

C H A P T E R

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Wettability control of metal-organic frameworks

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4.1 Introduction

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p0010 Metal-organic frameworks (MOFs) are crystalline materials consisting of inorganic nodes (metal ions or clusters) and multitopic organic linkers, which can be systematically tuned in terms of chemical composition and precise arrangement.^{1–5} This fine control over the organic and inorganic components of MOFs offers an extensive set of synthetically accessible and remarkable structures, distinguishing them from other porous materials such as activated carbon, polymers, and zeolites. As a consequence of these properties, MOFs have demonstrated their utility for a variety of applications including,^{6–8} but not limited to gas storage/separation,^{9–16} chemical separations,¹⁷ catalysis,^{18–20} and chemical sensing.^{21–23} However, they have not yet been widely applied in industry, and in many cases the deployment of MOFs is held back by a lack of long-term stability under environmental or application-specific conditions, leading to pore blockages and loss of accessible surface area. Therefore, in order to be applicable, the stability of the materials is of eminent importance.^{24–32} Given the ubiquity of water vapor in the atmosphere, or as a component in applications for which MOFs may find utility, water stability has been a defining topic in determining whether real-world applications are realized using MOFs.

p0015 It is well accepted that the decomposition of MOFs is typically due to the insertion of a water molecule, which breaks the metal–ligand

linkage.³³ Therefore, to achieve water stability in MOFs, two main methods have recently been developed, either thermodynamically by using metals and ligands that produce a stronger metal-oxide bond,^{34–36} or kinetically by designing a framework with steric protection of the M–O bonds from water.^{37–39} Specifically, the use of linkers with enhanced basic properties or metals in higher oxidation states leads to an improvement in the chemical stability as a result of the greatly increased strength of the M–O bond. Based on such design principles, numerous water-stable MOFs have been developed, significantly promoting the expansion of their application.^{40,41} While efforts are ongoing to prepare new hydrolytically stable materials, there exists an ample library of known MOFs with less stable structures. Kinetically blocking water from reacting with the MOFs can be utilized to enhance the stability of existing MOFs of known topology. Improving the water resistance of these MOFs is equally, if not more, important as finding new stable structures, with the consideration that numerous MOFs have been well studied and have been produced at scale by industry, and these findings can be directly leveraged for a range of current applications.^{42,43} Considering that a hydrolysis reaction can only progress if the water molecule can approach sufficiently closely to the metal atom to allow interaction between the orbitals on the electrophilic metal atom and the nucleophilic water molecule, preventing the water molecules from attacking the frameworks is clearly expected to enhance their water tolerance.

p0020 Wetting is an omnipresent phenomenon that can be observed anywhere from high tides on the beach to ion channels in cell membranes. Engineering the wettability of a material presents a rational, yet sophisticated solution to combat failure related to water absorptivity, which has attracted substantial attention in the practical applicability of materials.^{44–57} Imparting the MOF materials with hydrophobicity could not only repel water molecules, thereby protecting MOFs against hydrolysis, but also render them new properties. Given their low adhesion properties and/or the solid/liquid/gas three-phase contact model, chemical behavior on such surfaces is quite different than that on traditional solid/liquid two-phase interfaces. Consequently, in addition to the significant effort being devoted to improving the hydrolytic stability, recent research has focused on applications for these unique interfacial materials such as oil spill cleanup, hydrocarbon storage/separation, or water purification.^{58–63}

p0025 In this chapter, we will first introduce the evolution of the study of superwetable materials, mainly focusing on the fundamental rules for building these liquid-repellent materials. In the following sections, we will provide a comprehensive overview of the state of the art in hydrophobic MOF synthesis along with the discussion of the present

challenges and opportunities. The potential applications of hydrophobic MOFs and related composites in hydrocarbon separation, water purification, oil spill cleanup, and catalysis are then demonstrated. We will attempt to show the mutual benefits offered by the integration of surface chemistry with materials. Finally, we offer perspectives on future directions for this promising field. We believe these findings for the realization of hydrophobic MOFs will offer simple, straightforward approaches for the development of diverse hydrolytically stable MOFs for future applications.

4.2 Wettability of metal-organic framework surfaces

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Wetting can be defined as the ability of a liquid to maintain contact with a solid surface. Therefore the first rule informed by natural examples of superhydrophobicity is that the chemical compositions of the material surfaces should be hydrophobic. It is generally accepted that solid surfaces with water contact angle (CA) greater than 90 degrees are defined as hydrophobic according to Young's equation [Eq. (4.1)].

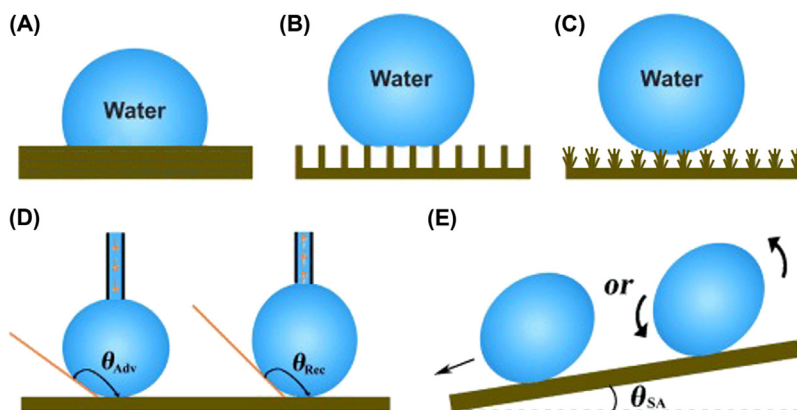
$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos\theta \quad (4.1)$$

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Herein, θ is the contact angle and γ_{sv} , γ_{sl} , and γ_{lv} are the surface tensions of solid/vapor, solid/liquid, and liquid/vapor involved in the system, respectively.⁶⁴ However, this equation cannot be used to describe the contact angle of a sessile drop on a rough surface like MOFs, given that the force balance at the three-phase contact line is affected by surface roughness. To address this concern, more complex approaches taking roughness into account are desired. Volger et al. demonstrated that rather than 90 degrees as in the mathematical concept, a CA of 65 degrees separates solid materials into hydrophobic and hydrophilic, derived from a surface force apparatus supported by ancillary techniques.^{65,66} Therefore two general rules can be summarized for targeting superhydrophobic materials: generating sufficient roughness on the material surfaces, and tailoring the chemical compositions of material surfaces to be hydrophobic with a water contact angle greater than 65 degrees.

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The hydrophilicity of a material is typically characterized by performing contact angle measurements, whereby a liquid drop is deposited on the surface, and the drop profiles of static and moving drops are then recorded. In addition to contact angle measurements, roll-off angle experiments are also frequently conducted to determine a substrate's wettability. To do this, a droplet is deposited on the surface of interest, and the surface is then slowly tilted until the drop rolls off, which will



f0010 **FIGURE 4.1** Effect of surface structure on the wetting behaviors of solid substrates in solid/air/water three-phase systems. (A) Diagram of Young's equation at the condition of a water droplet on a smooth surface with a contact angle θ . (B and C) Same system on a micro-structured substrate and micro/nanostructured substrate, respectively. (D) Advancing θ_{Adv} and receding contact angle θ_{Rec} . (E) Tilt angle, that is, the so-called roll-off angle or sliding angle θ_{SA} . Source: Reproduced with permission from Wen, L.; Tian, Y.; Jiang, L. *Bioinspired Super-Wettability from Fundamental Research to Practical Applications*. Angew. Chem. Int. Ed. 2015, 54, 3387–3399. Copyright 2015, John Wiley and Sons.

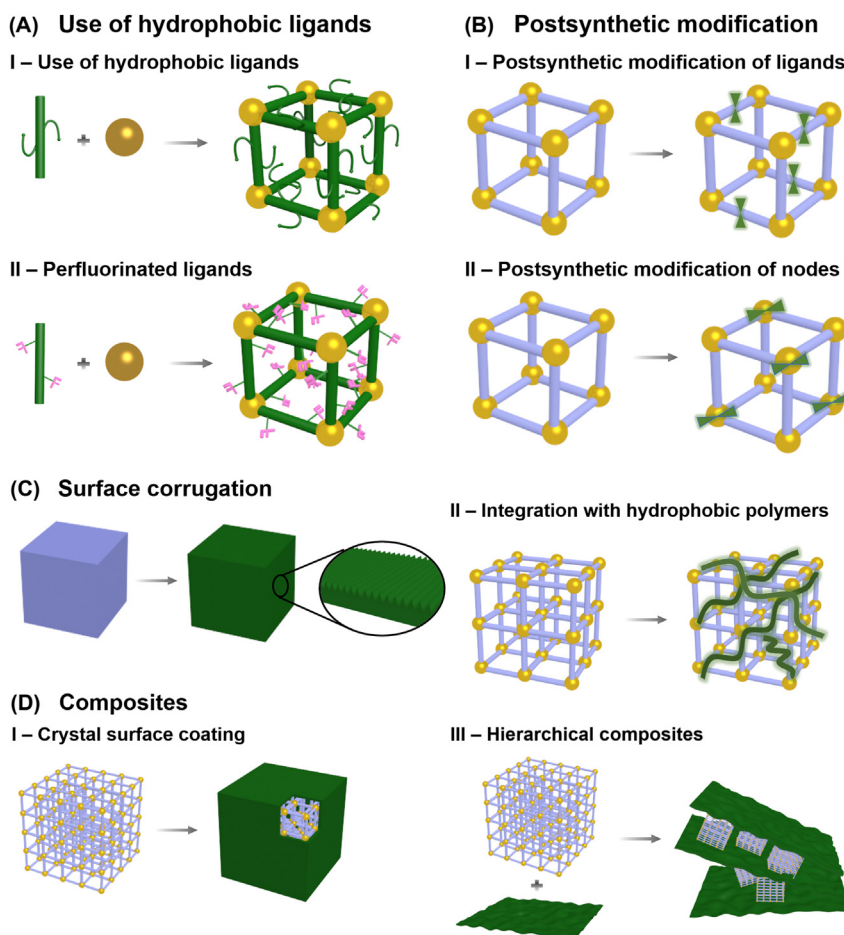
occur if the droplet's adhesion to the substrate is sufficiently low to be overcome by the gravimetric force acting on it. Materials with a higher hydrophobicity show small roll-off angles. In the dynamic case, however, this wettability is characterized by the advancing contact angle (θ_{Adv}) and the receding contact angle (θ_{Rec}). Both of these parameters are dependent on the adhesion of the materials. In general, superhydrophobicity means a high θ_{Adv} with a low contact-angle hysteresis, which is characterized by $\theta_{Adv}/\theta_{Rec}$ or the sliding angle θ_{SA} . With respect to porous materials, their performances in water/organic vapor adsorption have proven to be valid, which has the advantage of being more reproducible than contact angle measurements since they do not depend on the sample form and the choice of baseline and require no fitting (Fig. 4.1).⁶⁷

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4.3 Synthesis of hydrophobic metal-organic framework materials

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Considerable efforts have been devoted to the synthesis of hydrophobic MOFs as well as their related composites. In this section, we summarize the strategies that have been used to impart the MOFs with hydrophobicity (Fig. 4.2). The first approach involves decorating the



f0015 **FIGURE 4.2** Strategies for fabricating hydrophobic MOFs and composites. (A) Linker-based strategy. (B) Postsynthetic modification. (C) External surface corrugation of hydrophobic metal-organic frameworks. (D) Hydrophobic MOF composites by introduction of additional layers, integration with hydrophobic polymers, and formation of hierarchical composites.

