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Ring-Opening Reactions within Porous Metal−Organic Frameworks

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Two new metal−organic framework (MOF) structures, IRMOF-3b and -3c, were prepared by ring-opening reaction of 1,3-propanesultone and 2-methylaziridine with an amine functionalized MOF, IRMOF-3. The new structures are permanently functionalized with covalently linked sulfonate and alkyamine units, respectively. The underlying framework structure is retained after reaction as confirmed by powder X-ray diffraction. The high porosity of IRMOF-3 is also maintained, as evidenced by nitrogen adsorption experiments, which yield Brunauer−Emmett−Teller (BET) surface areas of 1380 and 530 m^2 g^{-1} compared to 2040 m^2 g^{-1} in the parent material. Ring-opening reactions provide a versatile route to irreversible binding of a range of functionalities that are otherwise difficult to access in MOFs.

Metal−organic frameworks (MOFs) are crystalline porous materials in which organic molecules link inorganic building units into well-defined structures.[1,2] Recently, synthetic transformations have been performed on these structures resulting in high-yielding functionalization throughout the crystal, in effect treating the entire crystal as a molecule.[3−6] By this method it is possible to access functionality that would be difficult or impossible to include through traditional synthetic methods due to interference of the desired functional group with the process of MOF structure formation and crystallization. Here we report the inclusion of sulfonate and ethylenediamine groups in IRMOF-3, an amine-containing MOF, by ring-opening reactions of 1,3-propanesultone and 2-methylaziridine (Figure 1). Sulfonate groups are rare in MOFs owing to their propensity to interact with the metal ions used in MOF synthesis.[7,8] Ethylenediamine has been included in MOFs by using one of the amine groups to covalently bind it to the framework.[9,10] The method of functionalization used in this report results in a covalently bound ligand wherein the ethylenediamine group is free. This functional group is potentially useful for subsequent metal chelation and carbon dioxide capture.[11]

IRMOF-3, which is composed of a link containing a free $-NH_2$ functionality, was synthesized according to published procedures and the pore contents fully exchanged for $CHCl_3$.[12,13] To the solid, which was immersed in $CHCl_3$, 1,3-propanesultone or 2-methylaziridne was added, and the mixture was held at 45 °C overnight. The $CHCl_3$ solvent was then repeatedly decanted and refreshed over three days to remove excess reagent.[14] The reaction products, here termed IRMOF-3b and IRMOF-3c respectively, maintained their structural topology throughout the reaction as evidenced by powder X-ray diffraction (PXRD) experiments (Figure 2).

The identity of the reaction products was confirmed by elemental analysis (EA)[14] and ^{13}C cross-polarization, magic angle spinning (CP/MAS) NMR (see the Supporting Information). NMR spectra of IFMOF-3b and -3c contain all peaks for IRMOF-3 in positions very close to the parent framework. Peaks corresponding to the reacted sultone molecule in IRMOF-3b are found at δ = 25 and 50 ppm. The former is assigned to the central carbon atom of the propylene group. The latter is assigned to the first and third carbon atoms of the propylene group, which are too close in chemical

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(12) A total of 3.35 g of 2-aminoterephthalic acid and 14.0 g of Zn(NO_3)$_2$·4H_2O were dissolved with sonication in 300 mL of *N*,*N*-dimethylformamide (DMF) and heated at 100 °C for 2 d. After cooling to room temperature, the mother liquor was decanted and the products washed with DMF. Products were immersed in $CHCl_3$, which was refreshed daily for 2 d. The brown crystalline products were used directly in the synthesis of IRMOF-3b or IRMOF-3c.

