

Metal–Organic Frameworks

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Switchable Surface Hydrophobicity–Hydrophilicity of a Metal–Organic Framework

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

Abstract: Materials with surfaces that 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. The MOF crystal-surface can be switched between hydrophobic and superhydrophilic through a chemical treatment to remove some of the building blocks.

Smart solid surfaces that exhibit switchable wettability, mainly between high (or super) hydrophobicity and superhydrophilicity, are actively being sought owing 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 respond to specific stimuli, they can exhibit switchable wettability. For instance,

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201609295. 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 could be used for fabricating such smart surfaces, comprise photo-sensitive inorganic oxides (for example, TiO₂^[4] and ZnO),^[6] organic polymers (for example, light-responsive azobenzene-containing polymers,^[7] temperature-responsive poly-*N*-isopropylacrylamide,^[8] and electrical-responsive polypyrrole),^[9] self-assembled monolayers (SAMs; for example, 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 and superhydrophilic properties. Researchers have recently begun to investigate hydrophobic and superhydrophobic MOFs to enhance the aqueous stability of the MOFs and enable new applications (for example, self-cleaning).^[13] Some advances have been made to this end. For instance, Kitagawa et al. reported a superhydrophobic MOF that 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 through the introduction of hydrophobic molecules as linkers (for example, 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] 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] (*o*CB-L, Figure 1 a) as a hydrophobic linker in combination with Zn-bdc (bdc = 1,4-benzenedicarboxylate). This switching behavior is achieved by alternatively exposing the MOF to a NaOH/DMF solution and a slightly acidic aqueous solution.

Reaction of $Zn(NO_3)_2$ ·6H₂O, H₂bdc, 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 °C for 48 h afforded a white crystalline material (yield: 49%). Single-crystal X-ray diffraction revealed a 3D network of formula $[Zn_4(\mu_4-bdc)_2(\mu_2-oCB-L)_2(\mu_3-O)_2-$

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^[*] Dr. S. Rodríguez-Hermida, C. Vignatti, Dr. K. C. Stylianou, Dr. V. Guillerm, Dr. J. Pérez-Carvajal, Dr. A. Verdaguer, Dr. I. Imaz, Prof. D. Maspoch Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology Campus UAB, Bellaterra, 08193 Barcelona (Spain) E-mail: daniel.maspoch@icn2.cat Dr. M. Y. Tsang, Prof. F. Teixidor, Prof. C. Viñas, Dr. J. Giner Planas Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) Bellaterra (Spain) E-mail: jginerplanas@icmab.es Dr. D. Choquesillo-Lazarte, Dr. C. Verdugo-Escamilla Laboratorio de Estudios Cristalográficos, IACT, CSIC-Universidad de Granada Av. de las Palmeras 4, 18100 Armilla, Granada (Spain) Dr. I. Peral Campus Limpertsberg, Université du Luxembourg 162 A, avenue de la Faïencerie, 1511 Luxembourg (Luxembourg) Dr. J. Juanhuix Alba Synchrotron Light Facility 08290 Cerdanyola del Vallés, Barcelona (Spain) Prof. D. Maspoch ICREA, Pg. Lluís Companys 23 08010 Barcelona (Spain)

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Figure 1. a) The oCB-L linker, b) $Zn_4(O)_2(OOC)_4$ cluster, and c) $Zn_4(bdc)_2$ layers 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 -oCB-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 (yellow), run along the *c* axis. Note that the carborane cores (dark blue) are pointed to the pore aperture. Zn = pink, O = red, C = gray, and H = white.

(DMF)₂]-4DMF, **oCB-MOF-1**, the purity of which was confirmed by elemental analysis, scanning electron microscopy, and powder X-ray diffraction (PXRD; Supporting Information, Figures S1–2 and Table S3). The basic unit of **oCB-MOF-1** is a tetranuclear $Zn_4(O)_2(OOC)_4$ cluster formed by two crystallographically independent Zn1 and Zn2 ions. Both Zn1 ions are {NO₃}-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 Zn2 ions are {NO₅}-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).