ligands of the MOF with low surface energy fluorine-containing or long-chain alkyl substituent linkers to alter the surface properties of the MOF. This strategy promotes stability in liquid water by creating a hydrophobic outer surface that inhibits the diffusion of water molecules into the pores of the MOF. The second approach involves so-called post-synthetic strategies, for example, grafting hydrophobic responsive groups onto preformed MOFs. Although both strategies can effectively exclude water from the MOF's pores, they may also render the inherent porosity of the resultant MOFs largely inaccessible, because of the steric

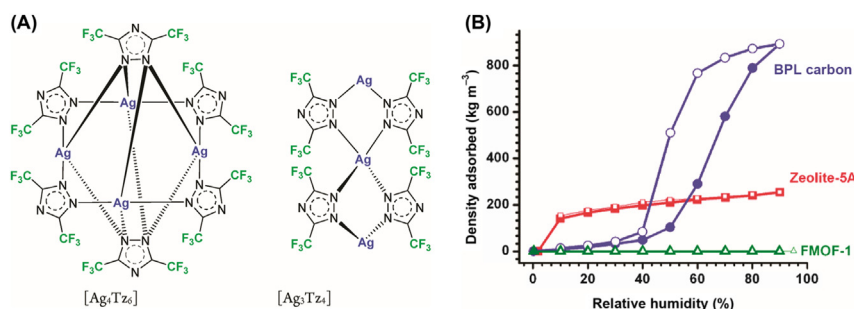
bulk of the groups attached to the ligand/outer surface. An alternative approach that generates highly hydrophobic exterior surfaces but preserves internal porosity involves creating high nano- to micrometer surface roughness. The final method involves the synthesis of hierarchical porous composites based on the hybridization of MOFs intercalated with hydrophobic materials.

4.4 Linker-based hydrophobic metal-organic frameworks

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p0045 Inspired by the low surface energy, extraordinary stability, and numerous applications of fluorinated molecules, Omary and coworkers have ignited an effort to explore the synthesis and functional properties of fluorinated metal-organic frameworks (FMOFs). They described the synthesis and structural characterization of two new highly fluorinated porous silver azolate MOFs, named FMOF-1 and FMOF-2.^{68,69} These MOFs were constructed by the association of three or four coordinated silver cations bound to 3,5-bis(trifluoromethyl)-1,2,4-triazolate linkers, yielding porous frameworks (Fig. 4.3A). Considering that the pore channels are densely decorated with low surface energy $-\text{CF}_3$ groups, this alignment affords only a weak water-framework interaction and thus repels the water molecules, exhibiting hydrophobicity. The measured contact angle for water on an FMOF-1 pellet is 158 degrees, indicative of superhydrophobicity.

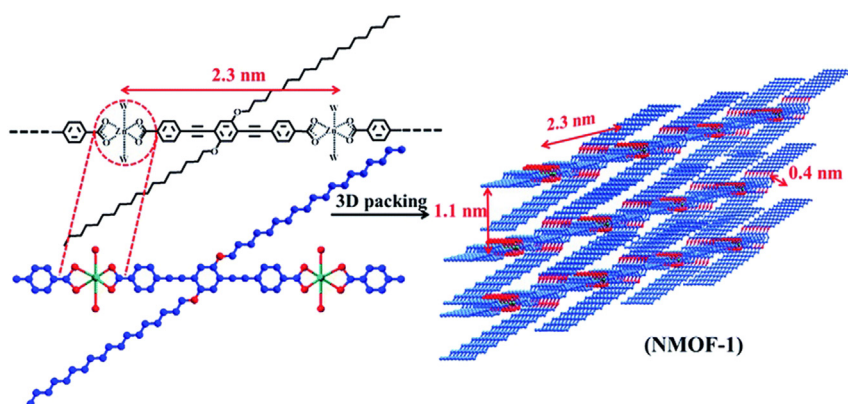
p0050 To further evaluate the resulting framework hydrophobicity, the authors analyzed the water adsorption isotherms of the resulting FMOF materials and contrasted them with those of a hydrophilic zeolite



f0020 **FIGURE 4.3** (A) Building Blocks of FMOF-1 (left) and FMOF-2 (right). (B) Water adsorption isotherms collected at room temperature for FMOF-1, zeolite-5A, and BPL carbon. Source: Reproduced with permission from Yang, C.; Kaipa, U.; Mather, Q.Z.; Wang, X.; Nesterov, V.; Venero, A.F.; Omary, M.A. *Fluorinated Metal-Organic Frameworks with Superior Adsorption and Hydrophobic Properties Toward Oil Spill Cleanup and Hydrocarbon Storage*. *J. Am. Chem. Soc.* 2011, 133, 18094–18097. Copyright 2011, American Chemical Society.

(zeolite-5A) and a hydrophobic activated carbon (BPL carbon). They showed that the hydrophobic character of the MOF materials appeared superior relative to that of the other adsorbents. No adsorption step and thus no water uptake is observed for FMOF-1 even near the saturation pressure (relative pressure of 0.9), whereas under the same conditions, activated carbon is fully saturated with water, and significant water adsorption was observed at a very low P/P_0 value (<0.1) for the hydrophilic zeolite (Fig. 4.3B). Impressively, such a hydrophobic character that fully prevents water molecules from entering into the pores means that FMOF-1 does not suffer from degradation even upon long-term exposure to boiling water, as verified by a combination of X-ray powder diffraction and IR spectroscopic analysis. After establishing the framework stability, to demonstrate the potential of these materials, the authors evaluated their performance in the adsorption of hydrocarbons of oil components, showing that the FMOFs exhibit high capacity and affinity to C_6 – C_8 fractions with retained efficiency even in the presence of water.⁶⁹ Considering that water vapor is a significant component of industrial flue gas ($\sim 10\%$) and cannot be neglected when examining adsorbents for CO_2 capture, a material with hydrophobicity is desired. Simulations and adsorption measurements show that FMOF-1 is hydrophobic, and water is not adsorbed in FMOF-1 at room temperature (Fig. 4.3B). CO_2 uptake capacity of FMOF-1 is not decreased even in the presence of 80% relative humidity (RH), suggesting that hydrophobic MOFs give promise for CO_2 capture from humid gas streams.⁷⁰

p0055 Later, Miljanić and colleagues reported three perfluorinated Cu-based MOFs built from perfluorinated ligands H_2OFBPD C (2,2',3,3',5,5',6,6'-octafluorobiphenyl-4,4'-dicarboxylic acid) and $H_2PFBPTZ$ [5,5'-(perfluorobiphenyl-4,4'-diyl)bis(1H-tetrazole)]. The most hydrophobic material among these new fluorinated MOFs is obtained by the reaction of H_2OFBPD C and $Cu(NO_3)_2$ in the presence of a bifunctional pillaring ligand 1,4-diazabicyclo[2.2.2]octane (DABCO). Evidence for the superhydrophobic behavior of the prepared MOFs came from the vapor adsorption studies and contact angle measurements, with a negligible water uptake capacity and a water contact angle of 151 degrees.⁷¹ The hydrophobic ligand strategy involves decorating the ligands of the MOF with functional groups that reduce the material's surface energy, such as perfluorinated aromatics, $-CF_3$ groups, or long alkyl or perfluoroalkyl chains. The use of ligands bearing perfluorinated aromatics in principle makes it possible to tune the hydrophobicity of any MOF whose ligands have one or more C–H bonds. Moreover, the de novo synthetic approach does not reduce the accessible pore space. However, fluorination changes the ligands' electronic structure and it is often essential to develop new synthetic strategies to access the desired framework

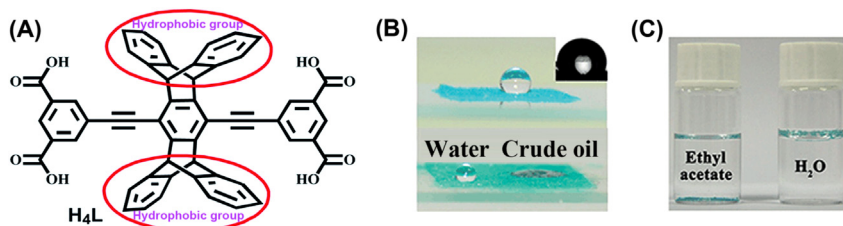


f0025 **FIGURE 4.4** Bottom-up approach for the fabrication of a self-cleaning MOF nanostructure by coordination driven self-assembly between Zn^{II} and OPE-C₁₈. Source: Reproduced with permission from Roy, S.; Suresh, V.M.; Maji, T.K. *Self-Cleaning MOF: Realization of Extreme Water Repellence in Coordination Driven Self-Assembled Nanostructures*. Chem. Sci. 2016, 7, 2251–2256. Copyright 2016, Royal Society of Chemistry.

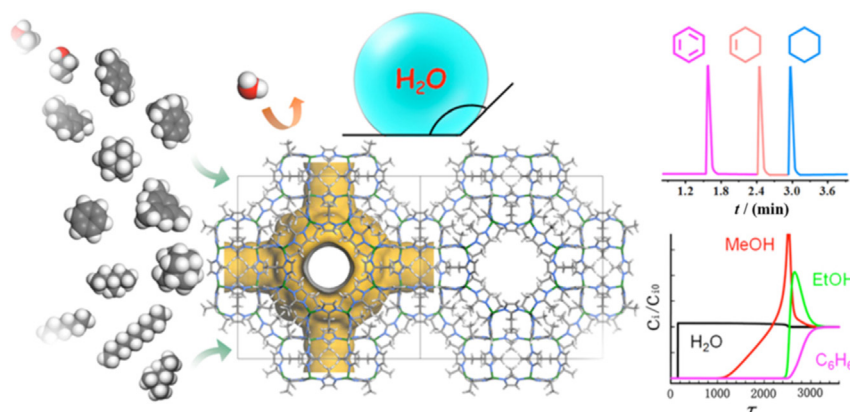
topologies. Furthermore, the preparation of complex perfluorinated ligands is, in itself, a challenging synthetic endeavor.

p0060 New approaches other than using fluorine-containing ligands are desired. Decorating the ligands of the MOF with alkyl substituent linkers has proven effective to alter the MOF's surface properties. Maji and coworkers reported a superhydrophobic coordination polymer (NMOF-1) assembled by an octadecoxy-functionalized organic linker oligo(*p*-phenyleneethynylene)dicarboxylate and Zn^{2+} ions (Fig. 4.4).⁷² Characterization results reveal that the NMOF-1 was assembled by 1D Zn-OPE-C₁₈ chains with octadecyl alkyl chains projecting outward, which reduces the surface free energy and leads to superhydrophobicity in NMOF-1 ($\text{CA} \approx 160$ degrees). To further prove the hydrophobic behavior of NMOF-1, benzene and water adsorption isotherms were collected at room temperature. It is worth noting that NMOF-1 has a contact angle of 162 degrees, indicative of superhydrophobicity. This is also supported by advancing and receding contact angle measurements. Impressively, the material's superhydrophobicity remains intact over a wide pH range of 1–9 and under high ionic concentrations, thereby advancing a new class of materials capable of water repellent applications.

p0065 Sun and coworkers report a MOF material (UPC-21) constructed from a pentiptycene-based organic ligand (H₄L). Due to the existence of multiaromatic hydrocarbon units in the central pentiptycene core of the ligand, UPC-21 exhibits high hydrophobicity with a water contact angle of 145 degrees and superoleophilicity with an oil contact angle of 0 degree.⁷³ Oil/water separation measurements reveal that this material can efficiently separate oil/water, with a separation efficiency above 99.0% (Fig. 4.5).