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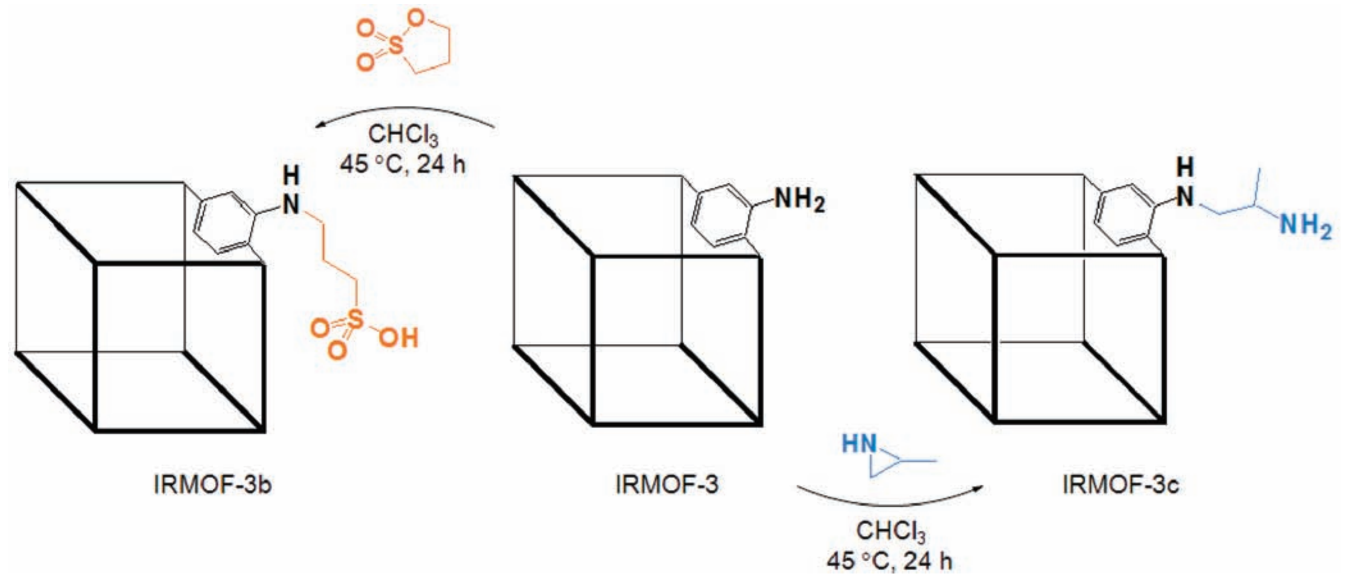

Figure 1. Ring-opening reactions performed on IRMOF-3 leading to covalently functionalized products IRMOF-3b and IRMOF-3c. The cage of the MOF is represented as a cube where vertices replace the metal clusters and edges replace the organic linkers.

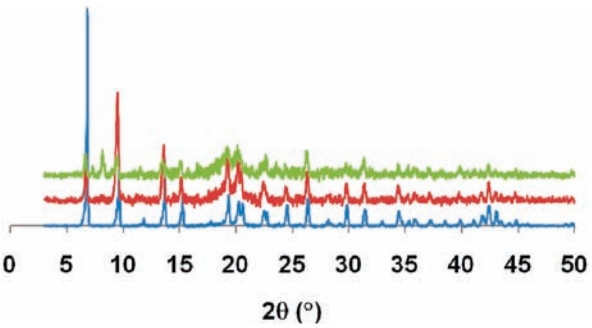

Figure 2. PXRD patterns of IRMOF-3 (blue), IRMOF-3b (red), and IRMOF-3c (green). Patterns are normalized and background corrected. The appearance of a peak around 8° 2*θ* in the IRMOF-3c pattern is attributed to partial hydrolysis of the framework on exposure to ambient air.

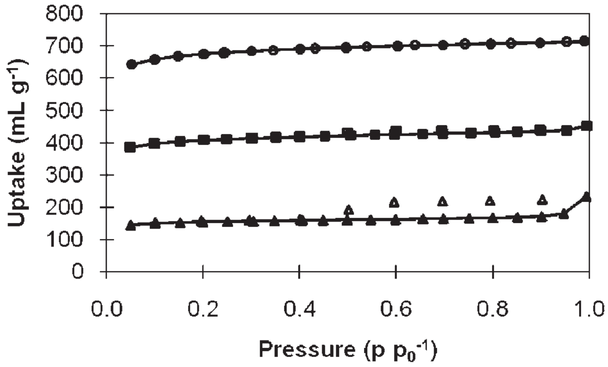

Figure 3. N_2 adsorption isotherms for IRMOF-3 (circles), IRMOF-3b (squares), and IRMOF-3c (triangles). Closed shapes represent adsorption while open shapes represent desorption. Lines connecting the adsorption curves are guides for the eye.

