Imparting amphiphobicity on single-crystalline porous materials

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The sophisticated control of surface wettability for target-specific applications has attracted widespread interest for use in a plethora of applications. Despite the recent advances in modification of non-porous materials, surface wettability control of porous materials, particularly single crystalline, remains undeveloped. Here we contribute a general method to impart amphiphobicity on single-crystalline porous materials as demonstrated by chemically coating the exterior of metal-organic framework (MOF) crystals with an amphiphobic surface. As amphiphobic porous materials, the resultant MOF crystals exhibit both superhydrophobicity and oleophobicity in addition to retaining high crystallinity and intact porosity. The chemical shielding effect resulting from the amphiphobicity of the MOFs is illustrated by their performances in water/organic vapour adsorption, as well as long-term ultrastability under highly humidified CO2 environments and exceptional chemical stability in acid/base aqueous solutions. Our work thereby pioneers a perspective to protect crystalline porous materials under various chemical environments for numerous applications.

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The custom design of surfaces with controlled wettability properties has been attracting continuous attention from both academia and industry\(^1\)-\(^7\). In particular, amphiphobic surfaces\(^8\)-\(^12\) that repel water and compounds with low surface tension (for example, oils) are of great interest due to their various prospective applications, such as oil transportation\(^1\), microfluidics\(^1\) and nano-object manipulation\(^1\). Albeit tremendous efforts have been devoted to creating such amphiphobic surfaces on a variety of substrates over the past several years\(^8\)-\(^12\), the impartment of amphiphobicity on porous materials, specifically single crystalline, has not yet been explored.

As an emerging class of porous materials with high single crystallinity, metal-organic frameworks (MOFs)\(^16\)-\(^18\), which feature amenability to design, high surface areas, tunable pore sizes and tailorability, have recently been extensively investigated for applications in gas storage\(^1\)\(^9\),\(^1\)\(^0\), separation\(^2\)\(^1\),\(^2\)\(^2\), carbon capture\(^3\)\(^-\)\(^4\),\(^2\)\(^4\),\(^2\)\(^5\),\(^2\)\(^8\), catalysis\(^2\)\(^5\)\(^-\)\(^2\)\(^8\),\(^2\)\(^9\),\(^3\)\(^0\)\(^-\)\(^3\)\(^4\) and so on (refs 31–34). However, an issue for their wide applications in practice includes the performance under a variety of environments (for example, stability in humid conditions, interferences by organic vapours in the atmosphere\(^3\)\(^5\)-\(^3\)\(^8\)), which necessitate the sophisticated control of the surface wettability of MOFs. Recent studies indicate the observation of framework degradation on the exposure of MOFs to wet CO\(_2\), even for those claimed with moisture stability\(^3\)\(^9\),\(^4\)\(^0\). To repel water molecules, thereby protecting MOFs against hydrolysis\(^4\)\(^1\)-\(^5\)\(^3\) while preserving crystallinity and intact porosity, some approaches have been developed to impart hydrophobicity/superhydrophobicity on the exterior surfaces of MOFs. For example, Jiang and colleagues\(^5\)\(^4\) recently developed a facile yet general coating approach to modify hydrophobic polydimethylsiloxane on the surfaces of MOF materials, which exhibited significant enhancement in moisture/water stability. However, some environments coexist with water and organic compounds. Therefore, amphiphobicity is needed to repel both water and organic molecules, to prevent the water attack while minimizing the interferences by organic compounds. Nonetheless, amphiphobic MOFs have not yet been achieved, despite their intriguing properties and attractive potentials for a variety of applications\(^1\)\(^3\)-\(^1\)\(^5\).

To impart amphiphobicity on the MOFs, in this contribution we rationally designed vinyl-functionalized linkers for targeted construction of MOFs, where the vinyl groups can remain intact during the formation process of MOF crystals, yet are sufficiently reactive for further chemical modifications\(^5\)\(^5\). After controllable functionalization of the exterior amphiphilic crystal surfaces with perfluoroalkyl groups via thiol-ene reaction, the resultant MOFs exhibit both superhydrophobicity and oleophobicity, while retaining high crystallinity and intact porosity.

