ACS APPLIED MATERIALS & INTERFACES

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Research Article

Evaluating the Robustness of Metal–Organic Frameworks for Synthetic Chemistry

Zihao Wang, Arvin Bilegsaikhan, Ronald T. Jerozal, Tristan A. Pitt, and Phillip J. Milner*

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 17517–17531

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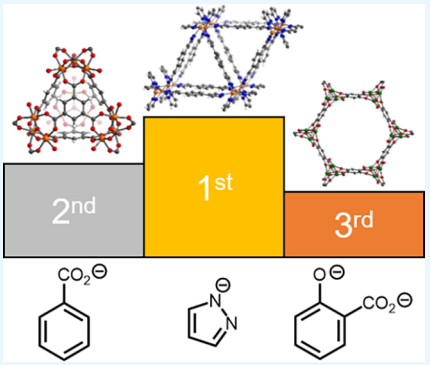
ABSTRACT: Metal–organic frameworks (MOFs) are emerging as sustainable reagents and catalysts with promising applications in synthetic chemistry. Although the hydrothermal stabilities of MOFs have been well studied, their robustness toward various reagents, including acids, bases, nucleophiles, electrophiles, oxidants, and reductants, remains poorly characterized. As such, heterogeneous platforms for promising catalysts are generally identified on an *ad hoc* basis and have largely been limited to carboxylate frameworks to date. To address these limitations, here we systematically characterize the robustness of 17 representative carboxylate, salicylate, and azolate MOFs toward 30 conditions representing the scope of synthetic organic chemistry. Specifically, analysis of the full width at half-maximum of powder X-ray diffraction patterns, as well as infrared spectroscopy, 77 K N_2 adsorption measurements, and scanning electron microscopy in select cases are employed to appraise framework degradation and dissolution under a range of representative conditions. Our studies demonstrate that azolate MOFs, such as $Fe_2(bdp)_3$ (bdp^{2-} = 4,4′-(1,4-phenylene)bis(pyrazolate)), generally possess excellent chemical stabilities under myriad conditions. In addition, we find that carboxylate and salicylate frameworks possess complementary stabilities, with carboxylate MOFs possessing superior robustness toward acids, electrophiles, and oxidants, and salicylate MOFs demonstrating improved robustness toward bases, nucleophiles, and reductants. The guidelines provided herein should facilitate the rational design of robust frameworks for applications in synthetic chemistry and guide the development of new strategies for the postsynthetic modification of MOFs as well.



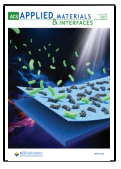
KEYWORDS: *metal–organic frameworks, catalysis, stability, robustness.*

INTRODUCTION

Metal–organic frameworks (MOFs), which are crystalline porous materials that self-assemble from organic linkers and inorganic nodes, are transformative candidates for a breadth of industrial applications, including chemical separations and gas storage.[1−4] Recently, MOFs have also emerged as unique heterogeneous catalysts and reagents for transformations relevant to synthetic organic and medicinal chemistry.[5−7] For these applications, a promising general strategy is to embed desired catalytic or reactive motifs within the organic linker, with the MOF serving as a heterogeneous support.[5] Due to their crystallinity, tunability, and porosity, MOFs are poised to overcome the limitations of traditional heterogeneous supports such as amorphous polymers, which remain underutilized in the pharmaceutical industry due to their poor reactivities compared to homogeneous systems.[8] Furthermore, MOFs offer the potential to change the inherent selectivities of transformations through confinement and secondary coordination sphere effects.[5] However, applications of MOFs in synthetic organic chemistry remain underdeveloped.

The utility of MOFs for separations has been greatly aided by structural guidelines for predicting their stability under relevant conditions, such as in the presence of water or corrosive gases.[9−13] Likewise, the development of homogeneous catalysts for synthetic chemistry has been accelerated by "robustness screens" that aid the assessment of their stabilities and activities in the presence of certain functional groups.[14] However, while the hydrothermal stabilities of MOFs have been well studied, little is known about their general stability to common reagents such as nucleophiles, electrophiles, oxidants, and reductants. A better understanding of the chemical robustness of different families of MOFs would facilitate the discovery of new platforms for hosting reactive species, which are currently identified largely by trial-and-error. A related challenge is that conflicting information exists in the literature due to differing experimental methods and criteria for evaluating robustness. For example, there are contradictory reports regarding the stability of the canonical framework ZIF-8 (ZIF = zeolitic imidazolate framework) toward water.[15]

Received: January 20, 2021
Accepted: March 24, 2021
Published: April 6, 2021



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ACS Appl. Mater. Interfaces 2021, 13, 17517–17531

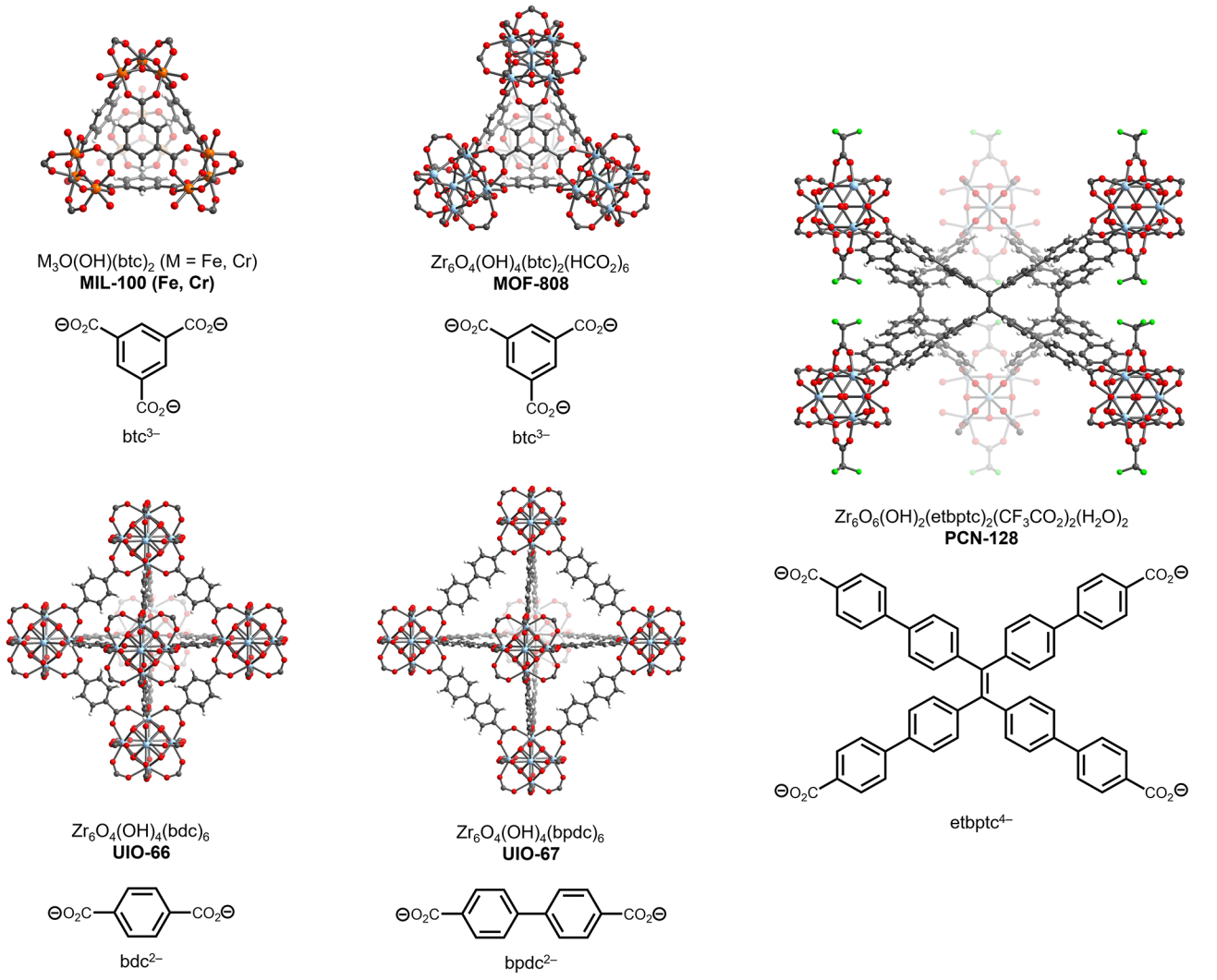

Figure 1. Carboxylate metal−organic frameworks studied as part of this work, including MIL-100 (Fe, Cr) or $M_3O(OH)(btc)_2$ (M = Fe, Cr), MOF-808 or $Zr_6O_4(OH)_4(btc)_2(HCO_2)_6$ (btc^{3-} = benzene-1,3,5-tricarboxylate), UiO-66 or $Zr_6O_4(OH)_4(bdc)_6$ (bdc^{2-} = benzene-1,4-dicarboxylate), UiO-67 or $Zr_6O_4(OH)_4(bpdc)_6$ ($bpdc^{2-}$ = 1,1′-biphenyl-4,4′-dicarboxylate), and PCN-128 or $Zr_6O_6(OH)_2(etbptc)_2(CF_3CO_2)_2(H_2O)_2$ ($etbptc^{4-}$ = 4′,4‴,4⁗,4⁗′′′′′-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1′-biphenyl]-4-carboxylate))). Gray, white, red, orange, pale blue, and bright green spheres represent carbon, hydrogen, oxygen, iron/chromium, zirconium, and fluorine, respectively.

