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

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Supporting Information Placeholder

ABSTRACT: Herein we report a series of novel mesoporous zirconium-based metal-organic frameworks (MOFs) with zeolitic sodalite (**sod**) underlying topology. Namely, 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 truncated rhombic dodecahedron mesopores with a diameter up to ≈ 43 Å, while the pore volume of $1.98 \text{ cm}^3 \cdot \text{g}^{-1}$ measured for Zr-**sod**-ZMOF-1 is the highest reported experimental value for zeolite like MOFs based on MBBs as tetrahedral nodes.

Metal-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 90's, tremendous efforts have been dedicated to explore their properties and potential applications as drug carrier,² separation agents,³ sensors,⁴ etc.

Among the 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 researchers are committing noticeable efforts toward expanding the repertoire of reticular chemistry.⁸ This is achievable by using complex ligands to deviate from “default” assemblies,⁹ or by developing advanced strategies, such as pillaring,¹⁰ supermolecular building layers¹¹ and supermolecular building blocks,¹² in order to promote the assembly into a precise underlying 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) 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 **sod**, **ana**, **rho** etc. topologies,¹⁴ alongside unprecedented ones (**med**)¹⁵ and ii) corner sharing of super-tetrahedra constructed from trimeric building blocks (Fe^{3+} , Cr^{3+} , etc) and linear (MIL-101)¹⁶ or triangular ligands (MIL-100),¹⁷ systematically to afford **mtn** underlying topology.¹⁸

The synthesis of ZMOFs with considerably expanded pores is a long-term pursuit and a persisting challenge, and several design strategies have been explored to expand and/or functionalize the pore system of the reported ZMOFs.¹³ The common approach to MOFs isorecticular expansion and/or decoration is by adjusting the metrics and functionalities of 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 slight modification in the specific angles and the positioning of the coordinating functional groups, with respect to the inorganic building block, prohibiting the isorectification 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, **dia** underlying topology.²⁰ In this context, the targeted frameworks must meet 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, **sod**) net has the highest occurrence, placing it as 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 with unique characteristics, due to the fact that the **sod** net is not self-dual and not prone to self-interpenetration, namely a high pore/aperture size ratio, large pore volume and contracted pore-aperture size, suitable for molecular entrapment for potential applications.^{13, 14b} In the present work, we introduce a *cantellation* design approach for the conception and directed assembly of novel mesoporous ZMOFs based on zirconium MBBs.

In order to successfully and rationally design a novel generation of

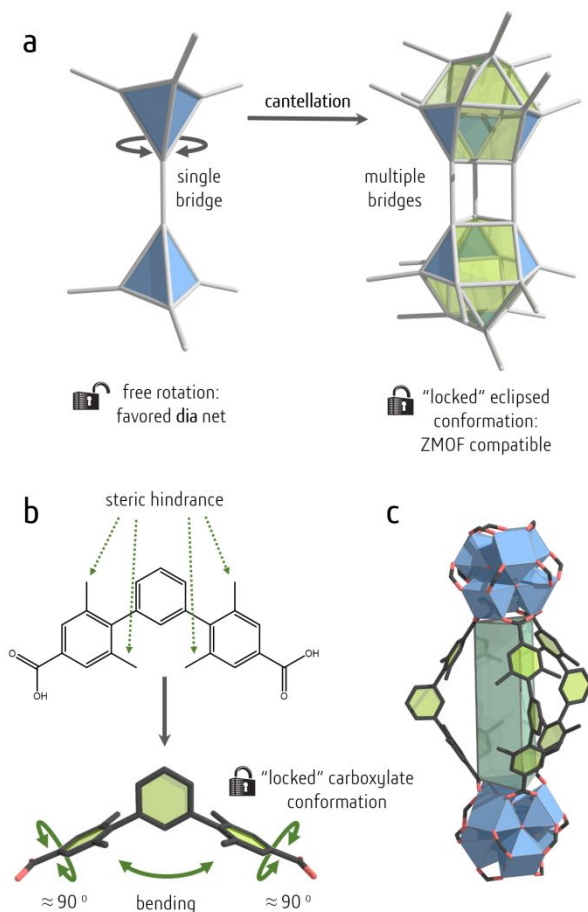


Figure 1. a) Schematic of the tetrahedra cantellation strategy leading to multiple bridges, allowing the building units to be “locked” in eclipsed conformation and b) design of a sterically hindered bent ligand, locking the carboxylic group in the appropriate position to c) form a triple bridge between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

isorecticular ZMOFs, we identified three main requirements:

