Switchable Surface Hydrophobicity-Hydrophilicity of a Metal-Organic Framework

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Abstract: Materials whose surface can be switched from high/superhydrophobicity to superhydrophilicity are useful for myriad applications. Herein we report a metal-organic framework (MOF) assembled from Zn^{II} ions, 1,4-benzenedicarboxylate and a hydrophobic carborane-based linker, whose crystal-surface can be switched between hydrophobic and superhydrophilic. Switching is achieved through chemical treatment to remove some of the building blocks.

Smart solid surfaces that exhibit switchable wettability – mainly between high or superhydrophobicity, and superhydrophilicity – are actively being sought due to their diverse potential applications such as self-cleaning materials, microfluidics, tunable optical lenses, drug delivery vectors, and sensors.[1, 2] In general, the wettability of a solid surface can be tuned by modifying its surface geometry and/or its chemical composition. For example, superhydrophobic surfaces can be fabricated by creating structures that mimic the rough surface of the lotus leaf.[3, 4] However, when such lotus leaf-like surfaces are built from materials that response to specific stimuli, they can exhibit switchable wettability. For instance, a lotus leaf-like surface built from the photosensitive material TiO_2 can exhibit light-dependent switching.[5] To date, the majority of materials that exhibit switchable wettability – and therefore, that could be used for fabricating such smart surfaces – comprise photo-sensitive inorganic oxides (*e.g.* TiO_2[4] and ZnO,[6]); organic polymers (*e.g.* light-responsive azobenzene-containing polymers,[7] temperature-responsive poly-*N*-isopropylacrylamide,[8] and electrical-responsive polypyrrole[9]); self-assembled monolayers (SAMs; *e.g.* electrical-responsive 16-mercaptohexanoic SAMs [10] and pH-responsive mixed SAMs[11]); and counterion exchange-responsive ionic liquids.[12]

Herein we report that metal-organic frameworks (MOFs) (also known as porous coordination polymers [PCPs]) can be a novel class of responsive materials that exhibit switching of their crystal surface, between hydrophobic to superhydrophilic. Researchers have recently begun to investigate hydrophobic and superhydrophobic MOFs to enhance their aqueous stability and enable new applications (*e.g.* self-cleaning).[13] Some advances have been made to this end. For instance, Kitagawa *et al.* reported a superhydrophobic MOF, which they obtained by controlling the corrugation of its crystal surface by using aromatic linkers.[14] However, the most common strategy to synthesize these hydrophobic MOFs is via introduction of hydrophobic molecules as linkers (*e.g.* trifluoromethyl groups,[15, 16] carboranes,[17] and alkyl chains[18, 19]) or as guests.[20]

Among these hydrophobic molecules, carboranes are an interesting class of exceptionally stable boron-rich clusters that possess material-favorable properties such as thermal and chemical stability.[21] Here, we have exploited this class of molecules to synthesize a responsive MOF that exhibits switching between hydrophobicity and superhydrophilicity. Specifically, we used an *ortho*-carborane functionalized with pyridylmethylalcohol groups at the C-positions[22] (hereafter, "*o*CB-L", Figure 1a) as a hydrophobic linker in combination with Zn-bdc (where bdc is 1,4-benzenedicarboxylate). This switching behaviour is achieved by alternatively exposing the MOF to NaOH/DMF solution and to slightly acidic aqueous solution.

Reaction of $Zn(NO_3)_2{\cdot}6H_2O$, H_2bdc, 1,2-bis{(pyridin-3-yl)methanol}-1,2-dicarba-closo-dodecarborane (*o*CB-L) and 2-methylimidazole (2-Hmim) in a 1:1 mixture of EtOH:DMF (4 mL) at 85 ºC for 48 h afforded a white crystalline material (yield: 49 %). Single-crystal X-ray diffraction revealed a 3D network of formula $[Zn_4(\mu_4\text{-bdc})_2(\mu_2\text{-}o\text{CB-L})_2(\mu_3\text{-O})_2(DMF)_2]{\cdot}4DMF$, ***o*CB-MOF-1**, which purity was confirmed by elemental analysis, Scanning Electron Microscopy and powder X-ray diffraction (PXRD, Supporting Information, Figures S1-2, Table S3). The basic unit of ***o*CB-MOF-1** is a tetranuclear $Zn_4(O)_2(OOC)_4$ cluster formed by two crystallographic independent Zn#1 and Zn#2 ions. Both Zn#1 ions are $\{NO_3\}$-tetrahedrally coordinated to two carboxylate groups of bdc linkers, one pyridine moiety of μ_2-*o*CB-L and a μ_3-O atom. Both Zn#2 ions are $\{NO_5\}$-octahedrally coordinated to two carboxylate groups of bdc linkers, one pyridine moiety of μ_2-*o*CB-L, two μ_3-O atoms and a guest DMF molecule (Figure 1b).