f0030 **FIGURE 4.5** (A) H_4L ligand with dangling hydrophobic groups. (B) Optical images of UPC-21 showing the hydrophobic character. The image of water droplet on the crystals of UPC-21 (top), the inset image in the right-hand corner is the image of the static water droplet (5 mL) and the image of crude oil diluted by hexane dropped on the crystals of UPC-21 (right). (C) Image of UPC-21 that can float on the water (right) and sink in ethyl acetate (left). Source: Reproduced with permission from Zhang, M.; Xin, X.; Xiao, Z.; Wang, R.; Zhang, L.; Sun, D. A Multi-Aromatic Hydrocarbon Unit Induced Hydrophobic Metal-Organic Framework for Efficient C2/C1 Hydrocarbon and Oil/Water Separation. *J. Mater. Chem. A* 2017, 5, 1168–1175. Copyright 2017, Royal Society of Chemistry.



f0035 **FIGURE 4.6** Perspective view of the coordination framework and pore surface structures of MAF-6, chromatograms on the MAF-6-coated capillary for gas chromatography separation of benzene, cyclohexene, and cyclohexane, as well as transient breakthrough calculations for an 85/5/5/5 water/methanol/ethanol/benzene mixture at 100 kPa in a packed bed of MAF-6 at 298K. Source: Reproduced with permission from He, C.-T.; Jiang, L.; Ye, Z.-M.; Krishna, R.; Zhong, Z.-S.; Liao, P.-Q.; Xu, J.; Ouyang, G.; Zhang, J.-P.; Chen, X.-M. Exceptional Hydrophobicity of a Large-Pore Metal – Organic Zeolite. *J. Am. Chem. Soc.* 2015, 137, 7217–7223. Copyright 2015, American Chemical Society.

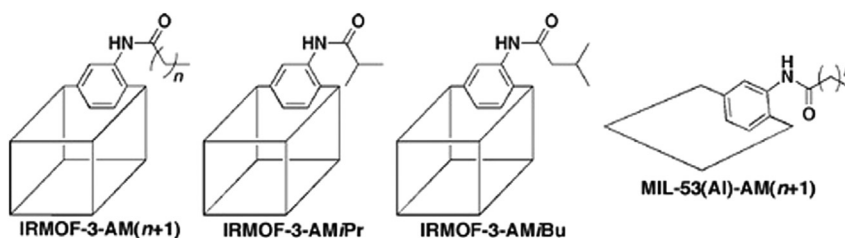
p0070 Taking advantage of the controllable coordination behavior of imidazolate derivatives, Zhang and coworkers reported that the pore surface hydrophilicity/hydrophobicity of metal azolate frameworks (MAFs) could be readily designed (Fig. 4.6). By varying the template, feeding order, and concentration of reactants during the crystallization of Zn(II)

2-ethylimidazolate isomers, a MAF material with a hydrophobic external crystal surface and pore channel named MAF-6 was obtained.⁷⁴ The terminated hydrophilic defects (unsaturated coordination sites) were successfully suppressed by careful control of the synthetic conditions. Gas and vapor adsorption isotherms, gas chromatography, water contact angle measurements, together with transient breakthrough and molecular dynamics simulations show that MAF-6 exhibits high porosity with a Langmuir surface area $1695 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.61 \text{ cm}^3 \text{ g}^{-1}$. The hydrophobicity and oleophilicity of MAF-6 are evidenced as follows: it can barely absorb water or be wetted by water with a water contact angle of 143 degrees, but readily adsorb large amounts of organic molecules including methanol, ethanol, mesitylene, adamantane, C_6 – C_{10} hydrocarbons, xylene isomers, and saturated/unsaturated analogues such as benzene/cyclohexene/cyclohexane or styrene/ethylbenzene. It can also separate these organic molecules from each other as well as from water by preferential adsorption/retention of those having higher hydrophobicity, lipophilicity, or oil/water partition coefficient. With these attributes, MAF-6 distinguishes itself with other porous materials such as SOD-[Zn(mim)₂] (Hmim = 2-methylimidazole, MAF-4/ZIF-8) with a hydrophobic pore surface but a hydrophilic crystal surface.

s0030 4.5 Induction of hydrophobicity by postsynthetic modification

p0075 With suitable attention to linker design by incorporating desired chemical functionality, direct approaches to MOF synthesis are effective for predictively modulating the wettability of the resulting materials. Installing desired functionalities directly, however, is not always possible. To this end, postsynthetic modification (PSM) of MOFs has been instrumental in obtaining frameworks that feature desired functionalities. This approach has the advantage that it can be applied to known MOFs to enhance their hydrolytic stability while retaining some of their intrinsic properties. Two variants of this approach can be distinguished: functionalization with organic substituents and modification with inorganic nodes. The first variant requires a framework with reactive substituents on the ligand that can undergo organic transformations for the introduction of hydrophobic moieties. The second variant necessitates the existence of coordinatively unsaturated metals, allowing for the installation of organic groups.

p0080 Cohen et al. pioneered the field in imparting hydrophobicity into the otherwise moisture-labile MOFs *via* PSM as exemplified by IRMOF-3 [Zn₄O(NH₂-BDC)₃; NH₂-BDC²⁻ = 2-amino-1,4-benzenedicarboxylate].⁷⁵ Alkyl chains with different lengths and degrees of branching can be introduced by the reaction of the amino groups with various carboxylic

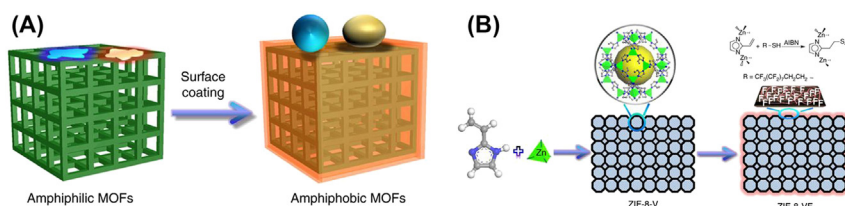


f0040 **FIGURE 4.7** Schematic illustration of the MOFs after postsynthetic modification. One modified organic ligand substituent is shown in each structure. *Source: Reproduced with permission from Nguyen, J.G.; Cohen, S.M. Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification. J. Am. Chem. Soc. 2010, 132, 4560–4561. Copyright 2010, American Chemical Society.*

acid anhydrides (Fig. 4.7). To establish the relationship between functional group and the extent of modification of the hydrophobic character of the resulting materials, a set of experiments was conducted showing that longer and branched alkyl chains more efficiently confer the material with hydrophobicity. Contact angle measurements are used to examine the hydrophobic/hydrophilic properties of materials. To assess changes in the moisture stability and hydrophobicity/hydrophilicity of the materials upon PSM, each material was exposed to ambient air or immersed in water and then characterized using powder X-ray diffraction (PXRD) and SEM to investigate the structural integrity. Reacting IRMOF-3 with valeric anhydride yielded the material IRMOF-3-AM₄, which has a contact angle above 116 degrees and is thus moderately hydrophobic. The hydrolytic stability of these resulting samples was assessed by exposure to ambient air. The addition of hydrophobic substituents stabilizes the bulk crystallinity of the IRMOF structure in air. PXRD patterns of IRMOF-3-AM₆ and IRMOF-3-AM₁₅ remain virtually unchanged over 4 days, with no new peaks and little loss in peak intensity, whereas all of the reflections for IRMOF-3 decrease over time, thereby indicating that hydrophobic modifications to the IRMOF lattice can appreciably safeguard the crystallinity of these materials under standard atmospheric conditions. The broader applicability of this methodology was confirmed by transferring it to the MIL-53(AI) structure, giving rise to superhydrophobic materials using the same reaction.)

p0085 The approach shown above can substantially increase moisture resistance; however, a great decrease in the framework's porosity was observed. To address this issue, Ma and coworkers contributed a general method to impart amphiphobicity on MOF crystals by chemically coating their exterior with a functional surface (Fig. 4.8A).⁷⁶ The authors rationally designed vinyl-functionalized linkers for construction of MOFs, since vinyl groups can remain intact during the MOF synthesis, yet are sufficiently reactive for further chemical modifications. To controllably introduce fluorinated groups

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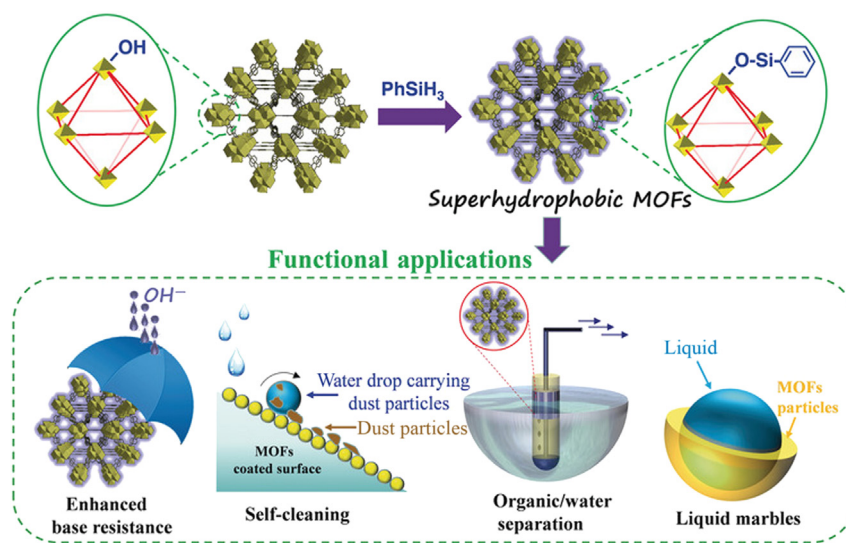
f0045 **FIGURE 4.8** (A) Amphiphobic surface engineering for MOFs. The resultant MOFs exhibit both superhydrophobicity and oleophobicity, while retaining high crystallinity and intact porosity. (B) Schematic illustration to impart amphiphobicity on ZIF-8-V. Synthetic route to create amphiphobic surface *via* grafting perfluoroalkyl groups on the exterior surface of the ZIF-8-V crystal. *Source: Reproduced with permission from Sun, Q.; He, H.; Gao, W.-Y.; Aguila, B.; Wojtas, L.; Dai, Z.; Li, J.; Chen, Y.-S.; Xiao, F.-S.; Ma, S. Imparting Amphiphobicity on Single-Crystalline Porous Materials. Nat. Commun. 2016, 7, 13300. Copyright 2016, Nature Publishing Group.*

onto the exterior surface of the resulting MOFs, a relatively bulky fluorinated compound, 1H,1H,2H,2H-perfluorodecanethiol, was employed, which is highly reactive toward the vinyl moiety through a thiol-ene click reaction. After treating the vinyl-functionalized MOFs, isostructural with ZIF-8, named ZIF-8-V, with 1H,1H,2H,2H-perfluorodecanethiol, the resulting MOFs (ZIF-8-VF) exhibit both superhydrophobicity and oleophobicity, while retaining high crystallinity and intact porosity, as revealed by contact angle measurements, vapor adsorption, gas adsorption, and PXRD (Fig. 4.8B). Notably, the contact angle of water on ZIF-8-VF sample is as high as 173 degrees, indicative of its extraordinarily superhydrophobic nature; by contrast, the pristine MOF, ZIF-8-V, gives a water contact angle of 89 degrees. Furthermore, ZIF-8-VF also shows oleophobicity, as evidenced by the fact that when a series of organic compounds with different surface tensions, including glycerol, 2-hydroxybenzaldehyde, benzonitrile, chlorobenzene, and dodecane, were contacted with the surface of ZIF-8-VF, contact angles of 150, 143, 130, 129, and 92 degrees, respectively, were observed. In contrast, these organic compounds can quickly penetrate the pristine MOF, giving rise to corresponding contact angles of 0 degree. Advantageously, given that the modification only occurs on the external surface of the MOFs, the crystallinity and porosity of the pristine MOFs are fully retained. The chemical shielding effect resulting from the amphiphobicity of the MOFs is illustrated by their performance in water/organic vapor adsorption, as well as by their long-term ultrastability under highly humidified CO₂ environments and exceptional chemical stability in acid/base aqueous solutions. More importantly, this strategy is generally applicable, as another vinyl-functionalized MOF (MOF-5-V), isostructural with MOF-5, can be readily conferred with amphiphobic properties, showing extraordinary tolerance to humidified CO₂. These results reinforce the utility of these materials in extended applications under harsh environments such as strong acidic and basic conditions.

