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Imparting surface hydrophobicity to metal–organic frameworks using a facile solution-immersion process to enhance water stability for CO₂ capture†

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The water sensitivity of metal–organic frameworks (MOFs) poses a critical issue for their large-scale applications. One effective method to solve this is to provide MOFs with a hydrophobic surface. Herein, we develop a facile solution-immersion process to deposit a hydrophobic coating on the MOFs' external surface without blocking their intrinsic pores. The water contact angle of the surface hydrophobic (SH) MOFs is ~146°. The hydrophobic coating not only greatly enhances MOFs' water stability but also provides durable protection against the attack of water molecules. When exposed to liquid water, the SH samples well retain their crystal structure, morphology, surface area and CO₂ uptake capacity. However, the as-synthesized (AS) samples nearly collapse and lose their porosity as well as CO₂ uptake capacity after the same exposure. This study opens up a new avenue for the MOFs' application of gas sorption in the presence of water.

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Introduction

Recently, a new class of porous crystals known as metal–organic frameworks (MOFs) have received remarkable attention.^{1–7} These crystals generally consist of metal clusters linked by organic ligands, which yields porous three-dimensional networks with large pore volumes and high internal surface areas.^{8–11} Therefore, much of the theoretical and experimental studies on MOFs' applications have been focused on gas sorption simulations and measurements.^{12–14} MOFs have shown high gas sorption capacities and selectivities for a series of gases. Nowadays investigations of gas storage and carbon dioxide capture from flue gas or ambient air have become a particular focus.¹⁵

MOFs' behaviour in the presence of water is an important criterion when considering these materials for adsorption applications. Water vapour is widely present in various industrial streams. Most industrial applications require MOFs that have a certain degree of stability towards water/moisture in order to facilitate handling and reduce costs. In most cases, however, water molecules are detrimental to the structural stability of MOFs.¹⁶ Clearly, when considering MOFs for gas adsorption, the structure stability and behaviour of MOFs in humid environments are critical properties that must be considered along with the adsorption capacities and selectivities of the target molecule. Water sensitivity has been regarded as a major drawback that limits MOFs' practical applications. The strength of the bond between the metal oxide cluster and the organic linker plays a key role in determining the water stability of the MOFs.^{17,18} MOFs with weak metal–ligand coordination bonds are generally vulnerable to water molecules and collapse in aqueous solutions as demonstrated by both theoretical and experimental results.¹⁶

Despite the importance of this issue, the strategies that have been reported for enhancing the water stability of MOFs or protecting them against the attack of water molecules have been addressed in a limited number of studies. To date, two main approaches have been adopted to enhance the water stability of MOFs. One is to obtain water-stable MOFs¹⁹ or hydrophobic MOFs^{20,21} by direct synthesis. The other one involves post-synthetic modification, including encapsulation

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of hydrophobic guest molecules (*e.g.*, fluorinated molecules,²² polyoxometalates,²³ and carbon nanotubes in their pores²⁴) and functionalization of their external surfaces *via* ligand replacement and exchange²⁵ or with carbon coatings by surface thermolysis²⁶ and so on.²⁷ One very attractive approach of post-synthetic modifications is to coat the MOFs' crystals with hydrophobic polymers to produce MOF@polymer composites, which exhibit better structural stability in water-containing media than the corresponding MOFs alone.^{28–32} Fernandez *et al.* coated a layer of hydrophobic Pluronic P123 polymer on the external surface of MOFs *via* physical adsorption.³⁰ The water stability of the polymer-functionalized MOFs is higher than the bare MOFs. However, the contact angle of the coated MOFs is around 22–27°, which is too small to provide sufficient protection. Jiang *et al.* recently developed a general coating approach to deposit hydrophobic polydimethylsiloxane on the surfaces of MOFs, which exhibited significant enhancement in moisture/water stability.²⁹ In addition, Ma *et al.* also contributed a general method to impart amphiphobicity on single-crystalline MOFs with 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol.³² Unfortunately, these methods usually have certain limitations, such as heating, tedious fabrication or the use of expensive hydrophobic polymers.