- i) Achieving the formation of a tetrahedral MBB;
- ii) Preventing the formation of **dia** net, the most regular edge-transitive net, considered as the default topology for the assembly of tetrahedra;²²
- iii) 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 face at each edge and vertex of a tetrahedron, affords the formation of cuboctahedron. Applying now the same cantellation 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 prevents any rotation and therefore “locks” 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.

After identifying the suitable inorganic MBB, 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 this conformation can be regarded as an exception as it is widely accepted that the favored topology would be **fcu**, exemplified by plethora examples.^{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 on the quest for the discovery of highly porous Zr-MOFs based on zeolite topologies, the ideal ligand should be: i) A ditopic linker, with a bent geometry allowing the triple bridging of MBBs without excessive constraint on the Zr-carboxylate bonds; and ii) the two carboxylates preferably oriented orthogonally to the plan of the ligand. Separately, these two requirements would not be sufficient to achieve the envisioned assembly. 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 *meta* positions. To fulfill the second criterion, we introduced steric hindrance by the means of methyl groups on the *ortho* positions (in 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 will overall minimize the coordination options, favors the triple bridging of the MBBs, virtually reducing their net-connectivity (points of extension) from 12 to 4: Each 12 coordinated 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 ZrCl₄ and L1 in presence of DMF and acetic acid resulted in the isolation rhombic dodecahedral crystals (Figure S16-a). Single-crystal X-ray diffraction studies revealed that, the obtained MOF encloses fully coordinated clusters (12-c) and 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** (cantellated **sodalite**), unveiled thanks to our design approach. It differs from **sod-a** net: it also allows to appreciate the presence and connectivity mode of the cuboctahedral building blocks, where a trigonal prism completes the tridimensional tiling (Figures S21-23).

Zr-**sod**-ZMOF-1 crystallizes in the *Im-3m* cubic space group with a unit cell parameter of 55.199(7) Å and a volume of 168190(60) Å³. The overall framework contains two types of cages: the large

