Hydrophobic Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) have diverse potential applications in catalysis, gas storage, separation, and drug delivery because of their nanoscale periodicity, permanent porosity, channel functionalization, and structural diversity. Despite these promising properties, the inherent structural features of even some of the best-performing MOFs make them moisture-sensitive and unstable in aqueous media, limiting their practical usefulness. This problem could be overcome by developing stable hydrophobic MOFs whose chemical composition is tuned to ensure that their metal–ligand bonds persist even in the presence of moisture and water. However, the design and fabrication of such hydrophobic MOFs pose a significant challenge. Reported syntheses of hydrophobic MOFs are critically summarized, highlighting issues relating to their design, characterization, and practical use. First, wetting of hydrophobic materials is introduced and the four main strategies for synthesizing hydrophobic MOFs are discussed. Afterward, critical challenges in quantifying the wettability of these hydrophobic porous surfaces and solutions to these challenges are discussed. Finally, the reported uses of hydrophobic MOFs in practical applications such as hydrocarbon storage/separation and their use in separating oil spills from water are summarized. Finally, the state of the art is summarized and promising future developments of hydrophobic MOFs are highlighted.

1. Introduction

Over the past two decades, novel hybrid nanoporous metal–organic frameworks (MOFs) have been developed as a new class of tunable hybrid materials comprised of ordered networks formed from organic ligands and metal cations. They are typically synthesized under mild conditions via coordination-directed self-assembly processes and are also known as metal–organic coordination networks and porous coordination polymers. Due to their high surface areas, large porosity, tunable pore sizes, and functionalities, MOFs have prospective applications in fields such as gas storage/separation, sensing or recognition, proton conduction, and magnetism. However, the advantageous unique structural features of even some of the best-performing MOFs are readily degraded because of their high moisture sensitivity, which may limit their practical applications.

Consequently, there is an ongoing search for highly hydrophobic, porous, sorbent materials to be employed in various large-scale applications in industry such as oil spill cleanup, hydrocarbon storage/separation, or water purification. Many academics, industrial scientists, and engineers have therefore conducted research on the fabrication of superhydrophobic surfaces, which involves hydrophobic surface modification and creating surface roughness on the micrometer- or nanoscale. Hydrophobic surfaces are defined as substrates with an apparent contact angle greater than 90° with respect to water. On superhydrophobic materials, water droplets have contact angles above 150° and show very low adhesion because the drops partially rest on an air cushion. The surface energy and roughness govern the wettability of hydrophobic surfaces. In general, lower surface energies and higher roughness are associated with larger contact angles, lower contact angle hysteresis, and robust superhydrophobicity. Because of their ultralow surface energies (10–20 mN m⁻¹), alkyl-based or fluorinated compounds are commonly used as hydrophobic modifiers to prepare surfaces with high intrinsic contact angles (>90°).

Recently, few methods have been developed for synthesizing hydrophobic MOFs including both pristine and composite systems. This review offers a comprehensive overview of the state of the art in hydrophobic MOF synthesis and the field's challenges and opportunities. Various synthetic strategies for preparing hydrophobic MOFs and their composites are introduced. We discuss the basics of wetting and critical challenges in the characterization of these hydrophobic materials. The potential applications of hydrophobic MOFs and related systems.
composites in hydrocarbon separation, water purification, oil spill cleanup, and catalysis are then elucidated. Finally, we offer perspectives on future directions for this promising field.

2. Wettability of (MOF) Surfaces

2.1. Describing Wettability: The Young Equation

Wettability determines the adhesion of droplets to window panes, paint to cars, and ice aggregation on airplanes. Wettabilibty is commonly tuned in printing, microfluidics, and heat transfer applications and also in MOF fabrication. Many natural surfaces such as the wings of insects and birds have unique nonwetting properties that are essential to their function.

The degree of wetting of a drop on a surface is determined by the interfacial tensions between the phases in contact, namely, the liquid, solid, and gas (air). The fundamental equation correlating the contact angle of a droplet with its interfacial tensions on an ideally flat, homogenous, solid surface was developed by Thomas Young in 1805:

\[ \cos \theta = \gamma_{SL} \cos \theta_{0} = \frac{\gamma_{LG} \cos \theta_{0} + \gamma_{SL}}{\gamma_{SG}} \]

Here, \( \gamma_{SG}, \gamma_{SL} \), and \( \gamma_{LG} \) are the solid–gas, solid–liquid, and liquid–gas interfacial tensions, respectively. The angle \( \theta \) is called the Young or intrinsic contact angle and is measured at the three-phase contact line where the liquid, solid, and gas phases meet. The Young equation describes the balance of forces acting parallel to the solid surface at the three-phase contact line in terms of surface tensions. It should be noted that all interfacial tensions are measured in units of force per unit length.

Surfaces with a water contact angle below 90° are considered hydrophilic, while those with water contact angles above 90° are considered to be hydrophobic (Figure 1a). Consequently, MOFs that show water contact angles above 90° are regarded as hydrophobic.

Young's equation cannot be used to describe the contact angle of a sessile drop on a rough or inhomogeneous surface like MOFs or MOF composites consisting of different materials because the force balance at the three-phase contact line is affected by surface roughness or inhomogeneities. More complex approaches taking roughness and heterogeneities into account are needed.

2.2. Wetting of Rough Surfaces: The Wenzel Equation

To account for surface roughness (Figure 2a), the roughness factor \( R \) was introduced by Wenzel. The roughness factor is the ratio of the actual surface area divided by the macroscopically apparent surface area and is thus larger than unity. The roughness factor \( R \) usually ranges between 1 and 2 but should not exceed 1/\( \cos \theta \) as \( \cos \theta_{w} \) cannot be larger than 1. The contact angle on a rough substrate is given by the Wenzel equation:

\[ \cos \theta_{w} = R \cdot \cos \theta \]

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Here, $\theta$ is the apparent contact angle a drop forms on a rough surface, i.e., on a length scale much larger than the surface roughness or protrusions, and $\theta$ is the material’s Young contact angle. In the Wenzel state, the liquid penetrates the rough surface’s pores. The introduction of surface roughness amplifies the material’s intrinsic wetting properties: it increases the contact angle if the surface is hydrophobic, and reduces the contact angle (or, in extreme cases, causes complete wetting) if the surface is hydrophilic.

### 2.3. Wetting of Heterogeneous Surfaces: The Cassie–Baxter Equation

The wetting of composite surfaces consisting of different materials can be described using the so-called Cassie–Baxter equation: \[ \cos \theta_c = \sum_i \phi_i \cos \theta_i \] (3)

### 2.4. Superhydrophobic Surfaces

Extremely hydrophobic surfaces on which water droplets adopt the Cassie state (contact angle >150°) and easily roll off while the surface is tilted by a few degrees (<10°) are known as superhydrophobic surfaces. The first artificial superhydrophobic surfaces were described over 50 years ago. In the late 1990s, the biologists Barthlott and Neinhuis analyzed and described the superhydrophobicity of various plants based on their microscopic structure. These authors’ groundbreaking publications prompted a substantial increase in academic and industrial research on artificial superhydrophobic surfaces. Natural superhydrophobic surfaces are found on the leaves of various plants such as the lotus and the body parts of some insects (e.g., the legs of water striders), among others. Super-hydrophobicity is often referred to as the lotus effect. Besides super-repellency, these surfaces are known for their exceptional self-cleaning properties. They have been used in various applications including anti-icing, anti-biofouling, drag reduction, gas exchange, and oil/water separation.

All surfaces of this type have two distinctive features: a high surface roughness on the micrometer- and/or nanoscale and a low surface energy, i.e., a hydrophobic surface with an intrinsic contact angle of close to 90° or above. The liquid–solid contact area is low, often below 10% of the total composite interface. Consequently, water droplets generally adhere poorly to these surfaces and roll off easily. Methods for preparing superhydrophobic surfaces include deposition of nanoparticulate coatings by spray or dip coating, candle soot deposition, lithography, chemical etching, plasma etching.
and electrospinning. Shortly after the emergence of hydrophobic MOFs, the first superhydrophobic MOF surfaces were reported. These materials either have an intrinsically hydrophobic and rough (micro-) structure or are formed by coating hydrophobic MOFs onto a rough substrate (for more details, see Section 3).

2.5. Surface Tension and Energy

The interfacial tension $\gamma$ can be interpreted as the work $\mathrm{d}W$ required to generate a new interfacial area $\mathrm{d}A$

$$\gamma = \frac{\mathrm{d}W}{\mathrm{d}A}$$

It takes units of energy per area (J m$^{-2}$) or force per unit length (N m$^{-1}$). It should be noted that the term “surface energy” is preferred for solids but “interfacial tension” or “surface tension” are more commonly used for liquids.

Molecules in the bulk are strongly attracted to one another because of dispersion forces, electrostatic interactions, and hydrogen bonds. At the surface, parts of these interactions are absent. Unlike molecules in the bulk, surface molecules are not completely surrounded by other molecules of the same type. Therefore, the transport of molecules from the bulk to the surface to increase the material’s surface area requires an input of energy to break intermolecular bonds. This energy is the surface energy. Liquids’ surface tensions are generally between 20 and 80 mN m$^{-1}$.[98] For instance, water has a surface tension of 72.5 mN m$^{-1}$ at 20 °C. However, some fluorinated liquids have surface tensions as low as 12 mN m$^{-1}$.[148]

Liquid surface tensions are easily measured with tensiometers utilizing a du Noüy ring or a Wilhelmy plate, or using the sessile or pendant drop method.[98] Measuring the surface energy of solids is less straightforward because the work required to deform a solid cannot easily be separated from that required to create new surface area. Therefore, surface energies are mostly measured indirectly. Most methods for determining a solid’s surface energy rely on the measurement of contact angles for liquids with different surface tensions. Methods of this kind include the Zisman plot,[151] Fowkes,[152] and Owens–Wendt–Rabel–Kaelble (OWRK) methods. However, these approaches are only applicable to materials with smooth, flat surfaces and cannot be applied to MOFs.

