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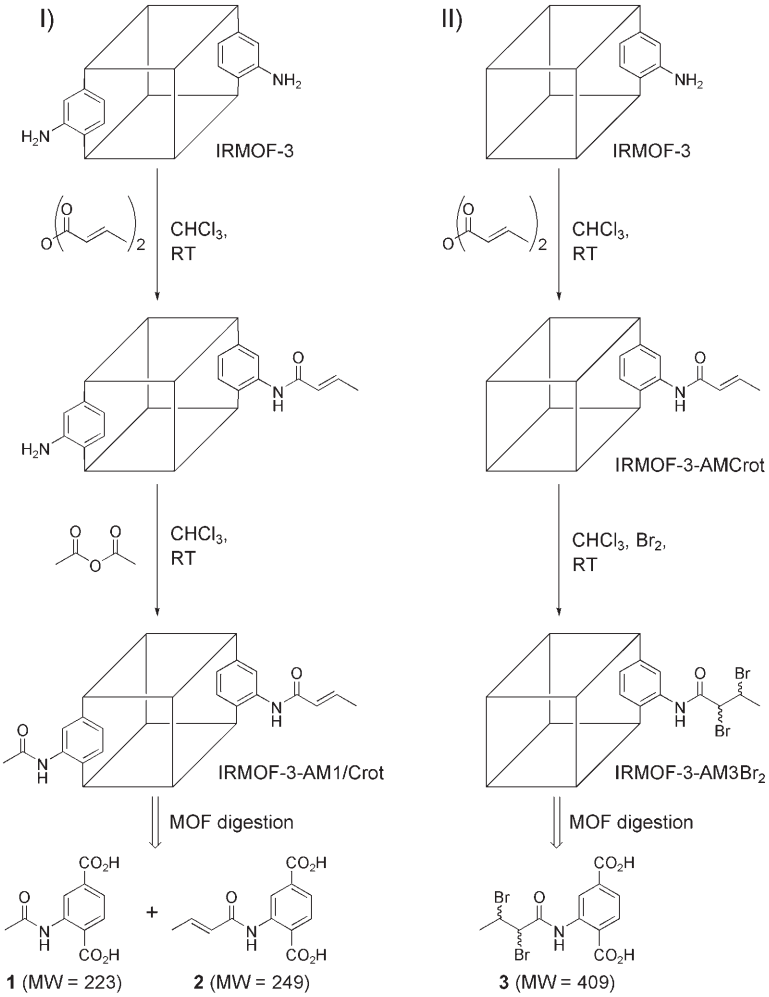
One of the challenges in the area of materials sciences is to develop reliable strategies that allow for the manipulation of physical and chemical properties of a given material in a controllable manner.[1] Materials chemists have played an enormously active role in achieving this goal, most notably through the ability to synthetically fine-tune the structures of materials on a molecular level. One recently emerged class of materials, metal-organic frameworks (MOFs), which contain metal ions or metal clusters as nodes and organic ligands as linkers, have attracted much attention because of their well-defined, adjustable, and often highly porous structures.[2–4] Some MOFs have already been utilized in various applications, including gas storage[5–8] and enantioselective catalysis.[9–12] However, optimization of MOF pore structure and hence material properties in a rational and systematic fashion remains a significant challenge.[9,11,13–15] We recently demonstrated that by targeting the organic linking component of the MOF, one can readily transform the MOF structure by means of postsynthetic covalent modification.[16] In particular, isoreticular metal-organic framework-3 (IRMOF-3), a cubic lattice prepared from $Zn(NO_3)_2 \cdot 4H_2O$ and 2-amino-1,4-benzenedicarboxylic acid (2-aminoterephthalic acid, NH_2-BDC),[7,17] can be efficiently modified by a heterogeneous acylation of its pendant amino groups with acetic anhydride, giving rise to a new MOF, IRMOF-3-AM1.[16] This postsynthetic modification approach may afford access to MOFs decorated with a variety of functionalities that are otherwise tedious or impossible to obtain by conventional MOF synthetic schemes, which generally employ solvothermal conditions.[3,7]



Scheme 1. Tandem modification strategies for postsynthetic functionalization of MOFs: I) IRMOF-3 is consecutively modified with crotonic anhydride and acetic anhydride; II) IRMOF-3 is first modified with crotonic anhydride and then further treated with bromine on the newly introduced alkenyl groups.