Organosilicone is a class of inexpensive high molecular polymers and exhibits hydrophobic properties after curing. Furthermore, due to its long chain structure, organosilicone can avoid deeply penetrating into the internal pores of MOFs. In this work, we report an effective approach to deposit a layer of hydrophobic organosilicone on the MOFs' external surface with enhanced water stability *via* a facile solution-immersion process. Our approach is simple, versatile and accomplished at room temperature (RT) without requiring heating. The hydrophobic coating is able to effectively protect the encapsulated MOF crystals against water molecules and therefore improves their water stability without significantly decreasing their initial sorption capacity in terms of porosity properties. To demonstrate the universality of our approach, three representative MOFs: NH₂-MIL-125(Ti),³³ ZIF-67³⁴ and HKUST-1,³⁵ have been chosen for investigation in detail.

Experimental

All chemicals were used as received without further purification.

MOF synthesis

Circular plate NH₂-MIL-125(Ti) crystals were synthesized in a mixed solvent containing *N,N*-dimethylformamide (DMF) and methanol according to a previous report.³⁶ Typically, 0.56 g of 2-amino-1,4-benzenedicarboxylic acid was dissolved in a mixed solvent of DMF and methanol in a volume ratio of 9 : 1. Then 0.6 ml titanium isopropoxide was added to the above solution. After ultrasonic concussion for 2 minutes, the mixed solution was transferred to a 100 ml Teflon-lined steel autoclave and then placed in an oven at 150 °C for 24 hours under static

conditions. After cooling naturally, the yellow precipitates were isolated by centrifugation and washed with DMF. Finally the precipitates were dried at 150 °C for 1 hour.

ZIF-67 microcrystals were synthesized based on our previous work.³⁷ 2.33 g of cobalt nitrate hexahydrate and 2.63 g of 2-methylimidazole were dissolved in 100 ml methanol, respectively. The above two solutions were then mixed and stirred thoroughly for 30 s. Subsequently, the mixed solution was incubated without stirring for 24 hours at RT. Subsequently, the supernatant was decanted away and the purple precipitates were collected by centrifugation followed by washing with methanol three times. Finally, they were vacuum-dried at 80 °C overnight.

HKUST-1 crystals were synthesized based upon our previously work.³⁸ Briefly, 1.82 g of copper nitrate trihydrate and 0.875 g of benzene-1,3,5-tricarboxylic acid were dissolved in 50 ml methanol under ultrasonication concussion, respectively. After this, the copper nitrate solution was transferred into the tricarboxylic acid solution. The mixed solution was kept at RT for 2 hours until MOFs' precipitation was complete. The blue precipitates were retrieved by centrifugation and washed with methanol three times. Finally, the blue powders were dried under vacuum at RT.

Fabrication of the surface hydrophobic (SH) coating on MOFs *via* the solution-immersion approach

First, DC 1-2577 (organosilicone, ~40 mg) was dissolved in 5 ml heptane. Then the above as-synthesized (AS) MOF powders (500 mg) were added to the organosilicone solution and ultrasonicated for 10 minutes. Finally, the turbid liquid was dried under vacuum at RT for 12 hours and the SH MOFs were obtained.

Water stability experiment

In order to quickly access the water stability of MOFs under humid conditions, ~200 mg AS or SH MOFs were directly dispersed in 10 ml deionized water and then sealed in a centrifugation tube. Subsequently, the tube was transferred into an oven at a constant temperature of 50 °C to obtain NH₂-MIL-125 (Ti) and ZIF-67. The water stability test for HKUST-1 was carried out at RT. After a predetermined time, the powders were centrifuged and dried at 80 °C for the following measurements. The above process was repeated until 5 days.

Materials characterization

The phase composition of the samples was characterized by using an X-ray powder diffractometer (XRD, HAOYUAN, DX-2800B) with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). Morphological features of the samples were observed using a field emission scanning electron microscope (FESEM, HITACHI, S4700) and transmission electron microscope (TEM, JEOL, 2100F) equipped with an energy dispersive spectrometer (EDS, Oxford). Prior to the nitrogen and carbon dioxide sorption measurements, the samples were degassed at 120 °C overnight. Nitrogen physisorption was conducted on an adsorption instrument (Micromeritics, ASAP 2020) at 77 K to measure

the surface area. The specific surface area is acquired using the Brunauer–Emmett–Teller (BET) method. The carbon dioxide adsorption–desorption isotherm was measured using an adsorption instrument (Micromeritics, 3Flex). The contact angle (CA) of water was measured at RT by using a CA meter (Data Physics, OCA20). Sessile water drops of 3 μl were used, and the value reported here was the average of three different positions.

