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Review Article

Increasing the Stability of Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are a new category of advanced porous materials undergoing study by many researchers for their vast variety of both novel structures and potentially useful properties arising from them. Their high porosities, tunable structures, and convenient process of introducing both customizable functional groups and unsaturated metal centers have afforded excellent gas sorption and separation ability, catalytic activity, luminescent properties, and more. However, the robustness and reactivity of a given framework are largely dependent on its metal-ligand interactions, where the metal-containing clusters are often vulnerable to ligand substitution by water or other nucleophiles, meaning that the frameworks may collapse upon exposure even to moist air. Other frameworks may collapse upon thermal or vacuum treatment or simply over time. This instability limits the practical uses of many MOFs. In order to further enhance the stability of the framework, many different approaches, such as the utilization of high-valence metal ions or nitrogen-donor ligands, were recently investigated. This review details the efforts of both our research group and others to synthesize MOFs possessing drastically increased chemical and thermal stability, in addition to exemplary performance for catalysis, gas sorption, and separation.

1. Introduction

Metal-organic frameworks are composed of metal-containing secondary building units (SBUs) connected by rigid or semirigid polytopic organic linkers. Depending on the geometry and connectivity of the SBUs, this can often create a structure with inherent porosity, with the void volume in the framework initially filled by solvent molecules [1]. These frameworks are often robust enough to survive a desolvation process termed activation by heating and/or vacuum, resulting in materials with extremely high surface areas. Some representative MOFs include MOF-5, MIL-101, HKUST-1, PCN-14, and UiO-66 [2–6]. MOF development has experienced a rapid expansion after the discovery of MOF-2 in 1998 [7]. Even though MOF-2 only possesses a modest porosity, it is one of the earliest MOFs that were demonstrated to have permanent porosity, as it was stable enough to survive solvent exchange with chloroform followed by vacuum desolvation or activation.

Soon after, MOF-5 was published, which is composed of $Zn_4(\mu_4\text{-O})$ SBUs (Figure 1) and benzene-1,4-dicarboxylate (BDC) linkers in a **pcu** topology. Subsequent sorption measurements showed an exceptional surface area, breaking all porosity records at the time. However, while MOF-5 is thermally stable to approximately 300°C, it is not water stable and thus cannot survive long after exposure to humid air [8]. The thermal and chemical stability of MOFs are both of great interest to researchers for multiple reasons. First, a MOF must be stable enough to undergo characterization. For example, a MOF that decomposes quickly is difficult to characterize by X-ray diffraction (XRD), and thus its crystal structure is difficult to determine. A MOF that collapses upon solvent removal cannot be said to be practically "porous," because its experimental surface area and gas sorption cannot be determined. Furthermore, many applications of MOFs, such as gas storage and separation, hinge on their chemical stability, as materials that are not air-stable are often much less cost-effective than materials that may have inferior absolute performance but that are more robust. Some applications may also rely on thermal stability, such as catalysis [9].

The vulnerability of MOFs typically lies in the lability of ligand-metal bonds. According to ligand field theory, because

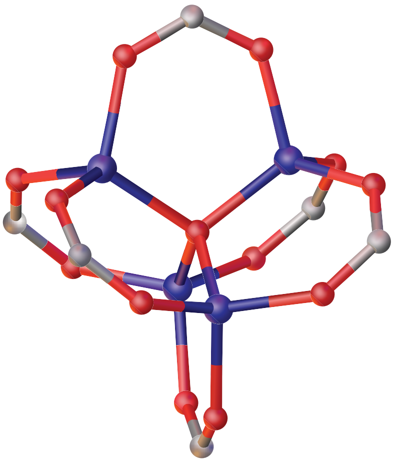

Figure 1: The $Zn_4(\mu_4\text{-O})$ unit of MOF-5 shown coordinated by 6 carboxylates [30].

Zn^{2+} is a transition metal ion with d^{10} electron configuration, it experiences no ligand field stabilization energy overall. Thus, its ligand environment will be controlled primarily by steric factors. This favors a tetrahedral environment but is not heavily destabilized when this environment is disturbed during ligand exchange. Facile ligand exchange allows the formation of a crystalline framework with high surface area and favors the formation of larger single crystals, allowing for more precise structural characterization through single-crystal XRD [10]. However, it also lowers the chemical stability of the resulting MOF, as easily exchanged carboxylates will be displaced by water or other nucleophiles, and if too many of the linking carboxylates are displaced, the framework will collapse. Even if the bond strength is high, if the energy barrier for ligand substitution is low, the MOF will not be chemically stable.

