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Switchable Surface Hydrophobicity-Hydrophilicity of a Metal-Organic Framework

Sabina Rodríguez-Hermida, a Min Ying Tsang, b Claudia Vignatti, a Kyriakos C. Stylianou, a Vincent Guillerm, a Javier Pérez-Carvajal, a Francesc Teixidor, b Clara Viñas, b Duane Choquesillo-Lazarte, c Cristóbal Verdugo-Escamilla, c Inmaculada Peral, d Jordi Juanhuix, e Albert Verdaguer, a Inhar Imaz, a Daniel Maspoch a, f and José Giner Planas b

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 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 devices, 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 respond to specific stimuli, they can exhibit switchable wettability. For instance, a lotus leaf-like surface built from the photosensitive material TiO2 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. TiO2 [6] 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 superhydrophobic. 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 (hereafter, "oCB-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(NO3)2·6H2O, Hbdc, 1,2-bis{(pyridin-3-yl)methanol}-1,2-dicarba-closo-dodecaborane (oCB-L) and 2-methylimidazole (2-Hmim) in a 1:1 mixture of EtOH:DMF (4 mL) at 85 °C for 48 h afforded a white crystalline material (yield: 49%). Single-crystal X-ray diffraction revealed a 3D network of formula [Zn6(µ4-bdc)(µ3-oCB-L)(µ3-O)2]2·(DMF)3]2·4DMF, oCB-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 oCB-MOF-1 is a tetranuclear Zn6(µ3-O)3(OOC)3 cluster formed by two crystallographic independent Zn#1 and Zn#2 ions. Both Zn#1 ions are [NO3]·tetrahedrally coordinated to two carboxylate groups of bdc linkers, one pyridine moiety of µ3-oCB-L and a µ3-O atom. Both Zn#2 ions are [NO3]-octahedrally coordinated to two carboxylate groups of bdc linkers, one pyridine moiety of µ3-oCB-L, two µ3-O atoms and a guest DMF molecule (Figure 1b).
Similar \( \text{M}_4\text{(O(H))}_6\text{(OOC)}_4 \) (\( \text{M} = \text{Zn}, \text{Co} \)) building units have previously been reported.\(^{[23]} \) In \( \text{oCB-MOF-1} \), each carboxylate group of the bdc linker bridges two \( \text{Zn}^{11} \) ions within the same \( \text{Zn}_4 \) unit, and each bdc linker connects two \( \text{Zn}_4 \) units, thereby forming square grid \( \text{Zn}_4\text{(bdc)}_2 \) layers that extend along the \( \text{ab} \) plane (Figure 1c). These layers are further connected through pillaring \( \mu_2\text{-oCB-L} \) 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 \( \mu_2\text{-oCB-L} \) linkers are located on the pore aperture surface.

Thermogravimetric analysis (TGA) of \( \text{oCB-MOF-1} \) shows a continuous weight loss of 22.3% from 90 °C to 250 °C, which we attributed to the loss of the four guest and two coordinated DMF molecules (calcd. 24.9%; Supporting Information, Figure S3). Above 350 °C, this framework decomposes over multiple steps. Elemental analysis, infrared (IR-ATR) and TGA measurements of a sample heated under vacuum at 85 °C 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 \( \text{oCB-MOF-1} \), evidenced by a strong peak at 1650 cm\(^{-1} \). In the same direction, TGA analysis of \( \text{oCB-MOF-1} \) revealed initial weight loss of 8.3%, from 120 °C to 250 °C, corresponding to loss of the two coordinated DMF molecules (calcd. 10.0%). Additionally, PXRD measurements showed that \( \text{oCB-MOF-1} \) retains its original structure. Sorption measurements revealed that desolvated \( \text{oCB-MOF-1} \) is non-porous to \( \text{N}_2 \) at 77 K and 1 bar. However, it is porous to \( \text{CO}_2 \) (69.4 cm\(^3\) g\(^{-1} \) at 0.9 bar; BET surface area: 296 m\(^2\) g\(^{-1} \)) 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 \( \text{CO}_2 \) but not for \( \text{N}_2 \) (kinetic diameters for \( \text{CO}_2 \): 3.30 Å and \( \text{N}_2 \): 3.7 Å). The isosteric heats of adsorption of \( \text{CO}_2 \) (\( Q_{st} \)) were derived from the Claussius-Clapeyron equation, using the adsorption branches of the isotherms measured at 288 K, 273 K and 258 K. The \( Q_{st} \) of \( \text{oCB-MOF-1} \) was 29.2 kJ mol\(^{-1} \).

