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Introducing a Cantellation Strategy for the Design of Mesoporous Zeolite-like Metal–Organic Frameworks: Zr-sod-ZMOFs as a Case Study

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ABSTRACT: Herein we report novel mesoporous zirconium-based metal—organic frameworks (MOFs) with zeolitic sodalite (sod) topology. Zr-sod-ZMOF-1 and -2 are constructed based on a novel cantellation design strategy. Distinctly, organic linkers are judiciously designed in order to promote the deployment of the 12-coordinated Zr hexanuclear molecular building block (MBB) as a tetrahedral secondary building unit, a prerequisite for zeolite-like nets. The resultant Zr-sod-ZMOFs exhibit mesopores with a diameter up to \approx 43 Å, while the pore volume of 1.98 cm³·g⁻¹ measured for Zr-sod-ZMOF-1 is the highest reported experimental value for zeolite-like MOFs based on MBBs as tetrahedral nodes.

M etal-organic frameworks (MOFs) are a unique class of crystalline materials, resulting from the assembly of organic and inorganic molecular building blocks (MBBs) into periodic structures.¹ Since the end of the 1990s, tremendous efforts have been dedicated to explore their properties and potential applications.²⁻⁴

Among almost 100 000 MOFs reported to date,⁵ the touch of rational design is increasingly visible, thanks to the principles of reticular chemistry and the associated RCSR database.⁶ Indeed, design strategies facilitated the assembly of MOFs with increasing complexity. If the assembly of common MBBs into MOFs based on the reticulation of edge-transitive nets is now widely applied,^{1c,7} then researchers are committing noticeable efforts toward expanding the repertoire of reticular chemistry.⁸ This is achievable by using complex ligands to deviate from "default" assemblies⁹ or by developing advanced strategies, such as pillaring¹⁰ and supermolecular building approaches^{11,12} in order to promote the assembly into a precise topology when multiple possibilities are plausible for the same basic building blocks.

Interestingly, some of these design strategies are inspired by the well-known porous materials zeolites. These so-called zeolite-like MOFs (ZMOFs) are constructed from tetrahedral building blocks.¹³ Two main ZMOFs design approaches can be distinguished, depending on their basic elements of construction: (i) those based on single-metal ion (Cu^{2+} , Zn^{2+} , Co^{2+} , In^{3+} , etc.) with functionalized imidazole (ZIFs) or imidazole dicarboxylate, leading to diverse structures with known topologies (**sod**, **ana**, **rho**, etc.)¹⁴ alongside unprecedented ones (**med**)¹⁵ and (ii) those with corner-sharing of super-tetrahedra constructed from trimeric building blocks and linear (MIL-101)¹⁶ or triangular ligands (MIL-100),¹⁷ systematically to afford **mtn** underlying topology.¹⁸

The synthesis of ZMOFs with expanded pores is a persisting challenge.¹³ The common approach to MOFs isoreticular

expansion is by adjusting the organic linker, e.g., length and/or width elongation.¹⁹ However, this strategy is less effective for obtaining highly porous ZMOFs.^{14c} This is due to the fact that there are hundreds of zeolitic topologies based on linking tetrahedral building units. Besides, linker expansion/elongation can induce modification in the specific angles and the positioning of the coordinating functional groups, prohibiting the isoreticulation of a specific ZMOF platform. It mostly affords amorphous solids or crystalline materials based on the "default" structure for the assembly of tetrahedral building units, the **dia** underlying topology.²⁰ In this context, the targeted frameworks must meet a specific arrangement of tetrahedral nodes at certain range of angles at the MBB level to reach the desired zeolitic net. As a semiregular edge-transitive net with simple tiling (transitivity 1121), the sodalite (sod) net has the highest occurrence, making it a suitable target for the design of expanded ZMOFs.²¹ Markedly, the reticulation of the sod net with expanded bridging linkers will permit access to open ZMOF structures, due to the fact that the sod net is not self-dual and not prone to self-interpenetration; that is, it has a high pore/aperture size ratio, large pore volume, and contracted pore-aperture size, suitable for molecular entrap-ment for potential applications.^{13,14b} Herein, we introduce a cantellation design approach for the directed assembly of mesoporous ZMOFs based on zirconium MBBs.

For the rational design of a novel generation of isoreticular ZMOFs, we identified three main requirements:

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- Achieving the formation of a tetrahedral MBB
- Preventing the formation of **dia** net, the most regular edge-transitive net, the default topology for the assembly of tetrahedra²²
- Obtaining an assembly mode that allows the tuning of the framework through ligand expansion and/or decoration

After a careful survey of existing structures and topologies, we reasoned that an efficient method to deviate from the default dia net while assembling tetrahedral nodes would be to propose a solution that prevents their stacking in staggered fashion. For this purpose, we propose a *cantellation* strategy (Figure 1): Second-order truncation of a tetrahedron, adding a



Figure 1. (a) Schematic of the tetrahedra cantellation strategy leading to multiple bridges, allowing building units to be "locked" in eclipsed conformation and (b) sterically hindered bent ligand, locking the carboxylic group in the appropriate position to form (c) a triple bridge between MBBs.

face at each edge and vertex of a tetrahedron, affords the formation of cuboctahedron. Applying the same cantellation strategy to a couple of tetrahedra stacked in an eclipsed fashion results in triply bridged cuboctahedra stacked in an eclipsed conformation. At this stage, the triple bridges between the cuboctahedra prevent any rotation and therefore "lock" them in the intended eclipsed fashion.