p0090 Similarly, Huang and coworkers synthesized a superhydrophobic zeolitic imidazolate framework (ZIF-90) through postfunctionalization *via* an amine condensation reaction between the free aldehyde in ZIF-90 and pentafluorobenzylamine. The resulting material showed high steam stability and has great promise as an effective and durable adsorbent for bio-alcohol recovery.⁷⁷

p0095 The aforementioned examples illustrate that PSM processes avoid the need for (potentially very challenging) synthesis of fluorinated ligands as well as the synthesis of the MOF itself, and many potentially suitable reagents for substitution are commercially available. However, this strategy also has some notable drawbacks: the MOF must be able to withstand the reaction conditions, it is only applicable to MOFs with suitable reactive sites, and the reagents must be able to penetrate into the MOF's pores.

p0100 The intrinsic presence of metal–OH groups at metal-oxo nodes of MOFs and their ability to be easily modified provide an alternative route for PSMs, which is advantageous over ligand modification processes that require extra functional groups as an anchor for postmodification steps. Kim and coworkers initiated an attempt to prepare superhydrophobic MOFs by modification of the metal-oxo nodes (Fig. 4.9).⁷⁸ Given the unique properties of NH₂-functionalized MOFs,



f0050 **FIGURE 4.9** Preparation of superhydrophobic NH₂-UiO-66-shp and its versatile applications. Source: Reproduced with permission from Sun, D.; Adiyala, P.R.; Yim, S.-J.; Kim, D.-P. Pore-Surface Engineering by Decorating Metal-Oxo Nodes with Phenylsilane to Give Versatile Super-Hydrophobic Metal-Organic Frameworks (MOFs). *Angew. Chem. Int. Ed.* 2019, 58, 7483–7487. Copyright 2019, John Wiley and Sons.

NH₂-UiO-66 was chosen as a model. After treating with phenyl silane, the resulting MOF (NH₂-UiO-66-shp) exhibited superhydrophobicity, leading to greatly improved base resistance, whereas the pristine MOF, NH₂-UiO-66, quickly decomposes under basic conditions. The superhydrophobicity and high stability of NH₂-UiO-66-shp also endow it with great promise for versatile applications, including organic/water separation, self-cleaning, and the formation of liquid marbles for microfluidic devices and sensing. This proof-of-concept study is important, given the wide prevalence of metal–OH groups in MOFs and their facile modification. The precise modification on the metal-oxo nodes of MOFs without blocking the windows of the pores maximizes the preservation of the accessibility of the pores, ensuring their availability in practical applications. This work not only provides a promising material for various functional applications but more importantly, also advances a new and general approach for designing superhydrophobic MOFs for practical uses.

p0105 In view of the strong interaction between phosphonic acid derivatives and Zr species, Ma and coworkers reported a facile method to modify the external surface of Zr-based MOFs with superhydrophobicity through the incorporation of *n*-octadecylphosphonic acid (OPA). Such modification has little effect on the inherent porosity and surface area of the pristine MOF while significantly improving the material's hydrophobicity, thereby rendering it with a high level of resistance to acidic/basic aqueous solutions and potential in fast removal of organic pollutants from water.⁷⁹ Han and coworkers developed a universal strategy of constructing superhydrophobic and superoleophilic MOF composites *via* the reaction between open metal sites on the activated MOFs and octadecylamine. The resulting MOF materials exhibit superhydrophobicity with fully retained porosity and crystallinity. They all demonstrated high adsorption capacities toward organic solvents and exhibited excellent oil–water separation performance (>99.5%) without external pressure.⁸⁰

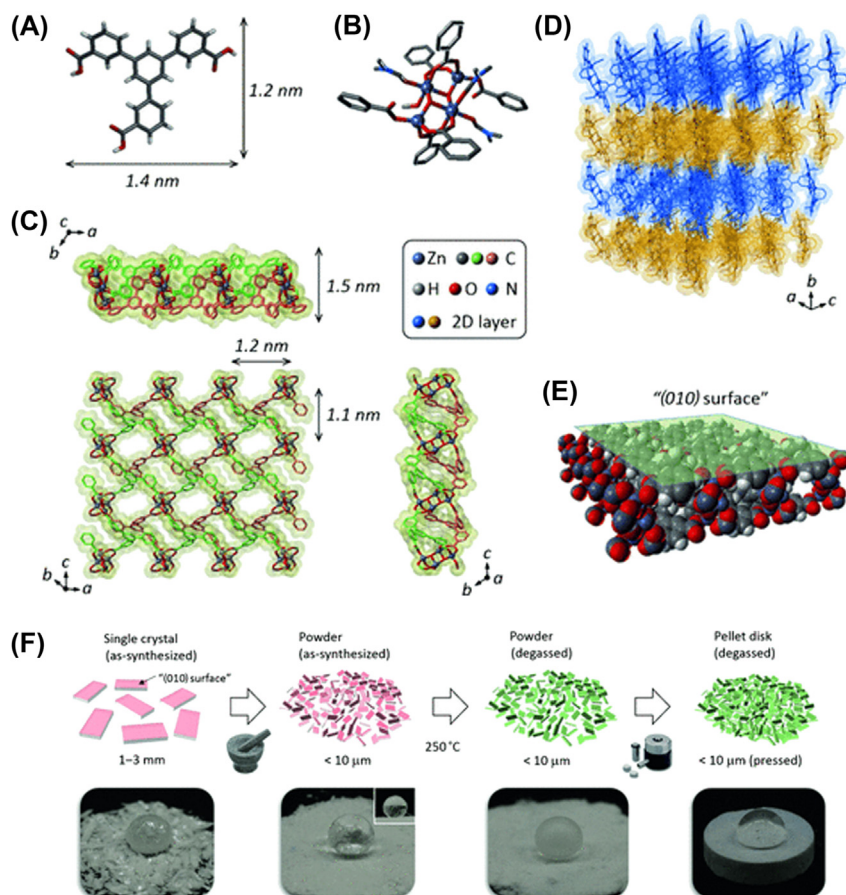
s0035 **4.6 Introduction of external surface corrugation by use of a hydrophobic unit**

p0110 Despite improving the moisture or water stability of MOFs, the approaches described earlier have some crucial drawbacks, such as reduced porosity and complex synthetic procedures. Inspired by the lotus effect, a wide variety of techniques have been employed to fabricate superhydrophobic surfaces by tailoring both surface chemistry and texture. An alternative strategy for providing highly hydrophobic exterior surfaces while retaining the internal porosity would be the

generation of surface roughness on the nano- to micrometer scale as it is well established that the texturing of a solid surface can significantly increase its hydrophobicity with respect to liquid water.^{81,82} It is envisioned that in the context of MOFs, ligands featuring an anisotropic crystal morphology with a predominant surface that is both highly corrugated and terminated by aromatic hydrocarbon moieties, which would provide a low-energy surface, are expected to provide a high level of hydrophobicity without the need for any modifications. Kitagawa and coworkers reported such a superhydrophobic MOF material by judicious choice of ligand.⁸³ 1,3,5-Tris(3-carboxyphenyl)benzene (H₃BTMB) was thus used to coordinate with a Zn species to yield [Zn₄(μ₃-OH)₂(BTMB)₂(DMF)₃(MeOH)], which possesses an aromatic hydrocarbon-terminated surface (Fig. 4.10). To examine the material's hydrophobic properties, contact angle measurements were performed on as-synthesized and activated powder, single crystals, and pellets, all of which yielded markedly different results, verifying that the nanosurface corrugation has a great impact on the material wettability. Recently, the same group extended such synthetic methods to preparing other MOFs with nanosurface corrugation, named PESD-2 and PESD-3 [Zn₂M₂(μ₃-OH)₂(BTMB)₂] (M=Co and Ni), with Co²⁺ or Ni²⁺ occupying the octahedrally coordinated Zn²⁺ positions.⁸⁴ The resulting materials exhibit outstanding superhydrophobic properties with retained performance even under elevated temperature condition. This material also exhibits oil spill cleanup from the water surface in the powder form as well as pellet form up to 385 wt.%. These studies open a new avenue for designing and engineering new composite superhydrophobic porous materials for better water and thermal stability, giving a significant promise for a wide range of applications such as catalysis, separation technology, and addressing environmental problems.

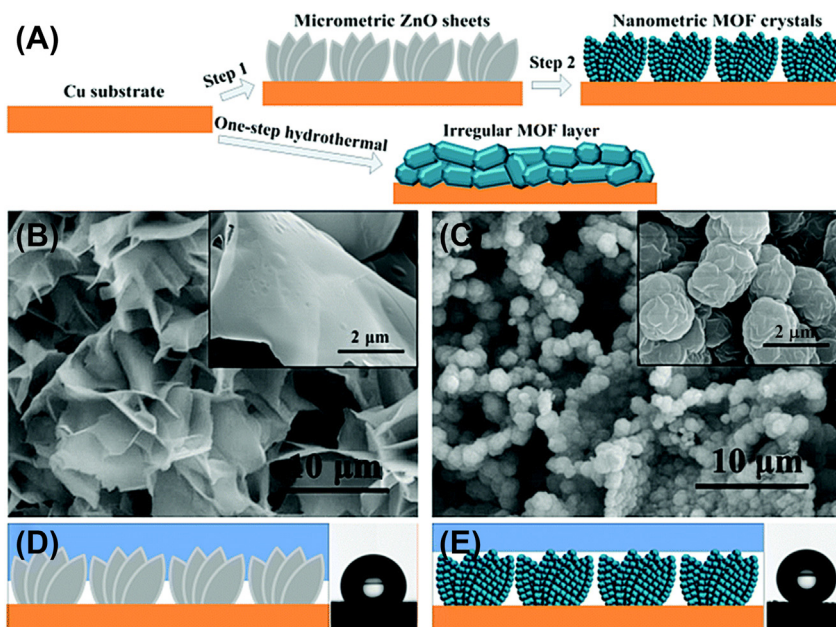
p0115 Given that multilevel topography could effectively reduce the adhesion and achieve robustness for improving hydrophobicity, Meng and coworkers fabricated a MOF array coating architecture on a copper substrate with a hierarchical micro-/nano-flowerlike architecture by in situ ligand-solvothermal transformations (Fig. 4.11). Benefiting from the unique hierarchical structure, the resulting material exhibits superhydrophobicity, showing a remarkable *n*-hexane permeate flux as high as $8.3 \times 10^4 \text{ L m}^{-2} \text{ h}^{-1}$ with a separation efficiency above 99.5%.⁸⁵

