Angewandte Highlights

Metal–Organic Frameworks

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Superhydrophobicity in Highly Fluorinated Porous Metal–Organic Frameworks**

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Porous metal–organic frameworks (MOFs) and porous coordination polymers (PCPs) are versatile classes of crystalline hybrid inorganic–organic solids that bear several key features over their traditional porous inorganic (zeolites, phosphates, and oxides) or organic (activated carbons) counterparts. In addition to their wide structural diversity with pore sizes ranging from a few angstroms to several nanometers and their sometimes flexible character, one of their main advantages consists in the possibility of their functionalization.[1] Realized either through direct synthesis or post-synthetic modifications using organic moieties or grafting on Lewis metal sites, amazing characteristics are conferred on the MOFs which allow the tuning of their sorption properties, particularly for separation-related applications. MOFs have, for instance, shown sorption properties suitable for the capture of greenhouse gases, separation of xylenes or propane from propylene, and capture of traces of N/S derivatives from fuels.[2–5] The impact of functionalization has been studied extensively to date, particularly for the capture of CO_2 or hydrogen storage, with a particular emphasis on materials bearing polar functional groups (NH_2, NO_2, Cl, Br, CO_2H, or SO_3H).[6] However, little has been done concerning the use of hydrophobicity to improve the efficacy of separation. In addition, most MOFs suffer from a weak hydrothermal stability that hampers their use under industrially relevant conditions because of the weakness of the metal–ligand bond relative to the metal–water bond.[7] The use of linkers with enhanced basic properties or metals in higher oxidation states leads nevertheless to an improvement in the chemical stability.[7] Furthermore, even when the water stability is sufficient, most MOFs show a sharp decrease in their performance under humid conditions as observed for the capture of CO_2 from flue gas.[8]

Hydrophobicity, through the presence of alkyl or fluorinated (F, CF_3…) groups, is an efficient way to improve the water stability of a given MOF, as shown recently through the modified analogs of the Zn terephthalate MOF-5. Omary and co-workers have recently reported the synthesis and structural characterization of two new highly fluorinated porous silver azolate MOFs, denoted FMOF-1 and FMOF-2. These MOFS were built by association of three or four coordinated silver cations bound to 3,5-bis(trifluoromethyl)-1,2,4-triazolate linkers which form 1.2 nm × 0.8 nm large hydrophobic channels (Figure 1).[9]

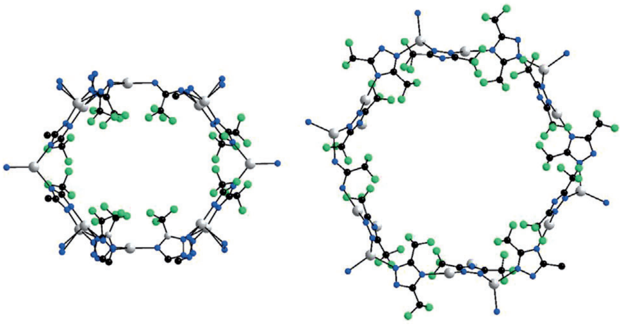

Figure 1. View of the crystal structures of FMOF-1 (left) and FMOF-2 (right) along the pore axis (the Ag, N, C, and F atoms are in light grey, blue, black, and green, respectively). Hydrogen atoms have been omitted for a better understanding.

First, the authors analyzed based on water adsorption isotherms the hydrophobic character of FMOF-1 and then, they showed that the hydrophobic character appears superior relative to other usual adsorbents, such as a hydrophilic zeolite, as expected, and a hydrophobic activated carbon. No adsorption step and thus no water uptake is observed for FMOF-1 even near the saturation pressure (relative pressure of 0.9), whereas activated carbon is, under the same conditions, fully saturated with water (Figure 2). Interestingly, as observed previously for other highly hydrophobic MOFs, Omary and co-workers denote, using a combination of X-ray powder diffraction and IR spectroscopic analysis, that FMOF-1 does not suffer from degradation upon long-term exposure to boiling water in agreement with the absence of any water adsorption.