Having determined that \( \text{oCB-MOF-1} \) 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 \( \text{oCB-MOF-1} \) and desolvated \( \text{oCB-MOF-1} \) packed on a glass surface. The contact angle (\( \Theta_c \)) in each case was 140° and 138°, respectively — values which are characteristic of a highly hydrophobic solid. We finally characterized the contact angle of \( \text{oCB-MOF-1} \) 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 \( \Theta_c \) 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.
The hydrophobic character of oCB-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), oCB-MOF-1' can barely adsorb water: at 95% relative humidity, it exhibits a very low uptake of only 0.05 g H₂O/g oCB-MOF-1' (Supporting Information, Figure S6). This low water adsorption clearly confirms that the pore surface of oCB-MOF-1' is hydrophobic and as such, would prevent entry of water into the pores. Due to the high hydrophobicity of oCB-MOF-1, it is highly stable in water. For example, oCB-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 oCB-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 oCB-MOF-1, either hand-packed or shaped in the form of a disk pellet, undergoes a switch from hydrophobic (Θw = 140° from the hand-packed; Θw = 108° from the pellet) to superhydrophilic (Θw = 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 hydrophilicity (Θw = 137° from the hand packed; Θw = 101° from the pellet) was fully recovered when hydrophobic oCB-MOF-1 was immersed in H₂O (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 oCB-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 35°. 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 oCB-MOF-1 crystals. Thus, we hypothesized that under basic conditions, the hydrophobic oCB-L linkers are selectively deboronated to their corresponding nido species and/or extracted from the crystal surface. The consequence of these processes would be that the more hydrophilic nido species and/or Zn⁺(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 ¹H- and ¹¹B-(¹H)-NMR spectroscopy, MS spectrometry and ICP-MS (Figures 2 and Supporting Information, Figures S9a, S10a, S11a). Remarkably, ¹¹B-(¹H)- and ¹H-NMR, and MS, indicated only the nido species resulting from the deboronation of the oCB-L linker (and not the closo form of the oCB-L and bdc linkers), whereas ICP measurements confirmed the absence of any Zn⁷⁺ ions. These observations are consistent with the fact that mainly oCB-L linkers from the crystal surface are selectively removed (either via deboronation and subsequent detachment, or vice versa), which exposes the more hydrophilic Zn⁺(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 Et₃N in DMF (85 °C, 3 h), NaOH in MeOH (r.t., 1 h), and NaOH in CH₃CN (r.t., 1 h) (Supporting Information, Figures S9b, S10b,
This deboronation reaction is well known to occur in carboranes by a wide variety of nucleophiles in various basic conditions. However, when we performed the treatment using aqueous NaOH (r.t., 1 h), we did not observe any changes in the crystal hydrophobicity (θW = 139° from hand-packed). We rationalized this result by considering the non-wettability of the highly hydrophobic crystal surface of as-synthesized oCB-MOF-1 to water (in sharp contrast to the organic solvents that we had tested: DMF, MeOH or CH3CN).

Contrariwise, we attributed the recovery of the initial hydrophobicity to the removal, mainly, of the hydrophilic Zn(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 oCB-L linkers exposed on the crystal surface. At this point, 1H- and 11B-1H)-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 Zn2+ ions during the treatment (13.5 ppm), whereas the MS spectrum showed mainly the bdc linker, plus a weak peak corresponding to the nido oCB-L linker. An ideal mechanism for such switching behavior is shown in Figure 3.

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 oCB-MOF-1 crystals to break them up and physically re-expose the hydrophobic oCB-L linkers on the crystal surface. As expected, we immediately observed a pronounced increase in the hydrophobicity of the ground crystals, which exhibited a θW 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 CO2 sorption capabilities of oCB-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 oCB-MOF-1 exhibited a type-II isotherm, but upon switching, the resultant hydrophilic oCB-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 g g⁻¹) in the hydrophilic oCB-MOF-1 was twice that in the hydrophobic one (0.05 g g⁻¹). A similar trend has been reported between ZIF-8 and its aldehyde-functionalized SIM-1 analog.[29] 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 oCB-MOF-1. Note here that initial type-II isotherm with a maximum uptake of 0.05 g g⁻¹ was recovered when switching again to the hydrophobic oCB-MOF-1 (Supporting Information, Figure S6).

In conclusion, we have reported a novel MOF, oCB-MOF-1, whose crystal-surface can be switched between hydrophobic and superhydrophobic via chemical treatment. It was assembled from Zn2+ ions, 1,4-benzenedicarboxylate and a hydrophobic carborane-based linker, which connects the constituent Zn(bdc)2 layers to yield the 3D network of the final MOF. We found that the carborane moieties confer enhanced hydrophobicity to this MOF (θW = 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 useful for obtaining smart porous surfaces (e.g. membranes and coatings) that exhibit switchable wettability.

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Figure 3. Ideal mechanism proposed for the switchable surface hydrophobicity-hydrophilicity of oCB-MOF-1. Pillaring oCB-L linkers are represented in blue and Zn(bdc)2 layers in green.


COMMUNICATION

A metal-organic framework, based on 2D layers of $\text{Zn}_4(bdc)_2$, 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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