**Results**

**Synthesis of vinyl prefunctionalized MOF.** As a representative example of MOFs, a vinyl-functionalized crystalline zeolite imidazole metal-organic framework was prepared using the protocol reported in the literature\(^5\)\(^6\) and it is isostructural with ZIF-8 as revealed by single-crystal X-ray diffraction (XRD) analysis (Supplementary Fig. 1). The guest solvent-free crystal product is designated as ZIF-8-V with a formula of Zn(C\(_3\)H\(_7\)N\(_2\))\(_2\) and the retention of vinyl groups on the linkers during the crystal formation process was further confirmed by liquid \(^1\)H NMR analysis of the digested ZIF-8-V sample (Supplementary Figs 2 and 3).

Crystal surface coating with perfluoroalkyl groups. To controllably introduce the fluorinated groups onto the exterior surface of ZIF-8-V, we hypothesize that, if a relatively bulky fluorinated compound that cannot permeate into the pore of the material is employed, the reaction would only occur on the exterior surface of the crystals. In addition, if these fluorocarbon chains are long enough, the surface energy of the sample would be significantly reduced\(^9\),\(^1\)\(^0\) (Fig. 1). To demonstrate this proof-of-concept, 1H,1H,2H,2H-perfluorodecanethiol was chosen as a typical compound for the surface modification of ZIF-8-V crystals, which was achieved via the thiol-ene click reaction\(^5\)\(^7\) to afford ZIF-8-VF (Fig. 2).

**Structural characterization.** Figure 3a shows powder XRD (PXRD) patterns of ZIF-8-V and ZIF-8-VF, which agree well with the calculated ones of ZIF-8-V, indicating the good retention of crystallinity and structural integrity during the post-synthetic modification process. N\(_2\) sorption isotherms collected at 77 K (Fig. 3b) reveal that both ZIF-8-V and ZIF-8-VF exhibit the classic type I adsorption behaviour, a characteristic of microporous materials. Derived from the N\(_2\) adsorption data, ZIF-8-V and ZIF-8-VF have similar Brunauer-Emmett-Teller (BET) surface areas (816 and 850 m\(^2\) g\(^{-1}\)) and pore volumes (0.42 cm\(^3\) g\(^{-1}\)), suggesting that the postmodification process should primarily occur on the exterior surface of the crystals with negligible blockage of the pores in the pristine material, thereby still accessible for guest gas molecules. The scanning electron microscopy (SEM) images (Fig. 3c,d) show that there is little change in the overall morphology of the crystals after the chemical modification reaction but the surfaces of the ZIF-8-VF crystals are rougher than those of ZIF-8-V crystals, further indicating the occurrence of the reaction on the exterior surface of the crystals. It is worth noting that such roughness of the surface has been reported to be beneficial to the enhancement of the hydrophobicity and oleophobicity\(^8\).

To identify the surface coating, the \(^1\)C and \(^1\)\(^9\)F MAS NMR spectra of ZIF-8-V and ZIF-8-VF were collected (Fig. 3e and Supplementary Fig. 4). Albeit no distinct difference in the \(^1\)C NMR spectra are observed for the two samples, ZIF-8-VF shows clear \(^1\)\(^9\)F NMR signals with the same chemical shifts as those of the 1H,1H,2H,2H-perfluorodecanethiol compound (Supplementary Fig. 5), which can be attributed to the much higher natural abundance of \(^1\)\(^9\)F nuclei than that of \(^1\)C nuclei. In addition, the Fourier transform infrared spectra of the ZIF-8-VF show the characteristic bands of C-F at 1,241 and 1,211 cm\(^{-1}\) as compared with the pristine ZIF-8-V (Supplementary Fig. 6). These results indicate that the perfluoroalkyl groups have been successfully introduced on ZIF-8-V, but the grafting degree is relatively low. To quantify the degree of postsynthetic modification, the ZIF-8-VF crystals were digested and analysed by the liquid \(^1\)H NMR spectroscopy (Supplementary Fig. 7). The results show that 98% of vinyl groups are still intact, which means that \(~2\)% of the vinyl groups are involved in the thiol-ene reaction.
probably occurring only on the exterior surface of the ZIF-8-V. To further prove the exterior surface modification, X-ray photoemission spectroscopy experiments were conducted (Fig. 3f and Supplementary Fig. 8), which reveal that ZIF-8-VF exhibits very strong signals associated with the F species. However, after the surface removal by Ar$^+$ ion-etching treatment (2 KeV, 100 s), the amount of residual F species is very small. These results suggest that the perfluoroalkyl groups should be mainly attached to the vinyl groups on the exterior surface of ZIF-8-V crystals, which is further confirmed by the energy-dispersive X-ray mapping of the ZIF-8-VF sample before and after surface plasma cleaning process (Supplementary Figs 9 and 10).