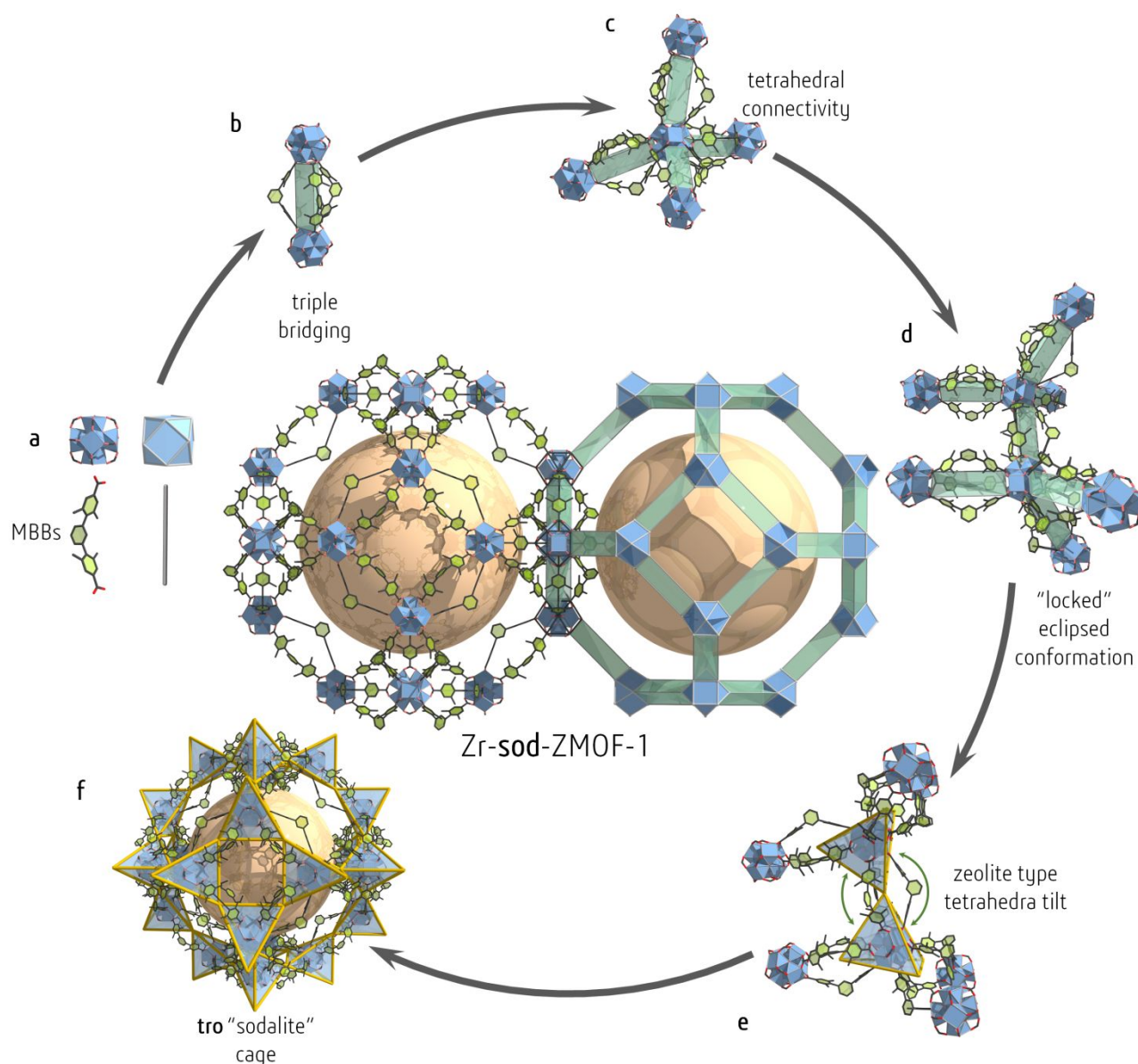


Figure 2. Illustration of the bottom up construction of Zr-sod-ZMOF-1 (center); a) organic and inorganic MBBs assemble through b) the formation of triple bridges. c) Each inorganic MBB is connected to four others in a tetrahedral fashion. d) The tetrahedral MBBs are oriented in an eclipsed fashion, with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

truncated rhombic dodecahedral cage typical from the sodalite net is mesoporous, with a diameter $\approx 43\text{\AA}$, accessible through square windows of $\approx 8\text{\AA}$ and hexagonal windows of $\approx 21\text{\AA}$ apertures. In addition, the structure encompasses microporous cages with a diameter of $\approx 6\text{\AA}$, resulting from the cantellation strategy, and delimited by the three ligands bridging adjacent clusters (Figure S19-a). Each unit cell of Zr-sod-ZMOF-1 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, in the present case, the **sod** net is favored, with an experimental T-X-T angle of 173.5° (Figure S18-c). 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, uninodal.

A careful look at the structure permits an interesting observation: Zr-sod-ZMOF-1 contains two crystallographically independent ligands, both present in each of the triple bridge between the clusters. The experimental bending angles of $2 \times 112.2^\circ$ and $1 \times 127^\circ$, away from the ideal 120° expected for this type of bending (Figure S18-a). This observation led us to conclude that thanks to the slight

