Metal–Organic Frameworks

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A Robust Infinite Zirconium Phenolate Building Unit to Enhance the Chemical Stability of Zr MOFs

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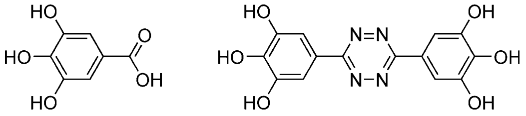
Abstract: *A novel Zr-chain based MOF, namely MIL-163, was designed and successfully synthesized using a bis-1,2,3-trioxobenzene ligand. Endowed with large square-shaped channels of 12 Å width, it shows remarkable water uptake (ca. 0.6 $cm^3 g^{-1}$ at saturating vapor pressure) and a remarkable stability in simulated physiological media, where archetypical Zr carboxylate MOFs readily degrade.*

Metal–organic frameworks (MOFs) have received considerable interest over the past two decades because of their potential application in several important fields, such as gas storage, separation, catalysis, and biomedecine.[1,2] A huge effort is still invested in the design of new porous and functional frameworks for targeted applications, although their chemical stability, especially in aqueous media[3] remains a very challenging issue. Low et al. showed that the bond strength between the metal cation M^n and the organic linker is one of the main criteria that drives the hydrothermal stability of MOFs.[4] Competitive species (such as carboxylates in the case of the separation of complex mixture from the biomass, or phosphates in bio-applications, but also cations[5]) could also play a critical role and profoundly affect the performances of the solid.

Hence, the most prominent strategy to build up chemically stable MOFs relies on strengthening the interaction between the metal cation and the ligand. This could be realized either by the use of ligands with a higher pK_a than carboxylate, such as azolate derivatives or/and highly charged M^n cations (especially $n \geq 3$).[6] Indeed, using highly charged cations has led to various carboxylate-based MOFs showing remarkable stability. Notably, Zr^{IV}-based MOFs, built up either from Zr_6 oxo/hydroxo clusters (UiO-66s, PCN-222,…)[7–16] or Zr oxide chains (MIL-140s),[17,18] fall into this category. In addition, the use of azolate derivatives has also yielded chemically stable MOFs, especially M^{II} imidazolates (ZIF-8,…)[19] and pyrazolates.[20–24] As a consequence, it might be expected that combining highly charged metal cations with high pK_a functional groups should offer frameworks with even higher chemical stability. Nevertheless, the pronounced oxophilic character of M^n ($n \geq 3$) cations might be an issue. Indeed, to our knowledge, only two porous Fe^{III} pyrazolates have been reported.[22,25] Oxygenated ligands, such as phosphonates[26,27] or the more basic phenolates thus appear appealing alternatives, although the control of the porosity could be a challenge. To date, a few open frameworks M^{II}[28–35] and one Ti^{IV}[36] carboxyphenolates or phenolates have been described.

Recently, through the systematic study of the reactivity of 3,4,5-trihydroxybenzoïc acid or gallic acid (see Scheme 1) with Zr^{IV} salts in *N*,*N*-dimethylformamide (DMF),[37] we identified a new one-dimensional coordination chain constituted solely from Zr^{IV} and 1,2,3-trioxobenzene moieties. This motif is built up of edge sharing ZrO_8 polyhedra, each Zr^{IV} being surrounded by four ligands and each ligand chelating two Zr^{IV} cations (see Figure S4 in the Supporting Information). From competitive coordination reactivity studies,[37] we also concluded that the 1,2,3-trioxobenzene moieties are more strongly bound to Zr^{IV} than the carboxylate groups, thus leading in the case of gallic acid to a dense 1D coordination polymer (MIL-153). Moreover, this motif appears robust, since the reaction of the same precursors in methanol rather than DMF led to a new 1D coordination polymer formulated $\{Zr(H\text{-}Gal\text{-}OMe)_2\}\cdot(MeOH, H_2O)_n$ (and later denoted MIL-157) built up from the same chain (space group $I4_1/a$ with $a = 23.3278(4)$ and $c = 14.9851(7)$ Å, see Figure S2 and S5 for the final Rietveld refinement and structure description, respectively). With this in mind, an original bis(1,2,3-trioxobenzene) ligand was prepared, and is suitable to produce a 3D solid. We



Scheme 1. Structural formula of gallic acid or H_4-Gal (left) and 5,5′-(1,2,4,5-tetrazine-3,6-diyl)bis(benzene-1,2,3-triol) or H_6-TzGal (right).