Figure 2 | 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.

Figure 3 | Structural characterization. (a) PXRD patterns, (b) $N_2$ sorption isotherms measured at 77 K, (c) SEM image of ZIF-8-V, (d) SEM image of ZIF-8-VF, (e) $^{19}$F MAS NMR curves and (f) X-ray photoemission spectra of ZIF-8-VF before and after surface Ar$^+$ ions etching (side band).
Examination of amphiphobic properties. The surface wettability of ZIF-8-V and ZIF-8-VF was characterized by contact-angle measurements. Figure 4a shows contact angles of water and a series of organic compounds on the surface of ZIF-8-VF. Notably, the contact angle of water on ZIF-8-VF sample is as high as 173°, indicating its extraordinarily superhydrophobic feature. In contrast, ZIF-8-V gives the water contact angle at 89° (Supplementary Fig. 11). These results confirm that the surface coating of perfluoroalkyl groups significantly enhances the hydrophobicity of the material. Furthermore, 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, the contact angles at 150°, 143°, 130°, 129° and 92°, respectively, were observed, indicating the oleophobic feature of ZIF-8-V. The results of the contact-angle experiments coupled with the permanent porosity, as revealed from the N₂ sorption measurement, thereby identify ZIF-8-VF as an amphiphobic porous material. In contrast, the contact angles of 2-hydroxybenzaldehyde, benzonitrile, chlorobenzene and dodecane on ZIF-8-V are <5° (Supplementary Fig. 12), indicating its superoleophilic nature. The superhydrophobic behaviour of the ZIF-8-VF was further illustrated by water vapour adsorption experiments (Fig. 4b). As a comparison, hydrophilic zeolite 13× exhibits strong affinity for water even at very low relative humidity (P/P₀ < 0.1). Hydrophobic ZIF-8-V exhibits a hysteresis loop at relative humidity >0.5, indicating that ZIF-8-V is capable of adsorbing water at high humidity. Interestingly, ZIF-8-VF adsorbs a negligible amount of water even at P/P₀ up to 0.9, which is anticipated to be effective to preclude the entrance of water within the interior pores of the MOF⁵⁸–⁶⁰. Toluene sorption isotherms collected at 298 K also reveal quite different adsorption behaviours for ZIF-8-V and ZIF-8-VF (Fig. 4c). For example, when P/P₀ is 0.15, it is observed that the adsorption capacity of toluene in ZIF-8-V and ZIF-8-VF is 143 and 7 mg g⁻¹, respectively. The repellency of ZIF-8-VF for toluene should stem from its excellent oleophobicity. The above results highlight that the surface-coated amphiphobic perfluoroalkyl groups serve as a shield to effectively prevent the access of water and organic compounds into the micropores of MOFs.