Cuboctahedral (cuo) MBBs are well-known in reticular chemistry, with the ubiquitous Zr hexanuclear cluster of UiO-66.²³ Therefore, Zr represents a natural candidate for further design of a novel class of ZMOFs.

Then, we embarked in the design of an organic ligand that would promote the formation of the necessary triple bridge between the **cuo** MBBs (Figure 1b,c). If such an example has been recently reported with linear terephthalic acid in an UiO-66 polymorph with **hex** topology,²⁴ then this conformation can be regarded as an exception as it is widely accepted that the favored topology would be **fcu.**^{23,25}

To deviate from the default **fcu** topology, one must modify the geometry of the ligand, i.e., introducing a geometry mismatch.⁹ Indeed, systematic explorations have shown that topological diversity can be achieved through the use of bent²⁶ or zigzag^{19c} ligands, as well as introducing steric hindrance to alter the orientation of the carboxylates.²⁷ To meet our needs, the ideal ligand (i) should be a ditopic linker, with a bent geometry allowing the triple bridging of MBBs without excessive constraint on the Zr-carboxylate bonds, and (ii) have the two carboxylates oriented orthogonally to the plan of the ligand. Separately, these two requirements would not be sufficient. Indeed, controlling only the bending angle on planar ligands afforded wide topological diversity, allowing the formation of MOFs with **fcu**,²⁸ **reo**,²⁹ **bon**,²⁶ **bct**,³⁰ **hbr**,³¹ **kag**,³² or **pcu** topologies.³³ In parallel, introducing steric hindrance on linear ligands favored the assembly of MOFs with **bcu** topology.²⁷

The insightful combination of these two geometrical requirements guided the design and synthesis of benzene-1,3-dimesitylenic acid (BDM, L1, Figure 1b). The ligand is based on a terphenyl core, where the central phenyl group is decorated by two benzoic groups in the meta positions. To fulfill the second criterion, we introduced steric hindrance by the means of methyl groups on the ortho positions (with respect to the central phenyl group) of each of the benzoic groups. In this way, introducing the methyl groups at these specific positions will act as a lock, limiting the rotation of the rings and keeping the peripheral carboxylate groups orthogonal to the plan of the ligand. This overall minimizes the coordination options and favors the triple bridging of the MBBs, virtually reducing their net-connectivity from 12 to 4. Each 12-coordinated (12-c) cluster is surrounded by 4 others in a tetrahedral fashion, as a result of the 12 ligands split into four triads converging to the same neighboring cluster (Figure 2c).

Reaction of $ZrCl_4$ and L1 in DMF and acetic acid resulted in isolation of rhombic dodecahedral crystals (Figure S16a). Single-crystal X-ray diffraction studies revealed that the obtained MOF encloses fully coordinated clusters (12-c) and that the overall MOF has the targeted underlying **sod** topology, observed for the first time in M^{IV}-based MOFs. Due to the triple bridging of the clusters by the ligands, a resulting cavity is not represented by the classic tiling of the **sod** topology. It is reflected by the unprecedented augmented net, **csd** (<u>c</u>antellated <u>sod</u>alite), unveiled thanks to our design approach. It differs from **sod-a** net, in that it also allows us to appreciate the presence and connectivity mode of the cuboctahedral building blocks, where a trigonal prism completes the tiling (Figures S21–S23).

Zr-sod-ZMOF-1 crystallizes in the $Im\overline{3}m$ cubic space group with a unit cell parameter of 55.199(7) Å and a volume of 168 190(60) Å³. The overall framework contains two types of cages: the large truncated rhombic dodecahedral cage typical from the sodalite net is mesoporous, with a diameter \approx 43 Å, accessible through square windows of \approx 8 Å and hexagonal windows of \approx 21 Å apertures. In addition, the structure

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Figure 2. Illustration of the bottom-up construction of Zr-sod-ZMOF-1 (center): (a) Organic and inorganic MBBs assemble through (b) the formation of triple bridges. (c) Each MBB connected to four others in a tetrahedral fashion. (d) Tetrahedral MBBs oriented in eclipsed fashion, with (e) a slight tilt characteristic of zeolites, allowing the overall formation of (f) the sodalite type cage.

encompasses microporous cages with a diameter of ≈ 6 Å, resulting from the cantellation strategy, and delimited by the three ligands bridging adjacent clusters (Figure S19a). Each unit cell contains 3672 atoms, ca. 13.3 and 102 times more than the unit cells of ZIF-8 (276 atoms) and the sodalite zeolite (36 atoms), respectively.