p0120 Chin and coworkers reported a simple strategy for the synthesis of microstructured surfaces *via* MOF self-assembly. The developed approach allows for localizing epitaxial growth of MOF at the tips of needle crystals to create mushroom-shaped structures, thus conferring reentrant textures to the MOF-functionalized surfaces. After the needles were subjected to continual growth and the MOF caps had been



f0055 **FIGURE 4.10** X-ray single-crystal structures showing (A) 1,3,5-tris(3-carboxyphenyl)benzene [H_3BTMB , from “benzene-1,3,5-tris(*m*-benzoic acid)”, (B) the coordination environment around a single $[Zn_4(\mu_3-OH)_2]^{6+}$ cluster, (C) views of a 2D layer consisting of the clusters shown in (B) linked by $BMTB^{3-}$ linkers, (D) the 3D stacking of individual 2D layers, and (E) the structure of the (010) surface, which affords a low-energy surface. Hydrogen atoms and solvent molecules have been omitted for clarity in many structures. (F) Schematic representation of PESD-1 in four states, and pictures of a water droplet on corresponding PESD-1 samples. The left two objects are as-synthesized forms and the right two objects are degassed forms. *Source: Reproduced with permission from Rao, K.P.; Higuchi, M.; Sumida, K.; Furukawa, S.; Duan, J.; Kitagawa, S. Design of Superhydrophobic Porous Coordination Polymers Through the Introduction of External Surface Corrugation by the Use of an Aromatic Hydrocarbon Building Unit. Angew. Chem. Int. Ed. 2014, 53, 8225–8230. Copyright 2014, John Wiley and Sons.*

functionalized with perfluorooctanoyl chloride, the anodized aluminum oxide (AAO)/MOF surfaces were found to be oleophobic, displaying contact angles of up to 100 degrees with *n*-hexadecane.⁸⁶



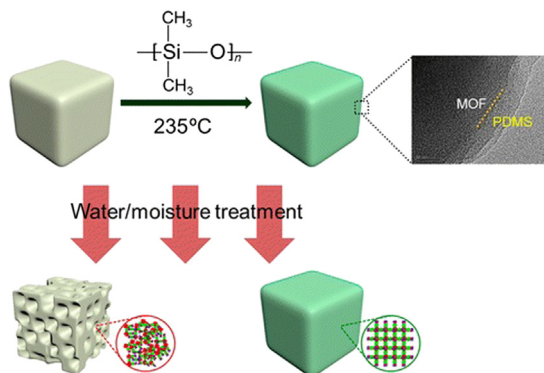
f0060 **FIGURE 4.11** (A) Scheme of the preparation process. Typical SEM images of the (B) ZnO array coatings and (C) micro-/nano-MOF array coatings; the insets are the corresponding magnified images. Schematic diagram of the contact state corresponding to the (D) ZnO array state and (E) MOF array state. *Source: Reprinted with permission from Zhang, G.; Zhang, J.; Su, P.; Xu, Z.; Li, W.; Shen, C.; Meng, Q. Non-Activation MOF Arrays as a Coating Layer to Fabricate a Stable Superhydrophobic Micro/Nano Flower-Like Architecture. Chem. Commun. 2017, 53, 8340–8343. Copyright 2017, Royal Society of Chemistry.*

4.7 Hydrophobic metal-organic framework composites

s0040

p0125

To provide a more general approach applicable to any MOFs, Yu and coworkers developed a facile vapor deposition technique by modifying the surfaces of MOF materials with hydrophobic polydimethylsiloxane (PDMS) to enhance their water and moisture resistance (Fig. 4.12).⁸⁷ MOF-5, HKUST-1, and ZnBT as representative vulnerable MOFs were successfully coated by PDMS, with well-inherited crystalline nature and pore characteristics. The resulting PDMS-coated MOFs all exhibit highly hydrophobicity with water contact angles of 130 ± 2 degrees, while their pristine MOFs show water contact angles close to 0 degree. It is worthy of mention that such coating is stable as evidenced by the hydrophobic behavior of the modified MOFs remaining unchanged, even after prolonged exposure to ambient air. To identify the presence of the PDMS layer on these representative MOFs, a composition line-scan was



f0065 **FIGURE 4.12** Illustration of PDMS coating on the surface of MOFs and the improvement of moisture/water resistance of MOFs. *Source: Reproduced with permission from Zhang, W.; Hu, Y.; Ge, J.; Jiang, H.-L.; Yu, S.-H. A Facile and General Coating Approach to Moisture/Water-Resistant Metal-Organic Frameworks with Intact Porosity. J. Am. Chem. Soc. 2014, 136, 16978–16981. Copyright 2014, American Chemical Society.*

performed, showing the homogeneous distribution of silica throughout the coated MOF, with a Si/Zn atomic ratio of $\sim 4.1\%$. These results inferred that the PDMS had been successfully coated on the MOF surface, which was further proven by high-resolution transmission electron microscopy (HRTEM), clearly showing a ~ 10 nm PDMS coating layer on the MOF surface. The coated PDMS layer significantly promotes the moisture/water resistance of these unstable MOFs, and thereby renders the coated MOFs with well-preserved performance in gas storage and catalysis under practical humid conditions.

p0130 Later, Zhu and coworkers reported a versatile and straightforward approach to deposit a layer of hydrophobic organosilicone on the MOFs' external surface with enhanced water stability *via* a simple solution-immersion process. The hydrophobic coating is able to protect the encapsulated MOF crystals against water molecules and therefore improves their water stability without significantly decreasing their initial sorption capacity in terms of porosity properties. This strategy is transferable as demonstrated that three representative MOFs (NH_2 -MIL-125(Ti), ZIF-, and HKUST-1) with different topologies and metal nodes have been successfully imparted with hydrophobicity.⁸⁸ Moreover, this approach seems very promising as it does not affect the accessibility of the pore space. However, to date the strategies mentioned earlier have only been applied to MOFs with micropores; it will be very interesting to see if this process can be applied to compounds with meso- and macropores without sacrificing porosity.

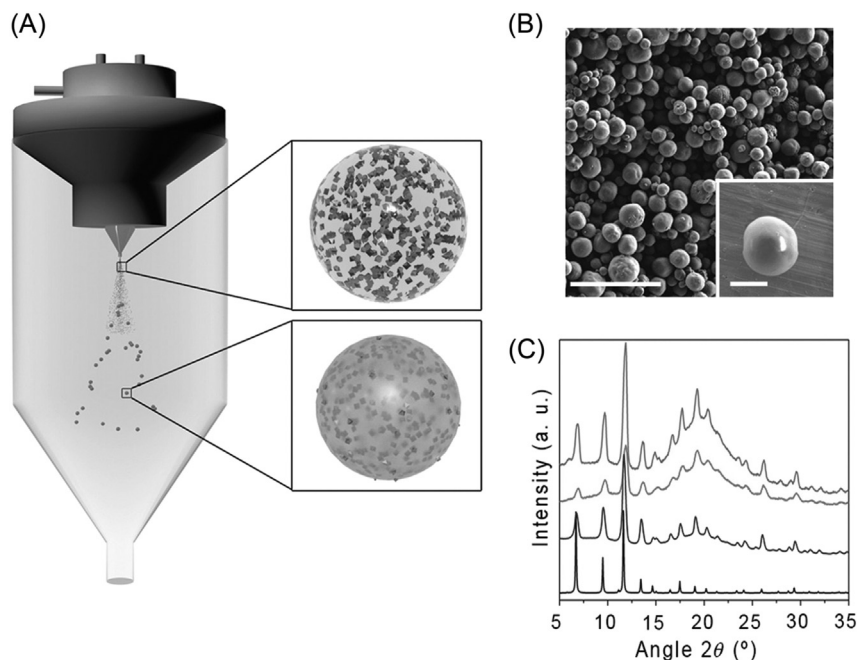
p0135 Matzger and coworkers developed another robust route for improving the hydrolytic stability of notoriously water-sensitive MOFs by the incorporation of hydrophobic linear polymer, as exemplified by the

synthesis of composites of MOF-5 and polystyrene (MOF-5-PS).⁸⁹ The MOF-5-PS composite is formed by neat heating styrene with MOF-5 at 65°C. The material produced after 24 h of heating (MOF-5-PS-24h) possesses remarkably increased hydrolytic stability over pristine MOF-5, as demonstrated by the fact that the pristine MOF-5 degraded at 53% RH within 4 h, whereas the MOF-5-PS composite was stable for over 3 months under otherwise identical conditions.

p0140 Maspoch and coworkers presented a rapid and scalable spray-drying (SD) synthesis of MOF@polymer composites with enhanced hydrolytic stabilities.⁹⁰ As a model study, HKUST-1 and polystyrene (PS) were the MOF and polymer of choice, respectively. The MOF crystals were encapsulated in the PS polymeric matrix by a spray dryer using a mixture of a colloidal HKUST-1 crystals suspension and a PS solution as a feed. This method does not require any purification or filtration steps, since the composites are obtained directly in a dried, pure form. In the resulting composites, the polymer protects the embedded MOF crystals against water molecules, without substantially decreasing their initial sorption capacity, and greatly increases their water resistance in terms of porosity properties (Fig. 4.13).

p0145 In contrast to forming a random composite of polymer and MOF, Wang et al. partitioned the channels of MOFs into confined, hydrophobic compartments by in situ polymerizations of aromatic acetylenes. Specifically, polynaphthylene was formed *via* a radical reaction inside the channels of MOF-5 and served as partitions without altering the underlying structure of the framework (Fig. 4.14). With the imparted hydrophobicity, not only the hydrolytic stability significantly improved but also the competitive adsorption of water versus CO₂, which drastically dampens their capacity and selectivity under real humid flue gas conditions, was reduced. Compared with pristine MOF-5, the resulting material (PN@MOF-5) exhibits a doubled CO₂ capacity (78 vs 38 cm³ g⁻¹ at 273K and 1 bar), 23 times higher CO₂/N₂ selectivity (212 vs 9), and significantly improved moisture stability, thereby showing great promise for CO₂ capture under real humid flue gas conditions.⁹¹

p0150 In addition to the use of polymer, Fischer and coworkers reported the synthesis of various MOF composites with fluorographene (FG), which allows functional groups to be incorporated into the basal plane of graphene rather than at the edges of the layers. The composites (HFGO@ZIF-8) were achieved by the combination of highly fluorinated graphene oxide (HFGO) with ZIFs. The PXRD of HFGO@ZIF-8 featured all planes corresponding to pristine ZIF-8.⁹² N₂ sorption isotherms reveal that the hybrid possesses hierarchical pore structure with a BET surface area of 590 m² g⁻¹. Characterization results indicate that the ZIF-8 nanocrystals act as pillars intercalated between HFGO layers by selective nucleation and controlled growth over oxygen functional groups, producing a hierarchical porous structure. Furthermore, the -CF₃



f0070 **FIGURE 4.13** (A) Schematic of the spray-drying synthesis of HKUST-1@PS composites. (B) Representative FESEM image of HKUST-1@PS_{18%} and a discrete composite sphere (inset). Scale bars: 10 and 2 μm (inset). (C) From bottom to the top: PXRD of the simulated patterns for HKUST-1, HKUST-1@PS₁₈, and the HKUST-1@PS₁₈ incubated overnight in either water or 10% HCl (v/v) solution. *Source: Reproduced with permission from Carné-Sánchez, A.; Stylianou, K.C.; Carbonell, C.; Naderi, M.; Imaz, I.; MasPOCH, D. Protecting Metal-Organic Framework Crystals from Hydrolytic Degradation by Spray-Dry Encapsulating Them into Polystyrene Microspheres. Adv. Mater. 2015, 27, 869–873. Copyright 2015, John Wiley and Sons.*

termination of the HFGO layers gives the composite very low surface energy. These features render the resulting composite with superhydrophobicity. Contact angle measurements showed the composite's water contact angle (162 degrees) and oil contact angle (0 degree), indicative of superoleophilicity and oleophilicity. The composite material HFGO@ZIF-8 (activated at 160°C) was further exploited for the absorption of oils and various organic solvents. ZIF-8 itself shows an absorption capacity in the range of 10–150 wt.%, while HFGO shows negligible uptake, whereas the absorption capacity of HFGO@ZIF-8 is much enhanced and ranges between 20 and 280 wt.%, outperforming those reported for resins and other porous composites (Fig. 4.15). In a continuation of this work, the same group reported an economically viable and readily scalable preparation of hydrophobic–oleophilic porous gels by simple mixing of hybrid composites of FGO and metal-organic gel (MOG) composed of Al³⁺ ions and 1,3,5-benzene-tricarboxylate (BTC) linkers and