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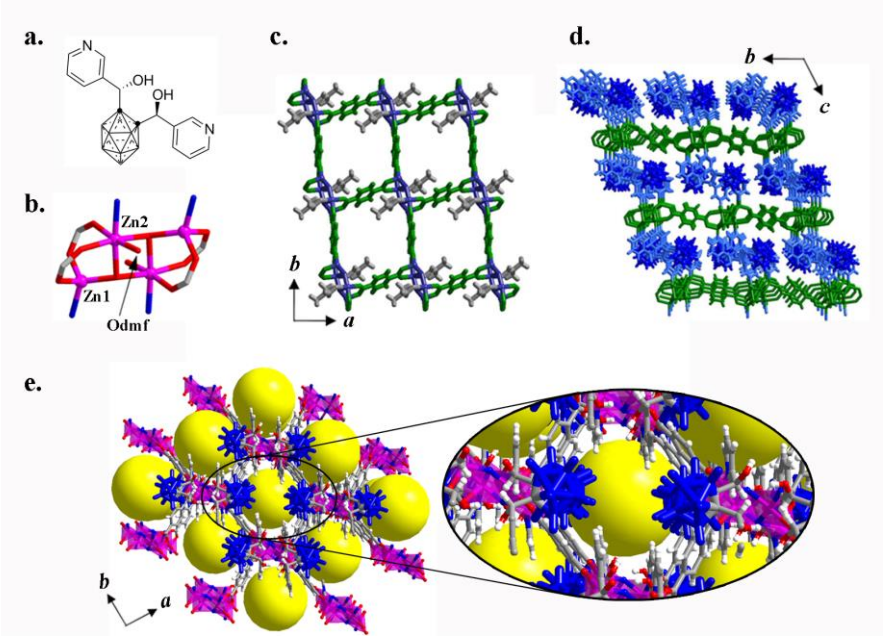

Figure 1. a) Representation of the *o*CB-L linker; b) $Zn_4(O)_2(OOC)_4$ cluster; c) $Zn_4(bdc)_2$ layers are extended in the *ab* plane. Bdc ligands are represented in green; coordinated DMF molecules, in gray; and $Zn_4(O)_2$ clusters, in blue; d) Pillaring μ_2-*o*CB-L linkers (blue) connect $Zn_4(bdc)_2$ layers (green), giving rise to a 3D structure. Carborane cores are represented in dark blue; e) 1D channels, formed by connected cavities (in yellow), run along the *c* axis. Note that the carborane cores (highlighted in dark blue) are pointed to the pore aperture. Color code (b, e): Zn (pink), O (red), C (gray), H (white).

Similar $M_4(O(H))_2(OOC)_4$ (M = Zn, Co) building units have previously been reported.[23] In ***o*CB-MOF-1**, each carboxylate group of the bdc linker bridges two Zn^{II} ions within the same Zn_4 unit, and each bdc linker connects two Zn_4 units, thereby forming square grid $Zn_4(bdc)_2$ layers that extend along the *ab* plane (Figure 1c). These layers are further connected through pillaring μ_2-*o*CB-L linkers to create a 3D structure (Figure 1d) that contains 1D channels (46% of void space in unit cell).[24] These channels are formed by cavities that can host a sphere of a diameter of 8.6 Å and that are connected by small apertures (3.2 x 6.4 Å, considering vdW radii) along the *c* axis (Figure 1e). These cavities are filled with four guest DMF molecules per formula unit. Importantly, the carborane moieties of μ_2-*o*CB-L linkers are located on the pore aperture surface.