Solid surface energies can be as low as 6 mN m$^{-1}$ and as high as several thousand mN m$^{-1}$.[156–158] Metals, metal oxides, and glasses have large surface energies due to their strong (polar) intermolecular bonds, and can form strong interactions with polar liquids such as water. Conversely, low surface energy solids are nonpolar. Therefore, the intermolecular interactions between water molecules are stronger than those between water molecules and the surface. Thus, water droplets on such surfaces show high contact angles to minimize the area of contact with the solid surface. Highly fluorinated surfaces have particularly low surface energies. An ideal surface fully covered with $-\text{CF}_3$ groups would have the lowest possible surface energy (6–7 mN m$^{-1}$).[158] Exchanging even one fluorine atom per $-\text{CF}_3$ group for hydrogen ($-\text{CF}_2\text{H}$) would raise the surface energy to 15 mN m$^{-1}$, and further exchange of fluorine for hydrogen would yield even higher

Figure 3. Natural and artificial superhydrophobic surfaces. a) Photograph of a lotus leaf. b), c) Micro- and nanostructure of the lotus leaf observed by scanning electron microscopy (SEM). Reproduced with permission.[115] Copyright 2011, Beilstein-Institut (CC BY 2.0). d) Model superhydrophobic surface consisting of SU-8 micropillar arrays. Reproduced with permission.[116] Copyright 2014, Royal Society of Chemistry. e) Artificial lotus-like superhydrophobic surface consisting of raspberry-like nanoparticles. Reproduced with permission.[117] Copyright 2011, Royal Society of Chemistry.
surface energies (Table 1). It was also found that surfaces covered with terminal groups (−CF, −CH) have lower surface energies than their nonterminal counterparts (−CF−CF−, −CH−CH−).[156]

Thus, to obtain low surface energies and high hydrophobicity, a surface or MOF material should have a high content of fluorocarbon compounds or at least large nonpolar hydrocarbon fragments. Section 3 discusses how to synthetically incorporate such low-energy groups and fragments into MOFs.

2.6. Surface Energy Measurements by Inverse Gas Chromatography

Determining the surface energy of microcrystalline materials such as MOF powders is a major challenge in surface science. As noted earlier, the contact angle–based techniques have several limitations relating to surface roughness and the presence of micropores and microcracks, which are difficult to control and can strongly affect measurement outcomes. Inverse gas chromatography (iGC) is an experimental technique that was pioneered in the 1950s and has matured into a widely used method for studying the surface properties of solids.[159,160] It is based on the dynamic exposure of a bed of powder to organic vapors. The vapors’ retention times are measured, taking into account the temperature, vapor tension, and flow rate (Figure 4). Linear alkanes are typically used to estimate the dispersion part of the surface energy, and it is assumed that the total surface energy \( \gamma_{SG} \) has two components: the dispersion \( \gamma_D \) and a specific/acid–base \( \gamma_{AB} \) component

\[
\gamma_{SG} = \gamma_D + \gamma_{AB}
\]

The measured net retention time corresponds to a specific net retention volume \( V \), which is related to the free energy of adsorption \( \Delta G_{ad} \) of a specific probe on the solid surface

\[
-\Delta G_{ad} = RT \ln V + \text{constant}
\]

Here, \( T \) the temperature and \( R \) is the universal gas constant. The constant term is related to a given reference state.[160] The relationship between the dispersion component of the surface energy \( \gamma_D (\gamma_{D,SG} \text{ for a solid–gas interface}) \) and the net retention volume can be derived by noting that the adhesion work \( W_a \) is related to the free energy of adsorption, applying Fowkes’ method[152]

\[
RT \ln V + \text{constant} = N_A r W_a = N_A r 2 \sqrt{\gamma_{D,SG} \gamma_{D,LG}}
\]

Here, \( N_A \) is the Avogadro constant, \( r \) is the probe cross section, and \( \gamma_{D,LG} \) is the surface tension of the liquid probe. Using \( n \)-alkane probes, Schultz et al.[161] showed that \( RT \ln V \) depends linearly on \( N_A r \sqrt{\gamma_{D,LG}} \), and Dorris and Gray[162] demonstrated that \( RT \ln V \) is linearly dependent on the alkane chain length (i.e., the number of carbon atoms, \#C, in the chain). If \( RT \ln V \) is plotted against \( N_A r \sqrt{\gamma_{D,LG}} \) or \#C using \( n \)-alkane probes (usually \( n \)-hexane, \( n \)-heptane, \( n \)-octane, and \( n \)-nonane), the dispersion surface energy \( \gamma_D \) can be determined from the slope of a linear fit of the resulting graph (Figure 4b). The specific/acid–base \( \gamma_{AB} \) component of the surface free energy can be determined by performing iGC experiments with a probe bearing an acidic

Table 1. Surface energies for various surface compositions and surfaces at 20 °C.[156–158]

| Surface composition/surface | Surface energy [mN m⁻¹] |
|-----------------------------|-------------------------|
| −CF₃                        | 6–7                     |
| −CF₂H                       | 15                      |
| −CF₂−CF₂−                   | 18                      |
| −CF₂−CH₂−                   | 25                      |
| −CH₃                        | 20–24                   |
| −CH₂−CH₂−                   | 31                      |
| −CH− (phenyl ring edge)     | 35                      |
| −CCl₂−CH₂−                  | 40                      |
| MgO (100)                   | 1200                    |
| Silicon (111)               | 1240                    |
and/or basic functional group. The specific $\gamma_{AB}$ component of $-\Delta G_{ad}$ is derived by subtracting the dispersion component (determined using n-alkane probes) from the measured $RT \ln V$ for the specific acid–base probe (Figure 4c). By using a range of specific probes, one can study the surface’s acid–base properties. It should be noted that various acid–base scales, and hence acid ($\gamma_i$) and base ($\gamma_j$) parameters, can be used for probes; commonly used scales include those of van Oss, Chaudhury, and Good (vOCG),[163] and Della Volpe.[164] Results obtained using different scales may differ substantially. Consequently, calculated acid–base surface energy profiles should only be used for relative comparisons of the acid–base properties of similar materials.[166] In addition, the measurements are performed at defined surface coverage ($\phi$) values, making it possible to create profiles of $\gamma_0$ (and $\gamma_{AB}$, $\gamma_i$, $\gamma_j$) as a function of $\phi$. Such profiles provide information about surface heterogeneity.[165] $\gamma_0$ values drop with increasing surface coverage because probes adsorb preferentially at sites of high surface energy, which usually correspond to structural or chemical surface defects. For instance, steps and cavities on the surface are high-energy adsorption sites in graphite/multilayer graphene.[166] The $\gamma_0$ versus $\phi$ profile also scales with the size of graphene flakes[167] and may provide valuable information that can be related to the material’s rheological, structural, and (electro)catalytic properties.[168]

The iGC technique can also provide other important information about surface properties, including isosteric adsorption enthalpies and entropies, the adsorption energy distribution, and specific surface areas for various probes. Recent reviews have discussed these applications in detail.[159,160,165] iGC measurements provide information about surface properties of powdered materials. The success of iGC in other fields of materials science suggests that it will be similarly useful for studying the surface properties of MOFs. In particular, it could be used to determine the surface energy of MOFs and its dispersion and acid–base components in order to estimate their interfacial tensions and hence their hydrophilicity/hydrophobicity.

### 2.7. Contact Angle Measurements

Hydrophobic and superhydrophobic surfaces are typically characterized by performing contact angle measurements with a goniometer. A liquid drop is deposited on the surface and observed using a camera from the side. The drop profiles of static and moving drops are then recorded.[169]

The contact angle is extracted from a fit of the drop profile. The fitting method used in this process should be chosen with care because it can affect the extracted contact angle. **Figure 5** shows the fitting of a droplet using four common fitting methods: ellipse, circle, tangent, and Young–Laplace fitting. These methods yield very different results (ranging from roughly $150^\circ$ to $180^\circ$) for the same recording.[170] The circle and the Young–Laplace fits assume that the contact angles at the right and left sides of the drop are identical. This is rarely true for rough surfaces because the three-phase contact line is pinned at protrusions. The elliptical and tangent fits permit different angles on the left- and right-hand sides of the drop profile. The tangent fit tries to match the slope of the meniscus close to the three-phase contact line. Several other parameters can influence contact angle measurements. For example, for MOFs it is important that the material is properly dried, and no humidity is adsorbed. Adsorbed molecules can change the surface energy or form a prewetting layer, and thus influence the contact angles. The camera settings can also influence the results; particularly important parameters include the illumination, brightness, contrast, and gamma. It is generally difficult to measure contact angles above $150^\circ$ because the narrow gap between the liquid and the solid greatly reduces the amount of light passing through the gap and hitting the camera, making it difficult to identify the real contact line. Conventional optical methods also typically cannot resolve details underneath droplets, such as whether the droplet is in the Cassie or Wenzel state.[120,170] This becomes even more severe for drop sizes above $>10 \mu$L where gravity influences the drop’s shape. It has recently been shown that contact angles can be measured with greatly improved accuracy using techniques such as laser scanning confocal microscopy.[171–173] Here, the lower side of the droplet is scanned using a laser. Reflected light at the liquid–air interface as well as fluorescence from the bulk liquid is captured using detectors. A 2D or 3D representation of the droplet can be obtained. However, this technique requires a transparent substrate.

### 2.8. Contact Angle Hysteresis

On real surfaces with finite roughness and heterogeneity, one must discriminate between the so-called static, advancing, and receding contact angles.[174,175] The static contact angle can
be measured directly after depositing the droplet on the surface. However, due to pinning of the three-phase contact line, surface deformation, evaporation, or slow spreading of the liquid, the static contact angle may change over time. Contact angles can also be influenced by the way the drop is deposited on the surface. The static contact angle is thus not a clearly defined quantity despite its importance for surface characterization. The static contact angle lies between the advancing and receding contact angles, which can be measured using two methods.