In general, MOFs with SBUs consisting of tetrahedral Zn^{2+} are not chemically stable. However, MOFs containing Zn^{2+} in a different coordination environment, such as MOF-69, have been shown to be more stable than those with purely tetrahedral Zn^{2+} ions. MOF-69 contains both tetrahedral and octahedral Zn centers which share oxygen to form infinite columns and exhibit chemical stability to exchange with a variety of solvents [11].

In order to increase the chemical stability of MOFs, early effort involved the employment of SBUs containing Cu^{2+} ions with d^9 configuration. Compared to a d^{10} transition metal like Zn, metal ions with d^9 configuration possess ligand field stabilization energy, regardless of what coordination environment those ions adopt. This increased ligand field stabilization energy should make the ligand substitution processes less favorable. HKUST-1, composed of copper paddlewheel SBUs (Figure 2) capped by axial water ligands and 1,3,5-benzene-tricarboxylate (BTC), displays an increased chemical stability and shelf-life over MOF-5 [12, 13]. When this material is activated, the water ligand on its axial position will be removed, leaving a relatively stable square planar coordination geometry on cupric SBUs in the activated sample. However, this material was reported to be unstable to direct contact with water, indicating only a limited increase in stability [14].

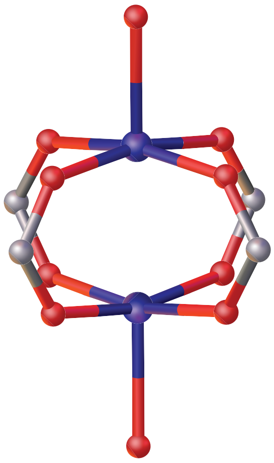

Figure 2: The copper paddlewheel unit of the PCN-6X series, found in many MOFs. Typically, it is coordinated equatorially by 4 ligand carboxylates, while the axial ligands are solvent molecules that may be removed by activation. The zinc paddlewheel is almost identical, but unlike the copper paddlewheel, attempted activation usually causes framework collapse.

Our group has reported the PCN-6X series of (3,24) connected isoreticular MOFs using copper paddlewheel SBUs and extended trigonal planar ligands with isophthalate groups as linkers on each arm, which exhibited both surface areas of up to 5109 $m^2\,g^{-1}$ and moderately good stability [15]. The framework structure itself can also impact the stability, as in PCN-61 where the mesoporous structure is stabilized by areas of less open connectivity, that is, the microwindows into the mesopores [16]. The control of framework topology and how it might impact framework stability were comprehensively reviewed elsewhere and will not be further covered here [17]. In general, the chemical stabilities of Cu-paddlewheel based MOFs were improved compared to $Zn_4(\mu_4\text{-O})$ based MOFs but are still insufficient for certain applications. For example, HKUST-1 was reported to undergo framework collapse under steaming conditions at temperatures above 343 K [12].

2. Framework Templating, Metal-Ion Metathesis, and High-Valent MOFs

Our group has explored a technique called framework templating, in which single crystals of an MOF using a more labile metal (such as zinc) are synthesized, which are then metal exchanged with a less labile metal (such as copper) that is still stable in the coordination environment produced in the Zn MOF. The lability of the metal-ligand bond is decreased and the stability is enhanced by replacing, for example, the zinc in a paddlewheel SBU with copper. Many frameworks based on Zn paddlewheel SBUs also possess an isostructural MOF with Cu paddlewheels [18]. Consequently, a zinc based MOF,

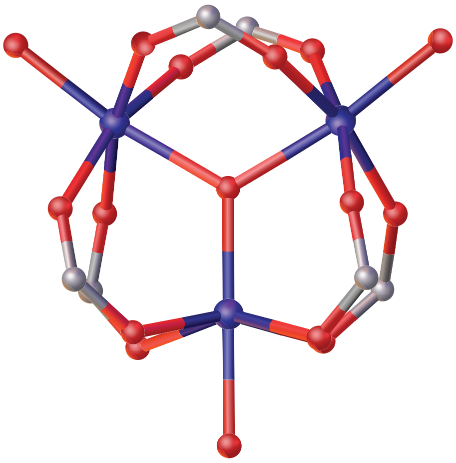

Figure 3: The $Cr_3(\mu_3\text{-}O)$ SBU of MIL-101 shown bound by 6 carboxylates and 3 solvent oxygen atoms.