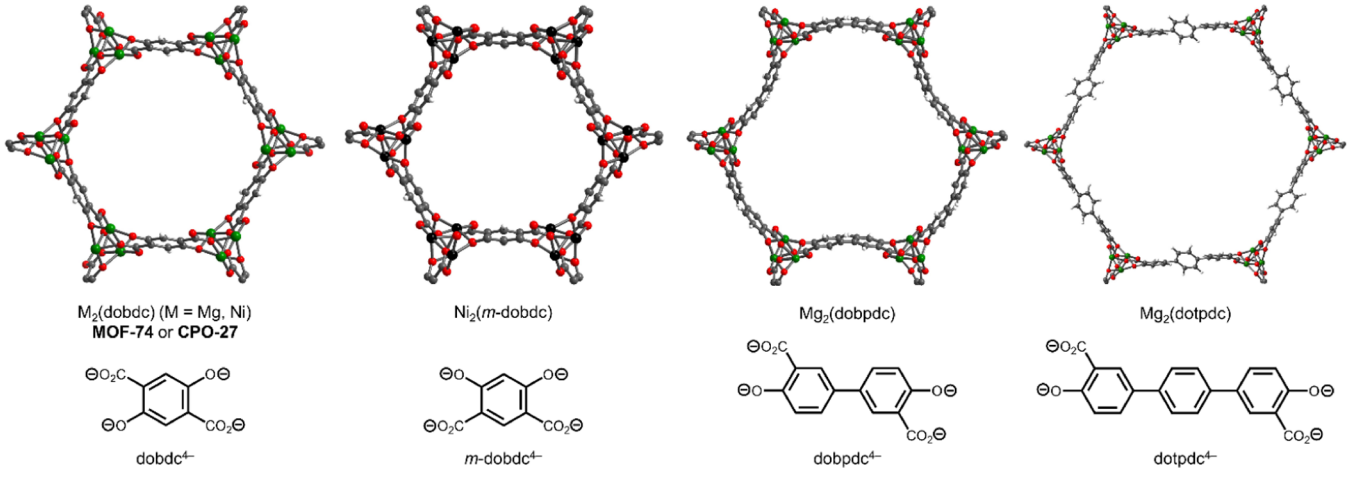

Figure 2. Salicylate metal−organic frameworks studied as part of this work, including MOF-74 or $M_2(dobdc)$ (M = Mg, Ni; $dobdc^{4-}$ = 2,5-dioxidobenzene-1,4-dicarboxylate), Ni_2(m-dobdc) (m-$dobdc^{4-}$ = 4,6-dioxidobenzene-1,3-dicarboxylate), Mg_2(dobpdc) ($dobpdc^{4-}$ = 4,4′-dioxido-1,1′-biphenyl-3,3′-dicarboxylate), and Mg_2(dotpdc) ($dotpdc^{4-}$ = 4,4″-dioxido-[1,1′:4′,1″-terphenyl]-3,3″-dicarboxylate). Gray, white, red, dark green, and black spheres represent carbon, hydrogen, oxygen, magnesium, and nickel, respectively.

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ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

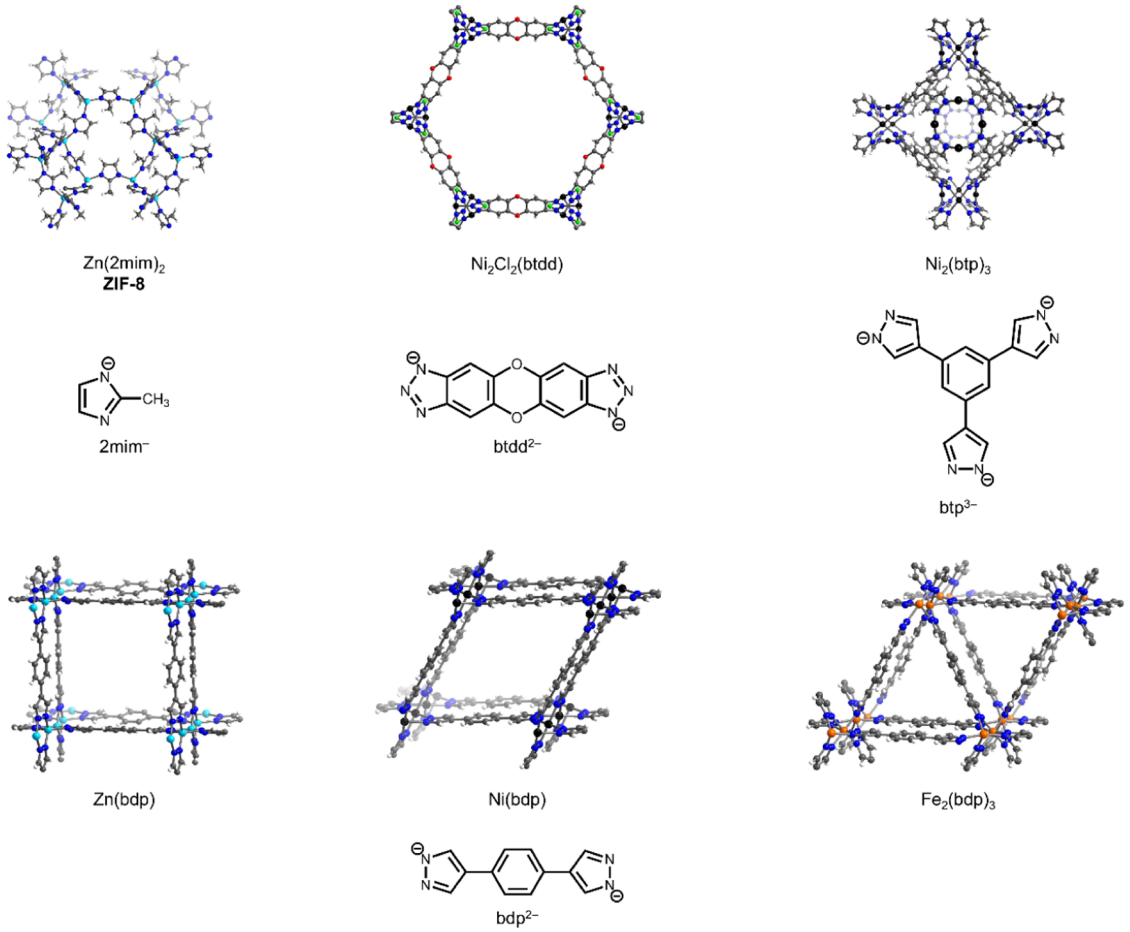

Figure 3. Azolate metal−organic frameworks studied as part of this work, including ZIF-8 or $Zn(2mim)_2$ ($2mim^-$ = 2-methylimidazolate), $Ni_2Cl_2(btdd)$ ($btdd^{2-}$ = bis(1,2,3-triazolo[4,5-*b*],[4′,5′-i])dibenzo[1,4]dioxin), $Ni_3(btp)_2$ (btp^{3-} = 4,4′,4″-(benzene-1,3,5-triyl)tris(pyrazolate)), Zn(bdp), Ni(bdp), and $Fe_2(bdp)_3$ (bdp^{2-} = 4,4′-(1,4-phenylene)bis(pyrazolate)). Gray, white, dark blue, sky blue, black, and orange spheres represent carbon, hydrogen, nitrogen, zinc, nickel, and iron, respectively.