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focused our attention on a *s*-tetrazine derivative (Scheme 1), as the electron-deficient character of this core[38] could potentially prevent the oxidation of the 1,2,3-trioxobenzene moieties under ambient conditions. Herein, we report the synthesis and characterization of a novel MOF, namely MIL-163, built up from this ligand and Zr^{IV}.

MIL-163, (formula $\{Zr(H_2\text{-TzGal})\}\cdot(\text{solvent})_n$, solvent = DMA, H_2O see below) was obtained in a good yield (ca. 80 %) by treating $ZrCl_4$ with two equivalents of H_6-TzGal in a mixture of DMF and water (2:3) under solvothermal conditions (see Experimental Section for details). It was isolated as a polycrystalline dark red powder and initially characterized by powder X-ray diffraction (PXRD). Because of its flexible character leading to a rapid pore contraction associated with a loss of crystallinity under air atmosphere (see below), high-resolution synchrotron data suitable for structure determination were collected while the solid was suspended in water (see Figure S3 for the final Rietveld refinement). MIL-163 crystallizes in a tetragonal setting (space group $P4_2/mmc$ with $a = 15.6152(2)$ and $c = 7.49628(9)$ Å). Its asymmetric unit consists of one Zr^{IV} and one quarter of TzGal^{6-}, all in particular positions as well as four water and one *N*,*N*-dimethylamine molecule with partial occupancies. As expected, each Zr^{IV} atom is chelated by two pairs of TzGal molecules, aligned along the [100] and [010] directions, respectively, yielding an eightfold coordination (Figure S6) with Zr–O distances lying in the usual range (2.142(1)–2.328(1) Å). Besides, each TzGal chelates four Zr ions (i.e. two Zr per 1,2,3-trioxobenzene group, see Figure S6). This affords edge-sharing ZrO_8 polyhedra defining the afore-mentioned chains running along the [001] direction (Figure 1 a).

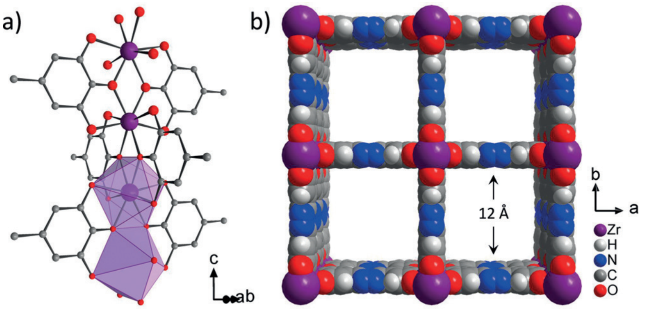

Figure 1. Crystal structure of MIL-163. a) View of a single chain showing the Zr^{IV} cations coordinated by 1,2,3-trioxobenzene groups. b) Perspective view of crystal structure along the [001] direction. Guest molecules are not represented for the sake of clarity.

The chains are connected to each other through TzGal linkers giving rise to a 3D open framework endowed with large square-shaped channels, with approximately 12 Å × 12 Å apertures (taking into account the van der Walls radii of the atoms) running parallel to the Zr chains (Figure 1 b). These channels are interconnected along the [100] and [010] directions through small apertures of about 2 Å × 4 Å (see Figure S7), likely accessible upon dynamic rotation of the tetrazine rings, and the total void volume estimated using the PLATON software[39] is 71 %.