PCN-921, by metal exchange with copper, was transformed to an isostructural MOF named PCN-922 via a single-crystal-to-single-crystal transformation. Zinc-based PCN-921 collapsed upon activation, while copper-based PCN-922 exhibited a BET surface area of 2006 $m^2 g^{-1}$ after activation, showing a permanent porosity [19]. Interestingly, it also changed its color from green to blue, which is consistent with copper's change in coordination environment from a distorted square-pyramidal geometry with an axially coordinated solvent molecule to a square planar one stabilized by the Jahn-Teller effect due to its d^9 configuration [20]. On the other hand, Zn^{2+}, upon loss of the axial solvent ligand, presumably twists into a tetrahedral geometry which destroys the framework [21]. Metal exchange like this is also known as metal-ion metathesis and has been used to synthesize many MOFs which were not able to be synthesized directly [22].

To further increase the chemical stability of MOFs, researchers can go further along the path of using high-valence metal ions, such as Cr^{3+}, Fe^{3+}, and Zr^{4+} [23]. With all the coordination environments being equal, an increased charge will decrease lability simply by increasing the electrostatic interaction between the metal ions and the ligands. This trend can also be rationalized by the hard/soft acid-base principle, where soft acids like low-oxidation state metals form less stable coordination bonds with harder bases like the oxygen donors on carboxylate ligands. It is not just the charge of the metal ion that increases stability but also the charge density. Small, hard ions with high charge density, such as Cr^{3+} or Zr^{4+}, are able to bond more strongly to carboxylates than larger, soft ions like Zn^{2+} could [24]. This was exploited in the synthesis of MIL-101, which has a complex structure consisting of large clusters of four smaller $Cr_3(\mu_3\text{-}O)$ SBUs (Figure 3) joined by BDC linkers. This produces a framework with both a high BET surface area (4100 $m^2 g^{-1}$) and very high chemical stability, being stable for several months in air and also being stable to various solvents and conditions [4].

Among metal units of a particular charge and coordination number, different metals can have ligand-metal exchange constants that are slower, which would result in a more chemically stable MOF. For example, $Ni(bdc)(ted)_{0.5}$ (BDC = 1,4-Benzenedicarboxylate, TED triethylene diamine) was shown to undergo slower ligand substitution with water vapor than $Cu(bdc)(ted)_{0.5}$, $Zn(bdc)(ted)_{0.5}$, or $Co(bdc)(ted)_{0.5}$, even though these MOFs were isostructural [13]. This is analogous to the differences found in the water exchange rate constants among the metal ions, though carboxylate-water exchanges will have different values than the known water-water exchange rate constants. Al^{3+} has a lower water exchange constant than Fe^{3+}, and Cr^{3+} is lower still, and so MOFs based on Cr^{3+} and Al^{3+} should be more water stable, all other things being equal, than isostructural MOFs based on Fe^{3+} or Ti^{3+}.

Increased chemical stability is also reported in UiO-66 and its isoreticular derivatives [3]. UiO-66 possesses 12-connected Zr_6O_8 SBUs in which the Zr^{4+} ions have stronger interactions with carboxylate ligands than copper or zinc, and thus these SBUs are less vulnerable to ligand substitution [25]. Additionally, the larger, more highly connected cluster means the framework suffers proportionally less disconnection if substitution was to occur. In general, higher nuclearity in the metal-containing unit of MOFs can increase stability in this manner. This is also shown by the increased stability of infinite chain SBUs. For example, as discussed earlier, MOF-69 is more chemically stable than Zn^{2+} MOFs containing tetrahedral Zn^{2+} paddlewheels and other discrete SBUs [11]. MIL-140, with its infinite Zr-oxide chains, as or more water stable than MOFs with a discrete Zr_6SBU such as the UiO-66 series [26, 27].