Similar $M_4(O(H))_2(OOC)_4$ (M = Zn, Co) building units have previously been reported.^[23] In **oCB-MOF-1**, each carboxylate group of the bdc linker bridges two Zn^{II} ions within the same Zn₄ unit, and each bdc linker connects two Zn₄ units, thereby forming square grid Zn₄(bdc)₂ layers that extend along the *ab* plane (Figure 1 c). These layers are further connected through pillaring μ_2 -oCB-L linkers to create a 3D structure (Figure 1 d) that contains 1D channels (46% of void space in the unit cell).^[24] These channels are formed by cavities that can host a sphere with a diameter of 8.6 Å and that are connected by small apertures (3.2 × 6.4 Å, considering vdW radii) along the *c* axis (Figure 1 e). These cavities are filled with four guest DMF molecules per formula unit. Importantly, the carborane moieties of μ_2 -oCB-L linkers are located on the pore aperture surface.

Thermogravimetric analysis (TGA) of **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 (calculated value of 24.6%; 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 and Table S3). The IR spectrum confirmed the presence of DMF molecules in the activated oCB-MOF-1', evidenced by a strong peak at 1650 cm⁻¹. In the same direction, TGA analysis of oCB-MOF-1' revealed an initial weight loss of 8.3%, from 120°C to 250°C, corresponding to the loss of the two coordinated DMF molecules (calculated value of 10.0%). Additionally, PXRD measurements showed that oCB-MOF-1' retains its original structure. Sorption measurements revealed that desolvated oCB-MOF-1' is non-porous to N₂ at 77 K and 1 bar. However, it is porous to CO₂ (69.4 cm³ g⁻¹ at 0.9 bar; BET surface $area = 296 \text{ m}^2 \text{g}^{-1}$) at 195 K and 0.8 bar, for which it showed reversible type-I isotherms (Supporting Information, Fig-

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ure S5). We reasoned that this selectivity could be explained by the pore aperture $(3.2 \times 6.4 \text{ Å})$, which is large enough to be accessible for CO₂ but not for N₂ (the kinetic diameters for CO₂ and N₂ are 3.3 and 3.7 Å, respectively). The isosteric heats of adsorption of CO₂ (*Qst*) were derived from the Clausius–Clapeyron equation, using the adsorption branches of the isotherms measured at 288, 273 and 258 K. The *Qst* of *o***CB-MOF-1**' was 29.2 kJ mol⁻¹ at low coverage, decreasing up to 26.4 kJ mol⁻¹ at high coverage. Note that when *o***CB-MOF-1** was heated at 200 °C for 12 h, all six DMF molecules were removed (Supporting Information, Figure S4 and Table S3). However, PXRD analysis showed a loss of crystallinity, and CO₂ sorption measurements revealed a decrease of 35% of the BET area compared to that of *o***CB-MOF-1**'.

Having determined that **oCB-MOF-1** retains porosity, we then evaluated the influence of the carborane units on its hydrophobic properties. Thus, we performed water contactangle measurements of crystalline powder of as-synthesized **oCB-MOF-1** and desolvated **oCB-MOF-1**' packed on a glass surface. The contact angle (θ_c) in each case was 140° and 138°, respectively, which are values characteristic of a highly hydrophobic solid. We finally characterized the contact angle of **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 θ_c of 108°. The measured

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Figure 2. a) Contact angle images of *o*CB-MOF-1 (left, disk pellet; right, 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 ¹H- and ¹¹B-{¹H}-NMR spectra of the supernatant. Treatment with water leads to release of the bdc linkers and Zn^{II} ions, as detected by ¹H- and ¹¹B-{¹H}-NMR and ICP, respectively; c) Photographs of the pressed disk pellet of *o*CB-MOF-1. d) Static contact angle values for two cycles of treatment.