Results and discussion

The phase composition of three AS MOFs was examined by XRD (Fig. S1[†]). It is seen that all the observed XRD patterns agree well with the simulated patterns, proving that phase-pure MOFs are obtained. After imparting surface hydrophobicity, the XRD pattern remains unchanged (Fig. S1[†]), which demonstrates that the solution-immersion process does not affect the MOFs' structure. The surface wettability of the AS and SH MOFs has been studied by CA measurements. As shown in Fig. 1a–c, the AS MOFs are hydrophilic. Water droplets can easily spread and can be quickly absorbed on them. The water CAs for AS NH₂-MIL-125(Ti), ZIF-67 and HKUST-1 are $16 \pm 2^\circ$, $16 \pm 2^\circ$ and $15 \pm 2^\circ$, respectively. However, after the solution-immersion process, the corresponding SH MOFs exhibit a water CA as large as $146 \pm 3^\circ$. Spherical water droplets can freely stand on the SH samples and cannot be absorbed (Fig. 1d–f). This reveals that a hydrophobic coating is formed on the MOFs' external surfaces. Apparently, this coating can repel water molecules from entering MOFs and is supposed to protect MOFs from their attack.

In order to confirm the presence of the hydrophobic coating, the SH NH₂-MIL-125(Ti) samples were observed by TEM (Fig. S2[†]). The image clearly shows there is a surface layer on the MOFs. Element mapping by EDS has also been conducted (Fig. S3[†]). The profile shows that the Si element uniformly distributes on the crystals' surfaces, undoubtedly demonstrating that organosilicone has been successfully coated on the MOFs. The existence of hydrophobic coating would be beneficial to improve MOFs' water stability.

The most straightforward evidence of the improved water stability for SH MOFs was obtained from the XRD results after

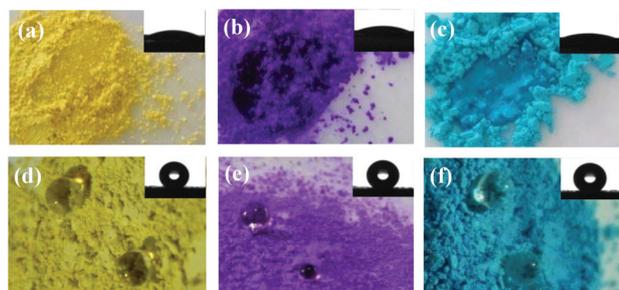


Fig. 1 Digital photographs of the AS (a) NH₂-MIL-125(Ti), (b) ZIF-67, (c) HKUST-1, and the SH (d) NH₂-MIL-125(Ti), (e) ZIF-67, (f) HKUST-1. The inset shows the CA image.

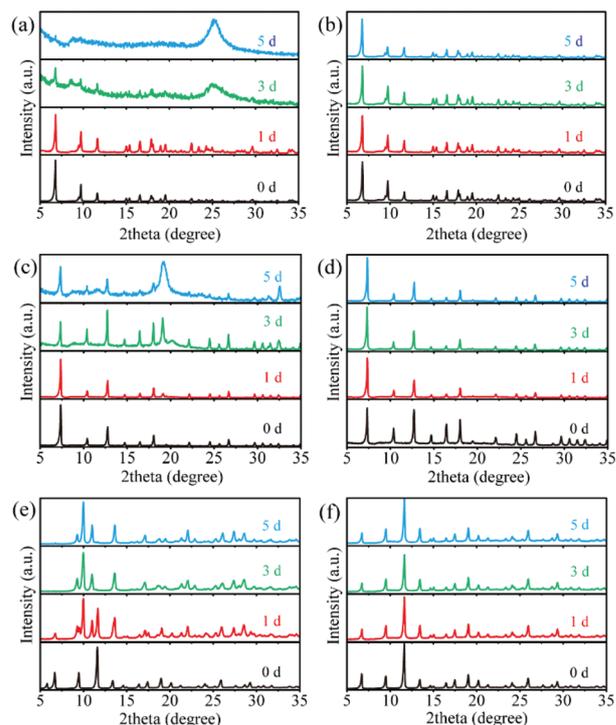


Fig. 2 XRD patterns of (a) AS NH₂-MIL-125(Ti), (b) SH NH₂-MIL-125(Ti), (c) AS ZIF-67, (d) SH ZIF-67, (e) AS HKUST-1 and (f) SH HKUST-1 after exposure to liquid water.