The first involves slow adding liquid to or removing liquid from a deposited droplet at a rate of around 0.5 \( \mu \text{L s}^{-1} \) or less (Figure 6). As liquid is added, the droplet expands and its contact angle increases. When the contact angle reaches the advancing contact angle \( \theta_{\text{Adv}} \), the contact line advances. Similarly, as liquid is removed from the droplet, it contacts, and its contact angle decreases until it reaches the receding contact angle \( \theta_{\text{Rec}} \) and the contact line recedes. The difference between the advancing and receding contact angles is defined as the contact angle hysteresis (CAH)\[169,175,176\]

\[
\text{CAH} = \theta_{\text{Adv}} - \theta_{\text{Rec}}
\] (9)

Another way to determine the advancing and receding contact angles is to deposit a droplet on a surface and gradually increase the surface's inclination \( \alpha \) (Figure 7a,b). At the moment immediately before the droplet starts to slide or roll down the inclined surface, the contact angles on the lower and upper sides of the droplet are equal to the advancing and receding contact angles, respectively. However, the droplet's adhesion to the surface is often too high for it to roll off, making it impossible to measure the advancing and receding angles using this method.\[120,177\]

Several factors and phenomena can cause contact angle hysteresis. One is surface roughness, whose effects can be explained by considering a simple case involving a droplet that is advancing over a surface with a microscopic protrusion or bump (Figure 8, left to right from position A). The droplet advances with an intrinsic contact angle of 90° until it reaches the protrusion. It then jumps to the middle of the protrusion, where it can again assume the intrinsic contact angle of 90° (Figure 8, position B). To advance further, the droplet's contact angle must exceed 90° (Figure 8, position C). Therefore, the contact line remains pinned until the contact angle at the droplet's front side exceeds the advancing contact angle \( \theta_{\text{Adv}} \). After overcoming the protrusion, the contact line can spread further, restoring its intrinsic contact angle of 90°. The same effect occurs for the receding contact line but in the opposite direction, leading to contact angles below 90°.\[98\]

The roughness of a surface can be understood as a measure of its density of microscopic protrusions. Consequently, surfaces of different roughness may exhibit different levels of contact angle hysteresis. However, the effect of roughness depends on the wetting state. For surfaces in the Wenzel state, surface roughness greatly increases contact angle hysteresis, \( \theta_{\text{Adv}} - \theta_{\text{Rec}} > 30° \) (the example shown in Figure 8 resembles the Wenzel state). For superhydrophobic surfaces, i.e., those on which droplets exist in the Cassie–Baxter state, contact angle hysteresis is typically below ≈20°.

Figure 6. Advancing and receding contact angles can be measured by adding and removing liquid from a droplet. a) As liquid is added to the droplet, it expands and the contact angle increases. The contact line starts advancing when the contact angle exceeds the critical advancing contact angle. b) As liquid is removed from the droplet, it shrinks and the contact angle decreases. The contact line starts receding when the contact angle falls below the critical receding angle. Reproduced with permission.\[176\] Copyright 2017, Wiley-VCH.

Figure 7. a) Illustration of a drop on a substrate tilted by the inclination angle \( \alpha \). The contact angles on the droplet's lower and upper sides are equal to the advancing and receding contact angles immediately before the droplet starts to slide/roll and as it is sliding/rolling. b) Experimental comparison between the static contact angle and the advancing/receding contact angles on an inclined substrate. Reproduced with permission.\[177\] Copyright 2009, American Chemical Society.
Another cause of contact angle hysteresis is surface inhomogeneity (either structural or chemical). Like surface roughness, inhomogeneities can cause pinning of the contact line. The advancing contact line may be pinned on areas exhibiting a higher lyophobicity (liquid repellency), whereas the receding contact line may be pinned on areas exhibiting a lower lyophobicity and thus a higher lyophilicity.

2.9. Roll-Off Angle Measurements

In addition to contact angle measurements, roll-off angle experiments (sometimes called sliding angle experiments) are commonly conducted to determine a substrate’s wettability. A droplet is deposited on the surface of interest, and the surface is then slowly tilted until the drop rolls off (Figure 7), which will occur if the droplet’s adhesion to the substrate is low enough to be overcome by the gravimetric force acting on it. Therefore, the droplet volume affects the tilting angle. Volumes of 5–10 µL are typically used. It should be noted that the term sliding angle may be inappropriate because it has been shown that droplets do not slide but roll. In particular, superhydrophobic surfaces and liquid-like surfaces show low roll-off angles. The roll-off angle is related to the contact angle hysteresis according to the following equation:

\[ F_{RA} = mg \sin \alpha = kw \gamma (\cos \theta_{Rec} - \cos \theta_{Adv}) \]  

(10)

Here, \( m = \rho V \) is the droplet’s mass, \( g \) is the gravimetric acceleration, and \( \alpha \) is the inclination of the surface (i.e., the roll-off angle). The factor \( k \) depends on the shape of the three-phase contact line and is usually taken to be 1. The contact width \( w \) of the droplet is measured perpendicular to the droplet’s movement. The contact angle hysteresis appears in the \( (\cos \theta_{Rec} - \cos \theta_{Adv}) \) term. Consequently, a low contact angle hysteresis will generate a low roll-off or sliding angle. Roll-off angle measurements have the advantage of being fast and more reproducible than contact angle measurements because they do not depend on the lighting and the choice of baseline and require no fitting.

3. Synthesis of Hydrophobic MOF Materials

Considerable research effort has been dedicated to the synthesis of numerous pristine hydrophobic metal–organic frameworks and composites, as shown in Figure 9. This section reviews the strategies that have been used to prepare these materials. The first approach involves decorating the ligands of the MOF with hydrophobic fluorine-containing and/or (long-chain) alkyl substituents linkers to alter the MOF’s surface properties (Figure 9a). This strategy promotes stability in liquid water by creating a hydrophobic outer surface that inhibits the diffusion of water molecules into the pores of MOF. The second approach involves so-called postsynthetic strategies, like hydrophobic responsive groups are grafted onto preformed MOFs (Figure 9b).

Although both strategies can effectively exclude water from the MOF’s pores, they also render the inherent porosity of resultant MOFs largely inaccessible, because of the sterically bulk of the groups attached to the ligand/outer surface. An alternative approach that generates highly hydrophobic outer surfaces but preserves internal porosity involves creating high nano- to micrometer surface roughness (Figure 9c). Although this approach is facile and applicable to many MOFs, it has mainly proved effective with microporous materials; reports describing its successful application to mesoporous MOFs are scarce. The most common way of synthesizing mesoporous MOFs involves using large organic linkers, but such frameworks often suffer from low thermal and mechanical stability as well as self-catenation. Consequently, there is a clear need to develop rational methods for fabricating robust hierarchical hydrophobic MOFs with tailored structures and wetting of surface areas. One way to avoid the limitations associated with tailoring the functional properties of hydrophobic MOFs solely by varying the combinations of nodes and linkers is to make hybrid of MOFs with other materials (i.e., 2D materials, polymers, etc.). The final approach involves the synthesis of hierarchical micro-mesoporous composites based on the hybridization of microporous MOFs intercalated with hydrophobic 2D layers/membranes (Figure 9d). After the initial steps of the development of different hydrophobic MOF materials and composites, recent studies on hydrophobic MOFs have focused on some critical challenges in the measurement of hydrophobicity by various methods, and the issues they create in practical applications.

3.1. Linker-Based Hydrophobic Metal–Organic Frameworks

Eddaoudi et al. introduced the principle of isoreticular synthesis in 2002. This principle states that frameworks with identical topologies but different functionalities pinned to the ligand backbone can be prepared by using ligands having different functionalities but identical connectivity. Since then, a plethora of different ligands have been prepared and used for the de novo synthesis of MOFs with tailored properties. Among other things, this approach has been used to introduce acidic sites or metal-chelating groups for catalysis, to modulate gas adsorption properties, or to confer flexibility. However, the attachment of overly large groups often alters the framework’s topology. There have been some efforts to induce hydrophobicity by incorporating ligands that are perfluorinated, possess fluorinated or alkyl side chains, or simply increase the surface corrugation and energy. The
preparation of ligands with alkyl chains and the use of perfluorinated ligands to construct MOFs have been explored by several groups. However, there are few reports describing the attachment of perfluorinated side chains, and very few in which the use of such side chains was a central aspect of the report.[190] Some representative hydrophobic ligands are listed in Table 2.

In 2007, Omary and coworkers described the superhydrophobic fluorous metal–organic frameworks FMOF-1 (Ag₄(Tz)₆) whose internal pores were linked with CF₃ groups. This framework is based on 3,5-bis(trifluoromethyl)-1,2,4-triazolate (Tz) organic linkers containing flexible CF₃ groups (Figure 10a). Later on, the authors reported FMOF-2 (Ag₄(Tz)₆).[59,195] The hydrophobicity of FMOF-1 was determined by water adsorption and comparison with the porous materials zeolite 5A and BPL carbon (Figure 10c). In contrast to zeolite 5A (significant water adsorption at a very low P/P₀ value (<0.1)) and BPL carbon (little uptake up to P/P₀ = 0.4, and significant uptake at P/P₀ = 0.8 with a typical type V hysteresis loop), FMOF-1 shows negligible uptake of water, even at saturation pressure. The large channels (1.2 nm x 0.8 nm) of FMOF-1 are inaccessible to water. Despite this, FMOF-1 adsorbs significant amounts of the hydrophobic hydrocarbons such as benzene, cyclohexane, n-hexane, toluene, and p-xylene (Figure 10b). FMOF-1 retains its powder crystal X-ray diffraction (PXRD) pattern even after soaking in water for several days, confirming its structural stability.

