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Moisture-Resistant and Superhydrophobic Metal−Organic Frameworks Obtained via Postsynthetic Modification

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Received February 1, 2010; E-mail: scohen@ucsd.edu

Metal−organic frameworks (MOFs) are porous, crystalline materials that are attractive for applications in gas adsorption,[1] separations,[2] and catalysis[3,4] because of their chemical tunability, high porosities, and good thermal stability.[5] Unfortunately, some of the most promising materials are limited because of an instability with respect to moisture.[6−8] Stabilizing these MOFs against ambient humidity would make these porous materials more suitable for specialized and industrial applications. The postsynthetic modification (PSM) approach, which has become an important tool in developing functionally diverse systems and introducing new physical and chemical properties into MOFs,[9] offers an opportunity to address this challenge.

Amine-containing MOFs can readily undergo PSM to form amide-functionalized MOFs.[10,11] It was hypothesized that the introduction of hydrophobic alkyl chains via PSM could improve the moisture resistance and change the physical properties (i.e., hydrophobicity) of these MOFs. The effect of PSM on two different MOF systems was examined (Figure 1). Isoreticular metal−organic frameworks (IRMOFs) are cubic frameworks comprised of Zn_4O clusters and dicarboxylate ligands. In this study, IRMOFs constructed of 1,4-benzenedicarboxylate (BDC, IRMOF-1), 2-amino-1,4-benzenedicarboxylate (NH_2-BDC, IRMOF-3), and PSM derivatives of the latter were investigated. The second MOF systems examined belong to the Material Institut Lavoisier (MIL) class of materials,[12] specifically, MIL-53(Al)-NH_2, a flexible MOF comprised of infinite Al^{3+} clusters and NH_2-BDC. The IRMOFs are generally considered sensitive to moisture, while the MILs are stable to water and other polar solvents (indeed MIL-53(Al)-NH_2 is synthesized in water). To assess changes in the moisture stability and hydrophobicity/philicity of the materials upon PSM, each material was exposed to ambient air or immersed in water and then characterized using contact angle measurements, powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM).

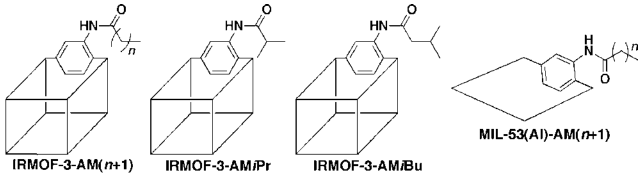

Figure 1. Schematic representations of the MOFs examined in this study. One modified organic ligand substituent is shown in each structure.

Contact angle measurements are commonly used to examine the hydrophobic/philic properties of materials. Hydrophilic materials display contact angles less than 90°. Contact angles between 90° and 150° are found for hydrophobic materials, and materials with contact angles >150° are considered superhydrophobic. IRMOF-1 and IRMOF-3 were found to be hydrophilic, absorbing water droplets and displaying contact angles close to 0° (Figure S1). Similarly, IRMOF-3-AM1, -AM2, and -AM3 also display 0° contact angles, simply absorbing the applied water droplet (-AM1 = "amide" with a one-carbon chain). However, IRMOFs modified with longer alkyl substituents (e.g., IRMOF-3-AM4 and longer) show contact angles ≥116° consistent with hydrophobic materials (Table 1). The contact angles of these hydrophobic samples remained unchanged even upon exposure to ambient air for several weeks. Smaller alkyl chains require a higher percentage of modification to effectively introduce hydrophobicity within the material. For example, a partially modified IRMOF-3-AM15 that has only 25% of the amine groups converted to amides (the maximum conversion obtained under the present reaction conditions) displays hydrophobicity as gauged by contact angle measurements. In contrast, for IRMOF-3-AM4 to be hydrophobic, at least 50% of the amine sites needed to be modified (Table S1, Figure S2). Branched alkyl substituents also enhanced hydrophobicity, as IRMOF-3-AM3 was hydrophilic, while IRMOF-3-AM*i*Pr was hydrophobic (Table 1). These experiments show that the functional group and the extent of modification are important factors that contribute to the introduction of hydrophobic properties within the materials.