Therefore, a systematic study in which the robustness of families of MOFs is evaluated under a standardized set of conditions would aid in the prediction of which frameworks can survive a given set of reaction conditions. Guidelines regarding the robustness of different families of MOFs toward various reagents would also accelerate the development of new strategies for postsynthetic modification as well.[16]

To fill in the knowledge gap regarding the chemical robustness of MOFs, here we systematically explore the stability of 17 "stable" MOFs representing three families of MOFs—carboxylate, salicylate, and azolate—to myriad conditions representing the scope of synthetic organic chemistry. In particular, we outline the robustness of these MOFs toward Brønsted acids, Brønsted bases, nucleophiles, electrophiles, oxidants, and reductants, by analyzing changes in the full width at half-maximum (FWHM) of powder X-ray diffraction (PXRD) reflections to monitor MOF dissolution and degradation.[17] The results of this evaluation will prove beneficial for the future identification of stable MOF-based platforms for applications in synthetic chemistry.

RESULTS AND DISCUSSION

Selection and Synthesis of Representative MOFs. In choosing representative MOFs for this study, we excluded frameworks that are known to be water sensitive, such as MOF-5[18] and HKUST-1 (HKUST = Hong Kong University of Science and Technology).[19] In addition, tetrazolate MOFs were excluded due to the known risk of explosion upon desolvating these frameworks.[20] In all, 17 representative stable frameworks from three families of linkers—carboxylates (Figure 1), salicylates (Figure 2), and azolates (Figure 3)—were chosen. By focusing on families of frameworks instead of individual MOFs, we hope to provide general trends for identifying which *type* of framework would be an ideal host for a given catalyst or reagent.

Frameworks constructed from polytopic carboxylates represent the largest and most well-studied family of topologically diverse MOFs (Figure 1).[4,21] Among these materials, carboxylate MOFs based on trigonal M_3O (M = Sc, V, Cr, Fe, Al)[22] and octahedral Zr_6 nodes[23] represent privileged materials owing to their excellent thermal stabilities. The hydrothermally stable MOFs MIL-100 (MIL = Materials Institute Lavoisier) or $M_3O(OH)(btc)_2$ (btc^{3-} = benzene-1,3,5-tricarboxylate; M = Fe, Cr) boast large (29 Å) pores and coordinatively unsaturated M^{3+} sites, making them intriguing heterogeneous Lewis acid catalysts.[24] The archetypical Zr-based MOFs UiO-66 (UiO = Universitetet i Oslo) or $Zr_6(OH)_4O_4(bdc)_6$ (bdc^{2-} = 1,4-benzenedicarboxylate)[25,26] and MOF-808 or $Zr_6O_4(OH)_4(btc)_2(HCO_2)_6$ (btc^{3-} = benzene-1,3,5-tricarboxylate)[27] are among the most stable of MOFs. Additionally, expanded versions of UiO-66, such as derivatives of UiO-67 or $Zr_6O_4(OH)_4(bpdc)_6$ ($bpdc^{2-}$ = 1,1′-

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

biphenyl-4,4′-dicarboxylate),[25] have been widely studied as hosts for catalytically active species. Similarly, Zr-based MOFs constructed from tetratopic linkers, such as PCN-128 or $Zr_6O_6(OH)_2(etbptc)_2(CF_3CO_2)_2(H_2O)_2$ ($etbptc^{4-}$ = 4′,4‴,4⁗′,4″″′″′-(ethene-1,1,2,2-tetrayl)tetrakis(([1,1′-biphenyl]-4-carboxylate))),[28] represent an emerging family of hosts for organometallic catalysts. Owing to their reported stabilities, MIL-100 (Fe, Cr), MOF-808, UiO-66, UiO-67, and PCN-128 were chosen as representative carboxylate MOFs.

The MOF-74, CPO-27, or $M_2(dobdc)$ (M = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd; $dobdc^{4-}$ = 2,5-dioxidobenzene-1,4-dicarboxylate) series of salicylate frameworks are a canonical family of MOFs (Figure 2).[29] These frameworks possess rigid one-dimensional channels lined with coordinatively unsaturated M^{2+} centers, which makes them promising catalysts for transformations such as C−H activation.[30] In addition, these frameworks can be readily expanded, for example to $M_2(dobpdc)$ (M = Mg, Mn, Fe, Co, Ni, Zn; $dobpdc^{4-}$ = 4,4′-dioxido-1,1′-biphenyl-3,3′-dicarboxylate)[31] and $M_2(dotpdc)$ (M = Mg, Fe; $dotpdc^{4-}$ = 4,4″-dioxido-[1,1′:4′,1″-terphenyl]-3,3″-dicarboxylate).[32,33] The large pores of these frameworks enable the diffusion of complex molecules to the metal sites, although these expanded frameworks have only recently been investigated as heterogeneous catalysts.[33] The versatility of the MOF-74 structure is also represented by the preparation of isomeric frameworks, such as the $M_2(m\text{-}dobdc)$ (M = Mg, Mn, Fe, Co, Ni; *m*-$dobdc^{4-}$ = 4,6-dioxidobenzene-1,3-dicarboxylate) series.[34] Importantly, Mg- and Ni-based MOF-74 variants are reported to be stable to water vapor.[32] As such, $M_2(dobdc)$ (M = Mg, Ni), $Ni_2(m\text{-}dobdc)$, $Mg_2(dobpdc)$, and $Mg_2(dotpdc)$ were selected as representative salicylate MOFs for further examination.

Azolate MOFs represent a diverse family of frameworks with generally excellent thermal stabilities (Figure 3).[35,36] Among these, the small-pore framework ZIF-8 or $Zn(2mim)_2$ ($2mim^-$ = 2-methylimidazolate) is by far the most widely studied.[37,38] The $M_2Cl_2(btdd)$ (M = V, Mn, Fe, Co, Ni, Cu; $btdd^{2-}$ = bis(1,2,3-triazolo[4,5-*b*],[4′,5′-i])dibenzo[1,4]dioxin) family of triazolate frameworks possess the MOF-74 topology and demonstrate excellent stabilities to air and water in certain cases.[39] Due to the high basicity of the linkers, pyrazolate MOFs also possess excellent hydrolytic stabilities. For example, $Ni_3(btp)_2$ (btp^{3-} = 4,4′,4″-(benzene-1,3,5-triyl)tris-(pyrazolate)), which possesses coordinatively unsaturated square planar Ni^{2+} centers, is stable to water at elevated temperatures.[40] Similarly, among the M(bdp) (M = Fe, Co, Ni, Zn; bdp^{2-} = 4,4′-(1,4-phenylene)bis(pyrazolate)) family of frameworks, the Zn and Ni variants retain crystallinity upon exposure to air and water.[41,42] Finally, the relatively new framework $Fe_2(bdp)_3$, which possesses triangular pores and strong Fe^{3+}−N bonds, was previously shown to exhibit high thermal and hydrolytic stability in preliminary tests.[43] Based on these findings, ZIF-8, $Ni_2Cl_2(btdd)$, $Ni_3(btp)_2$, M(bdp) (M = Ni, Zn), and $Fe_2(bdp)_3$ were chosen for further study as representative azolate MOFs. Outside of ZIFs, azolate MOFs remain understudied compared to carboxylate and salicylate MOFs, especially as heterogeneous hosts for reactive species.[26]

The precursors H_3btc, H_2bdc, H_2bpdc, H_2dobdc, and H_2mim were purchased from commercial sources, whereas $H_4(m\text{-}dobdc)$, $H_4dotpdc$, H_2btdd, $H_4etbptc$, $H_4dobpdc$, H_2bdp, and H_3btp were prepared according to (modified) literature procedures (see Section 2 of the Supporting Information or the SI for details). Every MOF was prepared on at least 0.5 g scale (see SI Sections 4−21 for details). In all but three cases—namely, PCN-128, $Mg_2(dotpdc)$, and Ni-(bdp)—this was achieved via a one-pot synthesis. After synthesis, the MOFs were thoroughly solvent-exchanged to remove soluble impurities, desolvated under vacuum, and analyzed by powder X-ray diffraction (PXRD) to confirm the formation of the correct phase. As every MOF in this work has been previously reported, 77 K N_2 adsorption isotherms were collected in the $0.2-1.0P/P_0$ range. The Langmuir surface areas of all MOFs are included in SI Table S18 and confirm the high quality of the MOFs prepared herein. One important consideration is that the conditions used to prepare certain frameworks, especially Zr-based MOFs, can affect the extent of defect formation and, as a result, their physical and chemical properties.[23] While the UiO-66 and UiO-67 samples used for the bulk of the experiments herein were prepared without acid modulators, we also prepared "defect-rich" analogues using hydrochloric acid[44] to preliminarily examine the effect of defects on MOF robustness. In most cases, the robustness of defect-rich UiO-66 and UiO-67 was found to mirror that of the unmodulated materials (see SI Section 25 for details).

