

Superhydrophobic perfluorinated metal–organic frameworks†

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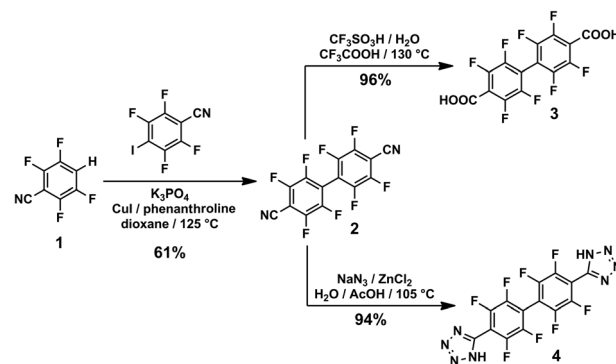
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Three perfluorinated Cu-based metal–organic frameworks (MOFs) were prepared starting from extensively fluorinated biphenyl-based ligands accessed via C–H functionalization. These new materials are highly hydrophobic: with water contact angles of up to $151 \pm 1^\circ$, they are among the most water-repellent MOFs ever reported.

Owing to their high thermal and chemical stability and unique physical properties, fluorinated polymers¹ are desirable materials in industrial and household applications. The recent explosion of interest in modularly synthesized metal–organic frameworks (MOFs)² quickly prompted efforts to amalgamate these two classes of materials through the preparation of extensively fluorinated MOFs. Such “Teflon-coated MOFs” promise to show superhydrophobic behavior and increased robustness towards moisture³ and their fluorophilic character could facilitate the sequestration and analysis of fluorinated pollutants, including Freons. Efforts to introduce heavily fluorinated linkers into MOFs were limited in their scope by the relatively small pool of readily available fluorinated organic linkers.⁴ Most significantly, fluorinated analogs of large aromatic oligocarboxylates—which currently represent a mainstay of MOF chemistry—are essentially unknown, with the notable exception of the commercially available perfluoroterephthalic acid.⁵ In this communication, we present a general strategy for the preparation of such large, perfluorinated and rigid aromatic carboxylic acids and tetrazoles, and proceed to demonstrate that these novel ligands can be reticulated into MOFs under solvothermal conditions. These new materials—which we propose to name MOFFs, highlighting their fluorinated character—have highly hydrophobic structures with H₂O contact angles as high as $151 \pm 1^\circ$.

Our investigations were initially aimed towards developing a method for the synthesis of fluorinated polyaryl ligands.



Scheme 1 Synthesis of ligands 3 and 4. See ESI† for experimental details.

The Cu-catalyzed deprotonative arylation of C–H bonds combines low cost of catalysts and high generality with respect to the coupling partners.⁶ This approach was successfully used to prepare linear perfluorinated carboxylic acid 3 and tetrazole 4 (Scheme 1). After extensive optimization of the reaction parameters, 2,3,5,6-tetrafluorobenzonitrile (1) was found to be an efficient cross-coupling partner in the Cu-catalyzed reaction with 2,3,5,6-tetrafluoro-4-iodobenzonitrile, affording the key dinitrile intermediate 2. Hydrolysis of 2 was achieved under strongly acidic conditions: heating compound 2 with an excess of triflic acid in trifluoroacetic acid solvent afforded diacid 3 in excellent yield. On the other hand, the reaction between dinitrile 2 and NaN₃ in the presence of ZnCl₂ provided bistetrazole 4 in high yield.⁷ The developed cross-coupling should be readily extendable to the synthesis of diversely substituted benzenes with polyfluoroarene substituents.⁸

With linkers 3 and 4 in hand, we proceeded to develop synthetic conditions for their incorporation into single-crystalline MOFs. Ligand 3 was combined with Cu(NO₃)₂·2½H₂O in a 1 : 18 : 1 mixture of *N,N*-dimethylformamide (DMF), MeOH and H₂O. After 4 d of heating at 40 °C, greenish-blue plate-shaped crystals of MOFF-1 were isolated. Their structural analysis using single crystal X-ray diffraction⁹ revealed an infinite two-dimensional network (Fig. 1), in which pairs of Cu atoms form paddlewheel-shaped Cu₂(COO)₄ clusters that are capped with one MeOH molecule at each Cu. This structure permits formulating the obtained material as Cu²⁺(3-2H⁺)(MeOH).