In 2013, Miljanic reported three perfluorinated Cu₂ paddlewheel MOFs incorporating the perfluorinated ligands H₂OFBPDC (2,2′,3,3′,5,5′,6,6′-octafluorobiphenyl-4,4′-dicarboxylic acid) and H₂PFBPTZ (5,5′-(perfluorobiphenyl-4,4′-diyl)bis(1H-tetrazole)) (Figure 11a).[74,77] Two frameworks using the H₂OFBPDC ligand were prepared, MOFF-1 (Cu₂(OFPBDC)₂(MeOH)₂) and MOFF-2 (Cu₂(OFPBDC)₂(DABCO); DABCO = diazabicyclo[2.2.2]-octane). The structures of these frameworks are shown in Figure 11a. MOFF-1 is prepared by combining H₂OFBPDC with Cu(NO₃)₂ under solvothermal conditions. Single-crystal X-ray diffraction (XRD) experiments revealed the formation of square grids of 2D Cu₂(OFPBDC)₂ layers capped by MeOH. The layers are aligned in a staggered fashion, with the Cu₂ paddlewheels above the void space of the adjacent layers, as also occurs in the nonfluorinated material MOF-118 (Figure 11b).[196] MOFF-2 features similar Cu₂(OFPBDC)₂ layers that are interconnected by DABCO pillars, generating a 3D framework (Figure 11c). Performing the same synthesis using the tetrazole-based linker H₂PFBPTZ results in the formation...
Table 2. Summary of hydrophobic MOFs/composites and applications.

| Ligand structure | Ligand abbreviation | MOF formula             | Responsible hydrophobicity                  | Contact angle [°] | Application                                                                 | Ref. |
|------------------|---------------------|-------------------------|--------------------------------------------|------------------|------------------------------------------------------------------------------|------|
| BDC2−-AM6        | MIL-53(Al)-AM6      | Al(OH)(BDC-AM6)         | Postsynthetic modification with alkyl chains | >150             | –                                                                            | [38] |
| Tz−              | FMOF-1              | Ag4Tz6                  | Perfluorinated ligand                      | –                | Hydrocarbon (C6–C8) storage                                                  | [59] |
| Tz−              | FMOF-2              | Ag4Tz4                  | Perfluorinated ligand                      | –                | Hydrocarbon (C6–C8) storage                                                  | [59] |
| OFBPDC2−         | MOFF-1              | Cu2(OFBPDC)2(MeOH)2     | Perfluorinated ligand                      | 108 ± 2          | –                                                                            | [74] |
| OFBPDC2−         | MOFF-2              | Cu2(OFBPDC)2(DABCO)     | Perfluorinated ligand                      | 151 ± 1          | –                                                                            | [74] |
| PFBPTZ2−         | MOFF-3              | Cu2(PFBPTZ)2(H2O)       | Perfluorinated aromatics                   | 135 ± 2          | –                                                                            | [74] |
| OPE-C182−        | NMOF-1              | Zn(OPE-C18)(H2O)2       | Ligand with alkyl chain                    | 160–162          | Self-cleaning                                                                | [147]|
| PEIP4−           | UPC-21              | Cu3(PEIP)1.5(H2O)3      | Hydrophobic ligand with extended aromatic system | 145 ± 1          | Hydrocarbon separation, oil spill separation from water                     | [199]|
| eIm−             | MAF-6               | RHO-Zn(eIm)2           | Hydrophobic internal pore and external crystal surface | 143 ± 1          | C6–C10 hydrocarbons                                                          | [56] |
| BTMB3−           | PESD-1              | Zn4(µ3-OH)2(BTMB)2     | Surface corrugation                        | 150              | Aromatic hydrocarbon storage                                                | [69] |
| mlm−             | HFGO@ZIF-8          | Hierarchical composite  | 162                                         | Oil–water separation, self-cleaning                                           | [211]|
| BTC5−            | FGO@MOG             | Hierarchical composite  | 150                                         | Oil–water separation                                                      | [212]|
| BTFPADB3−        | UHMOF-100/PDMS/PP   | Cu2(BTFPADB)2          | Fluorinated ligand                         | 176              | Aromatic hydrocarbon storage and oil–water separation                      | [84] |
Table 2. Continued.

| Ligand structure | Ligand abbreviation | MOF formula | Responsible hydrophobicity | Contact angle [°] | Application | Ref. |
|------------------|---------------------|-------------|---------------------------|------------------|-------------|-----|
| ![Image](image1.jpg) | HFPD<sup>4−</sup> | USTC-6 Cu<sub>2</sub>(HFPD) USTC-6@GO@sponge | Fluorinated ligand | 128 | Aromatic hydrocarbon storage Oil–water separation | [213] |
| ![Image](image2.jpg) | mlm<sup>−</sup> | SIM-2(C<sub>12</sub>) SIM-1 isostructural with ZIF-8 | Postsynthetic modification with alkyl chains | – | Catalysis Knoevenagel condensation | [71] |
| ![Image](image3.jpg) | BDC<sup>2−</sup>, 2,2′-DM-BIPY | SCUTC-18 | Linker functionalization | – | Toluene adsorption | [77] |
| ![Image](image4.jpg) | TPTC-OR<sup>−</sup> | Cu<sub>2</sub>(TPTC-OR) | Linker functionalization | – | Tuning moisture and thermal stability of MOFs | [91] |
| ![Image](image5.jpg) | NH<sub>2</sub>-BDC<sup>2−</sup> | UiO-66-NH<sub>2</sub>@MON-3 Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(NH<sub>2</sub>-BDC) <sub>12</sub> | Postsynthetic coating with microporous organic framework | 145 | Adsorption of organic compounds | [54] |
| ![Image](image6.jpg) | BTC<sup>3−</sup> | HKUST-1 Cu<sub>3</sub>(BTC)<sub>2</sub> | Postsynthetic coating with PDMS | 130 | Gas sorption catalysis | [60] |
| ![Image](image7.jpg) | BDC<sup>2−</sup> | UiO-66/Pd/PDMS Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(BDC)<sub>12</sub> | Postsynthetic coating with PDMS | 140 | Hydrogenation of styrene catalysis | [202] |
| ![Image](image8.jpg) | TCPP<sup>+</sup> | PCN-222(Fe)<sub>4</sub>-F<sub>7</sub> Zr<sub>6</sub>(OH)<sub>8</sub>(Fe-TCPP)<sub>4</sub> | Postsynthetic modification with perfluorinated alkyl chains | 135 | Catalysis | [226] |
| ![Image](image9.jpg) | BDC<sup>2−</sup> | MIL-101(Cr) Cr<sub>3</sub>O(OH)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>(BDC)<sub>12</sub> | Postsynthetic coating with silica | – | Catalysis | [49] |
| ![Image](image10.jpg) | DOBDC<sup>−</sup> | Ni<sub>2</sub>DOBDC | Postsynthetic modification with polymer chains (Pluronic P123) | – | Moisture stability | [44] |
of Cu(PFBPTZ)(H$_2$O). The bridging of Cu(H$_2$O) chains by the tetrazolate ligands in this framework gives rise to 1D channels similar to those seen in the dicarboxylate-based MOFs MIL-47 and MIL-53 (Figure 11d). [197, 198] To estimate the hydrophobic/hydrophilic properties of MOFF-1, MOFF-2, and MOFF-3, their water contact angles were measured before and after solvent removal from the pore space. MOFF-1 has water contact angles of 0° and 108° ± 2° before and after solvent removal, respectively. MOFF-2 crystallizes without solvent in the pore space and has a H$_2$O contact angle of 151° ± 1°. Finally, MOFF-3 has similar contact angles of 134° ± 1° and 135° ± 2° in the solvated and desolvated states, respectively.

| Ligand structure | Ligand abbreviation | MOF formula | Responsible hydrophobicity | Contact angle [°] | Application | Ref. |
|------------------|---------------------|-------------|---------------------------|------------------|-------------|-----|
| BTC$^{3-}$       | HKUST-1             | Cu$_3$(BTC)$_2$ | Postsynthetic coating with polyvinylidene difluoride (PVDF) | –                | Ammonia adsorption | [82] |
| BDC$^{2-}$       | MOF-5               | Zn$_4$(BDC)$_4$ | Postsynthetic modification with polymer (polynaphthylene) | –                | Carbon capture | [202] |
| tdc$^{2-}$ = 2,5-thiophenedicarboxylate | DUT-67-Pba | Postsynthetic modification with perfluorinated alkyl chains | 119 | Stability enhancement | [46] |
| TBAPy = 1,3,6,8-tetrakis(p-benzoate)pyrene | Pd@Fr-NU-1000 | Postsynthetic modification with perfluorinated alkyl chains | – | Catalysis | [50] |
| 1,2-Bis-1,2-dicarba-closo-dodecarborane (oCB-L) | [Zn$_4$(µ$_4$-bdc)$_2$(µ$_2$-cCB-L)$_2$(µ$_3$-O)$_2$(DMF)$_2$]·4DMF | Hydrophobic carborane-based linker | 140 | – | [70] |
| 2,4,6-Tr(pyridin-4-yl)-1,3,5-triazine | MFOF-1 | Fluoride- and sulfate-bridged cubane-type tetranuclear cobalt clusters | – | Aromatic vapor adsorption | [86] |
| mIm$^{-}$       | ZIF-8/carbon nitride foam | Postsynthetic coating with carbon nitride foam | 139 | Oil–water separation and chemical fixation of CO$_2$ | [68] |
| asp$^{2-}$       | Ni$_2$(l-asp)$_2$bipy@PDMS | Postsynthetic coating with PDMS | 130 | High flux of H$_2$O and acceptable separation factor | [203] |
| Benzimidazole    | ZIF-7 | Linker functionalization | 151 | Oil spill separation | [80] |
| BDC$^{2-}$       | UiO-66/mesh membranes | Postsynthetic coating with membrane | – | Oil–water separation | [191] |

Table 2. Continued.
In 2016, Maji and coworkers reported the superhydrophobic nanoscale coordination polymer Zn(OPE-C₁₈)(H₂O)₂ (NMOF-1) using an octadecoxy-functionalized organic linker oligo(p-phenyleneethynylene)dicarboxylate (OPE-C₁₈²⁻) and Zn²⁺ (Figure 12a).⁴ Using several characterization methods, the authors showed that this material forms 3D supramolecular framework via van der Waals interactions between adjacent C₁₈ alkyl chains. To investigate the hydrophobic behavior of NMOF-1, the authors performed benzene and water adsorption isotherms at room temperature (Figure 12b). It is worth noting that NMOF-1 has a contact angle of 162°, showing superhydrophobicity. This is supported by advancing and receding contact angle measurements (Figure 12c–e).