shift to be distinguished in the solid state. A small amount of unreacted sultone was observed with peak positions δ = 42 and 70 ppm. In the IRMOF-3c spectrum the peak at δ = 17 ppm corresponds to the terminal methyl group in the proposed structure while the peak at δ = 47 ppm corresponds to the two ethylene carbon atoms, which are too close in chemical shift to be distinguished in the solid state. We note that it was not possible to differentiate between the two possible ring-opening products in IRMOF-3c, where nucleophilic attack occurs at either the 2- or 3-position on the aziridine ring. We presume that attack occurs more favorably at the less substituted 3-position; however, a mixture of products is likely.

The approximate reaction yield per organic linker was obtained from EA.[14] In IRMOF-3b, 57% of the linkers are functionalized with alkylsulfonate groups. In IRMOF-3c more than one addition per linker is possible, as each addition results in a new primary amine group in the pore. EA indicates 1.08 aziridine additions per linker, which likely corresponds to a combination of linkers with zero, one, and two or more additions. Significant oligomerization is hindered by the pore structure of the MOF, as diffusion of aziridine becomes limited with successive additions.

The high posority of the parent IRMOF-3 structure is retained after reaction, as evidenced by nitrogen adsorption isotherms collected for the reaction products (Figure 3). IRMOF-3b has a calculated surface area of 1380 $m^2\ g^{-1}$ as determined by the Brunauer−Emmett−Teller (BET) method, which is 67% of IRMOF-3. This reduction in surface area is expected with the added mass of the alkylsulfonate groups.

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(14) **IRMOF-3b**. To ~2 g of IRMOF-3 in $CHCl_3$ was added 2 mL of 1,3-propanesultone. After sitting overnight, the products, which were slightly opaque in comparison to pristine IRMOF-3, were washed with $CHCl_3$. The solvent was exchanged daily for 2 d to remove any unreacted sultone. Under vacuum the products were dried and heated at 120 °C for 20 h prior to gas adsorption studies. Elemental analysis for the 57% functionalized material, $Zn_4O(C_8H_5NO_4)_{1.29}(C_{11}H_{11}NSO_7)_{2.71}$ (calculated values in parentheses): Zn, 25.93% (25.55%); C, 33.53 (34.17); H, 2.73 (2.49); N, 4.11 (4.10); S, 5.91 (5.36). **IRMOF-3c**. To ~2 g of IRMOF-3 in $CHCl_3$ was added 2 mL of 2-methylaziridine. The mixture was heated mildly (45 °C) for 4 h. After cooling to room temperature, the products, which were slightly opaque in comparison to pristine IRMOF-3, were washed with $CHCl_3$. The solvent was exchanged daily for 2 d to remove any unreacted aziridine. Under vacuum the products were dried and heated at 120 °C for 20 h prior to gas adsorption studies. Elemental analysis for the material functionalized 1.08 times per link, $Zn_4O(C_{11}H_{12}N_2O_4)_3(C_3H_7N)_{0.24}$ (calculated values in parentheses): Zn, 26.67% (27.41%); C, 38.49 (38.35); H, 3.75 (3.29); N, 8.65 (9.16).

IRMOF-3c has a BET surface area of 530 $m^2\ g^{-1}$, 26% of IRMOF-3. This reduction is more than what is expected for the added mass of alkylamine groups, though the material is still highly porous. It is possible that activation of IRMOF-3c is more challenging than the parent MOF due to the presence of the amine chains. It may be possible to improve activation conditions to attain optimal gas uptake.

The successful ring-opening modification of IRMOF-3 using two different reagents indicates that this method of functionalization is generalizable and may serve as a route to previously elusive functional groups throughout MOFs and related porous crystalline materials. Ring-opening reactions present several advantages as a route to new functionalities in MOFs. The wide variety of strained or reactive heterocycles readily available provides a range of functionalities that can be included. Such ring-opening reactions are irreversible, making it possible to use a functionalized MOF in gas adsorption, catalysis, or other application without loss of the relevant group. Finally, the groups added in this study have not proven to be readily accessible by traditional MOF synthesis.

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Supporting Information Available: ^{13}C CP/MAS NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.