exposure to liquid water for up to 5 days (Fig. 2). For the purpose of comparison, the results of AS samples are also presented. From powder XRD, it is seen that all the diffraction patterns of the AS MOFs have significantly changed and they have undergone structure transformation. NH₂-MIL-125(Ti) can only retain its crystal structure in 50 °C water for 1 day (Fig. 2a). Upon further exposure to water for 3 days, the diffraction peaks of NH₂-MIL-125(Ti) become very weak. Meanwhile, a broad peak at 2 theta = 25.2° appears, indicating the formation of a new phase. When exposed to water for 5 days, the diffraction peaks associated with NH₂-MIL-125(Ti) almost completely disappear, revealing the destruction of its crystal structure. In contrast, there is no obvious change in the peak positions and crystallinity level for SH NH₂-MIL-125(Ti), nor is there structural transformation observed when exposed to liquid water for up to 5 days (Fig. 2b). The crystal structure remains essentially unchanged after the same exposure. Obviously, the SH NH₂-MIL-125(Ti) exhibits much better water stability and surface hydrophobic coating effectively protects NH₂-MIL-125(Ti) against the attack of water molecules. The AS ZIF-67 can retain the crystal structure for 1 day (Fig. 2c). After exposure for 3 days, the diffraction peaks of ZIF-67 also become much weak and an extra peak emerges at 2 theta = 19.1°. When the AS ZIF-67 is exposed to water for 5 days, many of its diffraction peaks disappear and the extra peak becomes stronger. These results show that the structure of ZIF-67 is damaged and new phases are formed. However, there is no change in the XRD patterns of the SH ZIF-67 for up to 5-day

exposure (Fig. 2d). Again, the SH ZIF-67 shows better water stability. HKUST-1 has hydrophilic open-metal sites¹⁶ and is more sensitive to water. Upon immersing in RT water for 1 day, the peaks associated with HKUST-1 weaken and new sharp diffraction peaks appear (Fig. 2e), signifying that decomposition of HKUST-1 has occurred. After exposure for up to 3 days, the characteristic peaks of HKUST-1 completely disappear, leading to the formation of new phases *via* protonation of benzene-1,3,5-tricarboxylic acid ligands.²⁸ This result is in good agreement with previous work.³ After the same exposure to water, however, the SH HKUST-1 still shows the same XRD pattern as the original (Fig. 2f). Once again, it is proved that the SH HKUST-1 shows better water stability. In order to evaluate the stability and durability of the hydrophobic coating, a prolonged exposure experiment for up to 1 month was carried out. XRD shows that the SH MOFs can still maintain structural integrity after the extended exposure (Fig. S4†). This observation suggests that the surface hydrophobic coating is rather stable and offers durable protection.

The sample colour was investigated as a supplementary proof of water stability. It is seen that three SH MOFs show nearly the same colour as the AS counterpart MOFs (Fig. S5†). After the water stability experiment, the original bright yellow colour of the AS NH₂-MIL-125(Ti) turns dark yellow (Fig. S5a†), indicating structure transformation and/or the formation of new phases. However, the colour of the SH NH₂-MIL-125(Ti) remains almost the same as the original. Similar results are also observed for the other two MOFs (Fig. S4b and c†). These findings agree with the above XRD results.

The enhanced water stability of the SH MOFs was further testified by SEM morphology observation. As shown in Fig. 3a, the SEM image shows that the AS crystals of ZIF-67 exhibit a rhombic dodecahedral shape with 12 exposed {110} faces, which is a special crystal form of the crystallographic point