Herein, we describe two postsynthetic strategies that, although conceptually distinct, similarly permit stepwise "tandem" modification of MOFs. In strategy I, an MOF is partially modified with one reagent and then subsequently modified with a second reagent on the remaining reactive sites. In strategy II, an MOF is first modified with a reagent that contains a latent functional group, which, upon introduction into the MOF, is subject to further transformation with a second reagent (Scheme 1). Whereas strategy II enables transformation cascades somewhat similar to those typically seen in organic synthesis, strategy I provides a

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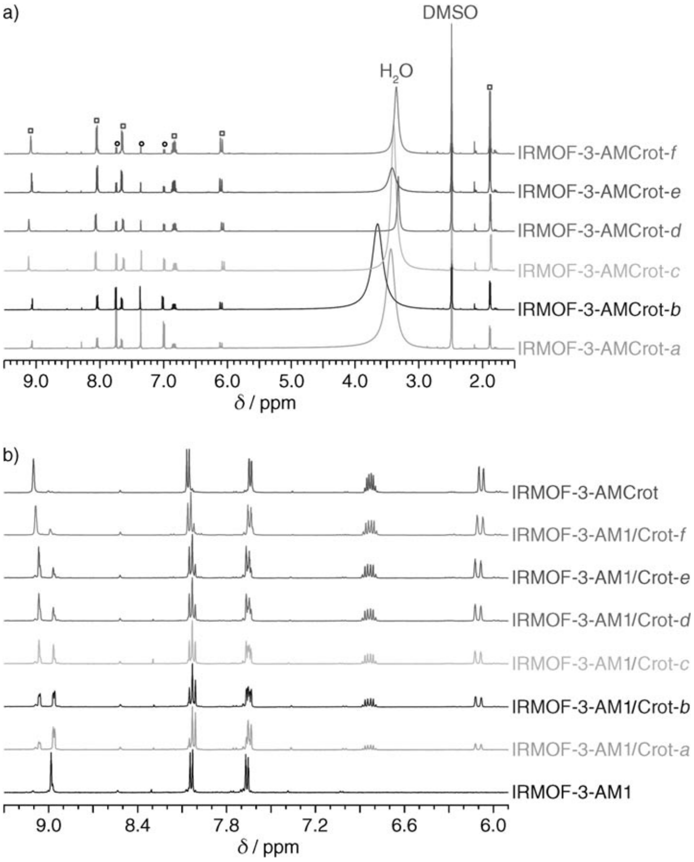

Figure 1. a) ^{1}H NMR spectra of IRMOF-3-AMCrot-*a–f* samples (digested in $DCl/D_2O/[D_6]DMSO$) possessing various percentages of amide groups. Squares and circles represent signals of **2** and NH_2-BDC, respectively. b) ^{1}H NMR spectra of IRMOF-3-AM1/Crot-*a–f* samples (digested in $DCl/D_2O/[D_6]DMSO$) possessing two different amide groups in various ratios and those of the fully converted IRMOF-3-AM1 and IRMOF-3-AMCrot.

simple, yet controlled approach to MOFs with multiple functional groups, a class of materials that are challenging to prepare by conventional methods.[18] We refer to these strategies as tandem postsynthetic modification, demonstrating that more than one chemical reaction, and hence more than one functional group, can be introduced into MOF structures by a postsynthetic strategy. IRMOF-3 is used as a model system[16] because of its high chemical stability, porosity, and robust structure. However, it is expected that this tandem modification concept will be applicable to any MOF with sufficient porosity and stability that contains reactive functional groups.

