Uncovering Structural Opportunities for Zirconium Metal–Organic Frameworks via Linker Desymmetrization

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The discovery of metal–organic frameworks (MOFs) mimicking inorganic minerals with intricate topologies requires elaborate linker design guidelines. Herein, the concept of linker desymmetrization into the design of tetratopic linker based Zr-MOFs is applied. A series of bent tetratopic linkers with various substituents are utilized to construct Zr-MOFs with distinct cluster connectivities and topologies. For example, the assembly between a bent linker L-SO₂ with C₂ᵥ symmetry and an 8-connected Zr₆ cluster leads to the formation of an scu topology, while another flu topology can be obtained by the combination of a novel 8-connected Zr₆ cluster and a bent linker L-O with C₁ symmetry. Further utilization of restricted bent linker [(L-(CH₃)₆)] gives rise to a fascinating (4, 6)-c cor net, originated from the corundum lattice, with an unprecedented 6-c Zr₆ cluster. In addition, the removal of toxic selenite ions in aqueous solution is performed by PCN-903-(CH₃)₆ which exhibits rapid and efficient detoxification. This work uncovers new structural opportunities for Zr-MOFs via linker desymmetrization and provides novel design strategies for the discovery of sophisticated topologies for practical applications.

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Metal–organic frameworks (MOFs), or porous coordination polymers, are a well-developed class of porous crystalline materials constructed from inorganic metal clusters and organic linkers.[1–9] As highly tunable structures through judicious linker design, MOFs attracted considerable interests in fields, such as gas storage, separation, heterogeneous catalysis, sensing, light harvesting, and drug delivery.[4,10,11] Among the numerous MOFs, zirconium MOFs have received increasing attention in recent years due to their highly stable feature originated from the robust Zr−O coordination bonds.[1,12] The high chemical stability of Zr-MOF ensures its economical large-scale production in water solution and also permits its structural intactness when exposed to harsh conditions.

The combination of Zr clusters and different organic linkers has contributed to the structural diversity and functional complexity of the MOF materials. Various synthetic approaches have been developed to synthesize Zr-MOFs with structural complexity, including linker design strategies, pillar strategies, postsynthetic methods, and preformed clusters.[1] For example, Zhou group reported the steric control over ditopic linker based Zr-PCN-700, where bulky substituents on the 2- and 2′-positions of BPDC (biphenyl-4,4′-dicarboxylate) were introduced to constrain the two carboxylates and phenyl rings into a perpendicular conformation.[13] Later Guillerm and co-workers described the topological influence of zigzag ligands during the assembly of bcu net.[14] Speaking of 4-connected linkers, the structural diversity based on Zr₆ clusters can also be expanded by tuning linker conformation. For example, various topologies including ftw, csq, shp, scu, she, and sqc can be accessed when square or rectangle tetratopic linkers are chosen.[15–20] The effects of linker geometry and flexibility influenced by the bulkiness of substituents can also be utilized to enhance the diversity of Zr-tetratopic carboxylate MOFs.[21] However, how to continue enhancing the structural and compositional compilation of Zr-tetratopic carboxylate MOFs poses a synthetic challenge.

Herein, we initiate a systematic study on Zr-tetracarboxylate frameworks constructed from a series of bent tetratopic linkers with various substituents. The utilization of a bent ligand with lower symmetry overcomes the traditional topology problems
limited by the rigid ligand backbones. The tunable linker geometries and conformations here by altering the composition of substituents generate a series of Zr-MOFs with varying topologies including \( \text{scu} \), \( \text{flu} \), and \( \text{cor} \). This work provides fresh insights into the discovery of Zr-tetracarboxylate frameworks with unprecedented topologies and conformations of building blocks, and highlights the importance of linker desymmetrization for dictating MOF architectures.

As shown in Figure 1a, four bent tetratopic ligands with various substituents (\( R_1 = -\text{H}, -\text{CH}_3; \ R_2 = -\text{NH}_2, -\text{CH}_3; \ R_3 = -\text{SO}_2, -\text{CH}_2, -\text{O} \)) were selected to construct Zr-based MOFs. Due to the bulkiness differences of \( R_1 \) substituents, the...
distances and angles between two central rings can be tuned. The presence of \( R_3 \) substituents can effectively influence the rotation angles between two peripheral phenyl rings near the central ring, while \( R_3 \) substituents are utilized to tune rotation degrees around the linker center.