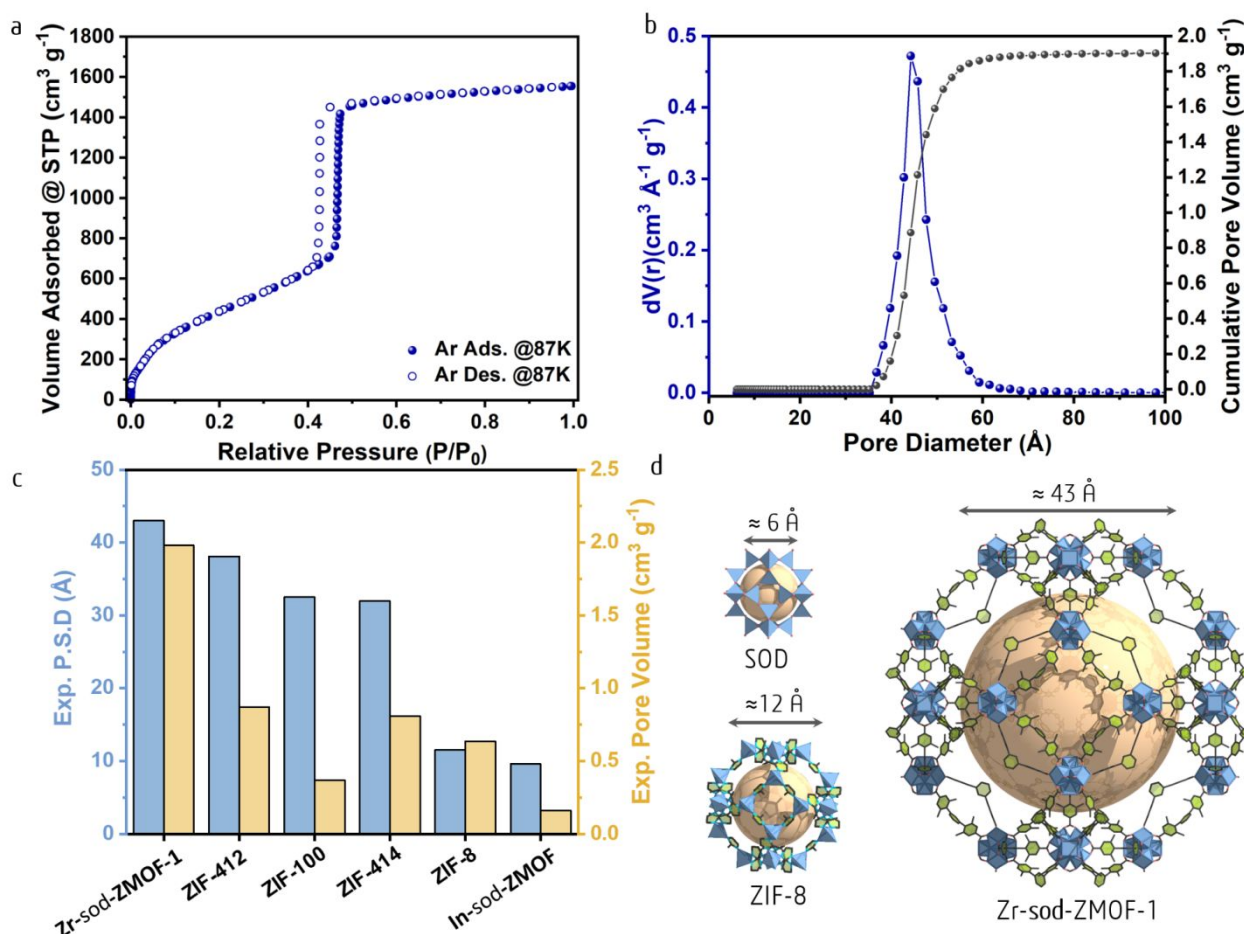


Figure 3. a) Type 4 Ar adsorption-desorption isotherm, b) the corresponding PSD and c) Experimental pore volume of Zr-**sod**-ZMOF-1 as compared to the highest reported values from frameworks based on tetrahedral nodes and with **sod** topology (ZIF-8 and In-**sod**-ZMOF) in gold. Experimental pore size distribution of Zr-**sod**-ZMOF-1 showing the highest reported experimental value among the same set of frameworks in blue. d) Cage size difference in Zeolitic SOD structure, ZIF-8 and Zr-**sod**-ZMOF-1.

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 argon sorption experiment carried out at 87 K, exhibiting a type-IV isotherm, characteristic of a mesoporous material with permanent porosity (Figure 3-a). The apparent Brunauer–Emmett–Teller (BET) surface area was estimated to be 1565 m²·g⁻¹. The experimental 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-c tetrahedral MBBs (Figure 3-c).³⁵ The pore size distribution shows a sharp pore size at 43 Å, in agreement with the crystallographic data for mesopores. 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/P₀ = 0.03), asserting the presence of micropores around 6.2 Å and their contribution to the overall porosity (Figure S24-c).