Thermogravimetric analysis (TGA) of ***o*CB-MOF-1** shows a continuous weight loss of 22.3% from 90 ºC to 250 ºC, which we attributed to the loss of the four guest and two coordinated DMF molecules (calcd. 24.9%; Supporting Information, Figure S3). Above 350 ºC, this framework decomposes over multiple steps. Elemental analysis, infrared (IR-ATR) and TGA measurements of a sample heated under vacuum at 85 ºC for 12 h confirmed the removal of the four guest DMF molecules (Supporting Information, Figure S4, Table S3). The IR spectrum confirmed the presence of DMF molecules in the activated ***o*CB-MOF-1'**, evidenced by a strong peak at 1650 cm^{-1}. In the same direction, TGA analysis of ***o*CB-MOF-1'** revealed initial weight loss of 8.3%, from 120 ºC to 250 ºC, corresponding to loss of the two coordinated DMF molecules (calcd. 10.0 %). Additionally, PXRD measurements showed that ***o*CB-MOF-1'** retains its original structure. Sorption measurements revealed that desolvated ***o*CB-MOF-1'** is non-porous to N_2 at 77 K and 1 bar. However, it is porous to CO_2 (69.4 cm^3g^{-1} at 0.9 bar; BET surface area: 296 m^2g^{-1}) at 195 K and 0.8 bar, for which it showed reversible type-I isotherms (Supporting Information, Figure S5). We reasoned that this selectivity could be explained by the pore aperture (3.2 x 6.4 Å), which is large enough to be accessible for CO_2 but not for N_2 (kinetic diameters for CO_2: 3.30 Å and N_2: 3.7 Å). The isosteric heats of adsorption of CO_2 (*Qst*) were derived from the Claussius-Clapeyron equation, using the adsorption branches of the isotherms measured at 288 K, 273 K and 258 K. The *Qst* of ***o*CB-MOF-1´** was 29.2 $kJmol^{-1}$ at low coverage, decreasing at a rate of up to 26.4 $kJmol^{-1}$ at high coverage. Note here that when ***o*CB-MOF-1** was heated at 200 ºC for 12 h, all six DMF molecules were removed (Supporting Information, Figure S4, Table S3). However, PXRD analysis showed a loss of crystallinity, and CO_2 sorption measurements revealed a decrease of 35% of the BET area compared to that of ***o*CB-MOF-1'**.

Having determined that ***o*CB-MOF-1** retains porosity, we then evaluated the influence of the carborane units on its hydrophobic properties. Thus, we performed water contact-angle measurements of crystalline powder of as-synthesized ***o*CB-MOF-1** and desolvated ***o*CB-MOF-1'** packed on a glass surface. The contact angle (Θ_c) in each case was 140° and 138°, respectively — values which are characteristic of a highly hydrophobic solid. We finally characterized the contact angle of ***o*CB-MOF-1** shaped in the form of a disk pellet (diameter = 13 mm), which was fabricated by pressing a dry crystalline powder under a pressure of 10 tons for 5 min (Figure 2). This pellet, which showed a roughness factor r (defined as the ratio of the actual area of the rough surface to its projected area on the horizontal plane) of 1.7 ± 0.1, was also found to be hydrophobic with a Θ_c of 108°. We also quantified the contact-angle hysteresis (CAH) that was found to be 32° (Supporting Information, Table S4). This relatively large CAH was attributed to the surface roughness of the disk pellet that can be the responsible for the contact line pinning.