Investigation of chemical shielding effect. The long-term stability under practical environments (for example, humidity) has been recognized as an issue for MOFs, which can be accessed via the method of accelerated ageing.⁵⁹ To evaluate the chemical shielding effect resulting from amphiphobicity, the PXRD patterns of various ZIF materials that are exposed to 100% relative humidity under CO₂ atmosphere at 45 °C were monitored for different duration times. When ZIF-8, one of the claimed very stable MOF materials⁵¹,⁶², was aged under the above conditions for 16 h, it was observed that some additional peaks associated to an unknown phase appeared, as shown by the black arrows in Fig. 5a. Moreover, the ratio of the unknown phase increases with the increase of exposure time. For instance, after 240 h, a large portion of ZIF-8 was transformed, indicative of structural degradation of ZIF-8. This conclusion is supported by N₂ sorption studies at 77 K, suggesting a remarkable reduction in the surface area (from 957 to 378 m² g⁻¹; Supplementary Fig. 13), as well as SEM images showing clear cracks of the crystals (Fig. 5b,c). Similar changes in the PXRD patterns were also observed for ZIF-8-V (Supplementary Fig. 14). In striking contrast, ZIF-8-VF does not experience any change in the PXRD patterns, even after ageing under the above conditions over 720 h.
The SEM images show that the ZIF-8-VF sample has maintained perfect crystal morphology and its surface area is also fully retained (802 m$^2$/g; Supplementary Fig. 15). These results highlight that the amphiphobic surface can serve as a chemical shield to effectively prevent ZIF-8-VF from being attacked by the mixture of H$_2$O and CO$_2$.

**Discussion**

To demonstrate the general applicability of the strategy presented herein, vinyl-functionalized MOF (MOF-5-V; Supplementary Fig. 16) isostructural with MOF-5, which is notoriously water/moisture unstable, was synthesized using the custom-designed ligand of 2-vinylterephthalic acid (Supplementary Fig. 17). After surface chemical coating of the perfluoroalkyl groups (Supplementary Figs 18–22), the resultant material (MOF-5-VF) demonstrates amphiphobic property (Supplementary Figs 23 and 24), which renders it with extraordinary tolerance to the humidified CO$_2$, as evidenced by its well-retained crystallinity, morphology and surface area after ageing under the aforementioned conditions for 7 days (Fig. 6e–h). In sharp contrast, as observed from PXRD patterns, MOF-5 starts to transform to the non-porous MOF-69 under the humidified CO$_2$ environment within <1.5 h and such a transformation almost
finishes after 4 h as indicated by the complete disappearance of MOF-5 phase in the PXRD patterns. Correspondingly, the SEM images show that the MOF-5 crystals underwent serious corrosion along with the complete loss of its porosity after 4 h (Fig. 6a–d). These results highlight the chemical shielding effect of amphiphobicity in protecting the highly unstable MOF-5 analogues under various conditions such as humidified CO2 atmosphere, environment with high humidity and aqueous solutions (Supplementary Figs 25–27). The greatly enhanced stability of amphiphobic MOFs over their pristine ones in both acidic and basic aqueous solutions further underscore the chemical shielding effect of amphiphobicity (Supplementary Figs 28–37).

In summary, we have demonstrated the successful impartment of amphiphobicity (that is, superhydrophobic and oleophobic) on the exterior surface of the highly single-crystalline porous materials of MOFs. Such amphiphobic surface can serve as a chemical shield to effectively prevent the MOFs from being attacked by water and organic compounds, thereby bestowing the chemical shield to effectively prevent the MOFs from being attacked by water and organic compounds, thereby bestowing the MOFs with ultrastability towards moisture/water and humidified CO2. Our approach contributed herein to create amphiphobic MOFs with ultrastability towards moisture/water and humidified CO2 atmosphere, environment with high humidity and aqueous solutions.

Data availability. The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information files and from the corresponding author upon reasonable request.

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Author contributions
Q.S., F.-X. and S.M. conceived and designed the research. Q.S. and B.A. and S.M. drafted the manuscript. Q.S., F.-S.X. and S.M. conceived and designed the research. Q.S., F.-S.X. and S.M. collected and analysed the single-crystal XRD data. Q.S. and B.A. and S.M. collected and analysed the single-crystal XRD data. Q.S. conducted the NMR characterization of the materials. Z.D. carried out the contact angle tests. J.L. contributed to the transmission electron microscopy tests. All authors discussed the results and gave approval to the final version of the manuscript.

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