Such a hydrophobic character that fully prevents water molecules from entering into the pores is due to the alignment of the perfluoro groups at the channel walls. This alignment affords only a weak water–framework interaction and thus forces the water molecules, as it is the case for superhydro-

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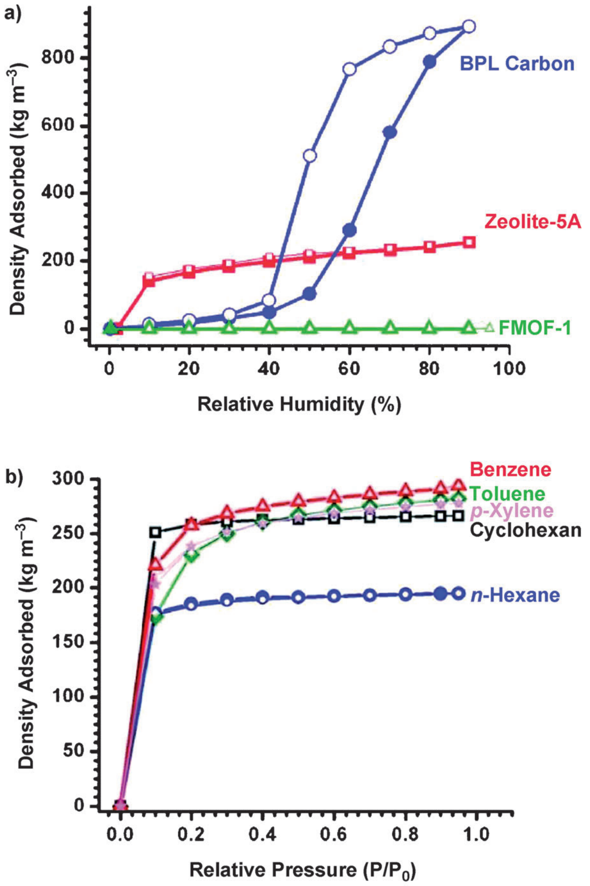

Figure 2. a) Room-temperature water adsorption isotherms of FMOF-1 compared to isotherms of other topical adsorbents (zeolite 5 A and BPL carbon). b) Room-temperature adsorption isotherms of benzene, toluene, *p*-xylene, cyclohexane, and n-hexane from FMOF-1 (extracted from Ref. [9]).

phobic materials, to produce a film of water at the external surface of the particles which blocks the adsorption of water molecules. The hydrophobic character is strengthened here because of the unprecedented high density of fluorinated groups ($F > 40$ w%) compared to other fluorinated porous MOFs.[10] In addition, there are no accessible hydrophilic groups, if one excludes the nitrogen atoms from the linker which are hardly accessible for guest molecules and would favor typically the formation of small pockets capable of accommodating free water molecules within the pores. To confirm the superhydrophobicity of these MOFs, the next step, as mentioned by the authors, would be to analyze quantitatively the hydrophobic character of FMOF materials through contact angle experiments and compare the results with those from traditional hydrophobic polymers, carbons, and silica materials.

Not only FMOF-1 behaves like a superhydrophobic material but it also exhibits a high and reversible sorption capacity of model aromatics and alkanes, reaching sorption capacities close to those of the most activated carbons or MOFs (Figure 2). Interestingly, when FMOF-1 is annealed, leading to a partial removal of organic linkers and a structural reorganization when exposed back to solvent, FMOF-2 is formed and shows a superior pore size (Figure 1) that affords a doubling in the sorption capacity of large apolar molecules such as toluene.

Finally, to confirm the potential of such materials, the next step is to evaluate the performance of these hydrophobic MOFs by multicomponent separation tests of mixtures of hydrophobic moities in the presence of water. Even if these tests at laboratory scale are successful, one shall bear in mind that the use of MOFs for practical applications will require not only their evaluation under industrial conditions (that is, mixtures in water and impurities), but also a comparison of costs to existing or other new hydrophobic MOFs based on low-cost abundant metals (Al, Fe, or Zn) and/or linkers.[10]

In conclusion, highly fluorinated superhydrophobic porous MOFs are not only of great interest for treatment of oil spills, but they also can be used for a wide range of applications that require both long-term stability and/or superhydrophobicity. Among the many potential applications of these MOFS some of the most promising are capture of hydrophobic biorenewable resources from water, separation or selective adsorption of gas/vapor mixtures under humid conditions (such as the capture of CO_2 from flue gases), and green heterogeneous catalysis in water.

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