In order to assess the strength of our cantellation design approach, we intended to prepare isorecticular Zr-**sod**-ZMOFs (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 isorecticular analogue to Zr-**sod**-ZMOF-1 (Tables S1-2).

The phase purity was further confirmed by powder X-ray diffraction pattern (PXRD, Figure S17). Due to the similarities between L1 and L2, Zr-**sod**-ZMOF-2 exhibit same type of cages. The large truncated rhombic dodecahedron mesopore cage, having a diameter of about 43.5 Å and a confined cage between the triple ligands of 4-6 Å, with two windows: square with 12 Å and hexagon with 22 Å (Figure S19-b). Similar to Zr-**sod**-ZMOF-1, there are two crystallographically independent ligands in the Zr-**sod**-ZMOF-2: 2x 118°, 1x 130.4° and the tetrahedral units show a T-X-T angle of 173° (Figure S18-a). In this structure, the dihedral angles between the benzoic moieties and the central core of the ligand are maintained at ca. 90°, “locked” by the steric hindrance.

In summary, we have developed a cantellation design approach that afforded the deployment of the 12-coordinated Zr-based MBB as a tetrahedral secondary building unit. Locked in eclipsed conformation through triple bridging by the organic ligands, the stacking of the MBBs prevents the formation of interpenetrated

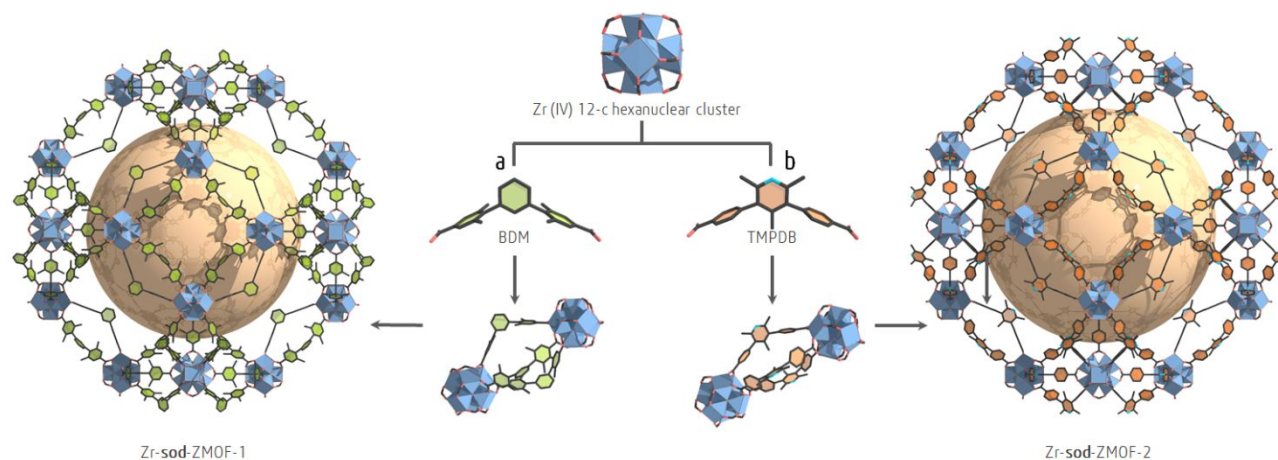


Figure 4. The relocation of the steric hindrance from a) the arms of the ligands (Zr-sod-ZMOF-1) to b) the central core allows the formation of an isorecticular analogue, Zr-sod-ZMOF-2.

MOFs with **dia** topology while allowing the formation of zeolitic-nets. Combined with appropriate ligand design, this strategy permitted the discovery of two isorecticular 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 (≈ 3.5 times higher than ZIF-8), as well as for any zeolitic material based on tetrahedral MBs. Finally, our cantellation strategy opens 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 on the ACS Publications website at DOI:.

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

Crystallographic data (CIF)

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The authors declare no competing financial interests.

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