However, the increased chemical stability reported for Cr^{3+}, Zr^{4+}, and other MOFs comes at a cost: the decreased lability that causes the higher chemical stability also makes it more difficult for the researchers to obtain high-quality single crystals for single crystal XRD purposes, typically producing only microcrystalline powders. Even Cu^{2+} MOFs are more difficult to crystallize than labile but unstable Zn^{2+} ones [19]. Lability and a relative equilibrium of ligand substitution are essential to the formation of single crystals. If the ligands bind very strongly to the metals with slow exchange and the equilibrium shifted toward precipitation, any nucleation will resort in the formation of either microcrystalline powder, or of amorphous products of typically low porosity and little use. Both laboratory research and industrial application of MOFs rely on accurate characterization of the products, and single-crystal XRD requires relatively large single crystals. Scientifically, development of MOFs requires study and understanding of the relationships between the structure of the MOF and its particular properties, which can only happen when the structure is well understood. Undoubtedly, many MOF and other products that may have had great application potential have been shelved or thrown away because of an inability to adequately characterize them, so synthesis of single-crystalline products over microcrystalline powders is very often highly preferred in a research setting.

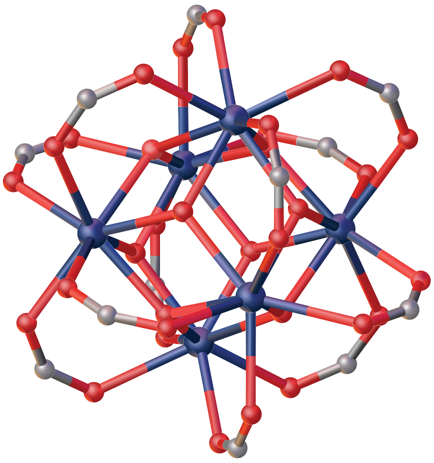

Figure 4: The Zr_6O_8“brick” of UiO-66 shown coordinated by 12 carboxylates.

3. Modulated Synthesis to Increase Crystal Size and Crystallinity of High-Valence MOFs

It is desirable to find suitable reaction conditions that give the MOF ligands high lability during synthesis, while producing a framework with extremely strong bonds and low ligand lability after synthesis is complete. In order to produce large single crystals with high chemical stability despite the fact that the metals producing this stability are correlated with decreased lability and lower crystal size and crystallinity, modulated synthesis, originally developed by Tsuruoka et al. [10] and very successfully used by Behrens [28], should be employed. In this approach, nonbridging ligands are used to influence crystal growth. The addition of modulating reagents, such as monocarboxylic acids, can allow the formation of large single crystals of a MOF that otherwise may have only been synthesized as a powder [24, 29].

MOFs containing high-valence Zr^{4+} cations such as UiO-66 (Figure 4), PIZOF-1, and PCN-222 have been demonstrated to be stable towards air and water [3, 29, 32]. Additionally, zirconium is attractive as a MOF component due to its high abundance and low cost [24]: both are important when designing novel catalysts or sorbents. Note that much said about zirconium-based MOFs can also be applied to isostructural hafnium based MOFs due to the two elements' high chemical similarity, but Hf-based MOFs are less studied due to that element's higher expense. As discussed above, there were previously few examples of Zr MOFs being isolated in a single-crystalline state, due to the fact that using less labile metal-ligand bonds simultaneously increases chemical stability and hinders the crystallization process. Through the use of carefully tuned modulated synthesis, our group has recently synthesized and characterized single crystals of several Zr-MOFs for both gas sorption and catalysis study [32–34]. This is done by adding a varying amount of acetic, trifluoroacetic, or other monocarboxylic acid that can both change the pH of the solution and bind competitively to the metal ions during crystal formation [10, 28]. Equilibria in chemical reactions are governed not only by the energetic differences between the different atoms and molecules, but also by the concentrations of the products and reactants. By simply introducing an excess amount of modulating ligand, we can drive the equilibria of crystal formation away from overly quick structure formation and towards the consecutive binding, release, and rebinding of ligands that allow ordered and large single crystal formation. However, since the mechanisms of crystal formation and solution equilibria under these conditions are difficult to predict, the exact amount and type of competing reagent must be tuned over many trials to produce large single crystals, as opposed to microcrystalline powders or no product at all. Catalysis is a possible application of MOFs that is especially demanding of chemical and thermal stability [35]. The MOF catalyst must not only possess appropriate sites, such as Lewis acidic or basic sites that are well exposed in accessible pores, but it must also be stable to the solvents, reagents, and temperatures that the reaction demands [36]. Based on synthesis conditions, the same catalytic cluster can exhibit different connectivity without compromising its stability. For instance, besides 12-connected Zr_6O_8 in UiO-66, 8-connected (in PCN-222 and PCN-521), and 6-connected (in PCN-225) Zr_6O_8 has also been found. Furthermore, by varying reaction conditions, MOFs based on cubic Zr_8O_6 have also been isolated in our laboratory.