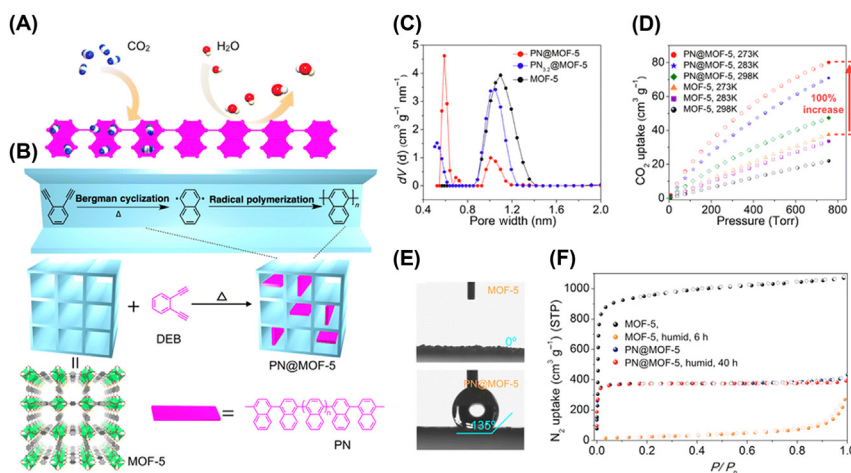


FIGURE 4.14 (A) Illustration of competitive adsorption of CO_2 against H_2O at the surface and edge of PN. (B) Polymerization of DEB in MOFs. (C) Pore size distributions of PN@MOF-5 , $\text{PN}_{3,2}\text{@MOF-5}$, and MOF-5 based on quenched solid-state density functional theory. (D) CO_2 sorption isotherms of PN@MOF-5 and MOF-5 at 273K, 283K, and 298K. (E) Contact angle measurements. (F) Nitrogen sorption profiles of PN@MOF-5 and MOF-5 after exposure to humidity for different times. Source: Reproduced with permission from Ding, N.; Li, H.; Feng, X.; Wang, Q.; Wang, S.; Ma, L.; Zhou, J.; Wang, B. Partitioning MOF-5 into Confined and Hydrophobic Compartments for Carbon Capture Under Humid Conditions. *J. Am. Chem. Soc.* 2016, 138, 10100–10103. Copyright 2015, American Chemical Society.

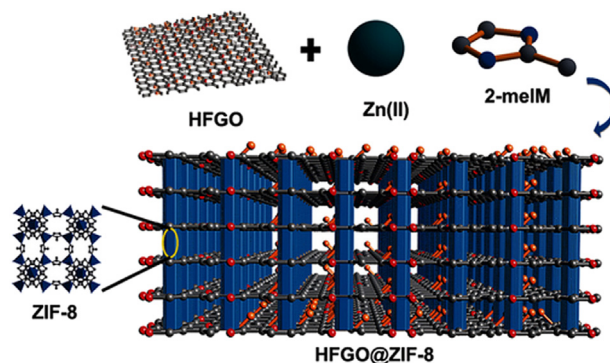
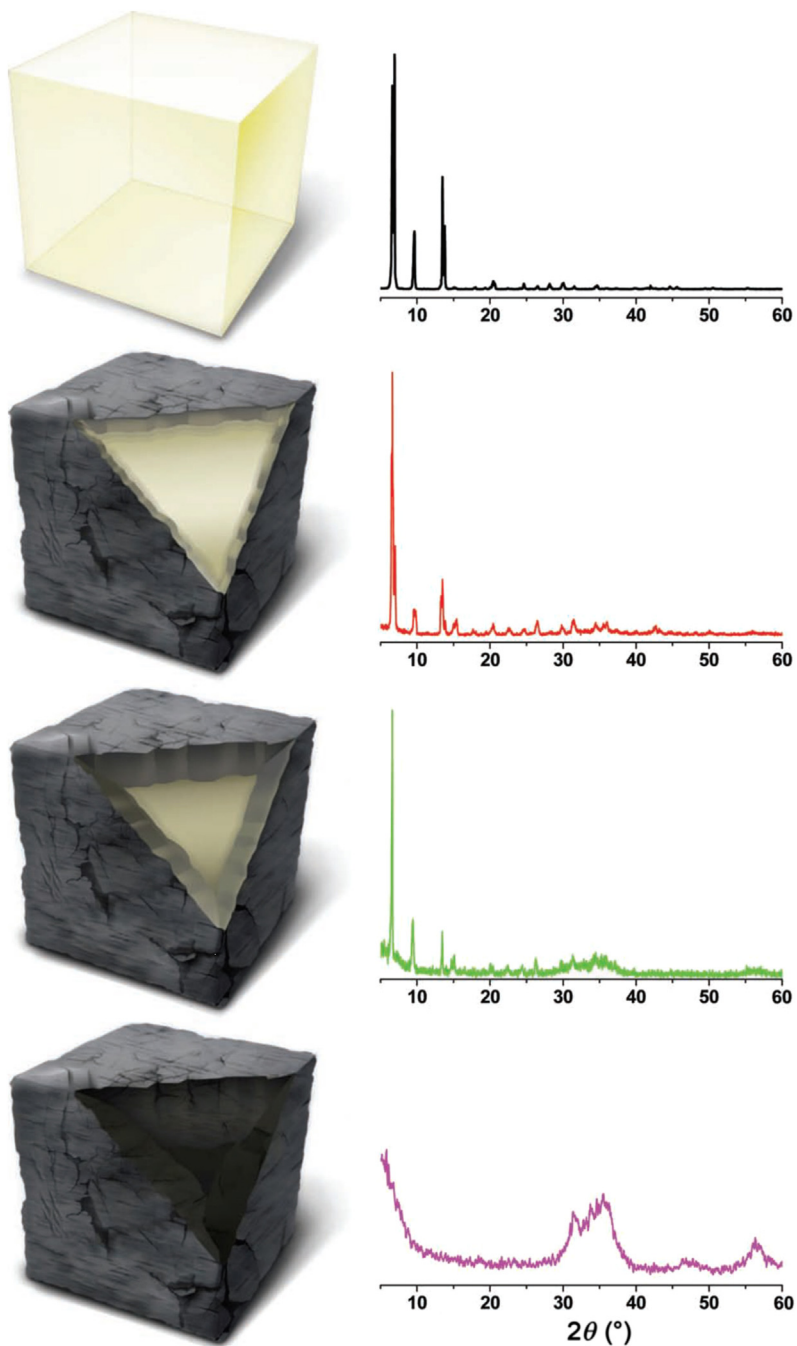


FIGURE 4.15 Illustration showing the concept of the formation and structure of HFGO@ZIF-8 . Source: Reproduced with permission from Jayaramulu, K.; Kumara, K.; Datta, R.; Rösler, C.; Petr, M.; Otyepka, M.; Zboril, R.; Fischer, R.A. Biomimetic Superhydrophobic/Superoleophilic Highly Fluorinated Graphene Oxide and ZIF-8 Composites for Oil-Water Separation. *Angew. Chem. Int. Ed.* 2016, 55, 1178–1182. Copyright 2016, John Wiley and Sons.



4. Metal organic frameworks

under solvothermal conditions. The water contact angle of FGO@MOG tablet was 126 ± 4 degrees indicating a highly hydrophobic behavior.⁹³

p0155 Ghosh and coworkers reported a hydrophobic MOF membrane UHMOF-100/PDMS/PP (UHMOF = ultrahydrophobic MOF; PP = polypropylene fabric). UHMOF-100 [Cu₂(BTFPADB)₂] consists of the fluorinated linker 4,4-[3,5-bis(trifluoromethyl)-phenyl]azanediylidibenzonic acid in the presence of copper nitrate. To examine the superhydrophobic behavior of UHMOF-100, contact angle measurements were conducted, with a water contact angle of 177 degrees and an oil contact angle of 0 degree, indicative of superoleophilicity. Vapor sorption isotherms collected at 298 K revealed that only negligible water uptake was recorded, but for hydrophobic organic vapor molecules (benzene, ethylbenzene, toluene, and *p*-xylene) significant uptake is observed. To utilize the properties of UHMOF-100, it was integrated into a device by spray coating the MOF onto a PDMS/PP membrane. The water contact angle of the prepared membrane was found to be 135 degrees highlighting the hydrophobic nature of the fabricated MOF membrane.⁹⁴

p0160 Willis and coworkers investigated an alternative method for postsynthetically modifying Cu-BTC by a plasma-enhanced chemical vapor deposition of perfluorohexane (PFH), enhancing the stability of Cu-BTC against degradation by water as a result of increased hydrophobicity. The overall crystal structure of Cu-BTC is maintained when submerged in water, and an enhancement of ammonia adsorption capacities gives Cu-BTC plasma broad appeal for many potential applications.⁹⁵ Through Monte Carlo simulations it was found that PFH sites itself in such a way within Cu-BTC as to prevent the formation of water clusters, hence preventing the decomposition of Cu-BTC by water. In view of that incorporation of "carbonaceous grease" is helpful to improve the hydrolytic stability of MOFs. Park and coworkers demonstrated that thermal modification of IRMOF-1 remarkably enhanced the stability of the framework against hydrolysis. Specifically, heat treatment of the IRMOF-1 samples led to the formation of an amorphous carbon coating on their surfaces, thus shielding the framework from decomposition under humid conditions. The thermally modified MOFs retained their crystal structure and pore characteristics, even after 14 days of exposure to ambient air.⁹⁶ This scalable and environment-friendly modification method opens new opportunities for the commercial preparation of water-resistant MOFs (Fig. 4.16).

f0066 **FIGURE 4.16** Schematic representations of IRMOF-1 (top) and IRMOF-1 after thermal modification to produce amorphous carbon-coated MOFs (middle) and, at higher temperature, ZnO nanoparticles@amorphous carbon (bottom). The corresponding XRD patterns are shown on the right. Source: Reproduced with permission from Yang, S.J.; Park, C.R. *Preparation of Highly Moisture-Resistant Black-Colored Metal-Organic Frameworks*. Adv. Mater. 2012, 24, 4010–4013. Copyright 2012, John Wiley and Sons.

p0165 It is well known that the practical applications of zeolitic imidazolate frameworks (ZIFs) have been hampered by their structural instability in humid acidic conditions. Guided by density functional theory calculations, Liang and coworkers demonstrated that the acidic stability of two polymorphic ZIFs (i.e., ZIF-8 and ZIF-L) can be enhanced by the incorporation of functional groups on polypeptides or DNA, which regulates the original Zn-N coordinative environment; concurrently the encapsulated biomolecules are stabilized by the ZIF exoskeleton, protecting them from denaturation.⁹⁷ A range of complementary synchrotron investigations into the local chemical structure and bonding environment suggest that the enhanced acid stability arises from the newly established coordinative interactions between the Zn centers and the inserted carboxylate (for polypeptides) or phosphate (for DNA) groups, both of which have lower pKa's than the imidazolate ligand. These findings introduce the principle of regulating the bonding environment to stabilize MOFs, paving the way for more sophisticated applications.

p0170 The integration of MOFs with other materials has been used successfully to prepare composites of MOFs with polymers, carbon materials, or biomolecules. This strategy is very promising because it appears to be universally applicable and the resulting composites couple the beneficial properties of microporous MOFs with the desirable qualities of the other component of the composite. Most reports describing these systems have been based on MOFs that are not inherently sensitive toward water; it would be interesting to see if other more sensitive MOFs could be protected by these hierarchical structures. In general, the combination of two or more of these synthetic concepts to trigger synergistic effects would be very exciting.

s0045 **4.8 Potential applications of hydrophobic metal-organic frameworks and their composites**

p0175 As discussed in the previous sections, hydrophobic MOF materials and related composites can be synthesized by various routes and have potential industrial applications in various fields. Although the industrial-scale use of hydrophobic MOFs is still distant, they have very attractive properties that make such uses quite plausible in the future. This section presents some key examples that highlight recent advances in the preparation and use of hydrophobic MOFs with potential applications in gas separation/storage, catalysis, and separation of oil spills from water.