Table 1. Percent Conversion and Contact Angle Measurements for IRMOF and MIL Materials

Compound	% Conversion	Contact Angle (deg)[a]
IRMOF-1	N/A	$\sim$0
IRMOF-3	N/A	$\sim$0
IRMOF-3-AM1	$\sim$99	$\sim$0
IRMOF-3-AM2	$\sim$99	$\sim$0
IRMOF-3-AM3	$\sim$99	$\sim$0
IRMOF-3-AM4	98 ± 3	116 ± 6
IRMOF-3-AM5	96 ± 3	119 ± 10
IRMOF-3-AM6	90 ± 3	124 ± 8
IRMOF-3-AM15	25 ± 3	123 ± 5
IRMOF-3-AM*i*Pr	$\sim$99	125 ± 12
IRMOF-3-AM*i*Bu	88	105 ± 11
MIL-53(Al)	N/A	$\sim$0
MIL-53(Al)-NH_2	N/A	$\sim$0
MIL-53(Al)-AM1	91	$\sim$0
MIL-53(Al)-AM4	44 ± 8	>150[b]
MIL-53(Al)-AM6	17 ± 9	>150[b]

[a] Values listed are an average (with standard deviations) of at least four independent experiments. [b] Water droplets were observed to rapidly roll off of the surface of the material.

MOF samples were exposed to air and examined using PXRD to provide insight on the integrity of the materials under ambient conditions. For these experiments, the samples were air-dried for approximately 15 min, crushed, and placed on a zero field sample holder for analysis. The samples were spun during the data collection, and the same sample was examined for 4 consecutive days. The instability of IRMOF-1 in ambient air is immediately noticeable with the formation of a new reflection at $2\theta = 8.9°$ (Figure S3), which is indicative of the transformation to MOF-69c.[6,7] Another indicator of degradation is the loss of the reflection at 2θ

10.1021/ja100900c

$= 6.9°$ within 24 h (Figure 2A). IRMOF-3 proved to be more stable than IRMOF-1 in ambient air. Over the period of 4 days, no new peaks appear for IRMOF-3, but all of the reflections for IRMOF-3 decrease over time, albeit at a much slower rate than observed for IRMOF-1 (Figure 2B). In contrast, the addition of hydrophobic substituents clearly stabilizes the bulk crystallinity of the IRMOF structure in air (Figure 2C). PXRD patterns of IRMOF-3-AM6 and IRMOF-3-AM15 remain essentially unchanged over four days, with no new peaks and little loss in peak intensity at $2\theta = 6.9°$ (Figure S7). The PXRD data indicate that hydrophobic modifications to the IRMOF lattice can appreciably safeguard the crystallinity of these materials under standard atmospheric conditions.

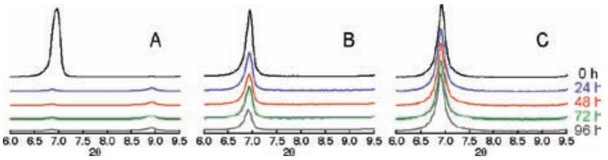

Figure 2. Representative PXRD patterns comparing peak intensity changes for (A) IRMOF-1, (B) IRMOF-3, and (C) IRMOF-3-AM15 over a period of 4 days.