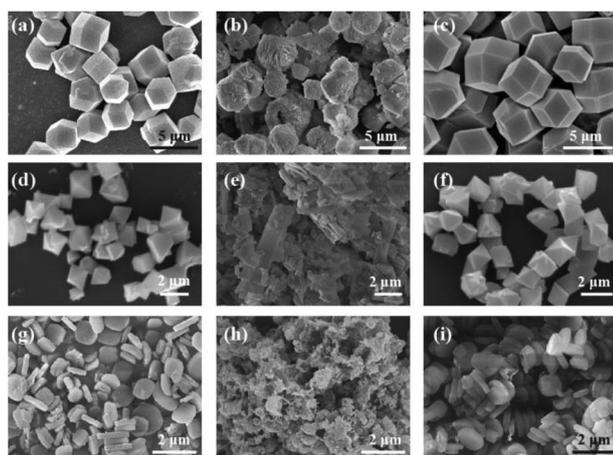


Fig. 3 SEM images of (a) the AS ZIF-67, (b) and (c) the AS ZIF-67 and SH ZIF-67 after exposure to water for 5 days, respectively, (d) the AS HKUST-1, (e) and (f) the AS HKUST-1 and SH HKUST-1 after exposure to water for 5 days, respectively, (g) the AS NH₂-MIL-125(Ti), (h) and (i) the AS NH₂-MIL-125(Ti) and SH NH₂-MIL-125(Ti) after exposure to water for 5 days, respectively.

group $\bar{4}3m$.³⁷ After exposure to liquid water for 5 days, the dodecahedral crystals are nearly destroyed and are full of cracks and cavities (Fig. 3b). It is discovered that the hydrophilic –N–H bonds of ZIF-67 on the external surface can adsorb significant amounts of water due to the terminated imidazole linkers.^{16,39} Therefore, this gives rise to a subsequent hydrolysis reaction and microstructure breakdown. However, there is no significant change in the crystal morphology and size of the SH ZIF-67 crystals after the same exposure to water (Fig. 3c). They remain intact and the dodecahedral morphology is well preserved. Apparently, the surface hydrophobic coating effectively protects ZIF-67 against the attack of water molecules by keeping them away and thus guarantees the MOFs' integrity. The SEM observation further verifies the above XRD results. The situations for HKUST-1 and NH₂-MIL-125(Ti) are similar to that of ZIF-67. The SH HKUST-1 and NH₂-MIL-125(Ti) could well retain their crystal shape whereas the AS MOFs collapse after the water stability test (Fig. 3d–i). Both XRD and SEM results clearly demonstrate the improvement of the water stability of the SH MOFs relative to the AS MOFs.

The improved water stability of the SH MOFs encouraged us to investigate their porosity properties and potential application in CO₂ capture. As shown in Fig. 4, the N₂ sorption and desorption isotherms of three AS MOFs at 77 K show a type I isotherm, indicating the permanent microporosity of the framework. The BET surface areas (S_{BET}) of the AS NH₂-MIL-125(Ti), ZIF-67 and HKUST-1 are measured to be 1134, 1587 and 1386 m² g^{−1}, respectively, which is in accordance with previously reported data.^{37,40–42} After exposure to water for 5 days, the N₂ adsorption and desorption curves of three AS MOFs are clearly decreased. The S_{BET} of AS NH₂-MIL-125(Ti) is significantly reduced by 80.2% from 1134 to 225 m² g^{−1} upon exposure, demonstrating that the porous structure of the framework collapses. However, the SH NH₂-MIL-125(Ti) shows only a minor decrease in N₂ sorption curves. 85% S_{BET} (968 m² g^{−1}) is retained after the same time period. The S_{BET} of AS ZIF-67 is also reduced significantly from

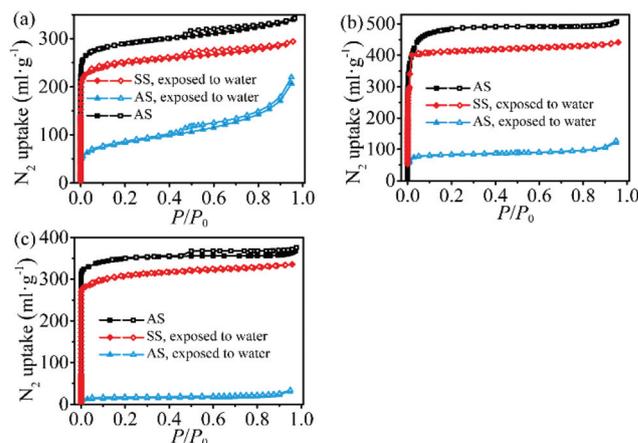


Fig. 4 N₂ sorption isotherms for (a) NH₂-MIL-125(Ti), (b) ZIF-67 and (c) HKUST-1 after exposure to liquid water for 5 days.