From a purely geometrical view, the assembly of eclipsed tetrahedra through our cantellation strategy should give an ideal T–X–T angle of 180° between the tetrahedral MBBs. There is however no net allowing such perfect orientation of eclipsed tetrahedra. Therefore, **mtn** or **mgz-x-d** nets, with T–X–T angles of 175° and 174.5°, respectively, could be the expected topologies.³⁴ Interestingly, the **sod** net is favored, with an experimental T–X–T angle of 173.5° (Figure S18c). This can be explained by its higher regularity; compared to the trinodal **mtn** and heptanodal **mgz-x-d** nets, the **sod** net is edge-transitive and uninodal.

Interestingly, Zr-**sod**-ZMOF-1 contains two crystallographically independent ligands, both present in each of the triple bridges between the clusters. The experimental bending angles of $2 \times 112.2^{\circ}$ and $1 \times 127^{\circ}$ were far from the ideal 120° expected for this type of bending (Figure S18a). This observation led us to conclude that thanks to the slight natural flexibility of the ligands the semiregular **sod** topology is ruling the MOF assembly over the more ideal but less regular tetrahedra stacking of **mtn** or **mgz-x-d**.

The porosity of Zr-**sod**-ZMOF-1 has been examined by an argon sorption experiment, exhibiting a type-IV isotherm, characteristic of a mesoporous material (Figure 3a). The apparent Brunauer–Emmett–Teller (BET) area was estimated to be 1565 m²·g⁻¹. The total pore volume was calculated to be 1.98 cm³·g⁻¹, in agreement with the theoretical value (2.4 cm³·g⁻¹). This experimental pore volume is the highest for **sod**-ZMOFs and even for ZMOFs based on 4-coordinated tetrahedral MBBs (Figure 3c).³⁵ The pore size distribution



Figure 3. (a) Ar adsorption-desorption isotherm. (b) Corresponding PSD and (c) Experimental pore volume and PSD for Zr-sod-ZMOF-1 as compared to highest reported values from frameworks based on tetrahedral nodes or with sod topology. (d) Cage size for SOD structure, ZIF-8, and Zr-sod-ZMOF-1.



Figure 4. Relocation of the steric hindrance from (a) the arms of the ligands (Zr-sod-ZMOF-1) to (b) the central core allows the formation of an isoreticular analogue, Zr-sod-ZMOF-2.

(PSD) shows a sharp pore size at 43 Å, in agreement with the crystallographic data. Since the primary pore system in Zr-**sod**-ZMOF-1 is mesoporous, the model deployed could not assess the contribution from the micropores. The micropores between the clusters generated by the cantellation with 3 bent ligands can be relatively estimated by using only low-pressure data points (up to $P/P_0 = 0.03$), asserting the

presence of micropores around 6.2 Å and their contribution to the overall porosity (Figure S24c).

In order to assess the strength of our cantellation design approach, we intended to prepare isoreticular Zr-**sod**-ZMOF (Figure 4), and a novel ligand was designed. 4,4'-(2,4,6-Trimethylpyridine)dibenzoic acid (TMPDB, L2) has the same angular characteristics as L1; however, its steric hindrance is now located in the central part of the ligand, on a pyridine ring. As expected, the use of ligand L2 allowed to obtain an isoreticular analogue to Zr-**sod**-ZMOF-1 (Tables S1 and S2).

The phase purity was further confirmed by powder X-ray diffraction (PXRD, Figure S17). Due to the similarities between L1 and L2, Zr-sod-ZMOF-2 exhibits the same type of cages: the mesoporous cage, having a diameter of about 43.5 Å, and a confined cage between the triple ligands of 4–6 Å with two windows, a square of 12 Å and a hexagon of 22 Å (Figure S19b). Similar to Zr-sod-ZMOF-1, there are two crystallographically independent ligands in the Zr-sod-ZMOF-2 (2× 118° and 1× 130.4°), and the tetrahedral units show a T–X–T angle of 173° (Figure S18a).

In summary, we developed a cantellation design approach that afforded the deployment of the 12-c Zr-based MBB as a tetrahedral secondary building unit. Locked in an eclipsed conformation through triple bridging by the ligands, the stacking of the MBBs prevents the formation of interpenetrated MOFs with dia topology while allowing the formation of zeolitic-nets. This strategy permitted the discovery of two isoreticular mesoporous Zr-sod-ZMOFs, the first examples of Zr-MOFs with zeolitic topology. Zr-sod-ZMOF-1 has the highest experimental pore volume reported for any sodalite type material so far (\approx 3.5 times higher than ZIF-8), as well as for any zeolitic material based on tetrahedral MBBs. Finally, our cantellation strategy offers new opportunities for the deliberate use of highly coordinated clusters as secondary building units with lower connectivity through multiple bridging.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c10007.

Synthesis, PXRD, TGA, and additional sorption data (PDF)

Crystallographic data for 1-periodic phase, Zr-sod-ZMOF-1, and Zr-sod-ZMOF-2 (CIF, CIF, and CIF)

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Notes

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