

Novel Metal–Organic Framework Based on Cubic and Trisectahedral Supermolecular Building Blocks: Topological Analysis and Photoluminescent Property

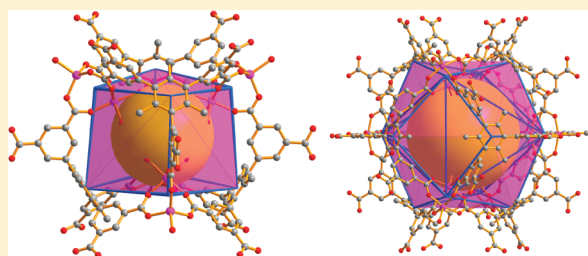
Xiaoliang Zhao,[†] Xiaoyang Wang,[†] Suna Wang,[‡] Jianmin Dou,[‡] Peipei Cui,[†] Zhen Chen,[†] Di Sun,^{*,†} Xingpo Wang,[†] and Daofeng Sun^{*,†}

[†]Key Lab of Colloid and Interface Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Shandong University, Jinan, Shandong, 250100, China

[‡]Department of Chemistry, Liaocheng University, Liaocheng 252059, P. R. China

Supporting Information

ABSTRACT: A novel supermolecular building blocks (SBBs) based metal–organic framework (MOF), with formula $[\text{Zn}_7(\text{TMBHB})_2 \cdot 2\text{NO}_3 \cdot 5\text{DMF} \cdot 4\text{CH}_3\text{CH}_2\text{OH} \cdot 6\text{H}_2\text{O}]_n$ (**SDU-1**), was constructed from C_3 -symmetric trimethyl substituted 3,3',3'',5,5',5''-benzene-1,3,5-triylhexabenzic acid (H_6TMBHB). Notably, the **SDU-1** consists of two kinds of rare secondary building units (SBUs), $[\text{Zn}_2(\text{COO})_3]$ and $[\text{Zn}_2(\text{COO})_4]$, which are linked by TMBHB to form cubic and trisectahedral SBBs, respectively. TOPOS software analysis of **SDU-1** indicates that two alternative simplifications based on different SBBs can produce (3,24)-connected **rht** or (4,12)-connected **ftw** topologies. Compared with a recently reported Zn-BHB ($\text{H}_6\text{BHB} = 3,3',3'',5,5',5''$ -benzene-1,3,5-triylhexabenzic acid) MOF, the structural dissimilarity between them was caused by the steric hindrance of three methyl groups, which makes three isophthalate units on TMBHB nearly perpendicular to the central phenyl ring, giving TMBHB a nonplanar conformation. The photoluminescence behavior of **SDU-1** was also discussed.



Porous metal–organic frameworks (MOFs) based upon combinations of metal centers and polydentate bridging ligands have attracted unparalleled attention in the past 20 years due to their appealing structural diversities and potential applications, such as gas storage and separation, luminescence, catalysis, drug delivery, and chemical sensing.¹ However, how to rationally realize the preferred structures with specific functionalities still remains a fundamental scientific challenge due to a number of factors that can influence the construction of MOFs.² Therefore, much effort should be continuously devoted to the design and controlled synthesis of porous MOFs. As we know, the supermolecular building blocks (SBBs) route has recently appeared as an effective strategy to design and construct porous MOFs with tailorable network topologies as well as pore size and surface characteristics.³ With this synthetic strategy, a huge number of porous MOFs have been prepared and characterized.⁴ An elegant example is the Zn^{II} benzenedicarboxylate MOF-5 based on the well-accepted $[\text{Zn}_4(\text{O})(\text{COO})_6]$ secondary building unit (SBU) showing high BET (Brunauer–Emmet–Teller) surface area and unusual stability.⁵ The strongest advantage of the SBB route mainly stems from the pre-designed carboxylate ligands.⁶ Although pure carboxylate ligands have been extensively studied,⁷ less methyl-substituted nonplanar polycarboxylate ligands were found to possess promising coordination chemistry for the synthesis of MOFs.⁸ As indicated by our previous work, the planarity of the