Large colorless crystals, PCN-901-SO\(_2\) (also named UPC-901-SO\(_2\)), were obtained with cuboid morphology after the solvothermal reactions between L-SO\(_2\) and ZrCl\(_4\) in the presence of trifluoroacetic acid as a modulator for 24 h (Figure 1b). The structure of PCN-901-SO\(_2\) was determined by single-crystal X-ray diffraction. Powder X-ray diffraction (PXRD) patterns indicate the phase purity of the obtained product (Figure 1d). PCN-901-SO\(_2\) crystallized in the tetragonal space group P4/mmm (Table S1, Supporting Information). Crystallographically, it contains an 8-connected Zr\(_6\) cluster \([\text{Zr}_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(H_2O)_4(COO)_8]\) and a bent tetratopic linker with \( C_{2v} \) symmetry. The overall structure was analyzed to be a 4,8-connected scu net with a point symbol of \{4\(^6\)6\(^{12}\)\}\(^{2}\) as determined by TOPOS 4.0 (Figure 2a).\(^{[22]}\) Note that this topology has been reported previously in NU-901 and PCN-606, which are constructed from rectangular planar nodes and cuboid nodes.\(^{[21,23]}\) In the structure of PCN-901-SO\(_2\), the arrangement of Zr\(_6\) clusters leads to two types of pores (Figure 2a). Remarkably, the linkers are restricted into a conformation with 113.6° dihedral angle between the two central phenyl rings, and 82.9° dihedral angle between the two peripheral phenyl rings and the central ones. The chemical stability of PCN-901-SO\(_2\) was further examined by immersing MOFs in various aqueous solutions for 24 h. PXRD patterns indicated that the PCN-901-SO\(_2\) has excellent chemical stability in solution with pH ranging from 0 to 12 as evidenced by the well-maintained crystallinity (Figure S14, Supporting Information).

Interestingly, we observed large crystals of PCN-902-O with a different morphology formed after the reaction between ZrCl\(_4\) and L-O under the same condition (Figure 1c). As indicated by single-crystal X-ray diffraction, L-O possessed a \( C_1 \) symmetry due to the bulkiness influence of the substituents (Figure 2b). Notably, the dihedral angle between the two central phenyl rings in L-O is 113.9° and the dihedral angles between the central phenyl ring and the two peripheral ones are around 60°. The corresponding phase purity of the products was supported by PXRD analysis (Figure 2d). PCN-902-O crystallized in the triclinic space group \( P\bar{1} \) (Table S1, Supporting Information). Crystallographically, it contains an 8-connected Zr\(_6\) cluster \([\text{Zr}_6(\mu_3-O)_4(\mu_3-OH)_4(OH)_4(H_2O)_4(COO)_8]\) and a 4-connected bent tetratopic linker with \( C_1 \) symmetry. The overall structure was determined to be a 4,8-connected flu net with a point symbol of \{4\(^{12}\)6\(^{12}\)8\(^{4}\)\}\(^{4}\) by TOPOS 4.0 (Figure 2b). Replacing L-O with a similar bent linker L-CH\(_2\) generated the isostructural PCN-902-CH\(_2\), as indicated by the PXRD pattern. The flu (fluorite) topology can be viewed as a cubic close packing (csc) of the Ca\(^{2+}\) cations where the F\(^{-}\) anions occupy all tetrahedral interstitial cavities (Figure 2a), leaving all the octahedral interstitial cavities vacant. MOFs with flu topology can be assembled through 4-connected linkers and 8-connected metal clusters.

Additionally, introducing bulky methyl groups onto the phenyl rings of L-CH\(_2\) can necessitate the two peripheral phenyl rings to exhibit a larger dihedral angle, leading to a different conformation for MOF construction. In order to obtain...
large single crystals, benzoic acid was used as the modulator to control the growth kinetics of PCN-903-(CH$_3$)$_6$, in which a truncated octahedron crystal with cor topology was built based upon an unprecedent 6-c Zr$_6$ cluster. Single-crystal X-ray analysis revealed that PCN-903-(CH$_3$)$_6$ crystallized in the trigonal space group $R$-$3c$ (Figure 3). It contains a novel 6-connected Zr$_6$ cluster [Zr$_6$(µ$_3$-O)$_4$(µ$_3$-OH)$_4$(OH)$_6$(H$_2$O)$_6$(COO)$_6$] and a tetra-topic linker with C$_1$ symmetry. Crystallographically, six bent tetratopic linkers bridged four neighboring Zr$_6$ clusters, which can be simplified into a fascinating (4, 6)-connected net with cor topology (Figure 3b).

Different from the traditional 6-connected Zr$_6$ cluster observed in MOF-808 and other 6-c Zr-MOFs, the Zr$_6$ cluster in PCN-903-(CH$_3$)$_6$ displays two types of dihedral angles, 64.7° and 22.1°, between the O–Zr–Zr–O plane and the equatorial plane (Figure 3e). This unusual asymmetric feature of Zr$_6$ clusters brings new opportunities to explore topology diversity within highly connected MOFs. The overall structure was analyzed to be a (4, 6)-connected net with a point symbol of {4$^3$.6$^6$}$_2$ as determined by TOPOS 4.0 (Figure 3b).