1587 to $67 \text{ m}^2 \text{ g}^{-1}$ upon exposure to water, while the S_{BET} of SH ZIF-67 remains as high as $1321 \text{ m}^2 \text{ g}^{-1}$. The water stability test for HKUST-1 leads to a similar result that the structure of AS HKUST-1 samples rapidly collapses and thus completely loses porosity after exposure for 5 days ($S_{\text{BET}} = 39.6 \text{ m}^2 \text{ g}^{-1}$), while the SH HKUST-1 maintains up to 87% S_{BET} ($1206 \text{ m}^2 \text{ g}^{-1}$), intact morphology and structure after the identical experiment. Decoste *et al.* introduced internal hydrophobicity in HKUST-1 to increase water stability by using a plasma-enhanced chemical vapour deposition approach with perfluorohexane.²² However, the S_{BET} and porosity of HKUST-1 were reduced by roughly 30%. In the current work, the surface hydrophobic coating enables the MOFs to maintain a higher specific surface area. All N_2 sorption results are in good agreement with the above structure and morphology investigations. The highly preserved S_{BET} of SH samples is certainly favourable for gas storage application.

MOFs have emerged as a class of excellent adsorbent materials for carbon dioxide capture from flue gas.^{43,44} However, the majority of them require the incoming gas stream to be completely dehydrated, as water can cause a drastic reduction in the CO_2 sorption capabilities.^{45,46} Here, as a proof-of-concept study, CO_2 sorption for the AS and SH MOFs has been conducted after exposure to liquid water (Fig. 5). The CO_2 sorption capabilities of the AS $\text{NH}_2\text{-MIL-125(Ti)}$, ZIF-67 and HKUST-1 reach 111, 34 and $149 \text{ cm}^3 \text{ g}^{-1}$ at 1 atm, respectively. After exposure to water, the CO_2 sorption and desorption curves of three AS MOFs become significantly lower, which is similar to that of N_2 sorption and desorption. As a result, only 21, 20 and 16% of the initial CO_2 sorption capacities at 1 atm can be retained, respectively, due to the structure breakdown caused by the attack of water molecules. It is seen that they almost lose their CO_2 uptake capacity. Taking into account their sensitivity to water, it is not surprising that the sorption capacity of the AS MOFs is dramatically diminished upon exposure to water. In the case of the SH MOFs after exposure, the CO_2 sorption and desorption curves

are close to those of the AS samples. 76, 83 and 86% of the initial CO_2 capacities are retained after the same treatment, respectively. Such a high residual capacity is definitely due to the intact structure of the frameworks.

The above results prove that the hydrophobic coating on the external surface of MOFs could significantly improve their water stability and is beneficial to maintain a high surface area and CO_2 adsorption capacity when MOFs are exposed to water. The present solution-immersion approach is not only facile but also shows significant superiority to maintain intrinsic porosity. It could be a universal approach to fabricate a thin hydrophobic coating on the MOFs' surface. By this approach, the water sensitive MOFs can still find potential applications in the presence of water.

Conclusions

In summary, this paper presents a facile solution-immersion method for fabricating the hydrophobic coatings on the external surfaces of three water sensitive MOFs. The hydrophobic coating not only greatly enhances MOFs' water stability but also provides MOFs with durable protection against the attack of water molecules. When exposed to liquid water, the surface hydrophobic MOFs well retain their crystal structure, morphology, surface area and CO_2 uptake capacity, whereas the as-synthesized MOFs quickly collapse and lose gas adsorption capacity. Our study would expand the potential applications of water sensitive MOFs in the presence of water or moisture.

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Notes and references

- 1 S. Q. Ma and H. C. Zhou, *Chem. Commun.*, 2010, **46**, 44–53.
- 2 K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.
- 3 J. Liu, P. K. Thallapally, B. P. McGrail, D. R. Brown and J. Liu, *Chem. Soc. Rev.*, 2012, **41**, 2308–2322.
- 4 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.