Overview of Robustness Assays. Robustness evaluations of MOFs were carried out by exposing frameworks to 30 different conditions to gauge their general stability to air, water, organic solvents, and different classes of reagents, including acids, bases, nucleophiles, electrophiles, oxidants, and reductants. To carry out specific assays, we subjected ∼10 mg of activated MOF to the indicated conditions for 24 h (using a large excess of the reagent of interest) and then characterized the resulting materials by PXRD to confirm retention of the original crystalline structure. In particular, analysis of the FWHM of PXRD reflections was employed to interrogate partial MOF dissolution or degradation under the reaction conditions.[17] While small fluctuations in the FWHM of PXRD reflections would be expected based on instrumentation effects, the partial amorphization or dissolution of frameworks should result in a significant decrease in the average crystallite size and thus a large increase in the FWHM, whereas the selective dissolution of small crystallites should result in a significant increase in the average crystallite size and a decrease in the FWHM. To guide the reader, here we represent our data as "heat maps," in which data entries are color-coded on a gradient from "cool" or blue (little-to-no degradation occurred) to "hot" or red (significant degradation occurred). In addition, we designate cases in which the desired phase was no longer present or the material completely dissolved with a × sign and color code these instances as red. Assays in which the original reflections as well as new reflections were observed by PXRD are highlighted as yellow. While complete loss of crystallinity or dissolution indicates that a material is unstable to the tested conditions, the retention of crystallinity does not necessarily mean that a MOF survived unchanged, as structural modifications that would be challenging to detect by PXRD (*e.g.*, anion/cation exchange, metal exchange, or linker functionalization) may have also occurred. In addition, it should be noted that these assays do not provide information about the stability of MOFs to the byproducts of reactions (*e.g.*, BH_3 produced upon H^- transfer from $LiBH_4$).

Air and Solvent Stability. We carried out a simple assay to evaluate the general robustness of the representative MOFs to ambient conditions after desolvation. Extended exposure to air on the benchtop was simulated by placing each fully

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

desolvated MOF in an oven heated to 120 or 180 °C under air for 24 h. The results of this assay are included in Table 1.

Table 1. Robustness of Representative MOFs to Air and Deionized (DI) Water, As Evaluated by PXRD[a,b]

MOF	120 °C Air % Change FWHM	180 °C Air % Change FWHM	DI Water % Change FWHM
MIL-100 (Fe)	9	9	Wash[a]
MIL-100 (Cr)	9	12	Wash[a]
MOF-808	1	−3	−16
UiO-66	1	6	4
UiO-67	3	25	×
PCN-128	6	−9	33
MOF-74 (Mg)	9	×	0
MOF-74 (Ni)	72	×	13
Ni_2(*m*-dobdc)	−1	×	11
Mg_2(dobpdc)	2	12	28[b]
Mg_2(dotpdc)	−3	−4	×
ZIF-8	5	−6	9
Ni_2Cl_2(btdd)	−5	−4	15
$Ni_3(btp)_2$	1	1	5
Zn(bdp)	2	5	−44
Ni(bdp)	−1	−1	−14[b]
$Fe_2(bdp)_3$	−3	−6	6

[a]Wash indicates that the material was washed with water during its preparation. [b]New reflections observed by PXRD.

Validating our choice of MOFs for this investigation, all but one of the MOFs was found to be stable to air at 120 °C, and all but three were stable at 180 °C. This stability is in contrast to Zn−carboxylate MOFs such as MOF-5, which rapidly lose crystallinity when handled in air at room temperature.[18]

All three of the frameworks found to be unstable to air at 180 °C, namely, MOF-74 (Mg), MOF-74 (Ni), and Ni_2(*m*-dobdc), are small-pore salicylate frameworks. We hypothesize that the modest air stability of these materials is likely due to oxidation of the linker, as all three possess two phenoxides on the same aromatic ring.[45] Indeed, it has previously been shown that strong oxidants can convert the linkers of MOF-74 to quinones (Figure 4).[46,47] The improved air stability of Ni_2(*m*-dobdc)—in which the oxygens on the linker are meta to one another—supports this hypothesis.[45] Interestingly, the expanded analogues of MOF-74, namely, Mg_2(dobpdc) and Mg_2(dotpdc), also demonstrate improved oxidative stability compared to MOF-74 (Mg) at high temperatures, likely due to the decreased favorability of quinone formation.[46] However, in our hands, Mg_2(dobpdc) was found to slowly change from white to blue upon extended vacuum filtration at room temperature, suggesting that its oxidative stability may be reduced in the presence of water. Nonetheless, these results represent a rare instance in which the robustness of a framework *increased* upon isoreticular expansion, as generally the opposite trend is observed.

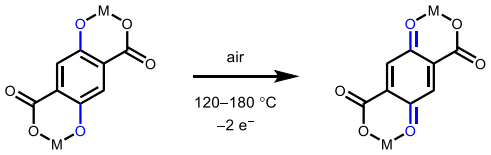

Figure 4. Proposed mechanism for the decomposition of MOF-74 frameworks in air via quinone formation.

The hydrolytic stability of representative MOFs was further assessed by submerging each MOF in neutral deionized (DI) water for 24 h (Table 1). With the exception of the large-pore frameworks UiO-67, Mg_2(dobpdc), and Mg_2(dotpdc), every MOF retained crystallinity under these conditions with minimal changes in the FWHM of PXRD reflections. Intriguingly, defect-rich UiO-67 displayed improved stability toward neutral water compared to the material prepared without modulator (SI, Figure S219). Notably, Ni(bdp) transitioned to a new crystalline phase, similar to the behavior that has been previously reported for the Zn analogue.[41] Furthermore, all of the MOFs in this work were found to retain crystallinity upon submersion in representative organic solvents, including methanol (MeOH), toluene (Tol), dichloromethane (CH_2Cl_2), and tetrahydrofuran (THF) (see the SI for details). These results confirm that stability assays carried out using reagents dissolved in organic solvents should reflect the stability of the MOF to the reagent, not to the solvent.

Brønsted Acids and Bases. The stability of MOFs toward aqueous Brønsted acids and bases has been widely studied. Typically, Brønsted acids (H^+) react with MOFs by protonating the linkers, resulting in framework dissolution. In contrast, nucleophilic aqueous hydroxide (OH^-) reacts with MOFs by displacing the linkers, leading to the formation of M−OH or M−O species.[48] Based on this mechanistic analysis, one would expect that aqueous and organic acids of comparable pK_a values should react similarly with MOFs, whereas sterically hindered, non-nucleophilic organic bases should possess reduced reactivity compared to aqueous OH^-. However, an often overlooked consideration is that framework decomposition under aqueous conditions consumes H^+ or OH^- ions, resulting in a shift in the solution pH over time that may account for conflicting reports regarding the aqueous stability of various MOFs.[49] One potential strategy to mitigate the effect of changing pH during robustness assays is to employ buffered aqueous solutions to minimize pH changes. However, a limitation of buffered solutions is that the stability of MOFs is contingent upon the exact salts used to prepare the buffer. For example, several MOFs that are stable to neutral deionized water, including UiO-66, PCN-128, and Ni_2Cl_2(btdd), were found to undergo significant degradation in widely used

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Table 2. Robustness of Representative MOFs toward Aqueous Brønsted Acids and Bases, as Evaluated by PXRD[a,b,c]