Sun and coworkers also reported a superhydrophobic MOF named UPC-21 (Cu₃(PEIP)₁·₅(H₂O)₃), comprised of a pentiptycene-based 4,4’-(pentiptycene-6,13-diyl-bis(ethyne-2,1-diyl)-isophthalic acid (H₄PEIP) linker and copper nitrate under solvothermal conditions (Figure 13a).⁵ The framework’s structure features 6 PEIP⁴⁻ ligands connecting 12 Cu₂ paddlewheel secondary building units (SBUs) to generate a Cu₂₄(PEIP)₆ tubular cage in which 6 paddlewheel SBUs arrange on the equator and 3 Cu₂ paddlewheels form triangular bottom and top faces (Figure 13b). Many of the benzene rings of PEIP⁴⁻ point into the cage, creating a hydrophobic cavity. The spindle-shaped cages are interconnected, giving rise to a 3D porous framework. The contact angles for UPC-21 are 145° ± 1°, suggesting a highly hydrophobic/oleophilic character owing to its multiaromatic carbon units in the framework (Figure 13c). Contact angle measurements were performed by placing water dropwise onto the surface of UPC-21 via syringe. If a substrate bearing UPC-21 powder was inclined after placing a droplet of water on its surface, a UPC-21-covered water droplet (a “liquid marble”) was formed; this is known to be a common occurrence with hydrophobic powders. The authors also measured UPC-21’s contact angles with crude oil diluted with hexane. The oil was adsorbed rapidly, confirming the material’s oleophilicity (Figure 13d).

3.2. Induction of Hydrophobicity by Postsynthetic Modification

Another way to enhance the stability of moisture- or water-sensitive MOFs is functionalization with hydrophobic fluoro- and/or alkyl/aromatic groups. This approach has the
advantages that synthetic pathways to known MOFs can be used and that some of their properties are retained when their wettability is changed. Two variants of this approach can be distinguished: functionalization with organic substituents and coating with a protective hydrophobic layer. The first variant requires a framework bearing reactive positions, either in the form of reactive substituents on the ligand that can undergo organic reactions under mild conditions (e.g., $\text{NH}_2$ or substituted with $\text{N}_3$ substituents that can undergo esterification or click reactions, respectively) or the existence of coordinatively unsaturated metals, that permit the installation of organic molecules (e.g., via solvent-assisted linker installation). The second variant entails adding polymeric layers over the outer surface of the MOF and requires that the material is stable toward the coating.

In 2011, Nguyen and Cohen reported the introduction of hydrophobicity into the otherwise moisture-labile IRMOF-3 ($\text{Zn}_4\text{O}(\text{NH}_2\text{-BDC})_3$; $\text{NH}_2\text{-BDC}^{2-} = 2\text{-amino-1,4-benzenedicarboxylate}$) via postsynthetic modification. The exposed framework’s amino groups were esterified with various carboxylic acid anhydrides with different alkyl chain lengths and degrees of branching. The parent frameworks IRMOF-1 ($\text{Zn}_4\text{O}(\text{BDC})_3$; $\text{BDC}^{2-} = 1,4\text{-benzenedicarboxylate}$) and IRMOF-3 are hydrophilic, with water contact angles of $\approx 0^\circ$ (Figure 14a). Functionalization with acetic anhydride (IRMOF-3-AM1), propionic anhydride (IRMOF-3-AM2), or butyric anhydride (IRMOF-3-AM3) also yielded hydrophilic materials with contact angles of $\approx 0^\circ$ (the structural details of these compounds are provided in Figure 14b). However, functionalization with valeric anhydride, which has a longer COOC$_4$H$_9$ side chain, yielded the material IRMOF-3-AM4, which has a contact angle above 116° and is thus moderately hydrophobic. The stability of these samples was assessed by performing powder XRD measurements after exposure to ambient air (Figure 14c). The nonfunctionalized IRMOF-1 exhibited a striking decrease in crystallinity after just 1 day, together with the formation of a parasitic phase, MOF-69c.

The inclusion of hydrophobic units increases stability of the IRMOF structure under ambient atmosphere. This is
Figure 12. a) Synthesis of NMOF-1 comprised of Zn$^{2+}$ and OPE-C$_{18}$$^{2-}$. b) Solvent vapor adsorption isotherms of NMOF-1 for water (red circles) and benzene (blue triangles) measured at 298 K. c) The material was coated on glass substrates and the resulting water contact angle amounts to 160–162° (circle fitting mode). d) Advancing and e) receding water contact angles of NMOF-1. Reproduced with permission.[147] Copyright 2016, Royal Society of Chemistry.

Figure 13. a) Structure of ligand H$_4$PEIP of UPC-21. b) View of 3D porous framework constructed with spindle-shaped cages. c) Top: optical image of water droplet shows its superhydrophobic behavior; bottom: quick oil uptake of MOF reveals oleophilic nature. d) UPC-21 sinking in ethyl acetate and floating in water. Reproduced with permission.[199] Copyright 2016, Royal Society of Chemistry.
confirmed by PXRD, which shows retention of the initial pattern for the esterified derivatives even after 4 days (Figure 14c–e). The applicability of this methodology to other systems was confirmed by transferring it to the MIL-53(Al) [Al(OH)(BDC)] structure. The amine-tagged MIL-53(Al)-NH$_2$ (Al(OH)(NH$_2$-BDC)) was modified by using three different alkyl anhydrides such as MIL-53(Al)-AM1, MIL-53(Al)-AM4, and MIL-53(Al)-AM6. The contact angle measurements show that unfunctionalized MIL-53(Al), MIL-53(Al)-NH$_2$, and MIL-53(Al)-AM1 were all hydrophilic (contact angles ≈0°) and functionalized MIL-53(Al)-AM4 and MIL-53(Al)-AM6 possess superhydrophobic behavior (contact angles above 150°).

In 2014, Hu and coworkers reported a postsynthetic route by modifying the surfaces of MOF materials with hydrophobic polydimethylsiloxane (PDMS) to enhance their water and moisture resistance using a facile vapor deposition technique (Figure 15a). The volatile PDMS precursor (PDMS stamp) is placed in a reactor with the pristine MOF powder, resulting in the formation of a hydrophobic PDMS coating. The authors surveyed three representative MOFs having three different metal SBUs, IRMOF-1 with Zn$_2$O clusters, HKUST-1 (Cu$_3$(BTC)$_2$; H$_3$BTC = 1,3,5-benzenetricarboxylate) with Cu$_2$ paddlewheel SBUs, and Zn$_2$(BDC)$_2$(DABCO) with DABCO pillared Zn$_2$ paddlewheels. IRMOF-1, HKUST-1, and Zn$_2$(BDC)$_2$(DABCO) are all hydrophilic and water-sensitive, with water contact angles close to 0°. However, the PDMS-coated derivatives of these MOFs exhibited water contact angles of 130° ± 2°, demonstrating their hydrophobicity. It should be noted that the hydrophobic behavior of these representative MOFs after coating remained unchanged, even after prolonged exposure to ambient air. To verify the presence of the PDMS layer on these representative MOFs, the distribution of elements within PDMS-coated IRMOF-1 was studied by acquiring a composition line-scan profile (Figure 15b,c). It shows homogeneous distribution of silica throughout the coated MOF, with a Si/Zn atomic ratio of ≈4.1%. Furthermore, scanning electron microscopy (SEM) images revealed that IRMOF-1 crystals have a regular cubic morphology with smooth surfaces. However, after exposure to a humid environment for 2 days, the material exhibited severe deterioration. The Brunauer–Emmet–Teller (BET) surface areas of pristine and PDMS-coated IRMOF-1 were calculated to be 3118 and 3159 m$^2$ g$^{-1}$, respectively. In 2016, Jiang and coworkers used this PDMS coating procedure to modify the surface hydrophobicity of Pd/UiO-66 (Zr$_6$O$_4$(OH)$_4$(BDC)$_6$), a composite containing an MOF and stabilized Pd nanoparticles (Figure 15d). The water contact angle of Pd/UiO-66 is 25°, and increases significantly upon PDMS coating to 115° (10 min vapor-phase coating) and 140° (20 min vapor-phase coating) (Figure 15e–h).

### 3.3. Introduction of External Surface Corrugation by the Use of a Hydrophobic Unit

Despite improving the moisture or water stability of MOFs, the approaches described earlier have some crucial drawbacks, such as...
as reduced porosity, complex synthetic procedures, or the need for advanced instrumentation. An alternative route for creating highly hydrophobic exterior surfaces without hampering the material’s internal porosity is the creation of rough surfaces, so-called corrugation, on the nano- to micrometer length scale. In 2014, Kitagawa and coworkers reported superhydrophobic MOF materials by using external surface corrugation originating from aromatic surface groups. [48,69] The authors reported a porous coordination polymer with external surface design (PESD), [Zn₄(µ₃-OH)₂(BTMB)₂(DMF)₃(MeOH)] using the organic linker BTMB₃⁻ (= 1,3,5-tris(3-carboxyphenyl)benzene), which possesses an aromatic hydrocarbon–terminated surface (Figure 16a). The material’s surface area is 295 m² g⁻¹ and powder XRD measurements of flake-shaped single crystals of PESD-1 reveal that the (010) surface is the material’s dominant surface (Figure 16c). Calculations based on single-crystal data confirm a nanometer-scale corrugation along this surface with a periodicity of 1.2 × 1.1 nm², caused by the surface termination by the aromatic hydrocarbons of the organic linker. Atomic force microscopy (AFM) characterization suggests that the (010) surface is relatively flat in larger length scales (Figure 16b,d). 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 (see discussion in section 3.5 about challenges in characterization). The authors additionally performed solvent adsorption at 298 K for water, benzene, cyclohexane, and toluene. In the water adsorption experiments, for hydrophobic materials rather untypical behavior is observed on PESD-1. Two significant steps at 0.27 and 2.3 kPa are observed on the adsorption isotherm. This indicates that while the exterior surface is repellant toward liquid water, the interior pore space is actually hydrophilic and accessible to water vapor (like a lotus leaf). The adsorption isotherm of hydrophobic organic solvents such as toluene and benzene shows a gate-opening adsorption isotherm, although cyclohexane was not adsorbed. These results indicate that PESD-1 has framework flexibility along with size-selective pores toward guest molecules. The same group recently reported a de novo synthetic method for preparing other MOF with nano-surface corrugation, including 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.[205] It should be noted that the reported bimetallic MOFs exhibit outstanding superhydrophobic behavior even at elevated temperatures. PESD-2(Co) exhibits a particularly large surface area and good uptake of solvents such as benzene, toluene, and cyclohexane.