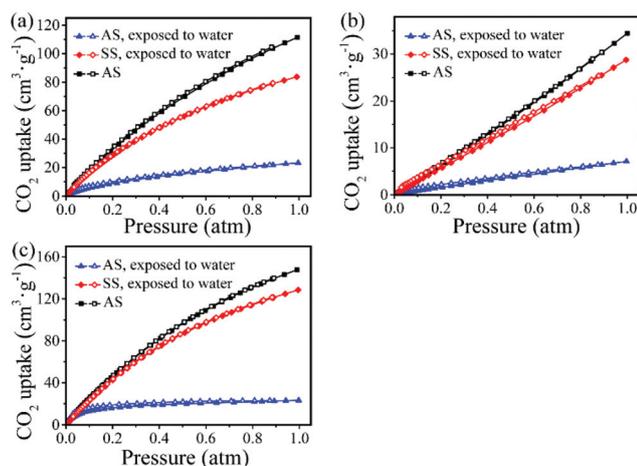


Fig. 5 CO_2 sorption isotherms for (a) $\text{NH}_2\text{-MIL-125(Ti)}$, (b) ZIF-67 and (c) HKUST-1 after exposure to liquid water for 5 days.

- 5 S. B. Wang and X. C. Wang, *Small*, 2015, **11**, 3097–3112.
- 6 A. J. Howarth, Y. Y. Liu, P. Li, Z. Y. Li, T. C. Wang, J. Hupp and O. K. Farha, *Nat. Rev. Mater.*, 2016, **1**, 15018.
- 7 D. Zacher, R. Schmid, C. Woll and R. A. Fischer, *Angew. Chem., Int. Ed.*, 2011, **50**, 176–199.
- 8 X. K. Qian, B. L. Yadian, R. B. Wu, Y. Long, K. Zhou, B. Zhu and Y. Z. Huang, *Int. J. Hydrogen Energy*, 2013, **38**, 16710–16715.
- 9 X. K. Qian, Z. Y. Zhong, B. L. Yadian, J. S. Wu, K. Zhou, J. S. K. Teo, L. W. Chen, Y. Long and Y. Z. Huang, *Int. J. Hydrogen Energy*, 2014, **39**, 14496–14502.
- 10 C. L. Cui, Y. Y. Liu, H. B. Xu, S. Z. Li, W. N. Zhang, P. Cui and F. W. Huo, *Small*, 2014, **10**, 3672–3676.
- 11 R. B. Wu, X. K. Qian, A. W. K. Law and K. Zhou, *RSC Adv.*, 2016, **6**, 50846–50850.
- 12 T. Pham, K. A. Forrest, W.-Y. Gao, S. Ma and B. Space, *ChemPhysChem*, 2015, **16**, 3170–3179.
- 13 P. Deria, D. A. Gomez-Gualdrón, W. Bury, H. T. Schaeff, T. C. Wang, P. K. Thallapally, A. A. Sarjeant, R. Q. Snurr, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 13183–13190.
- 14 T. Pham, K. A. Forrest, E. H. L. Falcao, J. Eckert and B. Space, *Phys. Chem. Chem. Phys.*, 2016, **18**, 1786–1796.
- 15 S. C. Xiang, Y. B. He, Z. J. Zhang, H. Wu, W. Zhou, R. Krishna and B. L. Chen, *Nat. Commun.*, 2012, **3**, 954.
- 16 N. C. Burtch, H. Jasuja and K. S. Walton, *Chem. Rev.*, 2014, **114**, 10575–10612.
- 17 J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 15834–15842.
- 18 K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser and Y. J. Chabal, *Chem. Mater.*, 2012, **24**, 3153–3167.
- 19 C. H. Wang, X. L. Liu, N. K. Demir, J. P. Chen and K. Li, *Chem. Soc. Rev.*, 2016, **45**, 5107–5134.
- 20 T. Wu, L. Shen, M. Luebbbers, C. Hu, Q. Chen, Z. Ni and R. I. Masel, *Chem. Commun.*, 2010, **46**, 6120–6122.
- 21 H. Jasuja, Y. G. Huang and K. S. Walton, *Langmuir*, 2012, **28**, 16874–16880.
- 22 J. B. Decoste, G. W. Peterson, M. W. Smith, C. A. Stone and C. R. Willis, *J. Am. Chem. Soc.*, 2012, **134**, 1486–1489.
- 23 D. Mustafa, E. Breynaert, S. R. Bajpe, J. A. Martens and C. E. A. Kirschhock, *Chem. Commun.*, 2011, **47**, 8037–8039.
- 24 S. J. Yang, J. Y. Choi, H. K. Chae, J. H. Cho, K. S. Nahm and C. R. Park, *Chem. Mater.*, 2009, **21**, 1893–1897.
- 25 X. Liu, Y. Li, Y. Ban, Y. Peng, H. Jin, H. Bux, L. Xu, J. Caro and W. Yang, *Chem. Commun.*, 2013, **49**, 9140–9142.
