Post-Synthetic Transformation

Adding to the Arsenal of Zirconium-Based Metal–Organic Frameworks: the Topology as a Platform for Solvent-Assisted Metal Incorporation


Abstract: Gaining control over the assembly of mesoporous Zr-based metal–organic frameworks (MOFs) with modifiable metal nodes remains a challenge. The topology is intriguing, particularly if considering postsynthetic modification, as it presents large sodalite-like cages surrounded by 12 interconnected 1D channels that allow for efficient diffusion of guest molecules

Introduction

Metal–organic frameworks (MOFs) are well-ordered and atomically defined porous materials that can act as heterogeneous scaffolds to bind small organic molecules, biomolecules, and metals for a number of applications ranging from gas storage to catalysis.[1] The structural diversity of MOFs, owing to the multitude of unique combinations of organic and inorganic building blocks that can be used to construct these materials, can be exploited to prepare frameworks with (1) high structural stability towards water and high temperatures, (2) exposed binding sites that can be used to anchor a variety of molecular entities,[2] and (3) interconnected mesoporous channels to promote rapid diffusion of molecules throughout the structure.[3]

MOFs containing Zr6 nodes are particularly intriguing, as they are stable at high temperatures and to aqueous solutions over a wide pH range.[4] The Zr6 cluster can be 12-, 10-, 8-, or 6-connected depending on the number of carboxylate linkers tethered to the Zr6 building unit (Figure 1).[4c,4d,5] Significant effort has been dedicated to the exploration of MOFs with partially unsaturated 8- or 6-connected Zr6 nodes, as the remaining coordination sites are occupied by terminal, labile hydroxy and aqua groups (–OH/H2O), which are available for substitution or site-limiting reactivity.[5g,6] Currently, only a limited number of 8- and 6-connected Zr6-based MOFs are suitable for postsynthetic node modification, and these MOFs are restricted to only a few topologies including csq,[4a,5g,7] bcu,[5c,8] and spn.[4c,9]

Therefore, the design and construction of new mesoporous frameworks,[9] especially those with new topologies, based on modifiable unsaturated Zr6 nodes continues to be of interest.

Figure 1. The “top” and “side” views of a 12-, 8-, and 6-connected Zr6 oxide node. The unsaturated 8- and 6-connected Zr6 nodes have potential anchoring points, as indicated by the arrows.

The use of di- and tetracarboxylic acid linkers with Zr6 clusters for the construction of MOFs has been well explored.[4c,4d,5g] For example, a number of isoreticular structures, expanded in size or containing peripheral covalent chemical modification, have been prepared for the fcu (2,12)-connected and ftw (4,12)-connected[10] topologies.[4d,5a,11] Tricarboxylic
acid linkers are not as commonly used to construct Zr$_6$-based MOFs but have been utilized to construct MOF-808 and PCN-777 (Figure 2, a). Using a 6-connected Zr$_6$ node with 1,3,5-benzenetricarboxylic acid (BTC) or 4,4′,4′′-tris-triazine-2,4,6-triyl-tribenzoic acid (TATB) gives the spn (3,6)-connected topology of MOF-808$^{[4c]}$ or PCN-777 (Figure 2, a)$^{[5i]}$ respectively. Obtaining a Zr$_6$-based MOF by using a threefold symmetric linker and an 8-connected node to prepare a the (3,8)-connected network should be possible but has not yet been achieved. The the topology consists of sodalite-like cages with postsynthetically modifiable nodes next to interconnected one-dimensional (1D) channels, which make it an ideal candidate for postsynthesis modification, in which every node is easily accessible. Herein, we control the geometry of an organic linker by introducing steric constraints to form a triangular prism, instead of a flat triangular, linker to obtain a new mesoporous, 8-connected Zr-based MOF with the topology, referred to as NU-1200 (Figure 2, b)$^{[12]}$. We also demonstrate the potential of NU-1200 for postsynthetic modification by using a reactive Ti$^{4+}$ precursor in solution.