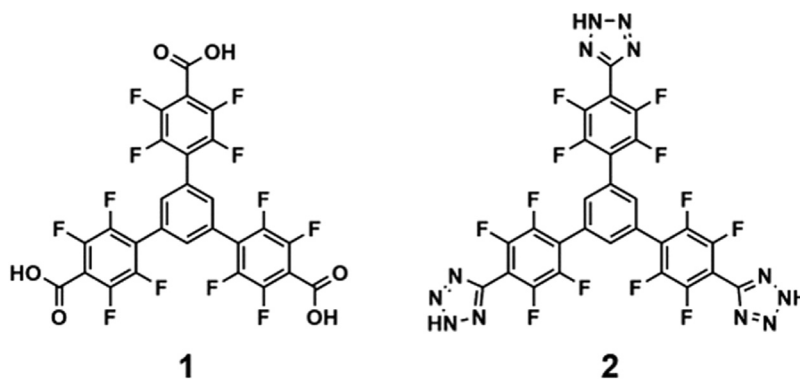
s0050 **4.9 Gas separation/storage**

p0180 The porosity of MOFs makes them attractive for gas storage applications, where the gaseous density within the framework may be increased relative to bulk gas due to framework – guest interactions. In

order to achieve separation between two or more components, there must be a differentiation between how the analyte gases interact with the framework, either by size or energetically. There are two primary energetic regimes of gas–framework interaction: chemisorption, where the uptake of the gas is dependent on a chemical transformation (e.g., bond formation or charge transfer) and physisorption, where the guest molecule interacts with the electric field produced by the framework.

p0185 Kitagawa and coworkers synthesized a perfluorobutyl-functionalized two-dimensional porous coordination polymer (PCP), $[\text{Cu}(\text{bpbtp})(\text{L})(\text{DMF}) \cdot (\text{DMF})]_n$ ($\text{H}_2\text{bpbtp} = 2,5\text{-bis}(\text{perfluorobutyl})\text{terephthalic acid}$, $\text{L} = 2,5\text{-bis}(\text{perfluorobutyl})\text{-1,4-bis}(4\text{-pyridyl})\text{benzene}$, $\text{DMF} = N,N\text{-dimethylformamide}$).⁹⁸ The pore surface of the PCP is decorated with pendent perfluorobutyl groups that create a densely fluorinated nanospace resulting in unique gas sorption properties. The unique adsorption properties such as preferential adsorption of CO_2 and O_2 and hysteresis loops in the isotherms for both gases can be attributable to the strong host–guest interactions.

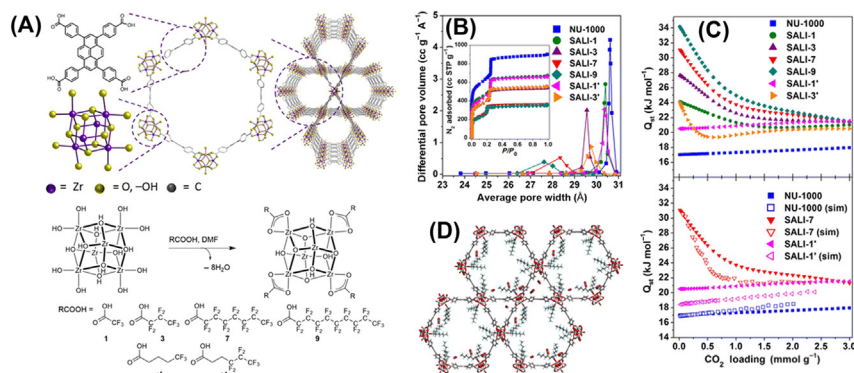
p0190 Due to the high polarity, fluorophilic character, and low affinity for moisture of fluorinated MOFs, they are a particularly appealing platform for the adsorption of fluorocarbons and chlorofluorocarbons, which are potent greenhouse species. Miljanić and coworkers reported the synthesis of two mesoporous fluorinated MOFs from extensively fluorinated tritopic carboxylate- and tetrazolate-based ligands (**1** and **2**, respectively, Fig. 4.17) with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$. The resulting tetrazolate-based framework MOFF-5 has an accessible surface area of $2445 \text{ m}^2 \text{ g}^{-1}$, the highest thus far achieved among fluorinated MOFs. MOFF-5 crystals exhibit unique affinity toward fluorocarbons and chlorofluorocarbons (CFCs), with weight capacities of up to 225% within seconds of exposure. In addition, this



f0090 **FIGURE 4.17** Extensively fluorinated tritopic MOF precursors **1** and **2**. Source: Reproduced with permission from Chen, T.-H.; Popov, I.; Kaveevititchai, W.; Chuang, Y.-C.; Chen, Y.-S.; Jacobson, A.J.; Miljanić, O.Š. Mesoporous Fluorinated Metal-Organic Frameworks with Exceptional Adsorption of Fluorocarbons and CFCs. *Angew. Chem. Int. Ed.* 2015, 54, 13902–13906. Copyright 2015, John Wiley and Sons.

mesoporous material shows unique CO₂ sorption isotherms and preference for nonspherical guest molecules, which could tentatively be rationalized by the low polarities of those guests, mismatched with the highly polarized environment inside fluorinated cavities.⁹⁹

p0195 Given their hydrophobicity and the presence of X–F dipoles, fluorinated MOFs have recently emerged as attractive candidates for CO₂ removal from fuel gas, whereby hydrophobicity should render the MOF stable toward water vapor, and the presence of C–F dipoles should lead to favorable interactions with the quadrupole of CO₂. Farha and coworkers developed a new functionalization technique named solvent-assisted ligand incorporation to incorporate perfluoroalkane carboxylates of various chain lengths (C₁–C₉) in the Zr-based MOF, NU-1000.¹⁰⁰ These fluoroalkane-functionalized mesoporous MOFs were studied experimentally and theoretically as potential CO₂ capture materials. CO₂ adsorption studies indicate that perfluoroalkane-functionalized nodes in the resulting system synergistically act as the primary CO₂ binding sites, manifesting in systematically higher values for isosteric heat of adsorption (Q_{st}), with increasing chain length. With a synthetic pathway to highly porous fluorinated MOFs, it is expected that exploration and understanding of their adsorption properties will increase. These promise to be distinctive, because of the highly polarized and fluorophilic pore surfaces, electron-deficient nature of aromatic nuclei, and the hydrophobicity of the framework (Fig. 4.18).



f0095 **FIGURE 4.18** (A) Molecular representations of NU-1000 and schematic representation of solvent-assisted ligand incorporation (SALI). (B) BJH pore size distributions and N₂ adsorption isotherms (inset) for NU-1000 and SALI-*n* samples. (C) Q_{st} of NU-1000, SALI-*n*, and SALI-*n'* samples: (top) calculated from experimental isotherm data and (bottom) comparison of simulated (sim) and experimental Q_{st} values for selected MOFs. (D) Simulated snapshot of CO₂ adsorption depicting the primary CO₂ binding sites in SALI-7. *Source: Reproduced with permission from Deria, P.; Mondloch, J.E.; Tylionakis, E.; Ghosh, P.; Bury, W.; Snurr, R.Q.; Hupp, J.T.; Farha, O.K. Perfluoroalkane Functionalization of NU-1000 via Solvent-Assisted Ligand Incorporation: Synthesis and CO₂ Adsorption Studies. J. Am. Chem. Soc. 2013, 135, 16801–16804. Copyright 2013, American Chemical Society.*

4.10 Oil spill cleanup

s0055

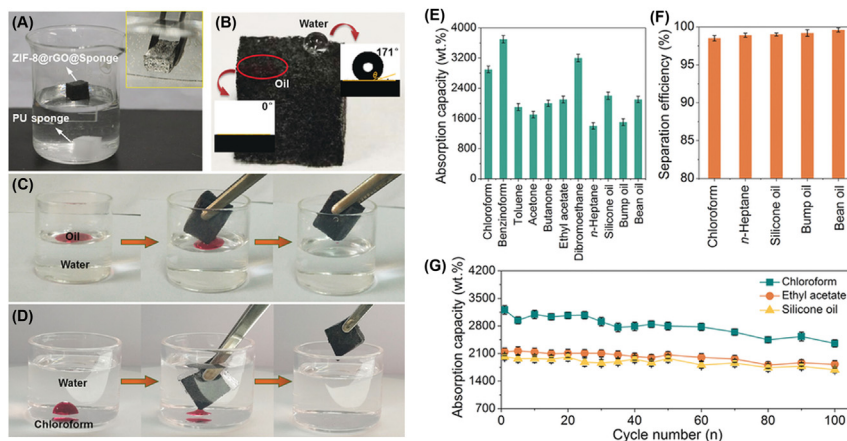
p0200 There will be a risk of spillages that may result in significant environmental damage and vast economic loss, as long as oil is prospected, transported, stored, and used. Worldwide, oil spill cleanup costs amount to over \$10 billion dollars annually. The adverse impact to ecosystems and the long-term effects of environmental pollution by these and other releases call for an urgent need to develop new materials for cleaning up oil from impacted areas. There are many adsorbents currently in use for oil spill cleanup, including sand, organoclays, and cotton fibers. These adsorbents, however, typically have a strong affinity for water, limiting their effectiveness in cleanup operations. Therefore the development of waterproof sorbents that are effective even at a very low concentration of oil residue remains an urgent challenge. The devastation resulting from the recent Deepwater Horizon oil spill raised awareness and underscored the urgent need for water-stable/-proof sorbents that can effectively remove oil residue in water, on land, and in the air.