In contrast, among the zeolitic imidazolate framework (ZIF) family, ZIF-8 (Zn(mIm)₂; mIm = 2-methylimidazole) has a hydrophobic pore surface due to its free flexible methyl groups but a hydrophilic crystal surface.[206–210] The ethylimidazole-based ZIF [Zn(eIm)₂] (also known as MAF-6, metal–azolate framework) shows hydrophobicity on both internal pore and external crystal surfaces.[56] To study the internal hydrophobic pore surfaces of MAF-6, solvent adsorption isotherms were obtained at room temperature. MAF-6 shows significant uptake of methanol, ethanol, and benzene (13.27, 9.15, and 6.36 mmol g⁻¹, respectively). The adsorption isotherm of ethanol and methanol shows typical type V curve, while benzene has a type IV adsorption isotherm, concluding hydrophobic behavior of MAF-6. The contact angle of MAF-6 amounts to 143° ± 1° due to large basins located on the (100) crystal surface that originate from its nearly mesoporous cavities. Therefore, the hydrophobicity of MAF-6 originated from highly corrugated crystal surface on the nanometer scale.
3.4. Hydrophobic MOF Composites

Despite the large number of hydrophobic MOFs based on fluorinated and long alkyl chain ligands, a great deal of research has been devoted to fabricating porous MOFs with hierarchical pores (both micro and meso), high surface areas, and large pore volumes. Hierarchical porous hydrophobic MOF composites can be synthesized, for instance, by growing MOF nanoparticles on various fluorine-based graphene layered materials. Our group recently reported the synthesis of various MOF composites with fluorographene (FG). FG was used in the preparation of these composites because it allows functional groups to be incorporated into the basal plane of graphene rather than at the edges of the layers.[211,212] Highly fluorinated graphene oxide (HFGO) was combined with ZIFs under solvothermal conditions (Figure 17a) to produce an MOF composite, HFGO@ZIF-8, with superhydrophobic–superoleophilic properties.[213] The powder XRD of this hybrid featured all planes corresponding to pristine ZIF-8. Interestingly, its nitrogen adsorption isotherm exhibited features of type I and type IV shapes, indicating the presence of micropores (presumably originating from ZIF-8) and mesopores (due to the stacking of ZIF-8 nanocrystals over HFGO layers), respectively. The hybrid has a BET surface area of 590 m² g⁻¹. Pore size distribution calculations using the nonlocalized density functional theory method suggest a distribution extending over both the microporous and mesoporous regimes (2–3 nm). X-ray photoelectron spectroscopy analysis of HFGO@ZIF-8 confirmed that the nature of its fluorinated groups was unaffected by the synthetic process; i.e., the pendant covalent C–F groups of HFGO were retained in the composite. These 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 termination of the HFGO layers gives the composite a very low surface energy, which is another prerequisite for hydrophobicity. Remarkably, contact angle measurements showed that the composite’s water contact angle (162°) exceeds those of pristine ZIF-8 and HFGO (56° and 125°, respectively; see Figure 17b–d). These results illustrate the interplay between two features—a hierarchical structure and a low surface energy—that make surfaces hydrophobic. Additionally, the composite took up oil droplets very rapidly (within 15 s); its oil contact angle is essentially 0°, indicating superoleophilicity (Figure 17e).

In a continuation of this work, we reported the economically viable and readily scalable preparation of hydrophobic-oleophilic porous gels by simple mixing of hybrid composites of...
metal–organic gel (MOG) composed of Al\(^{3+}\) ions and BTC\(^{-}\) linkers and fluorinated graphene oxide (FGO) under solvo-
thermal conditions (Figure 17f).

PXRD analyses of the composites indicated that their crystallinity was low, as only a few broad diffraction peaks were observed. Nevertheless, the data indicated that the material's structure is closely related to that of MIL-100(Al)(Al\(_3\)(X)(H\(_2\)O)\(_2\)O(BTC)\(_2\)) with X = OH\(^{-}\) or F\(^{-}\).

The FGO@MOG exhibits a typical type IV N\(_2\) adsorption/desorption isotherm, proving meso–macroporous nature with pore diameters of 2–70 nm. This demonstrates that hierarchical (micro/meso) pore structures can be obtained by using FGO to disrupt MOF crystal growth, promoting mismatched growth over oriented crystallization. It should be noted that the MOF nanoparticles initially go through controlled nucleation and nanoparticles selectively coordinated with the oxygen functionalities of the FGO sheets. The composite's hydrophobicity was assessed by measuring its advancing/receding contact angles (Figure 17g–l). The advancing water contact angle of the hybrid is 126° ± 4°, showing its hydrophobic behavior. Pristine FGO and MOG exhibit advancing water contact angles of 116° ± 4° and 0°, respectively. Its hexadecane contact angle was close to 0°, confirming the hydrophobic–oleophilic behavior of the FGO@MOG composite.

At the same time, hydrophobic–oleophilic composites based on a hydrophobic MOF incorporated in a graphene oxide (GO)/sponge composite were presented by Jiang and coworkers.\(^{[215]}\) The used MOF USTC-6 (Cu\(_2\)HFPD) consists of a tetracarboxylate-based organic linker H\(_4\)HFPD (4,4'-(hexafluoroisopropylidene)diphthalic acid) with a Cu\(_2\) paddlewheel SBU, prepared under solvothermal conditions (Figure 18a). Single-crystal XRD analysis reveals 2D layers in the ac plane with a wave-like surface with exposed pendant –CF\(_3\) groups between the 2D layers, which decrease the surface energy and induce the high hydrophobicity of USTC-6. The powder XRD data further confirm phase purity and more importantly preferential orientation along the (060) plane. The water contact angle measurements show angles of up to 132° for the crystals. Furthermore, for the preparation of an oil spill up cleaning device, the authors incorporated the obtained hydrophobic MOF on branched sponges functionalized with GO.

The GO surface has carboxylic, hydroxyl, and epoxy functional groups, which facilitate anchoring of USTC-6. The composite shows water contact angles in the range of 121° to 130° and oil droplets quickly adsorb into this sorbent. The hydrophobic/oleophilic nature of USTC-6 is transferred to the device, and the incorporation of USTC-6 changes the properties of
GO@sponge (Figure 18b). In a similar manner, 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 H₂BTFPADB (4,4-[3,5-bis(trifluoromethyl)phenyl]azanediyldibenzoic acid) in the presence of copper nitrate.[84]

Single-crystal XRD analysis shows a 2D grid-based framework structure with ultramicropores decorated with bis(trifluoromethyl) moieties (Figure 18c). To examine the superhydrophobic behavior of UHMOF-100, contact angle measurements were conducted, with a water contact angle of 177° and an oil contact angle of 0°, indicating superoleophilicity (Figure 18d–e). The authors recorded vapor sorption isotherms at 298 K. Due to the hydrophobic pores, only negligible water uptake was recorded, but for hydrophobic organic vapor molecules (benzene, ethylbenzene, toluene, and para-xylene) significant uptake is observed. These compounds are common oil components (i.e., C₆–C₈ hydrocarbons) (Figure 18f). To utilize the properties of UHMOF-1, it was integrated into a device, by spray coating the MOF onto a PDMS/PP membrane. The water contact angle of the prepared membrane amounts to 135° highlighting the hydrophobic nature of the fabricated MOF membrane.

3.5. Challenges in Characterization of Hydrophobic MOFs

Determining and characterizing MOFs’ hydrophobicity is challenging because standard methods such as contact angle measurements are often not readily applicable; there is a lack of unified and universal standard methods and protocols. The challenges can be illustrated by considering the example of a specific hydrophobic MOF, namely, PESD-1 (Zn₄(µ₃-OH)₂(BTMB)₂) (Figure 19).[69] This framework is based on the aromatic linker molecule H₃BTMB (benzene-1,3,5-tris(m-benzoic acid)) and is obtained in the form of single crystals with dimensions of 1–3 mm. Consequently, the surfaces made from these crystals have a very high roughness. Water droplets deposited on this MOF adopt near-spherical shapes and can roll off at <10° (Figure 19a). This demonstrates that the MOF is intrinsically hydrophobic (i.e., its intrinsic contact angle is close to or >90°), as otherwise the water would spread in accordance with the Wenzel equation. Upon grinding the crystals, a powder with a smaller grain size (<10 µm) is obtained. This powder is still sufficiently rough for deposited water droplets to adopt a high static contact angle (>150°) and a spherical shape (Figure 19b). After degassing the ground MOF powder to remove guest molecules (the grain size remains <10 µm; Figure 19c).
and pressing it into a pellet, the static contact angle decreased markedly, to \(\approx 110^\circ\). This indicates that a single MOF material can exist in at least four different states, each with different hydrophobicities. How then should we measure its behavior and what factors should be taken into account when doing so?

Most MOF materials and composites are obtained in the form of crystals or powder.\,[58,59,146] However, in some cases, an MOF may be coated on a substrate such as glass.\,[216] The treatment of the crystals or powder prior to the contact angle measurement is crucial because the substrate’s roughness significantly affects the wetting properties, as discussed earlier. Therefore, one can only meaningfully compare the measured contact angles of different MOF materials if their pretreatment was identical. Pressing a powder into a pellet disk significantly reduces its surface roughness and thus alters its wetting properties, allowing assessment of its intrinsic hydrophobicity.

Depending on the applied pressure and the powder’s characteristics, some residual roughness may remain. Because of the reduced roughness, water droplets resting on top of the pressed tablet should exist in the Wenzel state, with a contact angle between 90° and 120° (but potentially up to 130° depending on the remaining roughness and the material’s intrinsic contact angle; Figure 20a). The highest possible water contact angle on an ideally flat nonporous substrate is \(\approx 120^\circ\), which can solely be achieved by perfluorinated (\(-\text{CF}_3\)) surfaces.\,[151,158] Only the introduction of roughness can enhance the contact angle above 120°. Contact angles for bare powders can substantially exceed this limit because of their high roughness, which depends mainly on the crystallites’ grain size. In many cases, the roughness due to the grain size is sufficient to support the Cassie state (Figure 20b). In such cases, the drop rests on the topmost powder grains and air is trapped beneath it. The droplet can have a contact angle above 150° and be able to roll off (which will occur at inclinations below 10° for 5–10 \(\mu\)L water droplets). The observed contact angle thus largely depends on the surface morphology and structure, i.e., the grain size and arrangement. Consequently, a material of high intrinsic hydrophobicity could have a lower observed contact angle than a material with a lower intrinsic hydrophobicity but more suitable roughness.