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† Electronic supplementary information (ESI) available: Synthetic procedures and characterization data for all new compounds and MOFs, and crystallographic information files (CIFs) for MOFFs 1–3. CCDC 902654, 902655 and 902657. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc41564c

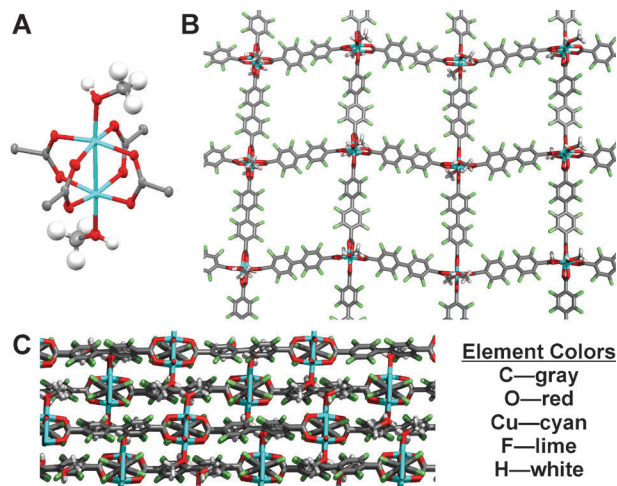


Fig. 1 X-ray crystal structure of MOFF-1, $\text{Cu}^{2+}(\text{3-2H}^+)(\text{MeOH})$. (A) Secondary building unit; (B) representative segment of the two-dimensional layer structure; (C) side-on view of interlayer orientation.

Two-dimensional sheets of MOFF-1 organize into a three-dimensional crystal through parallel offset stacks, in which the $\text{Cu}_2(\text{COO})_4$ cluster of one layer fits into the void space of the adjacent layers. The two-dimensional grid structure of this MOF is similar to that of its non-fluorinated analog MOF-118,¹⁰ but the two frameworks differ in their three-dimensional organization: while MOF-118 presents a rare interpenetrated square grid network, MOFF-1 is composed of parallel stacked two-dimensional layers.

In the presence of a bifunctional pillaring ligand 1,4-diazabicyclo[2.2.2]octane (DABCO), diacid **3** was converted into a pillared three-dimensional Cu-based framework MOFF-2. Specifically, heating a solution of ligand **3**, DABCO and $\text{Cu}(\text{NO}_3)_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ in a 3 : 18 : 1 mixture of DMF, MeOH and H_2O at 60 °C for 2 d resulted in greenish single crystals. Their analysis using X-ray diffraction revealed (Fig. 2) the expected constitution $\text{Cu}^{2+}(\text{3-2H}^+)(\text{DABCO})_2$ and the pillared arrangement of layers mediated by DABCO

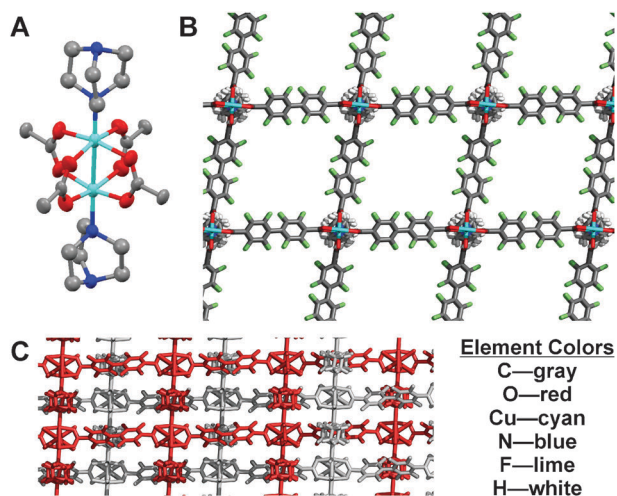


Fig. 2 X-ray crystal structure of MOFF-2, $\text{Cu}^{2+}(\text{3-2H}^+)(\text{DABCO})_2$. The disorder in the DABCO ligand is apparent. (A) Secondary building unit; (B) view along the one-dimensional channels in the structure; (C) side-on view of the interpenetrated framework, where two independent nets are shown in different colors.

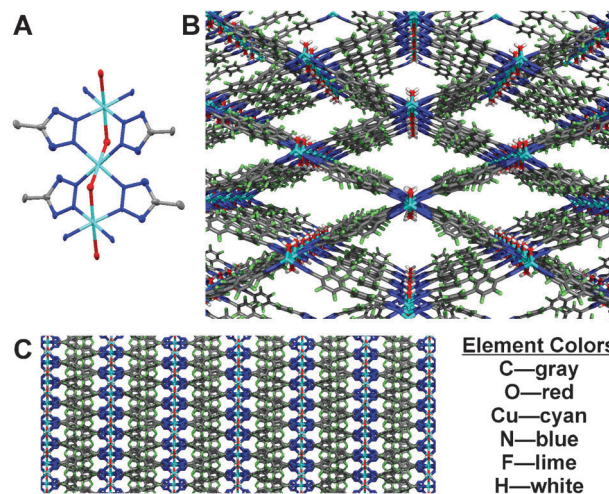


Fig. 3 X-ray crystal structure of MOFF-3, $\text{Cu}^{2+}(\text{4-2H}^+)(\text{H}_2\text{O})$. (A) Secondary building unit; (B) view along the one-dimensional channels in the structure; (C) view of the structure perpendicular to the orientation of the channels.