contact-angle hysteresis (CAH) was 32° (Supporting Information, Table S4). This relatively large CAH was attributed to the surface roughness of the disk pellet, which 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 (for example, ZIF-8 and perfluorinated MOFs),^[25] 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. Owing 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 handpacked or shaped in the form of a disk pellet, undergoes a switch from hydrophobic ($\theta_c = 140^\circ$ for the hand-packed; $\theta_{\rm c} = 108^{\circ}$ for the pellet) to superhydrophilic ($\theta_{\rm c} = 0^{\circ}$ in both cases) upon immersion in a solution of NaOH (10 equiv.) in DMF for 1 h at room temperature. Moreover, this switch was reversible; the initial hydrophobicity ($\theta_c = 137^\circ$ for the hand packed, $\theta_c = 101^\circ$ for the pellet) was fully recovered when hydrophilic **oCB-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 vary significantly during this switching process, evidencing that the chemical nature of oCB-MOF-1 is mainly responsible for 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 the latter, the CAH was 35°. Remarkably, we were able to demonstrate at least two complete cycles of switching without observing a significant loss in hydrophobicity (Figure 2d and the 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^[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 ¹H- and ¹¹B-{¹H}-NMR

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spectroscopy, mass spectrometry and ICP-MS (Figure 2 and the Supporting Information, Figures S9a, S10a, and S11a). Remarkably, ¹¹B-{¹H}- and ¹H-NMR, and mass spectra 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 through deboronation and subsequent detachment, or vice versa), which exposes the more hydrophilic Zn₄(bdc)₂ layers on the crystal surface.

We would like to highlight that we obtained identical results, when we performed the treatment with Et₃N in DMF (85 °C, 3 h), NaOH in MeOH (rt, 1 h), and NaOH in CH₃CN (rt, 1 h) (Supporting Information, Figures S9 b, S10 b, S12, and S13). This deboronation reaction is well known to occur in carboranes by a wide variety of nucleophiles under various basic conditions.^[21,26] However, when we performed the treatment using aqueous NaOH (rt, 1 h), we did not observe changes in the crystal hydrophobicity ($\theta_c = 139^\circ$ for handpacked). We rationalized this result by considering the non-wettability of the highly hydrophobic crystal surface of assynthesized *o*CB-MOF-1 to water (in sharp contrast to the organic solvents that we had tested; DMF, MeOH, or CH₃CN).

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 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 the carborane species (Supporting Information, Figures S9c, S10c, and S11b). Consistently, ICP measurements confirmed the release of Zn^{II} ions during the treatment (13.5 ppm), whereas the mass spectrum showed mainly the bdc linker and 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 reexpose the hydrophobic oCB-L linkers on the crystal surface.

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

As expected, we immediately observed a pronounced increase in the hydrophobicity of the ground crystals, which exhibited a θ_c of 129° (for hand-packed; Supporting Information, Figure S14). This result is consistent with the observation of no significant modifications in the crystallinity or in the CO₂ sorption capabilities of **oCB-MOF-1**' throughout the switching process (Supporting Information, Figures S15 and S16). 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 s^{-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 analogue.^[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 oCB-MOF-1. Note that the initial type-II isotherm with a maximum uptake of 0.05 g s^{-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 superhydrophilic properties through 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 ($\theta_c = 140^\circ$). Given the versatile compositions of MOFs and the fact that they can be fabricated by design, we hope that the present work 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 (for example, membranes and coatings) that exhibit switchable wettability.

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- C. Vignatti, K. C. Stylianou, V. Guillerm,
- J. Pérez-Carvajal, F. Teixidor, C. Viñas,
- D. Choquesillo-Lazarte,
- C. Verdugo-Escamilla, I. Peral, J. Juanhuix,
- A. Verdaguer, I. Imaz, D. Maspoch,*
- J. Giner Planas* _____ IIII-------

Switchable Surface Hydrophobicity– Hydrophilicity of a Metal–Organic Framework



Switching surfaces: A metal–organic framework, based on 2D layers of Zn_4 -(bdc)₂ connected through a pillaring hydrophobic carborane-based linker, switches from hydrophobic to superhydrophilic and vice versa, upon chemical treatment.

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