**Figure 19.** A typical hydrophobic MOF material (PESD-1) exhibiting different wetting properties depending on its state. a) Crystalline state with a large crystallite size of 1–3 mm; a deposited water droplet adopts a near-spherical shape. b) Grinded powder with a smaller grain size of <10 \(\mu\)m and a similar water contact angle. c) Degassed powder retaining the <10 \(\mu\)m grain size. d) Powder pressed into a pellet, reducing surface roughness and contact angles. Reproduced with permission.\,[69] Copyright 2014, Wiley-VCH.

**Figure 20.** a) Schematic illustration of a water droplet on a hydrophobic MOF powder pressed into a tablet adopting the Wenzel state. b) Water drop on hydrophobic MOF powder without further treatment. Air is entrapped underneath the droplet (Cassie state) between the powder grains due to the high surface roughness of the powder.
Powder-based measurements are also error-prone because powders are loose assemblies of grains that are easily “picked up” by droplets, potentially reducing the air–water interfacial tension. This is why it is difficult to measure contact angle hysteresis on MOF powders. The advancing contact angle can be measured with reasonable accuracy by increasing the droplet volume, but the removal of liquid to measure the receding contact angle can cause the droplet to pick up powder grains, which strongly influences the measurement and may lead to the formation of a “liquid marble.” Therefore, it is advisable to measure contact angle hysteresis on powders; such measurements should ideally only be performed on pressed pellet disks.

Contact angle–based methods for measuring the surface energy of MOF materials such as the Zisman plot or OWRK methods are unreliable because even pressed tablets exhibit residual roughness, and the MOF material is likely to adsorb the low surface tension liquids (alkanes, oils, alcohols) used in those methods due to the inherent porosity of the MOFs. Instead, methods such as iGCE (Section 2.6) should be used.

As noted earlier, the characterization of hydrophobic MOFs is very challenging. We therefore wish to offer a few suggestions that may help in the development of standardized protocols and procedures. Static (using 5–10 µL droplets) and advancing contact angles (≈5 µL initial drop size, with ≈20 µL being added) can and should be measured on powders. The resulting values should be reported in combination with a description of how the surface was prepared. To reduce the influence of the needle on the droplet and the measurement, hydrophobic needles are recommended, and the tip of the needle should be located ≈1 mm above the surface. The measurement should be conducted quickly after depositing the droplet since the contact angles can change in course of time, e.g., if the liquid penetrates the powder. Receding contact angles should not be measured on powders because the droplet will take up powder, influencing the measurement. However, roll-off angles can be measured on powders using small (5–10 µL) water droplets. In addition to performing measurements on powder, pressed tablets should be fabricated at a defined load, and the static (using 5–10 µL drops), advancing, and receding contact angles (≈5 and ≈25 µL initial droplet sizes for advancing and receding angles, respectively, with ≈20 µL being added/withdrawn) should be measured on those tablets. The contact angles should be reported together with the applied load. The surface roughness should ideally be estimated and listed, and the contact angle measurements should be carefully interpreted based on these results. Measurements on pressed pellet disks with a low roughness give the best indication of the intrinsic wetting properties of the MOF material. However, in this context, the stability of MOFs toward mechanical pressure must be kept in mind.

4. Potential Applications of Hydrophobic MOFs and Their Composites

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

4.1. Hydrocarbon Storage/Separation

Light hydrocarbon storage/separation is important in the chemical industry and the wider economy. Clean olefin feedstocks are necessary for the production of high-quality polymers, and their separation, currently achieved by cryodistillation, is one of the most energetically (and hence financially) expensive processes in the chemical industry. In addition, the storage of light aromatic hydrocarbons is vital for their conversion into bulk chemical products and their use as fuels.

Omary et al. developed hydrophobic fluorous MOFs (FMOF-1 and FMOF-2) that can be used to adsorb a variety of C6–C8 hydrocarbons commonly found in the gas oil fraction of crude oil. The uptakes of benzene, cyclohexane, n-hexane, p-xylene, and toluene by these materials were 290, 300, 190, 265, and 270 kg m\(^{-3}\), respectively (Figure 10b). These strong uptakes at low pressure indicate the presence of favorable host–guest interactions based on the confinement of the aromatic adsorbates. It should be noted that the uptake of hydrocarbon mainly depends on the internal hydrophobic pores and the size of the channels.

Another linker-based hydrophobic MOF is UPC-21, which was successfully used for the adsorption/separation of hydrocarbons (C\(_1\)–C\(_8\)). In addition to its hydrophobic pores, UPC-21 is lined with open metal sites, enabling the discrimination of olefins from paraffins and short-chain from long-chain hydrocarbons. UPC-21 exhibits a remarkable acetylene uptake of 139.5 cm\(^3\) g\(^{-1}\) at 295 K (Figure 21a). Its uptake capacities for C\(_2\)H\(_4\), C\(_3\)H\(_6\), C\(_4\)H\(_6\), and C\(_6\)H\(_6\) are also fairly high at 1 bar and amount to 98.4, 104.3, 110.1, and 103.0 cm\(^3\) g\(^{-1}\), respectively, at 295 K. The isosteric heats (Q\(_s\)) of adsorption for C\(_2\)H\(_4\), C\(_3\)H\(_6\), and C\(_4\)H\(_6\) are 38.8, 24.7, and 23.1 kJ mol\(^{-1}\), respectively, indicating strong interactions between the hydrocarbons and the coordination framework (Figure 21b). The overall capacity of UPC-21 for light hydrocarbons (C\(_2\)–C\(_4\)) at 295 K is much higher than those of other promising MOFs such as M’MOF-3a, UTSA-67, and Cu(etz). This was attributed to the synergistic effects of its high density of open Cu(II) sites, multiple aromatic rings, and optimized pore size. On the other hand, UPC-21 adsorbs only 25.7 cm\(^3\) g\(^{-1}\) of CH\(_4\) at 295 K. The calculated separation selectivities (expressed as molar ratios) for UPC-21 when exposed to equimolar mixtures of CH\(_4\) and C\(_2\)H\(_2\) amount to 38.1 at 1 bar (Figure 21c,d). It is worth observing that UPC-21 shows better selectivity for C\(_2\)H\(_2\) over CH\(_4\) at 295 K than previously reported MOFs such as MFM-130a (34.7), UTSA-36a (13.8), Zn\(_2\)(OH)\(_2\)(1,2,4-BTC)\(_2\) (14.7), and Zn\(_2\)(BTA)\(_6\)(TDA)\(_2\) (15.5). The same group also prepared a nanoporous hydrophobic MOF [(In\(_{1.5}\)(μ\(_3\)-O)\(_{0.5}\)(TPTA-F)\((H_2O)(OH)_{0.5}\)]·4DMF·4.5H\(_2\)O (UPC-104; H\(_2\)TPTA-F = 2-fluoro-[1,1′,3′,1″-terphenyl]-4,4″,5″-tricarboxylic acid) based...
on a fluorine-functionalized organic linker, and used it for hydrocarbon storage/separation.[221] This framework has high stability in acidic and basic aqueous solutions and is thermally stable up to 300 °C. Moreover, UPC-104 exhibits very high H₂ (230.8 cm³ g⁻¹, 2.06 wt% at 77 K and 1 bar), C₂H₂ (187.0 cm³ g⁻¹ at 273 K and 1 bar), and C₃H₆/C₃H₈ adsorption capacities (276.5 and 250.4 cm³ g⁻¹ for C₃H₆ and C₃H₈, respectively, at 273 K and 1 bar).

Chen and coworkers successfully used the hydrophobic zeolite imidazole framework MAF-6 to separate alcohols and aromatic hydrocarbons from water based on its large aperture size and inherent hydrophobicity (Figure 22a).[56,222] In their work, the separation of hydrocarbons was achieved by gas chromatography (GC) using a quartz capillary with microcrystalline MAF-6 grafted onto its inner surface. Interestingly, MAF-6 achieves good selectivity and excellent separation for diverse linear and aromatic hydrocarbons and adsorbs large quantities of organic molecules. Interestingly, the material is able to successfully separate saturated and unsaturated molecules with similar structures (Figure 22b–f). These results indicate that stable superhydrophobic MOFs could be useful for hydrocarbon storage and separation in the future.

4.2. Oil–Water Separation

Oil spills in oceans cause serious problems to human beings and marine life, presenting serious threats to environment and people’s health. Water purification from oils, without damaging ecosystems or causing environmental pollution, is a challenging task. The methods established for separation of oils from water by adsorptive separation hold the greatest promise due to its simplicity and economic viability.

A combination of hydrophobic and oleophilic graphene-based MOF composite materials was recently used successfully for oil separation: a superhydrophobic and oleophilic multiaromatic hydrophobic MOF exhibited 100% oil separation from water and removed 99.0% of all tested pollutants other than crude oil. Our group successfully used the hierarchical porous superhydrophobic–oleophilic composite HFGO@ZIF-8, which exhibits high absorption of oils and various organic solvents.[213] The uptake values for the composite (which ranged from 20 to 280 wt%) were appreciably higher than those for the parent hydrophobic MOF, ZIF-8 (10–150 wt%; see Figure 23a). We also modified the composite further by incorporating it into a sponge, yielding a material designated sponge@HFGO@ZIF-8. This sponge exhibited outstanding absorption uptake of various organic solvents and oils, with uptake values of 150–600 wt% depending on the oil or solvent (Figure 23b). We also prepared meso-macroporous hydrophobic–superoleophilic fibrous materials composed of MOGs with FGO. FGO@MOG exhibits significantly higher absorption capacity than those reported for hydrophobic MOFs in the literature, ranging from 200 to 500 wt% toward the selected oils and organic solvents (Figure 23c).[214] Another composite, UHMOF-100/PDMS/PP, features an MOF-coated polymer-based membrane and was used to absorb several oils, such as crude and marine oil, biodiesel, hexadecane, carbon tetrachloride, and toluene. Its absorption capacity (=40–70 wt%) and flux (85 ± 5 mL⁻² s⁻¹) are high and remained unchanged even after ten cycles (Figure 23d).[84] Chen and coworkers recently reported a UiO-66-coated mesh superoleophobic
membrane that shows significant separation efficiency, almost 99.99% oils from water. Moreover, a USTC-6@GO@sponge displays great uptake and absorption rates for organic solvents and oils ranging from 1200 to 4300 wt%. Its high absorption of oils was attributed to the microporous behavior of USTC-6 and the sorbent’s high meso-macroporosity. Moreover, the adsorbed oils were readily separated from the USTC-6@GO@sponge because of its decent elasticity and significant mechanical stability. The authors exploited the novel characteristics of this composite to construct a simple model apparatus that enabled the successful recovery of oil from a spill in water by a straightforward “adsorption–squeezing” process (Figure 24a). Even after prolonged cycling, the apparatus successfully recovered hexane from water (Figure 24b,c). Furthermore, the authors showed that the apparatus is capable of oil recovery even under harsh conditions (Figure 24d–f).