Results and Discussion

The fully saturated Zr$_6$ node [Zr$_6$O$_4$OH$_4$(COO)$_{12}$] possesses O$_h$ symmetry (e.g., UiO-66) and is compatible with many carboxylate-containing organic linkers. Careful inspection of the linker/node interactions in the tricarboxylic acid based frameworks MOF-808 and PCN-777 (Figure 2, a) reveals that all of the carboxylate groups of a single linker are coplanar, which renders the linker flat. From this it becomes apparent that if a tritopic linker is used that cannot be flat, a different topology with different node connectivity will form. Notably, there are very few examples of MOFs with the topology and those that do exist are mostly based on square-planner metals (Cu, Co, Mn, Zn, Cd, Ni, Fe, Ln) in 8-connected nodes and co-planer triangular 3-connected linkers.$^{[13]}$ Obtaining a material with the topology by using an 8-connected Zr$_6$ cluster and a triangular linker has not yet been realized.

With these considerations in mind, 4,4′,4′′-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (TMTB) was synthesized. The steric demand imparted by the inclusion of three methyl groups forces the appended benzoic acid groups to rotate and stay perpendicular to the plane of the benzenoid core. TMTB retains D$_3$h symmetry but forms a prismatic, not flat, structure with each carboxylic acid group parallel to the others. If mixed with ZrCl$_4$ and benzoic acid (as a modulator) under solvothermal conditions in DMF, this ligand directs the formation of a new Zr-based MOF with the topology. Large cubic single crystals (>20 μm) of NU-1200 were grown and found to be suitable for single-crystal X-ray diffraction (SC-XRD). In general, it is very challenging to obtain large, single crystals of Zr-based frameworks that are suitable for analysis by SC-XRD. The ability to obtain large crystals of NU-1200 adds to the appeal of this framework for studying postsynthetic modification techniques, as characterization by X-ray diffraction can be achieved. SC-XRD reveals that NU-1200 consists of sodalite-like cages and interconnected 1D channels, which is consistent with the topology (Figure 2, b). Interestingly, the terminal –OH/H$_2$O groups on the unsaturated 8-connected Zr$_6$ nodes in NU-1200 all point into the large (20 Å, nucleus to nucleus) mesoporous 1D channels, which makes this MOF particularly intriguing for postsynthetic node modifications. Nitrogen adsorption studies reveal that NU-1200 has a Brunauer–Emmett–Teller (BET) surface area of 2400 m$^2$ g$^{-1}$ (Figure 3) and a distinctive mesoporous step at a relative pressure ($p/p_0$) of 0.1. NU-1200 has a total pore volume of 1.42 cm$^3$ g$^{-1}$, and the DFT pore-size distribution indicates

![Figure 2](https://example.com/figure2.png)
pores with diameters of ca. 14 Å (consistent with the diameter of sodalite-like cage) and 20 Å (1D channel) (Figure S5, Supporting Information). Thermogravimetric analysis (TGA) and variable-temperature powder X-ray diffraction (VT-PXRD) demonstrate that NU-1200 is stable up to 300 °C. After activation with HCl to remove the excess amount of the benzoic acid modulator coordinated to the Zr6 node (Section S3), the presence of the terminal –OH/H2O groups in NU-1200 was confirmed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) (Figure S7). The sharp band at 3670 cm–1 is assigned to the terminal –OH groups on the Zr6(μ3-OH)8(OH)8 node, whereas the band at 2750 cm–1 corresponds to O–H stretches from hydrogen bonding of the terminal water ligands on the node.[6]