Additionally, solid-state magic-angle spinning (MAS) NMR spectroscopy was used to determine the pore content and the protonation state of the ligand. The 1D ^{13}C NMR spectrum (Figure S12) revealed the presence of one signal at low isotropic chemical shift ($\delta = 35$ ppm) corresponding to a *N*,*N*-dimethylamine molecule, likely arising from the degradation of DMF. In addition, seven narrow ^{13}C resonances of similar intensities, located between $\delta = 100$ and 170 ppm were observed. These signals are attributed to seven carbon atoms out of the fourteen belonging to one whole TzGal ligand (as shown in Figure S12), thus corresponding to one half of TzGal instead of one quarter deduced by diffraction. An explanation of this reduction of symmetry of the linker is given by the 1D ^1H MAS NMR spectrum, which presents a signal at $\delta = 17$ ppm (Figure S13). Such a resonance at particularly high isotropic chemical shift, which is also observed in MIL-153[37] and MIL-157 (Figure S9), corresponds to a very acidic proton bound to one of the two oxygen atoms the in *meta* position, as confirmed by the 2D ^1H-^{13}C NMR spectrum showing a correlation peak between this signal and the C(-O) atoms at $\delta \approx 145$–150 ppm (see Figure S10 and S14 for MIL-157 and MIL-163, respectively). As a consequence, differences in chemical shifts are observed between the two *meta* C-O carbon atoms (-C-O and -C-OH) and the two C-H carbon atoms, and the linker is partially protonated ($H_2\text{-TzGal}^{4-}$).

The thermal behavior of MIL-163 was evaluated by thermogravimetric analysis under oxygen flow (Figure S17). As observed in the case of other solids built up from gallic acid,[31,32,37,40] MIL-163 has a rather low decomposition temperature (ca. 210 °C) compared to Zr carboxylate MOFs.[7,17] This is most likely due to an oxidative degradation of the 1,2,3-trioxobenzene moieties.[37] At lower temperature, solvent loss is accompanied by a shift and a broadening of the Bragg peaks (Figure S18). This phenomenon, also observed on the MAS NMR data (Figure S15) is fully reversible, as the redispersion of the dry solid in a polar solvent (such as water, ethanol, or DMF, see Figure S20) leads to the complete recovery of the crystalline state and the initial pore opening (see Figure S19). Alternatively, when suspended in an apolar solvent (in this case toluene), the XRPD pattern is different (Figure S21). Its indexation (Figure S22) suggests a flexible behavior very similar to the one found in MIL-53s solids,[41] that is, a shrinkage of the channels (evolving from square-shaped to lozenge-shaped) without any structural change along the inorganic chain axis (see Figure S23 for a schematic representation). Addition of water, ethanol, and DMF to this solid leads to the recovery of the initial XRPD diagram (Figure S21), hence again confirming the reversibility of this transformation.