To examine the synthetic feasibility of strategy I, IRMOF-3 was consecutively modified with two different anhydrides, namely, crotonic anhydride and acetic anhydride. Single crystals of IRMOF-3 were synthesized by following reported procedures with minor modifications (see the Supporting Information).[16,17] The crystals were treated with a solution of crotonic anhydride in $CHCl_3$. Similar to the acetic anhydride case, the presence of crotonic anhydride readily triggered the acylation of IRMOF-3 on its pendant amino groups even under ambient conditions. The transformation was supported by both nuclear magnetic resonance (NMR) spectroscopy and electrospray ionization mass spectrometry (ESIMS). ^{1}H NMR spectra of the modified product, IRMOF-3-AMCrot, which was digested and dissolved in DCl/D_2O and $[D_6]DMSO$, showed new resonances at $\delta =$ 1.88, 6.01, 6.84, 7.66, 8.04, and 9.10 ppm, which is consistent with those of the expected modified ligand **2** (Scheme 1), whereas the negative mode ESIMS showed an anticipated base peak at *m*/*z* 248 (Figure S3 in the Supporting Information). More importantly, the heterogeneous nature of modification allowed the process to be manipulated, mostly by careful control of reaction time and/or reactant concentration, in such a way that IRMOF-3 was only partially modified. Indeed, by treating IRMOF-3 with crotonic anhydride for durations of one to six days, a series of new MOFs with an increasing degree of acylation, (IRMOF-3-AMCrot-*a–f*) were obtained (Figure 1). N_2 adsorption isotherms measured at 77 K indicated that these partially modified MOFs remained highly porous (BET surface areas range from 2297 to 1690 $m^2 g^{-1}$; Figure S4 in the Supporting Information). Such controlled modification of MOFs is by itself novel and deserves further attention as it immediately leads to new MOF structures with two distinct functionalities (i.e. amine and amide).

The partially converted IRMOF-3-AMCrot-*a–f*, with varying degrees of unreacted amine sites, were further treated with acetic anhydride in $CHCl_3$ until the remaining amino groups were almost completely acylated. The resulting solids were then separated from the reaction solutions and characterized by ^{1}H NMR spectroscopy, ESIMS, single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and gas adsorption. As shown in Figure 1, ^{1}H NMR spectra of the digested products (IRMOF-3-AM1/Crot-*a–f*) strongly suggested that not only did new MOFs decorated with two different substituents form, but the relative ratios of these two internal substitutes was also modulated. Furthermore, negative-mode ESIMS performed on individual single crystals (digested in H_2O) from the IRMOF-3-AM1/Crot-*a–f* samples confirmed the presence of both **1** and **2** (Figures S6–S11 in the Supporting Information). X-ray diffraction studies (on both single-crystalline and powder samples), TGA profiles, and N_2 adsorption isotherms of IRMOF-3-AM1/Crot-*a–f* established the structural integrity, thermal stability, and microporosity of these new MOFs (see the Supporting Information). Taken together, these results unambiguously support that the tandem modification strategy I leads to the generation of multifunctional MOFs characterized by the coexistence of different substituents within a single framework and not simply bulk mixtures of monofunctionalized MOFs.

Tandem modification strategy II was also tested on IRMOF-3. Single crystals of IRMOF-3 were treated with crotonic anhydride in $CHCl_3$ to yield IRMOF-3-AMCrot with near-complete conversion of all of the amino groups. The newly incorporated alkenyl groups, well known in organic chemistry for their myriad of reactivity with a wide range of reagents, provided reactive sites for further modification of IRMOF-3-AMCrot. As a representative exploration, halogenation reactions were targeted.

Bromine in $CHCl_3$ was thus added to IRMOF-3-AMCrot crystals and the heterogeneous mixtures were allowed to react in darkness. The reaction time and reactant concentration were carefully managed to allow a series of products with increasing degree of bromination (IRMOF-3-AM3Br_2-*a–c*) to be isolated at different stages of the reaction. Comparison of the ^{1}H NMR spectra of the digested IRMOF-3-AM3Br_2-*a–c* with that of the digested IRMOF-3-AMCrot revealed the expected upfield shifts for the resonances associated with the original alkenyl group (Figure 2), indicating formation of the vicinal dibromides (Scheme 1). Interestingly, the upfield shift effect appeared to be more dramatic ($\Delta\delta > 2.0$ ppm in [D_6]DMSO) for the protons adjacent to the methyl groups than those adjacent to the amide groups. Negative-mode ESIMS patterns obtained for individual single crystals (digested in H_2O) of IRMOF-3-AM3Br_2 matched the simulated pattern (Figure S16 in the Supporting Information), providing further evidence for the successful bromination of IRMOF-3-AMCrot. Although small amounts of impurities were also noted in the ^{1}H NMR spectra (Figure S15 in the Supporting Information), possibly because of some undesired side reactions, the crystallinity and thermal stability of the resultant IRMOF-3-AM3Br_2 were nevertheless confirmed by single-crystal X-ray diffraction, PXRD, and TGA experiments (see the Supporting Information). N_2 adsorption isotherms of IRMOF-3-AM3Br_2-*a–c* also suggested that microporosity was essentially maintained (Figure 2). Observed decreases in surface areas (ca. 500 m^2g^{-1} for IRMOF-3-AM3Br_2-*c* vs. ca. 1400 m^2g^{-1} for IRMOF-3-AMCrot) were largely attributed to both reduced free space available and increased overall weight of the new MOFs as a result of introducing large and heavy bromine atoms.