In PCN-222, our group synthesized single crystals of an extremely stable Zr-based MOF with porphyrin-containing ligands that can themselves bind different metal ions, enabling a variety of catalytic activities, which was enabled both by the actual catalytic sites and by the high pore size and water and temperature stability of this MOF [32]. PCN-222 is stable not only to air and boiling water, but also to immersion in concentrated HCl for 24 hours. Similar Zr-porphyrin MOFs PCN-224 and PCN-225 exhibited different catalytic activity [33] or pH-dependent fluorescence [34]. Additionally, by using similar Zr SBUs along with tetrahedral ligands, stability was maintained alongside a higher surface area (BET 3411 $m^2 g^{-1}$) in PCN-521 (Figure 5), which mimicked the topology of fluorite by exploiting the cubic nature of the 8-connected Zr_6O_8 clusters in combination with the 4-connected tetrahedral linkers [24]. All of these Zr-MOFs exhibited high chemical stability due to the strong Zr–O bonds, and all were synthesized as single crystals by carefully varying the type and amount of modulating reagent. However, while many Zr-MOFs have demonstrated stability to neutral or acidic aqueous solutions, their stability towards base was lower, with only NO_2-functionalized UiO-66 retaining its crystallinity in pH 14 aqueous NaOH among tagged UiO-66 derivatives and PCN-225 being stable from pH 1–11 [34, 37].

Behrens et al. developed a series of porous interpenetrated zirconium-organic frameworks (PIZOFs,) using Zr^{4+} and $HO_2C[PE\text{-}P(R^1,R^2)\text{-}EP]CO_2H$ linkers. These MOFs demonstrated high porosity, tunability, and high stability against moisture and temperature. The very long organic linkers in these MOFs retain chemical stability, unlike UiO-67 and other UiO-66 derivatives with extended ligands. This is an example of modulated synthesis being used to prepare single crystals of a high-valence metal containing MOF,

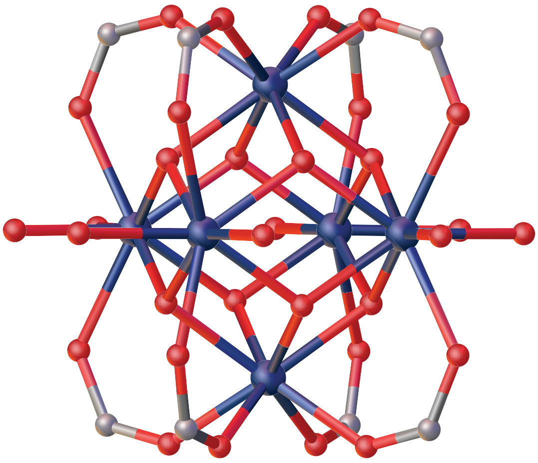

Figure 5: The Zr_6O_8unit of PCN-521, which is similar to that of UiO-66 except that it is 8-connected instead of 12 connected, having a "cubic" symmetry that is compatible with the tetrahedral ligands used. The equatorial Zr atoms are coordinated by hydroxyl groups on the periphery of the unit [24].

with single-crystal X-ray diffraction studies produced for PIZOF-1, -2, and -8 after they were synthesized with benzoic acid as modulating reagent [29]. Other examples of water-stable Zr^{4+}-based MOFs after the use of modulating reagents have also been published [38].

4. N-Donor Ligands

So far, carboxylates are the most commonly used ligands in MOF synthesis. Utilization of high-valence metals as hard acids appears to be the most straightforward approach for the construction of stable MOFs by taking advantage of the existing ligand database. In addition to this approach, the interactions between softer ligands (such as imidazolates, triazolates, tetrazolates, and other nitrogen containing heterocycle-incorporated ligands) with softer metal ions (such as Zn^{2+} and Co^{2+}) can also be exploited in stable MOF synthesis. An early example of this by the long group was the synthesis of a framework using Mn^{2+} and 1,3,5-benzenetristetrazolate [39]. Detailed stability measurements were not conducted, but a crystal remained single through activation at 150°C allowing single-crystal XRD structural determination of the desolvated framework, implying high stability. Chen et al. published Zn^{2+} MOFs with imidazolate ligands and zeolite topology that possessed high thermal stability, Eddaoudi et al. developed zeolite-like MOFs using indium and bis(bidentate) imidazoledicarboxylic acid ligands, and the Yaghi group also introduced zeolitic imidazolate frameworks (ZIFs), using soft Zn^{2+} and Co^{2+} and imidizolate linkers to construct a wide variety of highly stable frameworks that mimic zeolite topology, due to the metal ions adopting a tetrahedral environment while the imidazolates link them at angles similar to the oxides in zeolite minerals [40–42].