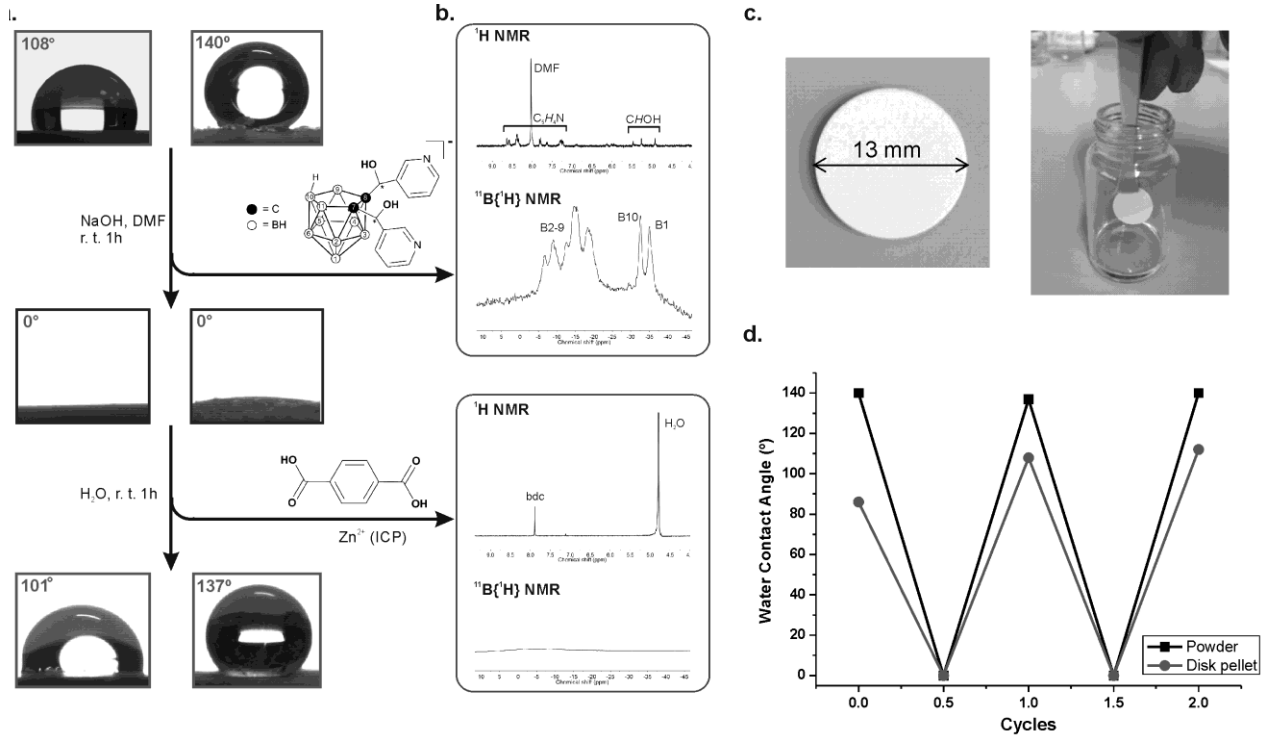

Figure 2. a) Contact angle images of ***o*CB-MOF-1** (left column, disk pellet; right column, hand-packed) before treatment (top), after immersion in a DMF solution containing 10 equivalents of NaOH (middle) and after immersion in H_2O (bottom).; b) In the first treatment, only carborane *nido* species were detected in the ^{1}H- and ^{11}B-{^{1}H}-NMR spectra of the supernatant. Treatment with water leads to release of the bdc linkers and Zn^{II} ions, as detected by ^{1}H- and ^{11}B-{^{1}H}-NMR and ICP, respectively; c) Photographs of the press disk pellet of ***o*CB-MOF-1**; d) Static contact angle values for two cycles of treatment (see text for details).

The hydrophobic character of ***o*CB-MOF-1'** is also revealed by water-vapor adsorption measurements. Similarly to other highly hydrophobic or superhydrophobic MOFs (*e.g.* ZIF-8 and perfluorinated MOFs),[25] ***o*CB-MOF-1'** can barely adsorb water: at 95% relative humidity, it exhibits a very low uptake of only 0.05 g H_2O/g ***o*CB-MOF-1'** (Supporting Information, Figure S6). This low water adsorption clearly confirms that the pore surface of ***o*CB-MOF-1'** is hydrophobic and as such, would prevent entry of water into the pores. Due to the high hydrophobicity of ***o*CB-MOF-1**, it is highly stable in water. For example, ***o*CB-MOF-1** is stable when incubated in liquid water over a wide pH range (from 2 to 12; pH adjusted with HCl or NaOH) for at least 15 h at room temperature (Supporting Information, Figure S8). Indeed, the simulated (derived from the single crystal structure of ***o*CB-MOF-1**) and experimental (resulting from the powders incubated at different pHs) PXRD patterns suggest that minor structural transformations occur under these conditions, which are however reversible after immersing these powders in DMF for 2 h.