- 26 S. J. Yang and C. R. Park, *Adv. Mater.*, 2012, **24**, 4010–4013.
- 27 C. V. McGuire and R. S. Forgan, *Chem. Commun.*, 2015, **51**, 5199–5217.
- 28 A. Carne-Sanchez, K. C. Stylianou, C. Carbonell, M. Naderi, I. Imaz and D. Maspocho, *Adv. Mater.*, 2015, **27**, 869–873.
- 29 W. Zhang, Y. L. Hu, J. Ge, H. L. Jiang and S. H. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 16978–16981.
- 30 C. A. Fernandez, S. K. Nune, H. V. Annappureddy, L. X. Dang, B. P. McGrail, F. Zheng, E. Polikarpov, D. L. King, C. Freeman and K. P. Brooks, *Dalton Trans.*, 2015, **44**, 13490–13497.
- 31 G. Huang, Q. H. Yang, Q. Xu, S. H. Yu and H. L. Jiang, *Angew. Chem., Int. Ed.*, 2016, **55**, 7379–7383.
- 32 Q. Sun, H. M. He, W. Y. Gao, B. Aguila, L. Wojtas, Z. F. Dai, J. X. Li, Y. S. Chen, F. S. Xiao and S. Q. Ma, *Nat. Commun.*, 2016, **7**, 13300.
- 33 C. Zlotea, D. Phanon, M. Mazaj, D. Heurtaux, V. Guillerme, C. Serre, P. Horcajada, T. Devic, E. Magnier, F. Cuevas, G. Ferey, P. L. Llewellyn and M. Latroche, *Dalton Trans.*, 2011, **40**, 4879–4881.
- 34 R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939–943.
- 35 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.
- 36 S. Hu, M. Liu, K. Y. Li, Y. Zuo, A. F. Zhang, C. S. Song, G. L. Zhang and X. W. Guo, *CrystEngComm*, 2014, **16**, 9645–9650.
- 37 H. Y. Wu, X. K. Qian, H. P. Zhu, S. H. Ma, G. S. Zhu and Y. Long, *RSC Adv.*, 2016, **6**, 6915–6920.
- 38 R. B. Wu, X. K. Qian, F. Yu, H. Liu, K. Zhou, J. Wei and Y. Z. Huang, *J. Mater. Chem. A*, 2013, **1**, 11126–11129.
- 39 P. Kuesgens, M. Rose, I. Senkovska, H. Froede, A. Henschel, S. Siegle and S. Kaskel, *Microporous Mesoporous Mater.*, 2009, **120**, 325–330.
- 40 B. Yuan, X. Q. Yin, X. Q. Liu, X. Y. Li and L. B. Sun, *ACS Appl. Mater. Interfaces*, 2016, **8**, 16457–16464.
- 41 H. Wang, X. Z. Yuan, Y. Wu, G. M. Zeng, X. H. Chen, L. J. Leng, Z. B. Wu, L. B. Jiang and H. Li, *J. Hazard. Mater.*, 2015, **286**, 187–194.
- 42 W. N. Zhang, Y. Y. Liu, G. Lu, Y. Wang, S. Z. Li, C. L. Cui, J. Wu, Z. L. Xu, D. B. Tian, W. Huang, J. S. DuCheneu, W. D. Wei, H. Y. Chen, Y. H. Yang and F. W. Huo, *Adv. Mater.*, 2015, **27**, 2923–2929.
- 43 Y. Y. Liu, Z. Y. U. Wang and H. C. Zhou, *Greenhouse Gases: Sci. Technol.*, 2012, **2**, 239–259.
- 44 N. T. T. Nguyen, H. Furukawa, F. Gandara, H. T. Nguyen, K. E. Cordova and O. M. Yaghi, *Angew. Chem., Int. Ed.*, 2014, **53**, 10645–10648.
- 45 A. C. Kizzie, A. G. Wong-Foy and A. J. Matzger, *Langmuir*, 2011, **27**, 6368–6373.
- 46 J. Liu, J. Tian, P. K. Thallapally and B. P. McGrail, *J. Phys. Chem. C*, 2012, **116**, 9575–9581.