The Rosi group synthesized a mesoporous framework bio-MOF-100, which is, to our knowledge, the highest BET surface area material known using N-donor ligands with 4,300 $m^2\,g^{-1}$ [43]. However, this material uses soft nitrogen containing adenine only to build Zn^{2+} SBUs with the SBUs linked by biphenyl dicarboxylate (BPDC) ligands. Thus, its overall stability would actually be expected to be much lower than that of Zn^{2+} MOFs linked exclusively by soft N-donor ligands, and this was confirmed by the fact that "gentle" supercritical CO_2 activation methods were required to achieve high porosity, with "harsh" conventional activation methods producing low N_2 adsorption consistent with collapse of the framework. This is in contrast with Bio-MOF-1 developed by the same group, which survived activation and demonstrated porosity at 125°C [44]. This is likely partially due simply to its relatively lower porosity compared to bio-MOF-100.

Similarly, our group reported another adenine-incorporated MOF, PCN-530, which consists of 2 distinct Zn-adenine SBUs forming 1D zinc-adenine chains linked by 4,4′,4″-*s*-triazine-2,4,6-triyl-tribenzoate (TATB) ligands [45]. Even though the porosity of this framework is not impressive due to the utilization of low symmetry ligands, this framework has demonstrated a significantly improved stability over the traditional Zn MOFs.

Using 1,3,5-tris(1H-pyrazol-4-yl)benzene (H_3BTP) and Ni, Co, Zn, and Co salts, Long et al. synthesized several different frameworks that are very stable both thermally and chemically compared to most carboxylate-based MOFs, due to the less labile linkages between the pyrazolate-based ligand and metal,. $Ni_3(BTP)_2$ in particular was stable to both 430°C in air and immersion in boiling acid (pH = 2) or base (pH = 14), while retaining crystallinity and possessing a BET surface area of 1650 $m^2\,g^{-1}$. This framework is both extremely stable and can expose Ni metal sites, making it promising for catalysis, even for reactions in harsh conditions [46]. The same group later reported $Fe_2(BDP)_3$, which has a BET surface area of 1230 $m^2\,g^{-1}$ and is based on a benzene dipyrazolate ligand. This material was stable to 280°C in air and boiling in aqueous acid (pH = 2) and base (pH = 10) for two weeks and was proven to be useful in separation of hexane isomers. Though the BET surface areas of these frameworks are not record breaking, their extreme stability while retaining high porosity makes them extremely promising materials that showcase the capabilities of N-based MOFs [47].

5. Ligands with Superhydrophobicity

Our group also attempted a method of synthesizing moisture-stable MOFs that did not involve altering the metal-containing units at all: synthesis of superhydrophobic MOFs by functionalizing the ligands with pendant hydrophobic groups. By partially filling the pores with $-O^n$Hex groups attached to [1,1′:4′,1″]terphenyl-3,3′,5,5′-tetracarboxylic acid (TPTC) ligands, the water stability was drastically increased as compared to the nonfunctionalized copper paddlewheel containing NOTT-10X structure or even compared to ligands functionalized with shorter hydrophobic groups [31]. Predictably, some porosity was sacrificed, but a moderate BET surface area of 1083 $m^2\,g^{-1}$ was retained. Most interesting was the superhydrophobic behavior of Cu_2TPTC-O^nHex,