The stability of the samples to direct contact with water was evaluated by using SEM. Images of MOF samples without direct exposure to water and following immersion in water were obtained (Figure 3). The unexposed samples of MOF crystals were taken from $CHCl_3$ solution and allowed to air-dry for 1.5 h. For exposed samples, the MOF crystals were placed in water for ∼30 min, after which the water was quickly removed, and the samples air-dried for ∼1 h prior to SEM imaging. As previously described, IRMOF-1 proved unstable even to ambient moisture in air as evidenced by the appearance of holes in the surface of the material (Figure 3A); when exposed to water, IRMOF-1 was completely decomposed (Figure 3B). IRMOF-3 appears unaltered under ambient conditions for short periods of time (Figure 3C), but when IRMOF-3 comes into direct contact with water, it immediately turns opaque. Although the bulk crystal morphology of IRMOF-3 appears preserved, the surface of the water-exposed IRMOF-3 sample is clearly degraded as shown by SEM (Figure 3D). In contrast, the hydrophobic IRMOF-3-AM6 (Figure S15) and IRMOF-3-AM15 appear unadulterated by ambient moisture (Figure 3E) or direct exposure to water (Figure 3F). Indeed, IRMOF-3-AM6 and IRMOF-3-AM15 crystals do not immerse in water (as do IRMOF-1 and IRMOF-3), but rather rest on the meniscus of the aqueous solution, providing additional evidence of the hydrophobicity observed in contact angle measurements. These results indicate that hydrophobic groups can protect IRMOFs from degradation upon contact with water.

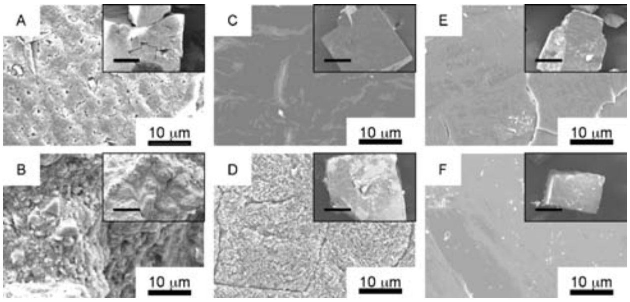

Figure 3. SEM micrographs of (A) IRMOF-1, (B) IRMOF-1 exposed to water, (C) IRMOF-3, (D) IRMOF-3 exposed to water, (E) IRMOF-3-AM15, and (F) IRMOF-3-AM15 exposed to water. The inset is the SEM micrographs of the crystals zoomed out (bar represents 200 μm, except for IRMOF-1, which is 100 μm).

While the introduction of hydrophobic groups to IRMOF-3 stabilizes it to ambient air and direct contact with water, we wanted to examine how the same functional groups would affect a more chemically robust MOF. Thus, MIL-53(Al)-NH_2 was modified with three different alkyl anhydrides (Supporting Information) to generate MIL-53(Al)-AM1, -AM4, and -AM6. Contact angle measurements of MIL-53(Al) (made with BDC),[13] MIL-53(Al)-NH_2 (made from NH_2-BDC), and MIL-53(Al)-AM1 showed contact angles of essential 0°. Surprisingly, both MIL-53(Al)-AM4 and MIL-53(Al)-AM6 appear to possess superhydrophobic properties with contact angles greater than 150° (Figure S13). We propose that it is the submicrometer crystallite size (Figure S17) combined with the hydrophobic functional groups that result in the observed superhydrophobicity.[14−16]

In conclusion, we have successfully demonstrated that hydrophobic properties can easily be incorporated within a MOF. The integration of medium to long alkyl groups within IRMOF-3 shields the moisture-sensitive MOF by turning it into a hydrophobic material. This valuable finding suggests that MOFs can be synthesized to possess certain desirable chemical and physical properties. This notion is further established by our ability to transform MIL-53(Al)-NH_2 into a material with superhydrophobic properties. Superhydrophobic properties are highly desirable and widely used in thin film materials to stabilize them against biofouling, inorganic, and organic pollutants.[14−16] The fabrication of thin film coatings of MOFs on various substrates is becoming common practice,[17,18] which provides an exciting opportunity to produce novel materials in satellite communications, textile fibers, and electrical engineering.

Acknowledgment. We thank Prof. S. Jin and C. N. Choi for help with contact angle measurements, R. Anderson and M. Clark for help with obtaining SEM images, and Dr. Y. Su for performing the mass spectrometry experiments. This work was supported by the National Science Foundation Award No. CHE-0546531 (new MOF synthesis) and the Department of Energy, Office of Basic Energy Sciences Award No. DE-FG02-08ER46519 (modification of MOFs for gas sorption). J.G.N. was supported by an NIH Training Grant (5T32DK007233).

Supporting Information Available: Experimental details, Table S1, Figures S1−S17. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA100900C