organic ligand has a significant effect on the topologies of the final structure.⁹ Hence, interesting MOFs with novel topologies could be achieved by applying nonplanar methyl-substituted terephthalic acid or 1,3,5-tricarboxylic acid, such as, 2,3,5,6-tetramethylterephthalic acid or 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid, which can be synthesized through the introduction of an methyl group in the carbon atoms beside the carboxylate groups.¹⁰ The carboxylate groups can rotate to form a large dihedral angle with respect to the central phenyl ring when they coordinate to metal ions in bidentate bridging coordination mode.

On the other hand, extension of ligand has been recognized as an efficient method toward the enhancement of the gas-uptake capabilities of MOFs.¹¹ However, increasing the surface area by larger ligands often leads to the interpenetration or self-interpenetration, which could be effectively alleviated by introduction of steric hindrance organic groups on linkers.^{7c} On the basis of the above-mentioned points and our previous work, we extend our previously used 2,4,6-trimethylbenzene-1,3,5-tricarboxylic acid to trimethyl substituted 3,3',3'',5,5',5''-benzene-1,3,5-triylhexabenzic acid (H_6TMBHB), and constructed a novel MOF (**SDU-1**) based on cubic and rare

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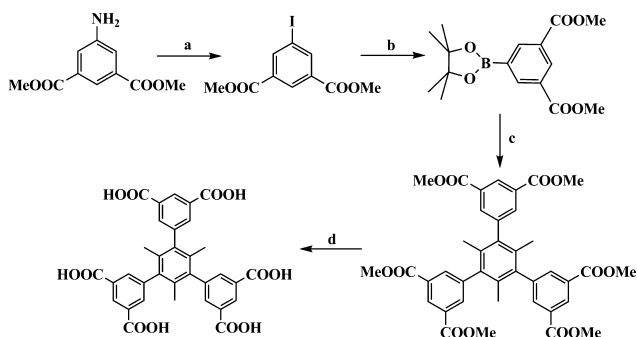
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trisoctahedron, in which two kinds of rare SBUs, $[\text{Zn}_2(\text{COO})_3]$ and $[\text{Zn}_2(\text{COO})_4]$, were observed. TOPOS software analysis of **SDU-1** indicates that two alternative simplifications based on different SBBs can produce (4,12)-connected **ftw** or (3,24)-connected **rht** topologies.

Ligand H_6TMBHB was synthesized using Suzuki reaction of dimethyl 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)isophthalate and 1,3,5-trimethyl-2,4,6-tribromobenzene (Scheme 1 and

Scheme 1. Synthetic Procedures of the H_6TMBHB ^a



^a(a) NaNO_2 , 2M HCl, KI; (b) triethylamine, $\text{PdCl}_2(\text{dppf})$, CH_3CN , 4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (c) $\text{Pd}(\text{PPh}_3)_4$, K_3PO_4 , 1,4-dioxane, 1,3,5-trimethyl-2,4,6-tribromobenzene; (d) 10 M NaOH, MeOH, tetrahydrofuran, 2 M HCl.

Supporting Information (SI)). Colorless polyhedral crystals of **SDU-1** were synthesized by solvothermal reaction of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_6TMBHB in the presence of 0.05 mL of HBF_4 in DMF–EtOH– H_2O (1 mL, v/v/v = 1:1:1, sealed tube, 90 °C). The phase purity is sustained by the powder X-ray diffraction patterns (Figure S1 in the SI). For **SDU-1**, most peak positions of the simulated and experimental patterns are in good agreement with each other. The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples. The solid FT-IR spectra (Figure S2 in the SI) of **SDU-1** show characteristic absorption bands for carboxyl groups.¹²