MOF	Conc. HCl % Change FWHM	pH = 1 % Change FWHM	pH = 4 % Change FWHM	pH = 7 % Change FWHM[a]	pH = 10 % Change FWHM	pH = 13 % Change FWHM	Sat. NaOH % Change FWHM
MIL-100 (Fe)	×	−19	23	5	×	×	×
MIL-100 (Cr)	7	7	6	9	×	×	×
MOF-808	×	7	15	5	×	×	×
UiO-66	×	8	1	×, 55[b]	×	×	×
UiO-67	×	×	×	×	×	×	×
PCN-128	×	×	×	×, 7[b]	×	×	×
MOF-74 (Mg)	×	×	×	×, ×[b]	27	−22	×
MOF-74 (Ni)	×	×	−6	−5, 6[b]	−10	−7	×
Ni_2(*m*-dobdc)	×	×	−7	−4	1	14	×
Mg_2(dobpdc)	×	×	×	×, ×[b]	×	×	×
Mg_2(dotpdc)	×	×	×	×	×	×	×
ZIF-8	×	×	−8[c]	−8	10	−4	86
Ni_2Cl_2(btdd)	×	1	35	−23[c], −10[b]	11[b]	34	×
$Ni_3(btp)_2$	×	×	8	−12	−21	−9	26
Zn(bdp)	×	×	48[c]	33[c]	−19[c]	−23[c]	×
Ni(bdp)	×	×	−26[c]	−19[c]	−8[c]	−18[c]	×
$Fe_2(bdp)_3$	×	−3	3	−1	−4	−5	−1

[a]Unless specified otherwise, determined using aqueous phosphate buffer (pH = 7). [b]Determined using aqueous tris buffer (pH = 7). [c]New reflections observed by PXRD.

aqueous phosphate buffer (pH = 7) but survive aqueous tris buffer (pH = 7) (Table 2). In contrast, MOF-74 (Mg) and Mg_2(dobpdc), which are (partially) stable in deionized water, underwent degradation in both pH = 7 buffered solutions, indicating that they may not possess good stability toward neutral water (Table 2). Finally, MOF-74 (Ni) was found to equally tolerate deionized water and both pH = 7 buffered solutions. These discrepancies highlight the need to consider the salts used to prepare aqueous solutions of varying pH values when assessing MOF robustness.

Consistent with previous reports and the results in Table 1, the representative carboxylate MOFs MIL-100 (Fe),[50] MIL-100 (Cr), MOF-808,[51,52] and UiO-66[49,53] are generally stable to water buffered at acidic and neutral pH values (1−7). This stability arises due to the low-thermodynamic driving force for protonating benzoates under weakly acidic conditions. However, the relatively weak nucleophilicity of benzoate linkers leads to poor stability toward aqueous OH^-.[49,51] In contrast, the larger pore Zr-MOFs, UiO-67 and PCN-128, were found to degrade under most tested aqueous conditions.[48] We hypothesized that the presence of basic, nucleophilic phenoxides in MOF-74 frameworks should lend these materials improved stability toward OH^- but reduced stability toward acids. Indeed, MOF-74 (Ni) and Ni_2(*m*-dobdc) were found to degrade in pH 1 buffered water but were stable in solutions buffered up to pH 13.[54,55] Given their poor stability to neutral water (Table 1), it is unsurprising that Mg_2(dobpdc) and Mg_2(dotpdc) were found to degrade under all tested aqueous conditions. Due to the superior hydrolytic stability of MOF-74 (Ni) and Ni_2(*m*-dobdc) compared to MOF-74 (Mg), the Ni-congeners of these expanded frameworks should possess improved stabilities under aqueous conditions.[56] Overall, our findings suggest that carboxylate and salicylate MOFs display complementary stabilities to acids and bases under aqueous conditions, but more work is required to identify water-stable large-pore frameworks.

ZIF-8,[38] $Ni_3(btp)_2$,[40] and $Fe_2(bdp)_3$[43] have all been previously shown to survive treatment with water at a range of pH values. Consistently, our representative azolate MOFs possess good to excellent hydrolytic stabilities, with $Ni_3(btp)_2$ and $Fe_2(bdp)_3$ even surviving extended exposure to saturated aqueous NaOH. We note that Zn(bdp) was previously reported to undergo a reversible phase change upon submersion in water,[41] which we also observe here for both

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Zn(bdp) and Ni(bdp). Overall, our findings suggest that azolate frameworks represent excellent platforms for synthetic transformations under aqueous or biphasic conditions.

In addition to aqueous Brønsted acids and bases, we also surveyed the stability of MOFs toward organic acids and bases (Table 3). As expected, the robustness of MOFs toward acetic acid ($MeCO_2H$, pK_a = 4.75) was found to closely match their robustness toward pH 4 buffered water. The lone exception was UiO-66, which is stable toward acidic water but unstable to acetic acid. This is likely due to the highly favorable formation of zirconium acetate by ligand exchange under the latter conditions.[57] We also examined the stability of MOFs toward the sterically hindered strong base lithium hexamethyldisilazide (LiHMDS, pK_a of conjugate acid ≈ 26) under anhydrous conditions. Despite being a significantly stronger base than OH^-, LiHMDS (as a 1.0 M solution in toluene) was found to degrade far fewer MOFs than aqueous NaOH (Table 2). While this is likely due in part to the inability of the LiHMDS dimer (~9 Å across) to penetrate smaller pore frameworks, the robustness of Mg_2(dotpdc) (28 Å pores) toward LiHMDS but not OH^- suggests that the reduced nucleophilicity of LiHMDS also plays a role in the observed reactivity difference. In a similar vein, LiHMDS was found to partially degrade the small-pore MOF ZIF-8 (3.4 and 11 Å pores), indicating that reagents incapable of entering the pores of a MOF are still capable of triggering decomposition. Overall, our preliminary results suggest that sterically hindered organic bases are preferable to OH^- when carrying out reactions under basic conditions.

Table 3. Robustness of Representative MOFs toward Organic Brønsted Acids and Bases, as Evaluated by PXRD

MOF	$MeCO_2H$ % Change FWHM	1.0 M LiHMDS/Tol % Change FWHM
MIL-100 (Fe)	7	10
MIL-100 (Cr)	6	6
MOF-808	13	67
UiO-66	×	5
UiO-67	×	×
PCN-128	×	×
MOF-74 (Mg)	×	5
MOF-74 (Ni)	−14	−7
Ni_2(*m*-dobdc)	1	1
Mg_2(dobpdc)	×	2
Mg_2(dotpdc)	×	−14
ZIF-8	×	50
Ni_2Cl_2(btdd)	−1	−3
Ni_3(btp)$_2$	8	−19
Zn(bdp)	×	−13
Ni(bdp)	×	94
Fe_2(bdp)$_3$	−4	17

Nucleophiles. The robustness of MOFs toward corrosive nucleophilic gases such as hydrogen sulfide (H_2S) and ammonia (NH_3) has been previously evaluated due to the industrial relevance of these gases.[12,58,59] Gaseous H_2S degrades several MOFs, including MIL-100 (Fe), HKUST-1, and derivatives of UiO-66,[60,61] whereas NH_3 has been shown to decompose amine-functionalized UiO-66.[39] In general, nucleophiles destroy MOFs by displacing the organic linkers from the metal nodes. Given the importance of nucleophilic species in synthetic chemistry and the dearth of systematic data regarding the stability of MOFs toward nucleophiles, here we studied the stability of MOFs to a range of representative neutral and anionic nucleophiles. These assays were rapidly carried out using 0.8−1.0 M solutions of these nucleophiles in organic solvents. The results of these experiments are included in Table 4.

The carboxylate MOFs studied here were found to be quite stable to an anhydrous 0.8 M solution of H_2S in THF, with the exception of MIL-100 (Fe), which was previously reported to rapidly form FeS in the presence of H_2S.[60,61] Likewise, all of the salicylate MOFs retained crystallinity upon treatment with H_2S in solution.[62] While ZIF-8 was previously reported to possess modest stability to 1000 ppm of dry H_2S,[60] in our hands this framework underwent complete loss of crystallinity in the solution state, likely to form ZnS. Similarly, the Zn-based pyrazolate framework Zn(bdp) also underwent complete decomposition in the presence of anhydrous H_2S. The excellent robustness of azolate MOFs constructed from metals other than Zn corroborates that Zn-based frameworks should be avoided for reactions involving thiols. Otherwise, the MOFs studied herein display promising stability toward strongly nucleophilic H_2S.

The reactivity of MOFs toward amines remains understudied outside of the context of postsynthetic modification. Therefore, the stability of MOFs toward *N*-based nucleophiles was evaluated using an anhydrous, air-free 1.0 M solution of NH_3 in methanol and a 1.0 M solution of *n*$BuNH_2$ in THF. With the exception of the large-pore framework PCN-128, the MOFs studied herein generally retained crystallinity in the presence of both nucleophiles. Overall, the robustness of MOFs toward neutral nucleophiles is excellent, which bodes well for their use in reactions that employ these species.