The intriguing cor topology originates from the lattice of corundum, a crystalline phase of aluminium oxide (Al$_2$O$_3$), where each Al atom is surrounded by six O atoms.[24] In the corundum lattice, the O atoms never locate at the corners of a regular octahedron, instead, they form a slightly distorted hexagonal close packing, where two-thirds of octahedral interstitial cavities are occupied by Al atoms. By replacing Al atoms with distorted 6-connected Zr clusters and O atoms with bent tetratopic ligands, the extension from an inorganic material to a porous inorganic–organic hybrid compound is achieved (Figure 3a). The assembly of 6-c Zr$_6$ clusters and C$_1$ ligands initially generates a supramolecular triangular bipyramid building unit, where all equatorial vertices are occupied by the ligand building units while both polar vertices are placed by the inorganic clusters (Figure 3d). As a result, a microporous cage with 6.4 Å size is formed. Further hierarchical assembly of these triangular bipyramid building units into 3D network can be visualized in Figure 3. Each triangular bipyramid unit is connected to neighboring six units, resulting in a second type of pore with 10.1 Å size between each two triangular bipyramid units.
structures with different topologies. For linker L-SO2, the linker in the frameworks, two lateral phenyl rings in the individual strained structure. Due to the constraints from Zr6 clusters, the formations were normalized by subtracting the energy of its unconstrained structure. The relative energy for a given linker fragment in different conformations have been explored through density functional theory and Table S2 (Supporting Information). For clarify, the energy of a given ligand is normalized through subtracting the energy of its unconstrained structure.

Further assembly of these units also generates a larger cage with 17.2 Å size (Figure 3c). The discovery of PCN-903-(CH3)6 presents a very rare case, and a new level of sophisticated assembly of Zr-cluster based MOFs involving multiple levels of structural hierarchy. It should be noted that there is a β-UH3-like topology based Zr-MOF constructed from 4-connected elongated linkers reported by Zhang and co-workers. Our work here presents a powerful strategy to ascertain new structural mysteries of MOFs which mimic complicated inorganic structures. In addition, there is also a Zn-MOF, Zn2O(BenzTB)3/2 (DUT-13) with very densely packed building blocks, PCN-902 and PCN-903 showed relatively low N2 uptake and surface areas.

The effects of center functional groups on linker conformation have been explored through density functional theory calculations. The relative energies of selected linkers in PCN-901, PCN-902, and PCN-903 were calculated and listed in Figure 4 and Table S2 (Supporting Information). For clarify, the energies of a given linker fragment in different conformations were normalized by subtracting the energy of its unconstrained structure. Due to the constraints from Zr6 clusters in the frameworks, two lateral phenyl rings in the individual ligand will exhibit distinct torsion angles in the corresponding structures with different topologies. For linker L-SO2, the linker is too rigid to distort, making the formation of conformations observed in PCN-902 and PCN-903 unfavorable. The energy difference of L-O in PCN-901 and PCN-902 is approximately 20.6 kJ mol⁻¹, while the difference is 14.4 kJ mol⁻¹ for L-O in PCN-902 and PCN-903. This result indicates that the bent conformation of L-O in PCN-902 allows for the gyration of two lateral phenyl rings, which is beneficial for the formation of PCN-902 with flu topology. For L-CH2 with a similar conformation, the formation of flu topology is also favorable as indicated by the relative energies in PCN-90X with varying topologies. Considering the linker L-(CH3)6, its conformation is latched by bulky methyl groups. By comparing the relative energies of linkers in PCN-90X, we observed that linkers with bulky groups such as -CH3 tend to be obtained with a larger torsion angle, so only PCN-903 with cor topology will be adapted in this case.