p0205

Hydrophobic MOFs have shown potential for oil cleanup. However, these MOFs were synthesized as microcrystalline powders, and therefore their applications in real-world separation could be affected by poor processability and handling. In addition, the limited pore volume of the MOF material restricts its adsorption capacity. To address these concerns, researchers were motivated to incorporate superhydrophobic MOF coatings onto other substrates to increase applicability. Jiang and coworkers also reported a hydrophobic–oleophilic composite by the integration of a hydrophobic MOF with graphene oxide (GO)/sponge composite. The MOF used in this study, USTC-6 (Cu_2HFPD), is constructed from a tetracarboxylate-based organic linker 4,4'-(hexafluoroisopropylidene)diphthalic acid with a Cu_2 paddlewheel secondary building unit (SBU). Single-crystal XRD analysis reveals 2D layers in the *ac* plane with a wavelike surface pendent $-\text{CF}_3$ groups between the 2D layers, which decrease the surface energy and induce the high hydrophobicity of USTC-6, giving a water contact angle of 132 degrees. The authors incorporated the obtained hydrophobic MOF on branched sponges functionalized with GO, which facilitate anchoring of USTC-6. The resulting composite retains the hydrophobic/oleophilic nature of USTC-6.¹⁰¹ Remarkably, the sorbent can be further assembled with tubes and a self-priming pump to build a model apparatus that affords consecutive and efficient oil recovery from water. The easy and fast recovery of oils/organic solvents from water based on such an apparatus indicates that it has great potential for future water purification and treatment.

p0210

Meng and coworkers developed novel superhydrophobic/superoleophilic materials composed of wrinkled microspherical MOF@rGO composites, which possess a unique micro/nanohierarchical architecture consisting of crumpled rGO nanosheets intercalated with well-dispersed MOF



f0100 **FIGURE 4.19** (A) Digital photographs of pure PU sponge and ZIF-8@rGO@Sponge in water. (B) Silicone oil and water droplets on the ZIF-8@rGO@Sponge with inserted profiles and contact-angle values. (C and D) Digital photographs showing the absorption of dyed silicone oil (C) and chloroform (D) from water by ZIF-8@rGO@Sponge. (E) Oil- and organic-solvent-absorption capacity of the ZIF-8@rGO@Sponge. (F) Separation efficiency of the ZIF-8@rGO@Sponge. (G) Absorption recyclability test of the ZIF-8@rGO@Sponge. The errors are estimated to vary from 2.7% to 6.0% for the absorption capacity and from 0.2% to 0.4% for the separation efficiency. *Source: Reproduced with permission from Gu, J.; Fan, H.; Li, C.; Caro, J.; Meng, H. Robust Superhydrophobic/Superoleophilic Wrinkled Microspherical MOF@rGO Composites for Efficient Oil-Water Separation. Angew. Chem. Int. Ed. 2019, 58, 5297–5301. Copyright 2019, John Wiley and Sons.*

nanoparticles.¹⁰² Due to the synergistic effects of superwettability and high meso/microporosity, the formed MOF@rGO composites display a higher absorption capacity and selectivity for the removal of organic solvents and oils from water than the individual constituents. Furthermore, a ZIF-8@rGO@Sponge adsorbent made from a commercial polyurethane (PU) sponge showed prominent oil–water separation performance and good recyclability. This study not only provides a promising material for oil spill cleaning and wastewater treatment for organic contaminants, but also a new concept for the structural and multifunctional exploitation of graphene/MOF-based composite materials (Fig. 4.19).

4.11 Catalysis

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p0215 Control of the wettability of a catalyst surface is widely known to be of great importance in the regulation of interactions between heterogeneous catalysts and reactants, which is directly related to catalytic activity and selectivity. Jiang and coworkers reported that hydrophobic modification can enhance catalytic performance. They performed styrene

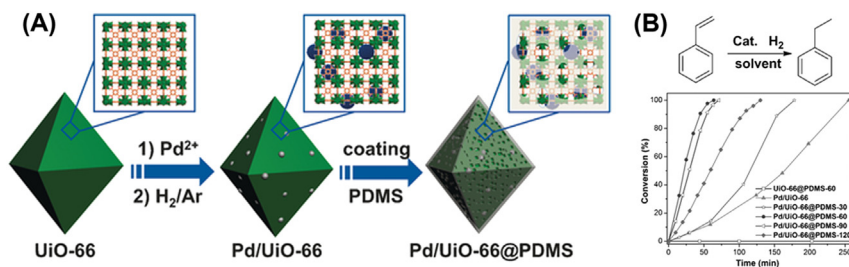
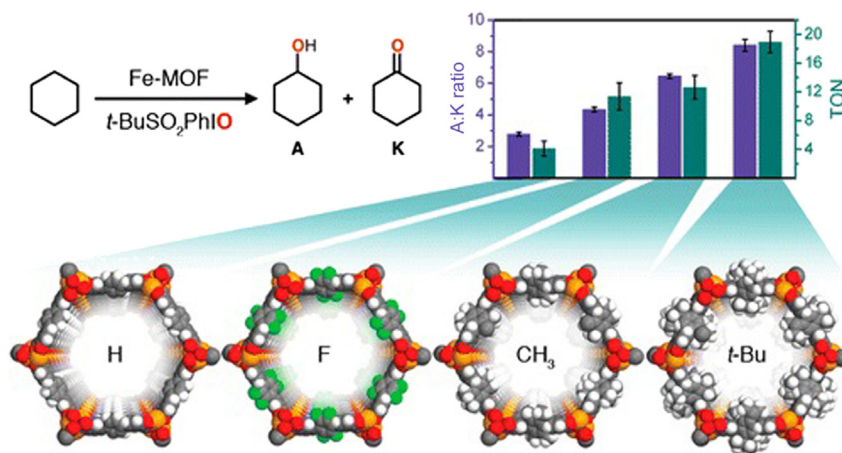


FIGURE 4.20 (A) Preparative route for Pd/Uio-66@PDMS. (B) Catalytic hydrogenation of styrene over Uio-66@PDMS, Pd/Uio-66, and Pd/Uio-66@PDMS (1:150 Pd:styrene molar ratio). Source: Reproduced with permission from Huang, G.; Yang, Q.; Xu, Q.; Yu, S.-H.; Jiang, H.-L. Polydimethylsiloxane Coating for a Palladium/MOF Composite: Highly Improved Catalytic Performance by Surface Hydrophobization. *Angew. Chem. Int. Ed.* 2016, 55, 7379–7383. Copyright 2016, John Wiley and Sons.

hydrogenation in a batch reaction over the pristine composite Pd/Uio-66 and a PDMS-modified hydrophobic hybrid, Pd/Uio-66@PDMS.¹⁰³ The parent Pd/Uio-66 required 255 min to achieve complete hydrogenation. By contrast, the PDMS-coated hybrid afforded full conversion within 65 min. The enhanced activity of the Pd/Uio-66@PDMS hybrid could thus be primarily ascribed to the hydrophobic responsive PDMS surface modification of the Pd surface, leading to the enhanced affinity for hydrophobic substrates. The composite Pd/Uio-66@PDMS catalyst also showed superior performance in the hydrogenation of other hydrophobic substrates such as nitrobenzene and cinnamaldehyde (Fig. 4.20).

Long and coworkers investigated the effects of a local hydrophobic environment on product selectivity and catalyst stability with respect to cyclohexane oxidation in expanded analogues of Fe₂(dobdc) (dobdc⁴⁻ = 2,5-dioxido-1,4-benzenedicarboxylate), a MOF featuring exposed iron(II) sites.¹⁰⁴ A threefold enhancement of the alcohol:ketone (A:K) product ratio and an order of magnitude increase in turnover number can be achieved by simply altering the framework pore diameter and installing nonpolar, hydrophobic functional groups near the iron center. Detailed Mössbauer spectroscopy, kinetic isotope effect, and adsorption studies suggest that the incorporation of simple nonpolar groups remarkably increases both the selectivity and stability of framework-embedded iron sites for cyclohexane oxidation catalysis without directly affecting the structure or reactivity of the iron centers themselves. Outer coordination sphere and pore environment effects may prove to be significant in the context of many other MOF-catalyzed reactions and are well worthy of further investigation (Fig. 4.21).

Hu and coworkers reported the effect of hydrophobic modification in the catalytic hydrogenation of cinnamaldehyde using iron(III)



f0110 **FIGURE 4.21** Oxidation of cyclohexane to cyclohexanol and cyclohexanone in $\text{Fe}_2(\text{dobdc})$ and expanded pore derivatives and view of one-dimensional hexagonal pores of $\text{Fe}_2(\text{dobdc})$, with an inset showing the local coordination environment around each coordinatively unsaturated iron(II) site and the corresponding TON values in oxidation of cyclohexane. Source: Reproduced with permission from Xiao, D.J.; Oktawiec, J.; Milner, P.J.; Long, J.R. *Pore Environment Effects on Catalytic Cyclohexane Oxidation in Expanded $\text{Fe}_2(\text{dobdc})$ Analogues*. *J. Am. Chem. Soc.* 2016, 138, 14371–14379. Copyright 2016, American Chemical Society.

porphyrin (FeP-CMP) to modify the surface of MIL-101@Pt and prepare MIL-101@Pt@FeP-CMP. In the same work, the authors proved that MIL-101@Pt@FeP-CMP sponge has a higher turnover frequency (1516.1 h^{-1}), with 97.3% selectivity for cinnamyl alcohol in 97.6% yield.¹⁰⁵

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4.12 Conclusions and perspectives

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In this chapter, we provide a comprehensive summary of the design concept, preparation, and applications of hydrophobic MOFs and their composites, highlighting state-of-the-art strategies. We discussed the basics of wetting of hydrophobic materials, followed by four strategies for preparing hydrophobic MOFs, namely, (1) the use of hydrophobic ligands, (2) postsynthetic grafting of hydrophobic side chains onto reactive sites (ligand or metal node), (3) the targeted exploitation of surface corrugation to induce hydrophobicity, and (4) the preparation of hydrophobic composites. While ligand functionalization is the most well-studied approach, it is restricted to structures where nonpolar entities can be incorporated without compromising the structural nature of the framework. Surface modification approaches based on core–shell models hold promise for a number of further systems provided there is

compatibility in the binding domain for the core and shell entities. Imparting crystal surface hydrophobicity *via* hydrophobic polymer coating approaches is perhaps one of the simplest and most generalizable approaches for improving MOF water stability, in view of the fully retained specific surface area and crystal textural properties of the resulting composites. Given the low adhesion of water molecules, MOF materials with hydrophobicity could not only repel water molecules, thereby protecting MOFs against hydrolysis, but also render them with new properties. We give examples of intriguing properties of MOFs and related composites with hydrophobicity for various applications. This summary of the wettability control of MOFs and its ability to increase their hydrolytic stability and confer new properties upon them lays important groundwork that will help accelerate their practical application. Building upon these achievements, further insight into how the modification strategy affects the MOF adsorption properties and processibility in the target application still need to be explored.

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NON-PRINT ITEM

Abstract

Metal-organic frameworks (MOFs) allow compositional and structural diversity beyond conventional solid-state materials. Their modular structure and extraordinarily broad chemical and topological variety can be translated into property tunability. This, in turn, has motivated their investigation as materials for numerous potential applications. However, the deployment of MOFs is held back by a lack of long-term stability under humid conditions. In this chapter, we summarize some of the research efforts toward imparting hydrophobicity on MOFs to kinetically block water from reacting with the MOFs and thereby enhance their tolerance toward humidity. For each functionalization strategy, we first describe its chemical basis along with the requirements for its successful implementation. We then present a small number of examples, with the emphasis on those that convey the underlying concepts to achieve the desired properties. The examples, however, are only illustrative, and a significant body of work exists. Emphasis is also placed on further applications as the integrated hydrophobicity influences the potential for MOFs in gas separation, environmental remediation, and catalytic applications.

Keywords: Wettability; hydrophobicity; metal-organic frameworks; water resistance; postsynthetic modification; hierarchical composites