This flexible behavior was further confirmed by gas and vapor sorption measurements. N_2 sorption isotherms recorded at 77 K showed only small amounts of adsorbed gas (Figure S24), leading to a BET areas of around 90 $m^2\,g^{-1}$ and 170 $m^2\,g^{-1}$ after classical and supercritical CO_2 activation, respectively. Experiments carried out at 298 K up to 25 bar (Figure S25) revealed that MIL-163 adsorbs about 6 $mmol\,g^{-1}$ of CO_2 at 25 bar and small amounts of N_2 and CH_4 (around 1 $mmol\,g^{-1}$ at 25 bar). All these values are significantly lower than would be expected from the structural analysis based on a large-pores crystal structure. In contrast, the H_2O sorption isotherm recorded at 298 K exhibits a multi-step adsorption profile (Figure 2) with two marked steps between $p/p^0 \approx 0.5$–0.6 (A in Figure 2) and 0.6–0.7 (B in Figure 2). These steps are also clearly visible on the desorption branch, although with a shift to lower p/p^0. All these results are in line with the flexible character of MIL-163. In the case of gases (N_2, CH_4, CO_2), it is likely that gas–framework interactions are probably not strong enough to overcome intraframework interactions and thus provoke any pore opening.[42–44] However, such interactions are most probably stronger in the case of water, thus leading to a stepwise pore opening. At saturation ($p/p^0 = 0.9$), MIL-163 adsorbs 32 mmol g^{-1} of water, corresponding to approximately 0.6 cm^3 g^{-1}, a value in agreement with the theoretical pore volume estimated from the crystal structure of the fully open structure (see above).This value compares very well with those found in benchmark MOFs (uptake of H_2O in DUT-67: 0.3 cm^3 g^{-1}, UiO-66: 0.4 cm^3 g^{-1}, CPO-27(Ni): 0.5 cm^3 g^{-1}, HKUST-1: 0.5 cm^3 g^{-1}, MIL-100: 0.8 cm^3 g^{-1}, MIL-101: 1.4 cm^3 g^{-1}).[45]

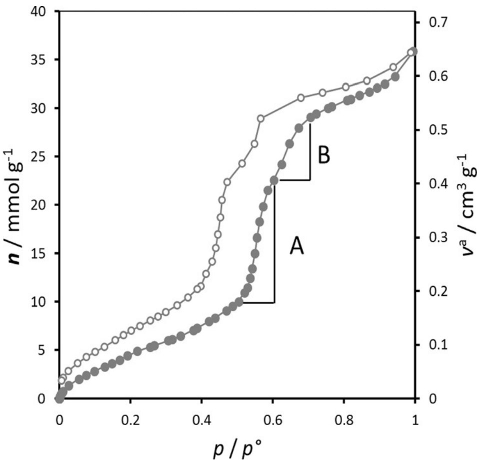

Figure 2. Water sorption isotherms recorded at 298 K for MIL-163. Filled symbols: adsorption; open symbols: desorption. See text for details.

Finally, the long-term chemical stability of MIL-163 in aqueous media was evaluated and compared with Zr^{IV} carboxylates built up from a linker of similar size (4,4′-biphenyldicarboxylate), namely UiO-67 and MIL-140C. Two tests were undertaken by analyzing the solids suspended ($C_m = 1$ mg mL^{-1}) in either boiling water or a phosphate buffer saline solution (PBS; pH 7.4) at 37 °C. This PBS condition gives a first good indication of the stability of the solids in physiological media, a prerequisite for various biomedical applications.[46] Moreover, it has already been shown that hydrolytically stable MOFs could readily degrade in PBS, owing to the presence of phosphate ions competing with the ligand for the complexation of the cations.[46,47]

PXRD patterns of the resulting solids are shown Figure 3, and Figures S26 and S27 for MIL-163, UiO-67, and MIL-140C, respectively. Depending on their structure and composition, the solids behave differently. While the exact nature of the hydrolytic instability of UiO-67 is still under debate,[14,17,48] under our experimental conditions, an irreversible peak broadening (Figure S26) is observed after suspension in boiling water for 24 h. In PBS after 24 h, a complete amorphization occurs (Figure S26) in agreement with previous findings on UiO-66.[47] MIL-140C presents an intermediate behavior. It remains intact in boiling water for at least two weeks, but degrades in PBS solution, since, after just 24 h, no more diffraction peaks could be discerned (Figure S27). In sharp contrast, even after two weeks in both media, MIL-163 remains intact, as indicated by the PXRD (Figure 3) but also MAS NMR analysis (Figure S16). A similar behavior is observed for MIL-157 (see Figure S11 and S28 for XRPD patterns and NMR analysis, respectively).