To gauge the robustness of MOFs toward strongly nucleophilic carbanions, which are a bedrock of synthetic organic chemistry, we evaluated the crystallinity of MOFs after exposure to an anhydrous 1.0 M solution of PhMgBr in THF. Again, with the exception of the large-pore carboxylate MOFs UiO-67 and PCN-128, the MOFs studied herein displayed good stabilities toward Grignard reagents at room temperature, which could likely be further improved at lower temperatures. Notably, the superior robustness of Ni_2Cl_2(btdd) and Mg_2(dotpdc) toward both nucleophiles and LiHMDS compared to UiO-67 and PCN-128 suggests that they are more stable mesoporous frameworks, especially in the presence of nucleophiles.

https://doi.org/10.1021/acsami.1c01329
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Table 4. Robustness of Representative MOFs toward Nucleophiles, as Evaluated by PXRD[a]

MOF	0.8 M H_2S/THF % Change FWHM	1.0 M NH_3/MeOH % Change FWHM	1.0 M *n*$BuNH_2$/THF % Change FWHM	1.0 M PhMgBr/THF % Change FWHM	1.0 M TBAF/THF % Change FWHM
MIL-100 (Fe)	×	2	4	−32	48
MIL-100 (Cr)	6	4	13	2	×
MOF-808	12	17	−2	149	4
UiO-66	3	20	−3	−4	×
UiO-67	12	×	15	×	×
PCN-128	22	×	×	×	×
MOF-74 (Mg)	−8	−6	9	25	8
MOF-74 (Ni)	−12	7	−13	−20	−8
Ni_2(*m*-dobdc)	−8	14	−10	−8	9
Mg_2(dobpdc)	55	3	8	150	×
Mg_2(dotpdc)	−8	−16	−14	−10	×
ZIF-8	×	−2	2	3	2
Ni_2Cl_2(btdd)	4	−5	−5	1	8
Ni_3(btp)$_2$	−16	7	−12	−8	10
Zn(bdp)	×	−35	−41[a]	28	−20[a]
Ni(bdp)	33	−3	30	73	40
Fe_2(bdp)$_3$	−3	−6	−2	−4	−4

[a]New reflections observed by PXRD.

Fluoride is a critical nucleophile in medicinal chemistry given the ubiquity of C−F bonds in small-molecule pharmaceuticals. To gauge the general stability of MOFs toward nucleophilic and soluble fluoride, we examined their robustness toward a 1 M solution of TBAF in THF under air-free conditions. In general, MOFs constructed from "hard" Zr^{4+}, Cr^{3+}, and Mg^{2+} cations underwent partial or complete decomposition in the presence of TBAF, likely due to the favorable formation of M−F bonds, whereas other MOFs retained crystallinity under these conditions. Consistent with these results, HF is commonly used to digest Zr-MOFs.[63] Surprisingly, the Zr-based framework MOF-808 was found to be stable toward fluoride, reflecting its exemplary stability among Zr-MOFs.[51] Overall, our findings confirm that Fe-, Zn-, and Ni-based frameworks are promising platforms for catalytic transformations involving nucleophilic fluoride.

Electrophiles. To date, the stability of MOFs toward electrophiles, such as alkyl halides, isocyanates, and halogens (see Oxidants below), has primarily been studied in the context of postsynthetic modification. Similar to Brønsted acids, strong electrophiles would be expected to decompose MOFs by reacting with the anionic linkers. As such, we initially hypothesized that the electrophilic stability trend of MOFs should inversely correlate with the nucleophilicity of the linkers, that is, carboxylates > salicylates > azolates. To evaluate the robustness of the representative MOFs toward electrophiles, we characterized their stability toward a range of reagents, including trimethylchlorosilane (Me_3SiCl), acetyl chloride (MeCOCl), sulfuryl chloride (SO_2Cl_2), and dimethyl sulfate (Me_2SO_4), as solutions in CH_2Cl_2. The results of these studies are summarized in Table 5.

The silylating reagent Me_3SiCl has previously been used to postsynthetically generate catalytic sites in Zn-based MOFs.[64] We found that most MOFs survived treatment with a 1.0 M solution of Me_3SiCl in CH_2Cl_2, with only Mg-based salicylate MOFs decomposing to a significant degree. Notably, the Ni-based salicylate MOFs MOF-74 (Ni) and Ni_2(*m*-dobdc) retained crystallinity in the presence of Me_3SiCl, consistent with their superior stability toward Brønsted acids compared to their Mg analogues (Table 2). These results suggest that Me_3SiCl may be broadly useful for activating catalytic sites within MOFs.

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Table 5. Robustness of Representative MOFs toward Electrophiles, as Evaluated by PXRD[a]

MOF	1.0 M Me_3SiCl/CH_2Cl_2 % Change FWHM	1.0 M $MeCOCl/CH_2Cl_2$ % Change FWHM	1.0 M SO_2Cl_2/CH_2Cl_2 % Change FWHM	1.0 M Me_2SO_4/CH_2Cl_2 % Change FWHM
MIL-100 (Fe)	−29	×	−23	−17
MIL-100 (Cr)	6	7	6	7
MOF-808	7	−16	−1	3
UiO-66	−7	−8	8	11
UiO-67	69	49	70	118
PCN-128	12	57	×	22[a]
MOF-74 (Mg)	×	96	106	1
MOF-74 (Ni)	−8	−1	×	−17
Ni_2(*m*-dobdc)	−23	−17	×	10
Mg_2(dobpdc)	×	×	×	−2
Mg_2(dotpdc)	×	×	×	−5
ZIF-8	−15	×	×	−3
Ni_2Cl_2(btdd)	5	−7	508	−5
$Ni_3(btp)_2$	−28	×	×	−5
Zn(bdp)	−14[a]	×	×	−55[a]
Ni(bdp)	16	×	×	23
$Fe_2(bdp)_3$	27	−3	−3	−5

[a]Additional reflection(s) observed by PXRD.

Unfortunately, we found that many MOFs possess significantly reduced stability toward the stronger electrophiles MeCOCl and SO_2Cl_2. Although the majority of chosen carboxylate and small-pore salicylate MOFs survived treatment with a 1.0 M solution of MeCOCl in CH_2Cl_2, large-pore salicylate and the bulk of azolate MOFs did not. We hypothesize that the degradation of these materials likely occurs by acetylation of the nucleophilic linkers, although the generation of HCl from the reaction of MeCOCl with nucleophiles likely also contributes to the observed degradation patterns. Nonetheless, the stable frameworks Ni_2Cl_2(btdd) and $Fe_2(bdp)_3$ were unique among azolate MOFs in surviving treatment with MeCOCl. Following a similar trend, only select carboxylate MOFs, along with Ni_2Cl_2(btdd) and $Fe_2(bdp)_3$, were found to (partially) survive submersion in a 1.0 M solution of SO_2Cl_2 in CH_2Cl_2. In contrast, most MOFs survived exposure to the strong alkylating agent Me_2SO_4. Overall, these results corroborate that carboxylate MOFs are generally suitable for reactions involving strong electrophiles, although the azolate MOFs Ni_2Cl_2(btdd) and $Fe_2(bdp)_3$ are also compatible despite their nucleophilic *N*-based linkers.

Oxidants. The stability of MOFs under oxidizing conditions remains understudied. Previous studies have shown that O_2 and Cl_2 can oxidize the linkers[47] or metal centers[65] of MOFs. Beyond O_2, the most widely studied oxidants in this context are I_2,[66] which is known to adsorb reversibly in MIL-100 (Fe),[67] and Br_2, which adsorbs reversibly in Co_2Cl_2(btdd).[65] Initially, we hypothesized that salicylate MOFs would possess poor stability toward oxidants given the redox noninnocence of their linkers (Table 1). Likewise, electron-rich azolate MOFs would also be expected to readily undergo oxidation. For this study, we chose I_2 and Br_2, as well as pyridinium chlorochromate (PCC) and *meta*-chloroperoxybenzoic acid (MCPBA), as representative oxidants for evaluation as solutions in CH_2C_{l2}. The results of these assays are included in Table 6.