connectors. The structure is two-fold interpenetrated, in contrast to its non-fluorinated constitutional analog DMOF-1-bpdc.¹¹

Finally, linker **4** was used to demonstrate that perfluorinated tetrazolate-based linkers can also be coordinated into MOFs. A solution of **4** and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in DMF was heated at 70 °C for 4 d. Blue rod-shaped single crystals that resulted were analyzed using X-ray diffraction, revealing (Fig. 3) a porous three-dimensional structure of MOFF-3. In this structure, octahedral Cu atoms are coordinated to peripheral tetrazolate nitrogens in four separate molecules of **4**, and an H_2O molecule acts as a bridge between each pair of adjacent Cu centers. This structure is analogous to Long's previously reported example of Cu-bistetrazolate MOFs,¹² and it also changes significantly upon heating as the coordinated H_2O molecules are removed.

Thermal stabilities of MOFFs 1–3 were evaluated using thermogravimetric analysis (TGA, see ESI† for details). MOFF-1 shows a relatively featureless TGA trace, suggesting that the initial slow loss of coordinated and encapsulated solvent overlaps with the more rapid weight loss caused by framework decomposition occurring at around 220 °C.¹³ MOFF-2 does not crystallize with included solvent and thus shows no weight loss until it starts to rapidly decompose at around 270 °C. For MOFF-3, loss of solvent (14.5% weight) occurs under 80 °C; the desolvated framework then remains stable until ~230 °C, when final decomposition begins. Decomposition temperatures for these MOFs are comparable to those for similar non-fluorinated networks, suggesting that the cleavage of the strong C–F bond (110–120 kcal mol^{−1}) is unlikely during framework decomposition.

Nitrogen sorption (see ESI† for details) within the pores of MOFF-1 and MOFF-2 was characterized by typical type I isotherms—with the corresponding BET surface areas of 580 and 444 m² g^{−1}, respectively. In contrast, MOFF-3 showed the highest and very hysteretic uptake of N_2 , perhaps indicative of its breathing behavior; this issue will be further explored in the forthcoming full paper.

To evaluate the hydrophobic/philic characteristics of MOFFs 1–3, we performed contact angle measurements with H_2O (Table 1). Samples of MOFF-1 are wettable by H_2O if air-dried,

Table 1 Water contact angle measurements for MOFFs 1–3^a

Framework	MOFF-1	MOFF-2	MOFF-3
Contact angle	$\sim 0^\circ$ ^b $108 \pm 2^\circ$ ^c	$151 \pm 1^\circ$ ^c	$134 \pm 1^\circ$ ^c $135 \pm 2^\circ$ ^d

^a Average of three measurements. ^b Air-dried. ^c Dried in a vacuum oven (120 °C, 24 h). ^d Dried with supercritical CO₂, see ESI for details.

which is probably caused by the coordinated hydrophilic molecules of MeOH. Upon oven-drying, these solvent molecules are removed and the residual framework becomes water-repellent (H₂O contact angle of $108 \pm 2^\circ$), as does oven-dried MOFF-3 (H₂O contact angle of $134 \pm 1^\circ$). The most hydrophobic material among these new fluorinated MOFs is MOFF-2, with a H₂O contact angle of $151 \pm 1^\circ$. As MOFF-2 crystallizes without included solvent molecules, its structure and hydrophobicity are unaffected upon drying. Further evidence for the superhydrophobic behavior of the prepared MOFFs came from the water vapor adsorption studies (see ESI† for details). These revealed that MOFFs 1–3 adsorb negligible amounts of water, even at 90% relative humidity ($< 2 \text{ kg m}^{-3}$)—which is comparable to the very low water adsorption of Omary's perfluorinated FMOF-1.³ Since other large perfluorinated ligands are expected to be hydrophobic, this direct-synthesis route to highly hydrophobic MOFs appears to be broadly applicable and complementary to Cohen's postsynthetic functionalization approach¹⁴ to superhydrophobic MOFs.

In summary, we have utilized C–H functionalization to access novel perfluorinated aromatic linkers, which were in turn reticulated into highly hydrophobic, extensively fluorinated metal–organic frameworks (MOFFs). The preparative route to ligands presented here is simple and general, and other extensively fluorinated ligands (and the derived MOFs) could be generated through straightforward adaptation of our protocol. As the extended aromatic ligands shown here open up pathways to highly porous fluorinated MOFs, it should be possible to explore and capitalize upon unique adsorption and binding properties anticipated for these materials. Finally, these new fluorinated precursors have ~ 300 times higher acidities than their non-fluorinated counterparts,¹⁵ and can be coordinated into MOFs at temperatures as low as 40 °C—which could be of interest in the effort to produce high-resolution patterned MOF arrays on surfaces.¹⁶

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