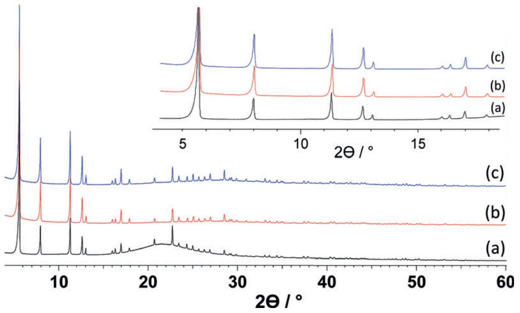

Figure 3. PXRD patterns ($\lambda = 1.5406$ Å) for MIL-163: a) pristine, b) after two weeks in boiling water and c) after two weeks in PBS at 37 °C. Bumps arise from the solvent in which the solid was suspended prior running the diffraction experiment (EtOH, water, and PBS, respectively). Inset: expanded region.

The stability in aqueous media is considered to be driven primarily by the strength of the cation–ligand bond, together with the solubility of the components (the more soluble such components are, the less stable the solid) and the presence of coordinatively accessible metal sites (which might promote the chemical degradation).[47] In this case, owing to its high polarity, the TzGal ligand is far more soluble than the 4,4′-biphenyldicarboxylic acid, while none of the tested solids presents a significant number of accessible metal sites (only defects). Thus, the superior stability of MIL-163 arises from the stronger ligand–Zr interaction. In the case of pure water, the Zr–carboxylate bonds are strong enough to resist, even sometimes in the presence of strongly complexing molecules.[49] Phosphates (similarly to phosphonates[50]) are known to bind more strongly to Zr^{IV} than carboxylates, leading in the case of UiO-67 and MIL-140C, to a complete amorphization. In contrast, the 1,2,3-trioxobenzene moieties seem to interact more strongly with Zr than phosphates, as attested by the structural integrity of MIL-163. The results of these stability tests are, at first sight, mainly driven by the strength of the Zr^{IV}–ligand interaction, which then follows the order $H_2O <$ carboxylate < phosphate < 1,2,3-trioxobenzene. It is still not possible to completely rule out the effect of the inorganic ligands on the (un)stability: μ_3-oxo and -hydroxo bridges found in the Zr^{IV} carboxylates UiO-67[7] and MIL-140C[17] might also act as "weak points". Nevertheless, their absence in MIL-163 (although prepared in the presence of water), as well as in MIL-157 and MIL-153, is also likely the consequence of the stronger ability of the 1,2,3-trioxobenzene moieties to bind to Zr^{IV}.[37]

To summarize, we report herein a new porous Zr MOF built up from a robust, 1D subunit arising from the 1,2,3-trioxobenzene complexing group. Because of its composition, this solid has distinct stability attributes compared to archetypical Zr carboxylates: while its thermal stability is rather limited (ca. 210 °C), it appears highly stable in the presence of competitive coordinative species, such as phosphate ions. Whereas MOFs built up from such an inorganic unit will certainly not be suitable for high-temperature applications, they are promising for low to medium-temperature "real" processes involving strongly complexing agents, that is, working conditions where most hydrolytically stable carboxylate MOFs would not be stable.

Experimental Section

Synthesis of MIL-163: In a 25 mL Teflon-lined steel autoclave, $ZrCl_4$ (0.2 mmol; 47 mg) was added to a solution H_6-TzGal (0.4 mmol; 132 mg) in DMF (2 mL) at room temperature. Water (3 mL) was then added under stirring, autoclave sealed and placed in the oven for 24 h at 130 °C. After cooling to room temperature, the solution was filtered and MIL-163 was recovered as a dark-red fine powder. The solid was then washed in DMF (ca. 10 mL) and EtOH (ca. 10 mL) for one night with each, before being filtered and dried in air (105 mg, yield ca. 80 %).

All synthetic procedures, information on apparatus and measurements, structure resolution details and refinement parameters, stability tests conditions and additional characterization information are given in the Supporting Information. CCDC 1415775 (MIL-157) and 1415776 (MIL-163) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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