Encouragingly, the majority of the MOFs studied in this work were found to retain crystallinity upon exposure to a 1.0 M solution of I_2 in CH_2Cl_2, likely due to its weakly oxidizing nature (E° = +0.54 V vs SHE). Indeed, only PCN-128 lost crystallinity in the presence of I_2. Likewise, with the exception of the poorly stable large-pore MOFs PCN-128 and Mg_2(dobpdc), the representative MOFs were found to largely

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Table 6. Robustness of Representative MOFs toward Oxidants, as Evaluated by PXRD

MOF	1.0 M I_2/CH_2Cl_2 % Change FWHM	Sat. PCC/CH_2Cl_2 % Change FWHM	1.0 M Br_2/CH_2Cl_2 % Change FWHM	Sat. MCPBA/CH_2Cl_2 % Change FWHM
MIL-100 (Fe)	11	5	15	9
MIL-100 (Cr)	1	8	6	10
MOF-808	−6	19	−4	6
UiO-66	2	4	−6	18
UiO-67	25	36	×	×
PCN-128	156	×	−22	×
MOF-74 (Mg)	−38	29	×	×
MOF-74 (Ni)	−12	−5	42	17
Ni_2(*m*-dobdc)	1	7	×	×
Mg_2(dobpdc)	10	764	×	×
Mg_2(dotpdc)	−10	−20	×	×
ZIF-8	−18	44	×	×
Ni_2Cl_2(btdd)	−1	9	×	×
$Ni_3(btp)_2$	−27	−22	×	×
Zn(bdp)	−13	−21	×	×
Ni(bdp)	28	59	×	×
$Fe_2(bdp)_3$	−2	6	2	×

tolerate the presence of oxidizing PCC in the form of a saturated solution in CH_2Cl_2. The poor stability of PCN-128 and Mg_2(dobpdc) toward PCC may be due to its acidic nature ($pK_a \approx 5.1$). Overall, our findings suggest that the majority of studied MOFs are capable of surviving weakly oxidizing conditions.

In contrast, exposing MOFs to strong oxidants, namely, a 1.0 M solution of Br_2 in CH_2Cl_2 ($E°$ = +1.066 V vs SHE) and a saturated solution of MCPBA in CH_2Cl_2 ($E°$ of peracetic acid = +1.76 V vs SHE) led to significant decomposition for most of the evaluated frameworks. As expected, these oxidants decompose most salicylate and azolate MOFs, although $Fe_2(bdp)_3$ uniquely retained crystallinity upon exposure to Br_2 among azolate MOFs. In contrast, the carboxylate MOFs MIL-100 (Fe, Cr), MOF-808, and UiO-66 retained crystallinity even under harshly oxidizing conditions. We note that partial oxidation of MOFs by Br_2 and MCPBA should produce acids (HBr and *meta*-chlorobenzoic acid, respectively) that may accelerate framework decomposition; likewise, MCPBA contains *meta*-chlorobenzoic acid and water as stabilizers, which may have contributed to the degradation of MOFs. Nonetheless, our results demonstrate that while most MOFs can tolerate weakly oxidizing conditions, stable carboxylate MOFs and $Fe_2(bdp)_3$ are ideally suited to survive reactions requiring strong (and acidic) oxidants.

Reductants. Although the stability of MOFs under reducing conditions also remains underexplored, the reversible electrochemical reduction of metal centers and redox-active linkers in MOFs has been demonstrated.[68] Samarium iodide (SmI_2) is a widely used single-electron reductant in synthesis (E^0 as low as −2.05 V),[69] and thus a commercially available 0.1 M solution in THF was chosen to evaluate the stability of MOFs under harshly reducing air-free conditions. Similarly, a commercially available solution of $LiBH_4$ in THF (diluted to 1.0 M) was employed due to the strongly reducing nature of H^- in solution (E^0 = −2.3 V). The results of these experiments are included in Table 7.

We found mixed results regarding the robustness of MOFs toward strongly reducing SmI_2. The majority of carboxylate MOFs underwent partial or complete decomposition in the presence of this reagent, with the exception of the highly stable MIL-100 (Cr). Likewise, SmI_2 degraded the bulk of azolate MOFs studied herein, with the exceptions of ZIF-8 and $Fe_2(bdp)_3$. In contrast, salicylate MOFs demonstrated promising stability toward SmI_2. These trends may arise in part due to the ability of SmI_2 to readily reduce Fe^{3+} (E^0 = −0.04 V), Ni^{2+} (E^0 = −0.25 V), and Zn^{2+} (E^0 = −0.76 V)

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Table 7. Robustness of Representative MOFs toward Reductants, as Evaluated by PXRD

MOF	0.1 M SmI_2/THF % Change FWHM	1.0 M $LiBH_4$/THF % Change FWHM
MIL-100 (Fe)	×	×
MIL-100 (Cr)	12	6
MOF-808	341	76
UiO-66	39	187
UiO-67	67	138
PCN-128	×	294
MOF-74 (Mg)	−13	25
MOF-74 (Ni)	115	9
Ni_2(*m*-dobdc)	−9	13
Mg_2(dobpdc)	−22	23
Mg_2(dotpdc)	−7	−2
ZIF-8	18	19
Ni_2Cl_2(btdd)	163	×
Ni_3(btp)$_2$	68	−21
Zn(bdp)	×	−23
Ni(bdp)	54	49
Fe_2(bdp)$_3$	12	−4

centers, but not Zr^{4+} (E^0 of $ZrO(OH_2)$ = −2.36 V) or Mg^{2+} (E^0 = −2.37 V) sites. Similar trends were observed with $LiBH_4$, as carboxylate MOFs generally degraded in the presence of this reagent, with the exception again of MIL-100 (Cr), whereas salicylate and azolate MOFs largely survived. The only azolate MOF that underwent significant decomposition in the presence of $LiBH_4$ was Ni_2Cl_2(btdd), which is constructed from Cl^- anions that may exchange with H^- prior to framework degradation. Therefore, our results suggest that salicylate MOFs, UiO-66, UiO-67, ZIF-8, and Fe_2(bdp)$_3$ are promising platforms for transformations that require harshly reducing conditions.

Further Evaluation of Stable Frameworks. To summarize the robustness of the representative MOFs studied in this work, we devised a qualitative scoring system in which each assay received a score on a scale from 0.00 to 1.00 determined by subtracting the absolute percentage change in FWHM from 100 and dividing the resulting value by 100 (*e.g.*, 0% change in FWHM would result in a score of 1.00). Assays that resulted in >100% change in FWHM or a complete loss of crystallinity received a score of 0.00, whereas assays that produced additional reflections by PXRD received a score penalty of 0.25 points. By averaging the scores of assays involving similar classes of reagents for a given MOF, a final score for each combination of MOF and class of reagent could be determined (Table 8). The concentrated HCl assay was excluded from this analysis because every MOF except for MIL-100 (Cr) degraded under these conditions. While somewhat arbitrary, these scores facilitate rapid comparisons of the overall stabilities of different classes of MOFs to different types of reagents. By comparing the average scores for different classes of MOFs (Table 9), we can conclude that carboxylate MOFs are generally the most stable toward acids, electrophiles, and oxidants, salicylate MOFs are generally the most stable toward nucleophiles and reductants, and azolate MOFs are generally robust but particularly stable toward bases and nucleophiles. The relatively understudied azolate MOF Fe_2(bdp)$_3$ was by far the most robust MOF studied in this work, as it retained its crystalline structure under nearly all of the conditions tested. Therefore, Fe_2(bdp)$_3$ and its pore-expanded analogues[70] represent a potentially new platform for hosting active catalytic species of interest in synthetic organic and medicinal chemistry. Perhaps less surprisingly, MIL-100 (Cr) and MOF-808 were the second- and third-most robust frameworks identified by our assays, respectively. Among salicylate frameworks, Ni_2(dobdc) and Ni_2(*m*-dobdc) are similarly robust and superior to Mg-based frameworks. In contrast, the mesoporous frameworks PCN-128 and Mg_2(dobpdc) were among the least robust MOFs evaluated.

Although analysis by PXRD provides insight into retention or loss of crystallinity, it is less useful for elucidating structural changes such as linker modification. Therefore, we further evaluated robust frameworks from each family of MOFs, namely Fe_2(bdp)$_3$, MOF-808, and MOF-74 (Ni), by infrared (IR) spectroscopy, 77 K N_2 adsorption measurements, and scanning electron microscopy in select cases (see Supporting Information Sections 22−24 for details). Characterization of all three MOFs by IR spectroscopy before and after successful robustness assays revealed minimal changes, confirming a lack of chemical modification after exposure to various reagents. In addition, we conducted representative stability assays for each MOF on large (∼50 mg scale) and confirmed retention of crystallinity and porosity in all cases. In particular, 77 K N_2 Langmuir surface areas and pore volumes of Fe_2(bdp)$_3$ and MOF-74 (Ni) were found to be largely unchanged after selected robustness assays, whereas those of MOF-808 samples decreased slightly (Table 10). In addition, scanning electron microscopy images further support the retention of well-defined Fe_2(bdp)$_3$ crystallites after exposure to Br_2, $LiBH_4$, and TBAF (SI Figures S204−S207). Therefore, our results suggest that Fe_2(bdp)$_3$, MIL-100 (Cr), MOF-808, and MOF-74 (Ni) are exceptionally robust frameworks capable of surviving a range of reaction conditions.