Interestingly, we observed that ***o*CB-MOF-1**, either hand-packed or shaped in the form of a disk pellet, undergoes a switch from hydrophobic (Θ_c = 140° from the hand-packed; Θ_c = 108° from the pellet) to superhydrophilic (Θ_c = 0° in both cases) upon immersion in a solution of NaOH (10 eq.) in DMF for 1 h at room temperature. Moreover, this switch was reversible: initial hydrophobicity (Θ_c = 137° from the hand packed; Θ_c = 101° from the pellet) was fully recovered when hydrophilic ***o*CB-MOF-1** was immersed in H_2O (pH < 6.5) for 1 h at room temperature (Figure 2). Note that the roughness factor r of the disk pellet as well as the CAH did not varied significantly during this switching process, evidencing that the chemical nature of ***o*CB-MOF-1** is mainly responsible of this switching phenomena. The r value calculated from the hydrophilic disk pellet was 1.7 ± 0.1, whereas that from the recovered hydrophobic pellet was 1.5 ± 0.1. In this latter, the CAH was found to be 35º. Remarkably, we were able to demonstrate at least two complete cycles of switching without observing any significant loss in hydrophobicity (Figure 2d and Supporting Information, Figure S8).

We attributed the switching phenomenon to changes in the surface chemistry of the ***o*CB-MOF-1** crystals. Thus, we hypothesized that under basic conditions, the hydrophobic *o*CB-L linkers are selectively deboronated to their corresponding *nido* species[26] and/or extracted[27] from the crystal surface. The consequence of these processes would be that the more hydrophilic *nido* species and/or $Zn_4(bdc)_2$ layers are mainly exposed to the crystal surface, making it hydrophilic. To verify these assumptions, we analyzed the supernatant from the NaOH/DMF treatment by ^{1}H- and ^{11}B-{^{1}H}-NMR spectroscopy, MS spectrometry and ICP-MS (Figures 2 and Supporting Information, Figures S9a, S10a, S11a). Remarkably, ^{11}B-{^{1}H}- and ^{1}H-NMR, and MS, indicated only the *nido* species resulting from the deboronation of the *o*CB-L linker (and not the *closo* form of the *o*CB-L and bdc linkers), whereas ICP measurements confirmed the absence of any Zn^{II} ions. These observations are consistent with the fact that mainly *o*CB-L linkers from the crystal surface are selectively removed (either via deboronation and subsequent detachment, or vice versa), which exposes the more hydrophilic $Zn_4(bdc)_2$ layers on the crystal surface.

Here, we would like to highlight that we obtained identical results as above, when we performed the treatment with Et_3N in DMF (85 ºC, 3 h), NaOH in MeOH (r.t., 1 h), and NaOH in CH_3CN (r.t., 1 h) (Supporting Information, Figures S9b, S10b,

S12-13). This deboronation reaction is well known to occur in carboranes by a wide variety of nucleophiles in various basic conditions.[21,26] However, when we performed the treatment using aqueous NaOH (r.t., 1 h), we did not observe any changes in the crystal hydrophobicity (Θ_c = 139° from hand-packed). We rationalized this result by considering the non-wettability of the highly hydrophobic crystal surface of as-synthesized ***o*CB-MOF-1** to water (in sharp contrast to the organic solvents that we had tested: DMF, MeOH or CH_3CN).

Contrariwise, we attributed the recovery of the initial hydrophobicity to the removal, mainly, of the hydrophilic $Zn_4(bdc)_2$ layers under slightly acidic aqueous conditions (which is probably due to the protonation of bdc linkers). This removal would again leave the hydrophobic *o*CB-L linkers exposed on the crystal surface. At this point, ^{1}H- and ^{11}B-{^{1}H}-NMR spectra of the supernatant showed the presence of the bdc linker but not of any carborane species (Supporting Information, Figures S9c, S10c, S11b). Consistently, ICP measurements confirmed the release of Zn^{II} ions during the treatment (13.5 ppm), whereas the MS spectrum showed mainly the bdc linker, plus a weak peak corresponding to the *nido o*CB-L linker. An ideal mechanism for such switching behavior is shown in Figure 3.