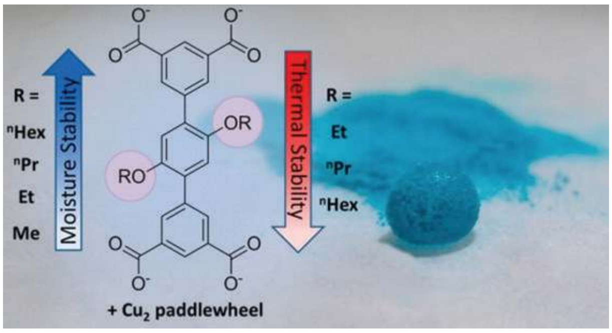

Figure 6: Superhydrophobicity shown in Cu_2TPTC-O^{n}Hex. (Reprinted with permission from [31]. Copyright 2013 American Chemical Society).

which completely resisted any absorption of water under standard conditions. However, this behavior was inversely proportional to the thermal stability of the material, with a loss of crystallinity found in the –O^{n}hex variant at 292°C as compared to 315°C for the –O^{n}Et variant (Figure 6).

The Omary group developed the fluorous MOFs FMOF-1 and FMOF-2, which showed no water adsorption found near 100% relative humidity and no solvent adsorption after being immersed in distilled water for extended periods, despite its large channels that show high and selective adsorption of C_6–C_8 hydrocarbons [48]. FMOF-1 is built from 3,5-bis(trifluoromethyl)-1,2,4-triazolate and Ag^+, and FMOF-2 is produced by annealing FMOF-1 followed by resynthesis from a toluene and acetonitrile solution, so these can also be counted as examples of stable N-based MOFs. Serre et al. studied a series of MIL-88 derivatives with many different functional groups attached to the terephthalate and 4,4′-biphenyl dicarboxylate ligands of the Fe^{3+} MOFs, including various fluorinated ligands. Permanent porosity was retained in the 2CF_3 versions of MIL-88B, with a BET surface area of 330 $m^2\,g^{-1}$, while very little surface area was found in the 4F derivative, likely because the pore size in that version is too small to accommodate N_2 molecules. This study mainly covered how the functional groups changed the flexibility and swelling of the framework, but it also showed that most functional groups (except for the BDC-2OH linker) did not cause a large change in the thermal stability of the framework [49].

Another example of superhydrophobic N-based MOFs stable to moisture was the Ni- bis-pyrazolate MOFs developed by Padial et al. [50]. These were designed to take advantage of the more stable bonds between azolates and softer "borderline" metal ions [51]. Their hydrophobicity was tuned by changing the ligand length to change pore size, and by using trifluoromethyl and methyl-functionalized ligands. $[Ni_8(L5\text{-}CF_3)_6]$, the most hydrophobic MOF presented, effectively captured a flow of diethylsulfide, a hydrophobic and volatile organic compound, under 80% relative humidity, unlike similar nonhydrophobic MOFs. High water stability was further demonstrated by water adsorption-desorption isotherms.

6. Conclusion and Perspective

MOF research, though based on decades of research on coordination polymers and traditional porous materials (such as zeolites or mesoporous silica), blossomed after the discovery of porous, functionalizable Zn^{2+} and Cu^{2+} frameworks that could be grown as single crystals and thus easily characterized [2, 5]. Due to the limited stability of the early frameworks, researchers tried various methods to create more robust frameworks. One of the most popular and successful methods, incorporation of high-valence metals, had the downside of decreasing crystal size and crystallinity [3]. This has caused difficulties in structural characterization that have been partially surmounted through the use of novel techniques [52] for deeper elucidation of MOF structures [53]. A modulated synthesis strategy for the growth of larger single crystals of stable high-valence MOFs can also be used to allow structural characterization through single crystal X-ray diffraction [10, 28].

As discussed in a recent review of our work and other works on the rational design of MOFs [36], it should also be noted that modulated synthesis techniques have also been reported to increase the porosity and catalytic activity of UiO-66, due to the introduction of defects that leave coordinated modulator in place of some proportion of the linking ligands [54, 55]. However, it is possible that this defect creation may reduce the stability of the resulting MOF as well. Our group has used these techniques to synthesize a variety of Zr-MOFs of lower cost and high stability and porosity, as well as exploring the use of soft N-donor and hydrophobic ligands to increase the stability of MOFs using bivalent metals. Many promising recently reported MOFs for gas storage and catalysis have used high-valence metals that have low ligand exchange rates, and so promising avenues of near future MOF research likely involve the use of modulating reagents, metal exchange, and other new techniques to synthesize highly porous and stable MOFs from other readily available high-valence metals, such as iron, chromium, or aluminum.