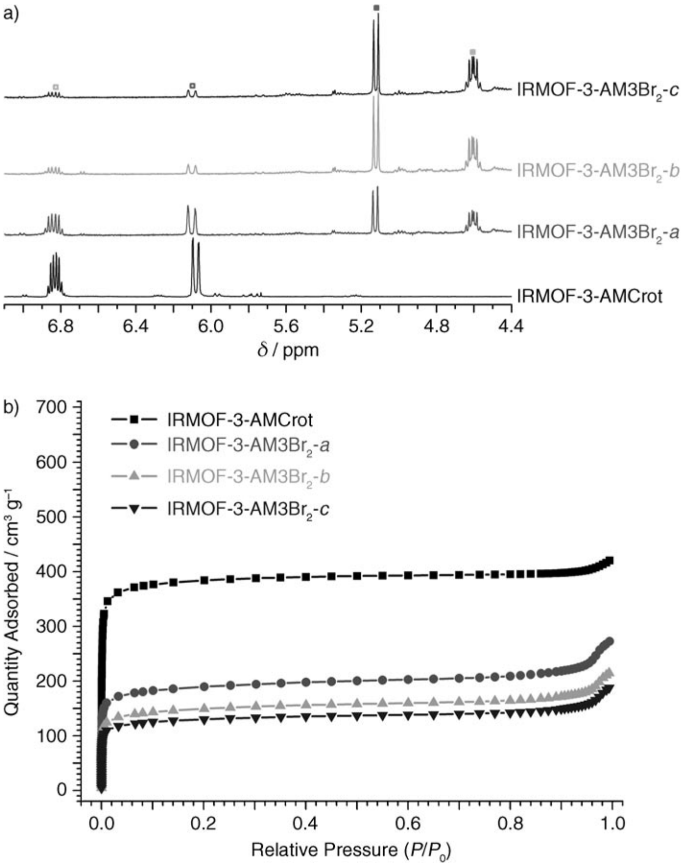

Figure 2. a) ^{1}H NMR spectra of IRMOF-3-AMCrot and IRMOF-3-AM3Br_2-*a–c* samples (digested in DCl/D_2O/[D_6]DMSO) showing up-field shifts for the original alkenyl protons. Empty squares and filled squares represent signals of **2** and **3**, respectively. b) N_2 adsorption isotherms (at 77 K) of IRMOF-3-AM3Br_2-*a–c* and IRMOF-3-AMCrot.

The two tandem modification methods discussed above each exemplify a highly efficient and controllable approach to the functionalization of MOFs. The ease of using stepwise synthetic operations, facilitated by the heterogeneous postsynthetic protocols, provides us with the capability to fine-tune the internal molecular environments of MOFs and offers unprecedented opportunities to systematically evaluate and improve the performance of MOF materials. In particular, strategy I appears to be well suited for generating multifunctional MOFs that are modulated with various chemical entities. Although we have only focused herein on amide-coupling reactions and two different anhydrides, it is not difficult to envision that the same principle could be easily applied to a wide variety of other types of reactions and reagents as well as much more complex combinations. Strategy II not only expands the scope of postsynthetic modification of MOFs, but also demonstrates the feasibility of serial manipulation of MOFs. Perhaps even more significant is the possibility of combining both strategies in the same MOF. In fact, it is possible to propose further modifications on IRMOF-3-AM1/Crot-*a–f*, which result from strategy I and can undergo bromination reactions demonstrated in strategy II. This approach will in turn give rise to an even larger pool of diverse MOF structures. We expect the postsynthetic modification approach to have significant implications for MOF chemistry, as we have, in effect, demonstrated a viable route to the solid-state version of diversity-oriented synthesis (DOS).[19] This study might eventually lead to development of combinatory libraries of MOFs. Efforts toward exploring new properties on the postsynthetically functionalized MOFs are currently underway in our laboratory.

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