4.3. Catalysis

The surface wettability of heterogeneous catalysts can profoundly affect their activity and selectivity by modulating their interactions with reactants and products. In 2016, Jiang and coworkers reported that hydrophobic modification can enhance catalytic performance. They performed styrene hydrogenation in a batch reaction over the pristine composite Pd/UIO-66 and a PDMS-modified hydrophobic hybrid, Pd/UIO-66@PDMS. The parent Pd/UIO-66 required 255 min to achieve complete hydrogenation (Figure 25a,b). However, the PDMS-coated hybrid afforded 100% conversion within 65 min. The authors also showed that varying the thickness of the PDMS coating had no effect on the hybrid’s size, electronic configuration, or (more importantly) catalytic efficiency. The enhanced activity of the Pd/UIO-66@PDMS hybrid can thus be primarily ascribed to the hydrophobic responsive PDMS surface modification of the Pd surface. The composite Pd/UIO-66@PDMS catalyst was also used to hydrogenate other hydrophobic substrates such as nitrobenzene and cinnamaldehyde. Additionally, Janiak and coworkers reported that hydrophobic silica coating of MIL-101(Cr) nanoparticles improved catalytic performance and catalyst reusability for the oxidation of indene with H₂O₂ in acetonitrile (Figure 25c). MIL-101Cr@mSiO₂ shows superior catalytic activity to pristine MIL-101(Cr) (Figure 25d,e). Furthermore, the turnover frequency of MIL-101Cr@mSiO₂ (95.2 mmol g⁻¹ h⁻¹) was superior to that of MIL-101Cr (76.8 mmol g⁻¹ h⁻¹).

In the same approach, Hu and coworkers reported the effect of hydrophobic modification in the catalytic hydrogenation of cinnamaldehyde using iron(III) porphyrin (FeP-CMP) to modify the surface of MIL-101@Pdsto and prepare MIL-101@Pt@FeP-CMP (Figure 26a). In the same work, the authors proved that MIL-101@Pt@FeP-CMP sponge has a greater turnover frequency (1516.1 h⁻¹), with 97.3% selectivity for cinnamyl alcohol at 97.6% yield (Figure 26b). Jiang and coworkers reported hydrophobic pore surface modification of iron–porphyrinic MOF, PCN-222(Fe), and successfully exploited for catalytic performance in cyclohexane oxidation (Figure 26c).Remarkably, perfluorinated alkyl substituent–based iron–porphyrinic MOFs significantly enhanced the MOF’s activity and hydrophobicity, and improved its interactions with cyclohexane, resulting in improved conversion and selectivity for KA oil (Figure 26d,e). Long and coworkers showed the profound effect the
Figure 23. a) Absorption of oils and organic solvents by HFGO@ZIF-8 (red) and pristine ZIF-8 (black). b) Oil absorption capacity of hybrid with sponge@HFGO@ZIF-8. c) Absorption of various oils and organic solvents for FGO@MOG (red bars) and MOG (black bars). d) Bar diagram representations of the absorption capacities of UHMOF-100/PDMS/PP toward different oils. Reproduced with permission.\cite{213} Copyright 2015, Wiley-VCH. Reproduced with permission.\cite{214} Copyright 2017, Wiley-VCH. Reproduced with permission.\cite{84} Copyright 2016, Wiley-VCH.

Figure 24. a) Schematic illustration of the system using USTC-6@GO@sponge to consecutively collect oil from water. Photographs showing b) the apparatus collecting floating oil (dyed red) in a continuous fashion from a water surface (dyed blue) in motion, and c) system’s status after completed oil–water separation. Illustration of the different stages of the oil recovery process: d) floating oil aspiration; e) removal of adsorbed oil above the tube nozzle; and f) formation of air channel inside the sorbent. Reproduced under the terms of the Creative Commons CC BY 4.0 License.\cite{215} Copyright 2016, Nature.
5. Conclusions and Perspectives

This review provides a comprehensive summary of the characterization, preparation, and applications of hydrophobic MOFs and their composites, highlighting state-of-the-art strategies. The hydrophobicity of the pore environment has a significant impact on the catalytic cyclohexane oxidation by functionalized Fe(DOTPDC) (DOTPDC$^{4-} = \text{4,4''-dioxido-[1,1':4',1''-terphenyl]-3,3''-dicarboxylate}$) frameworks. By attaching larger and more hydrophobic groups to the linker backbone, the turnover frequency was improved, and the selectivity toward cyclohexanone over cyclohexanol was dramatically increased. Finally, Coskun and coworkers recently reported carbon nitride foam/ZIF-8 composites for separating oil spills from water and the highly competent conversion of CO$_2$ into chloroprene carbonate, achieving quantitative yield and excellent product selectivity.$^{[68]}$
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, 3) the targeted exploitation of surface corrugation to induce hydrophobicity, and 4) the preparation of hydrophobic hierarchical porous composite structures. 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, −CF₃ 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, this concept does not reduce the accessible pore space as much as the use of bulky side chains. However, fluorination changes the ligands' electronic structure and it is often essential to develop new synthetic strategies to access the desired framework topologies. Furthermore, the preparation of complex perfluorinated ligands is a challenging synthetic endeavor. An alternative is to use ligands bearing long hydrophobic alkyl chains that are anchored to the ligand backbone by condensation/esterification/amidation reactions. However, as noted earlier, although this strategy significantly increases hydrophobicity, it also dramatically reduces accessible pore space. The use of perfluoroalkanes in this context is still very rare and in its infancy, but the preparation of fluororous nanocages/layers in this way is certainly an appealing idea for some applications, such as the adsorption of chlorofluorocarbons or oxygen.

Further advancement in this field will require the development of new synthetic routes and conditions that will allow perfluorinated ligands to be combined with many different SBUs in order to access the plethora of topologies that have been prepared using hydrocarbon-based linker backbones. This will also facilitate the creation of mesoporous perfluorinated MOFs, which have many practical advantages (e.g., superior mass transport through their pores).

An alternative to direct synthesis of hydrophobic MOFs is postsynthetic modification of conventional MOFs. This strategy has the advantage of being applicable to any MOF with reactive handles (e.g., open metal coordination sites or ligands bearing reactive groups). Moreover, it avoids the need for a (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 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.

An alternative to postsynthetic modification by chemical reactions is to coat the framework with a hydrophobic polymer. This approach seems very promising because it apparently does not affect the accessibility of the pore space. However, to date it has only been applied to MOFs with micropores; it will be very interesting to see if this process can be transferred to compounds with meso- and macropores without sacrificing porosity.

Surface corrugation is a method that is seemingly applicable to diverse surfaces and enables selective transformation whereby the outer surface is made hydrophobic while the inner surface remains hydrophilic. At present, it can only be applied to MOFs with very specific types of ligands, but it could be a very powerful strategy if general methods for roughening the surface of (ideally) any type of MOF material were developed.

The final strategy that has been used successfully involves preparing hierarchical porous composites of metal–organic frameworks with membranes or 2D carbon materials. 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 can 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 interesting.

The characterization of hydrophobic MOFs poses another challenge with many pitfalls because hydrophobic MOFs often have hydrophobic pores as well as external hydrophobic surfaces. The inherent hydrophobic pores can be thoroughly characterized by measuring vapor-phase adsorption isotherms for water and/or aromatic hydrocarbons. However, no standardized measurement protocol utilizing consistent pressure ranges and measurement temperatures has yet been developed. Hydrophobic pores usually do not show any appreciable water uptake, but they typically outperform traditional porous materials with respect to the uptake of benzene. The outer hydrophobic surface can be characterized by contact angle measurements. Although many advances have been made in this area, contact angle measurements still have many limitations, and there is a clear lack of standardization in this area.

This review has highlighted some critical challenges relating to contact angle measurements on the surfaces of powders, crystals, and pressed pellets before and after the evacuation of solvent molecules. While some intriguing high contact angles have been reported for various hydrophobic MOFs, contact angle measurements of supposedly hydrophobic MOFs are only rarely performed. Furthermore, it must be noted that the pressure applied during the preparation of pellets could mechanically alter some MOF structures. We also highlighted inverse gas chromatography as a promising method for surface characterization of MOFs based on the adsorption of various solvent vapor molecules.

Many hydrophobic MOFs/composites have potential applications in alcohol adsorption, hydrocarbon separation/storage, oil spill separation from water, and catalysis, and there are undoubtedly many other potential applications that have yet to be discovered and explored. Despite their great promise, the industrial applications of hydrophobic MOFs are currently in their infancy and are limited by the chemical, physical, and mechanical stability of most reported MOF materials. Therefore, the synthesis of highly stable/hierarchical porous hydrophobic MOFs and their composites has the potential to create new opportunities, e.g., in energy (storage) applications or sensing where the enrichment of certain species from solution is important. The design and coupling of photocatalytically active and hydrophobic MOF is another interesting avenue.
that could enable the preparation of water-stable photocatalytic water splitting devices. Furthermore, there is the prospect of developing hydrophobic hierarchical materials that combine different functions in one material, such as MOF/2D material/sponge hybrids for oil spill cleanup, in which a certain fraction of the crude oil is strongly adsorbed in the MOF and the other fraction in the mesopores, enabling the splitting of the oil fractions during cleanup. We expect rapid development in this field and further optimization of hydrophobic MOFs and their composites for various applications, but standardized characterization methods will be needed to achieve this and to ensure comparability between different systems and their properties.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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