Due to the existing large amount of coordinately unsaturated sites on Zr6 clusters, the highly defective PCN-903-(CH3)6 was tested for its ability to adsorb and remove selenite anions from aqueous solutions. Although trace amounts of selenium are vital for nutritional needs of animals, it becomes extremely toxic at high concentrations (400 μg d⁻¹). The maximum acceptable concentrations were set as 40 and 50 ppb, respectively, by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA). The uptake ability of PCN-903-(CH3)6 toward toxic SeO3²⁻ was first tested via a series of SeO3²⁻-aqueous solution from 10 to 500 ppm. To reach adsorption equilibrium, 10 mg PCN-903-(CH3)6 was immersed in the aqueous solutions for 24 h, which was followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis of supernatant fraction to determine the remaining SeO3²⁻ concentration. As indicated by Figure 5a, the adsorb amounts of SeO3²⁻ in the MOF absorbent increase as the initial concentrations of SeO3²⁻ increase. The maximum Se capacity of PCN-903-(CH3)6 was calculated as 7.55 mg g⁻¹, which exhibits one of the highest adsorption capacities among MOF absorbents (Figure 5a and Table S4, Supporting Information). Remarkably, PCN-903-(CH3)6 exhibits rapid removal, >90% of SeO3²⁻ within 7 min, >99% removal within 1 h and complete removal, >99.9%, of SeO3²⁻ within 3 h. The excellent selenite removal efficiency places PCN-903-(CH3)6 as a promising porous absorbent for detoxification.

In conclusion, we have synthesized four new Zr-MOFs based on desymmetrized tetrapodal linkers with various substituents. For example, PCN-901-SO2 is constructed from the assembly between a bent linker L-SO2 with C2v symmetry and an 8-connected Zr6 cluster; PCN-902-O/CH2 contains a novel 8-connected Zr6 cluster and a bent linker L-O/CH2 with C2v symmetry, exhibiting a GaF4-like flu topology; further utilization of restricted bent linker [(L-(CH3)6)] gives rise to PCN-903-(CH3)6 with a fascinating Al2O3-like (4, 6)-cor topology. Additionally, the highly defective PCN-903-(CH3)6 showed efficient removal of toxic selenite ions in aqueous solutions, achieving >90% of SeO3²⁻ within 7 min, and complete removal, >99.9%, of SeO3²⁻ within 3 h. This work points out a fresh direction for developing functional and stable Zr-MOFs with unprecedented topologies by linker design.

Experimental Section

Linker Synthesis: The detailed synthetic approaches of organic linkers including L-SO2, L-CH2, L-SO2, and L-(CH3)6, are provided in the Supporting Information.

Synthesis of PCN-901(Zr)-SO2: ZrCl4 (20 mg), L-SO2 (10 mg), and DMF (3 mL) were charged into a 10 mL vial, followed by the addition of...
0.15 mL trifluoroacetic acid. The mixture was heated in 115 °C oven for 2 d. After cooling down to room temperature, the colorless crystals of PCN-901(Zr)-SO₂ were harvested (yield: 75%).

**Synthesis of PCN-902(Zr)-O**: ZrCl₄ (20 mg), L-O (10 mg), and DMF (3 mL) were charged into a 10 mL vial, followed by the addition of 0.10 mL trifluoroacetic acid. The mixture was heated in 120 °C oven for 2 d. After cooling down to room temperature, the colorless crystals of PCN-902(Zr)-O were harvested (yield: 70%).

**Synthesis of PCN-902(Zr)-CH₂**: ZrCl₄ (20 mg), L-CH₂ (10 mg), and DMF (3 mL) were charged into a 10 mL vial, followed by the addition of 0.10 mL trifluoroacetic acid. The mixture was heated in 120 °C oven for 2 d. After cooling down to room temperature, the colorless crystals of PCN-902(Zr)-CH₂ were harvested (yield: 71%).

**Synthesis of PCN-903(Zr-CH₃)₆**: ZrCl₄ (20 mg), L-(CH₃)₆ (10 mg), benzoic acid (500 mg), and DMF (3 mL) were charged into a 10 mL vial. The mixture was heated in 120 °C oven for 2 d. After cooling down to room temperature, the colorless crystals of PCN-903(Zr-CH₃)₆ were harvested (yield: 62%).

**Adsorption Isotherm Measurement**: PCN-903-(CH₃)₆ (10 mg) was mixed with a 10 mL stock solution of selenite (SeO₃²⁻) with various concentrations. The mixture was kept at room temperature for 24 h to ensure complete adsorption. The ion concentration in the supernatant solutions was determined by ICP-MS.

**Adsorption Kinetics Measurement**: PCN-903-(CH₃)₆ (10 mg) was mixed with a 10 mL stock solution of selenite (SeO₃²⁻) at a concentration of 10 ppm. The mixture was kept at room temperature for various periods. During the adsorption process, the ion concentration in the supernatant solutions was analyzed by ICP-MS.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

linker design, linker desymmetrization, metal–organic frameworks, topology, zirconium

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Figure 5. Efficient removal of toxic selenite ions by PCN-903-(CH₃)₆. a) Sorption isotherms for selenite (SeO₃²⁻) by PCN-903-(CH₃)₆. b) Sorption kinetics curves for selenite (SeO₃²⁻) by PCN-903-(CH₃)₆.
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