CONCLUSIONS

The extensive assays in this work highlight several trends regarding the stability of MOFs under various synthetic conditions. For example, the stability of MOFs toward nucleophiles is excellent, favoring their application in transformations involving these reagents. However, their robustness toward aqueous acids and strong electrophiles remains modest. In addition, the generally poor stability of large-pore frameworks, such as UiO-67 and PCN-128, restricts the use of MOFs for functionalizing large complex molecules. In this

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

Table 8. Breakdown of Robustness Scores as a Function of Reagent Category and MOF

MOF	Air (2)	Acids (3)	Bases (4)	Nucleophiles (5)	Electrophiles (4)	Oxidants (4)	Reductants (2)
MIL-100 (Fe)	0.91	0.84	0.23	0.63	0.58	0.90	0.00
MIL-100 (Cr)	0.90	0.94	0.24	0.75	0.94	0.94	0.91
MOF-808	0.98	0.88	0.08	0.73	0.93	0.91	0.12
UiO-66	0.97	0.64	0.24	0.74	0.92	0.93	0.31
UiO-67	0.86	0.00	0.00	0.35	0.28	0.35	0.17
PCN-128	0.93	0.00	0.00	0.16	0.46	0.20	0.00
MOF-74 (Mg)	0.46	0.00	0.62	0.89	0.26	0.33	0.81
MOF-74 (Ni)	0.14	0.60	0.69	0.88	0.69	0.81	0.46
Ni_2(*m*-dobdc)	0.50	0.64	0.71	0.90	0.63	0.48	0.89
Mg_2(dobpdc)	0.93	0.00	0.25	0.47	0.25	0.23	0.78
Mg_2(dotpdc)	0.97	0.00	0.22	0.70	0.24	0.43	0.96
ZIF-8	0.95	0.22	0.63	0.78	0.46	0.35	0.82
Ni_2Cl_2(btdd)	0.96	0.88	0.57	0.95	0.71	0.48	0.00
Ni_3(btp)$_2$	0.99	0.61	0.81	0.89	0.42	0.38	0.56
Zn(bdp)	0.97	0.09	0.49	0.45	0.27	0.42	0.39
Ni(bdp)	0.99	0.16	0.33	0.64	0.40	0.28	0.49
Fe_2(bdp)$_3$	0.96	0.97	0.93	0.96	0.91	0.73	0.92
$0 \le S < 0.20$		$0.20 \le S < 0.40$		$0.40 \le S < 0.60$		$0.60 \le S < 0.80$	$0.80 \le S \le 1.00$

Table 9. Summary of Robustness Scores for Different Families of MOFs

MOF	Air (2)	Acids (3)	Bases (4)	Nucleophiles (5)	Electrophiles (4)	Oxidants (4)	Reductants (2)
Carboxylate (6)	0.93	0.55	0.13	0.56	0.69	0.71	0.25
Salicylate (5)	0.60	0.25	0.50	0.77	0.41	0.46	0.78
Azolate (6)	0.97	0.49	0.63	0.78	0.53	0.44	0.53
$0 \le S < 0.20$		$0.20 \le S < 0.40$		$0.40 \le S < 0.60$		$0.60 \le S < 0.80$	$0.80 \le S \le 1.00$

Table 10. Langmuir Surface Areas and Pore Volumes of Fe_2(bdp)$_3$, MOF-808, and MOF-74 (Ni) after Large-Scale Robustness Assays

MOF	condition	77 K N_2 Langmuir surface area (m^2/g)	pore volume at $P/P_0 \approx 0.9$ (cm^3/g)
Fe_2(bdp)$_3$	initial	989 ± 9	0.32
	after TBAF	920 ± 4	0.34
	after $LiBH_4$	986 ± 7	0.37
MOF-808	initial	1574 ± 12	0.64
	after PCC	1245 ± 14	0.52
	after $nBuNH_2$	1152 ± 12	0.48
MOF-74 (Ni)	initial	1406 ± 46	0.47
	after I_2	1352 ± 17	0.49
	after AcOH	1106 ± 1	0.42

regard, mesoporous MOFs, such as MIL-100 (Cr), Mg_2(dotpdc), MOF-808, and Ni_2Cl_2(btdd), represent a promising starting point for the design of chemically robust, large-pore frameworks. That being said, our preliminary results (SI Section 25) suggest that defect engineering may provide an avenue to improve the chemical robustness of large-pore frameworks such as UiO-67; we will explore this possibility further in future work.

Among oxygen-based MOFs, our findings suggest an almost perfect complementarity between carboxylate and salicylate MOFs, with carboxylate MOFs presenting superior robustness toward acids, electrophiles, and oxidants due to their weakly nucleophilic/basic linkers, and salicylate MOFs presenting superior robustness toward bases, nucleophiles, and reductants due to their strongly nucleophilic linkers (Table 9). Among carboxylate frameworks, MIL-100 (Cr) and MOF-808 are the most robust, although the toxicity of Cr salts likely restricts the applicability of MIL-100 (Cr) in industry. Likewise, MOF-74 (Ni) and Ni_2(*m*-dobdc) represent the pinnacles of salicylate MOFs, although the poor air stability of MOF-74 (Ni) represents a challenge for its broad utility (Table 1).

While the thermal and hydrolytic stability of azolate frameworks has long been recognized,[36] one of the most critical highlights provided by this systematic study is their similarly broad chemical stability. In particular, Fe_2(bdp)$_3$ demonstrates unparalleled robustness among MOFs, retaining crystallinity under all but the harshest of conditions. As the bulk of synthetic applications in organic synthesis to date have focused on carboxylate MOFs, this finding represents a prospective new direction for identifying platforms for stabilizing reactive moieties—namely, high-valent metal azolate frameworks. Our findings suggest that large-pore azolate frameworks are particularly promising for the future design of broadly applicable heterogeneous catalysts and reagents for applications in organic synthesis. Likewise, our results suggest that azolate frameworks represent an understudied alternative to Zr-based MOFs for the installation of desired functionality via postsynthetic modification as well. Finally, our work underscores the importance of analyzing the FWHM of PXRD reflections, not just the reflections

https://doi.org/10.1021/acsami.1c01329
ACS Appl. Mater. Interfaces 2021, 13, 17517−17531

themselves, to monitor the degradation and dissolution of MOFs in future work.[17]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c01329.

Characterization of all organic linkers and metal−organic frameworks, as well as the results of all stability assays (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Phillip J. Milner − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States*; orcid.org/0000-0002-2618-013X; Email: pjm347@cornell.edu

Authors

Zihao Wang − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States*

Arvin Bilegsaikhan − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States*

Ronald T. Jerozal − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States*

Tristan A. Pitt − *Department of Chemistry and Chemical Biology, Cornell University, Ithaca, New York 14850, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.1c01329

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version.

Notes

The authors declare the following competing financial interest(s): P.J.M. is listed as an inventor on several patents that include functionalized variants of salicylate MOFs.

■ ACKNOWLEDGMENTS

We acknowledge Cornell University for initial support of this work. Further support for this work was provided by the National Institute of General Medical Sciences of the National Institutes of Health under award number R35GM138165. The content is solely the responsibility of the authors and does not necessarily represent the official views of the National Institutes of Health. We additionally thank Nankai University for the financial support of Z.W. and Cornell University for a Summer Experience Grant for A.B. This work made use of the mail-in service at Beamline 11-BM of the Advanced Photon Source. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. The ^{1}H NMR spectra in this work were collected on a Bruker INOVA 500 MHZ spectrometer that was purchased with support from the National Science Foundation (CHE-1531632). This work made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (DMR-1719875). We thank Drs. Dianne Xiao (University of Washington, Seattle) and Adam Jaffe (University of California, Berkeley) for helpful comments during the preparation of this manuscript.

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