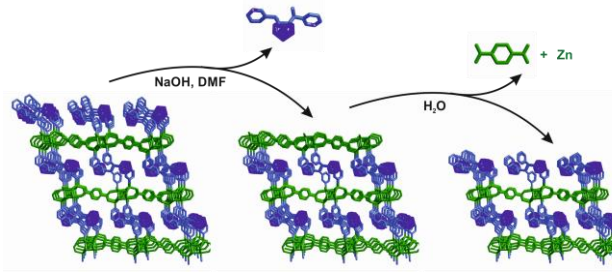

Figure 3. Ideal mechanism proposed for the switchable surface hydrophobicity-hydrophilicity of ***o*CB-MOF-1**. Pillaring *o*CB-L linkers are represented in blue and $Zn_4(bdc)_2$ layers in green.

To demonstrate that this switchable phenomenon is due chiefly to the crystal surface and not to any internal modifications, we ground a sample of superhydrophilic ***o*CB-MOF-1** crystals to break them up and physically re-expose the hydrophobic *o*CB-L linkers on the crystal surface. As expected, we immediately observed a pronounced increase in the hydrophobicity of the ground crystals, which exhibited a Θ_c of 129° (from hand-packed; Supporting Information, Figure S14). This result is consistent with the non-observation of any significant modifications in the crystallinity or in the CO_2 sorption capabilities of ***o*CB-MOF-1'** throughout the switching process (Supporting Information, Figures S15-16). In fact, the only significant variation that we observed during this process was in the water sorption properties. Initially, the hydrophobic ***o*CB-MOF-1'** exhibited a type-II isotherm, but upon switching, the resultant hydrophilic ***o*CB-MOF-1'** showed a type-V isotherm, which corresponds to an increase in uptake at a relative pressure of 0.3 (Supporting Information, Figure S6). Although neither sample showed any significant water uptake, the uptake (0.09 gg^{-1}) in the hydrophilic ***o*CB-MOF-1'** was twice that in the hydrophobic one (0.05 gg^{-1}). A similar trend has been reported between ZIF-8 and its aldehyde-functionalized SIM-1 analog.[28] These differences at low pressure can be attributed to the presence of a higher number of polar groups on the crystal surface in the hydrophilic ***o*CB-MOF-1**. Note here that initial type-II isotherm with a maximum uptake of 0.05 gg^{-1} was recovered when switching again to the hydrophobic ***o*CB-MOF-1** (Supporting Information, Figure S6).

In conclusion, we have reported a novel MOF, ***o*CB-MOF-1**, whose crystal-surface can be switched between hydrophobic and superhydrophilic via chemical treatment. It was assembled from Zn^{II} ions, 1,4-benzenedicarboxylate and a hydrophobic carborane-based linker, which connects the constituent $Zn_4(bdc)_2$ 2D layers to yield the 3D network of the final MOF. We found that the carborane moieties confer enhanced hydrophobicity to this MOF (Θ_c = 140°). Given the versatile compositions of MOFs, and the fact that they can be fabricated by design, we hope that our work here facilitates development of MOFs with reversible wettability properties triggered by stimuli such as light, temperature or pH. Such materials would ultimately prove utile for obtaining smart porous surfaces (*e.g.* membranes and coatings) that exhibit switchable wettability.

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Keywords: Metal-organic frameworks • hydrophobicity • hydrophilicity • carborane • switching

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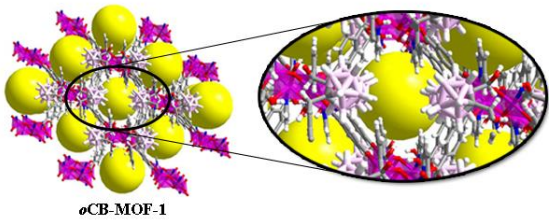
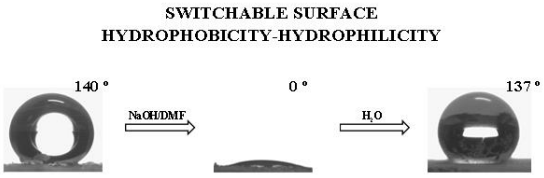
COMMUNICATION

A metal-organic framework, based on 2D layers of $Zn_4(bdc)_2$ connected through a pillaring hydrophobic carborane based linker, undergoes a switching from hydrophobic to superhydrophilic, and vice versa, upon chemical treatment.





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Switchable Surface Hydrophobicity-Hydrophilicity of a Metal-Organic Framework