So far, most stability measurements on MOFs have been concentrated on their thermal and water stabilities, but further avenues of possible research are to determine their stabilities towards contaminants such as salts, body fluids, or corrosive molecules such as H_2S or NH_3. Some studies of this sort have been done, especially on MOFs designed for drug delivery, and have been reviewed elsewhere [56]. As future MOFs are developed for more widespread application, their stability towards more varied chemicals and contaminants should be determined, and application-built MOFs should be rationally designed to be stable towards conditions present in their targeted environment.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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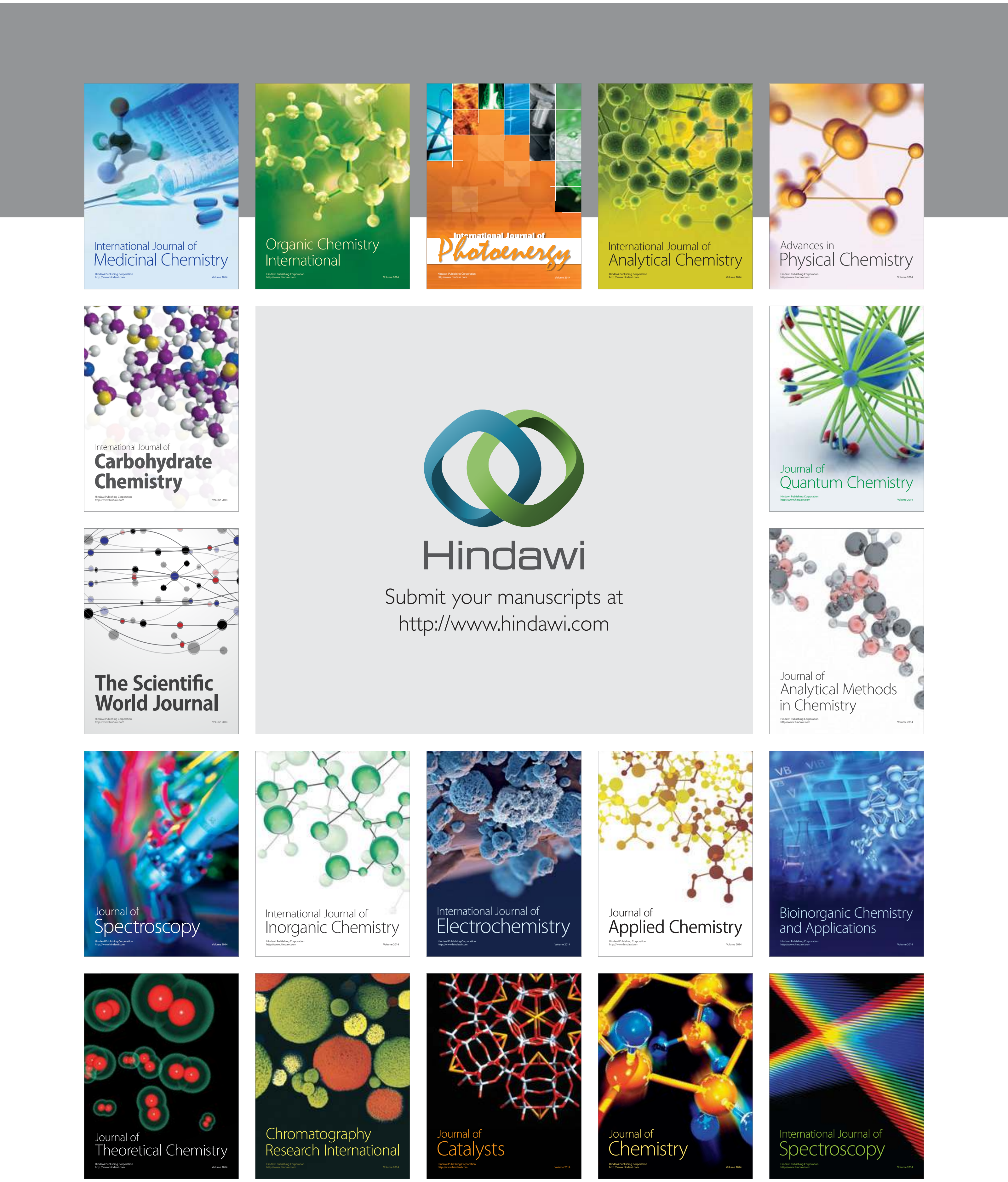
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