To demonstrate the ease by which the exposed –OH/H2O groups on the unsaturated 8-connected Zr6 nodes can be modified, we turned to a solution-based technique we term solvent-assisted metal incorporation (SAMI).[14] For efficient metal incorporation, several criteria should be considered: (1) the metal source should be very reactive to the –OH and H2O functionalities, (2) the solvent must dissolve the reactive metal complex but must not make strong coordination complexes with the metal source, (3) the conjugate acid, following ligand exchange on the desired metal ion, must not destroy the framework, and finally (4) metalation should not result in significant node distortion,[15] as this would hinder the use of the framework as a general heterogeneous support. We chose titanium isopropoxide [Ti(iPrO)4] to modify NU-1200 in dichloromethane (CH2Cl2) (Section S4). The noncoordinating solvent readily dissolves the metal precursor and the 2-propanol product formed during SAMI is nondestructive. PXRD measurements show that NU-1200 remains crystalline throughout the SAMI process. To further uncover the atomic structure, the post-SAMI NU-1200 was examined by SC-XRD. The crystal structure reveals the successful preparation of NU-1200–Ti with two Ti4+ atoms per Zr6 node (Figure 4). Specifically, each node contains four distinct Ti4+ sites that are each 50 % occupied. Each Ti4+ is attached to two oxygen atoms from the Zr6 cluster and four oxygen atoms from hydroxy/aqua ligands. The average loading of two Ti atoms per Zr6 node was corroborated for a bulk sample by using inductively coupled plasma optical emission spectrometry (ICP-OES) (Section S10). Additionally, the metalation occurs with insignificant distortion of the Zr6 node, as confirmed by SC-XRD. SAMI holds great promise as an approach to form immobilized single-site metal atoms/clusters by using reactive metal precursors, and we are currently working to generalize this technique.

In summary, we designed a new Zr-MOF, NU-1200, by carefully controlling the steric environment of a threefold symmetric organic linker. NU-1200 displays a topology with sodalite-like cages next to large interconnected 1D channels. Exposed –OH and H2O groups attached to the unsaturated Zr6 nodes and pointing into the mesoporous channels were readily functionalized with a reactive Ti4+ species, and the product, NU-1200–Ti, was characterized with atomic precision by using single-crystal X-ray diffraction. NU-1200 represents the first Zr-based MOF with an open and easily modifiable topology. These structural characteristics allow NU-1200 to serve as an atomically defined and robust platform for future targeted applications requiring postsynthetic modifications.

Experimental Section

Synthesis of NU-1200: A 4 mL Pyrex vial was charged with ZrCl4 (0.05 mmol, 12 mg), 4,4',4''-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid (TMTB) (0.02 mmol, 10 mg), benzoic acid (2.87 mmol, 350 mg) and DMF (2 mL). The mixture was heated in a 120 °C oven for 48 h. The solution was removed immediately, and the solid residue was washed with fresh DMF (3x). Colorless cubic-shape crystals were harvested with a yield of 70 % (8 mg) based on TMTB ligand.

Conclusion

Figure 3. N2 sorption isotherm at 77 K for NU-1200 after activation with 4 M HCl. The inlay shows the large >20 μm cubic crystals of NU-1200.

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SAMI of Ti Inside NU-1200: Residual DMF was removed from the as-synthesized NU-1200 (20 mg) through solvent exchange with CH₂Cl₂ (5 mL) at room temperature (18 °C) over the course of 24 h. The solvent was decanted, and the NU-1200 was suspended in CH₂Cl₂ (5 mL). Ti(PrO)₃ (0.15 mL) was added to this suspension under an atmosphere of nitrogen, and the sample was heated at 60 °C for 24 h. After cooling to room temperature, the sample was washed with CH₂Cl₂ (3 × 10 mL) and dried at room temperature.

CCDC 1481852 (for NU-1200) and 1481853 (for NU-1200–Ti) 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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[8] Solution-phase metatlation for the Zr6 node by using SAMI is complementary to gas-phase metatlation of the node by using atomic layer deposition (ALD) with volatile metal precursors. ALD in MOFs (AIM) is an ongoing field of study, see ref[6].


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NU-1200 is a Zr-based metal–organic framework (MOF) with the topology. Consisting of unsaturated Zr₆ oxide nodes and triangular linkers with large interconnected channels, this MOF is an ideal candidate for postsynthesis metalation. 

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