The crystal structure of **SDU-1** was determined by single-crystal X-ray diffraction analysis (see SI). **SDU-1** crystallizes in the cubic space group $Fm\bar{3}m$ with $a = 38.5910(8)$ Å and is a cationic 3D framework. In the asymmetric unit, there are four crystallographically independent Zn^{II} ions with three different coordination environments. As shown in Figure 1a, both Zn1 and Zn2 locate in a distorted square pyramidal coordination geometry and are linked by four carboxyl groups to form a paddle-wheel $[\text{Zn}_2(\text{COO})_4]$ SBU. Zn3 and Zn4 are coordinated by six and four O atoms, respectively, and they are linked together by three carboxyl groups to form a $[\text{Zn}_2(\text{COO})_3]$ SBU (Figure 1b). It should be pointed out that, compared to the usual $[\text{Zn}_4(\text{O})(\text{COO})_6]$ SBU, the three-connected $[\text{Zn}_2(\text{COO})_3]$ and four-connected $[\text{Zn}_2(\text{COO})_4]$ SBUs are quite rare in the construction of functional MOFs.¹³ Interestingly, six $[\text{Zn}_2(\text{COO})_4]$ SBUs are bonded together by eight TMBHB ligands to form a rare convex polyhedral SBB, namely, a trisoctahedron (Figure 1c) with a diameter of ca. 20 Å, that also can be seen as an eight-capped octahedron. On the other hand, four $[\text{Zn}_2(\text{COO})_3]$ SBUs and four TMBHB ligands constitute another Platonic polyhedral SBB, a cube (Figure 1d), with the dimensions of $7.8986(2) \times 7.8986(2) \times 7.8986(2)$ Å³. Two different kinds of polyhedra were packed into a complicated 3D framework. As we know, the simplest and

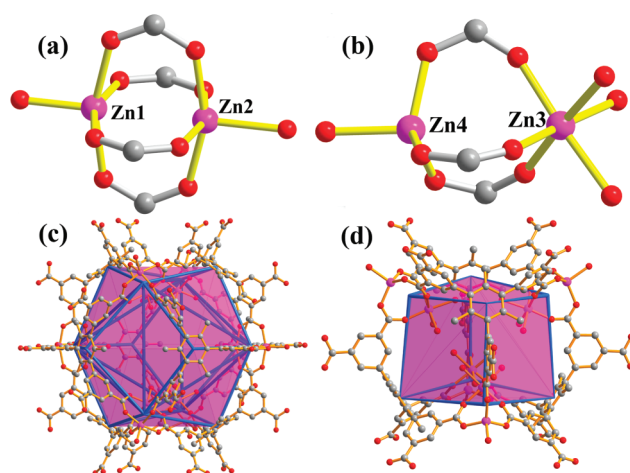


Figure 1. Ball-and-stick representation of $[\text{Zn}_2(\text{COO})_4]$ (a) and $[\text{Zn}_2(\text{COO})_3]$ (b) SBUs in **1**. Polyhedral representation of trisoctahedral (c) and cubic (d) SBBs.

most widely recognized polyhedra are tetrahedron, cube, octahedron, dodecahedron, and icosahedron, which are constructed from one type of regular polygon and belong to the Platonic solids.¹⁴ Another common class of polyhedra closely associated to Platonic solids are the Archimedean solids, which contain no less than two kinds of polygons in each Archimedean polyhedron.¹⁵ However, there are two different polyhedra, namely, cube and trisoctahedron in **SDU-1**, and the latter one belongs to the class convex polyhedron, being very rare in SBB-based MOFs.

An appealing structural feature of **SDU-1** is that the 3D framework can be alternatively simplified to two different networks with high-connected topologies based on different SBB nodes. First, taking the $[\text{Zn}_2(\text{COO})_3]$ SBU as a 3-connected node (Figure 2a), each trisoctahedral SBB (Figure 2b) is extended by 24 $[\text{Zn}_2(\text{COO})_3]$ SBUs to form the

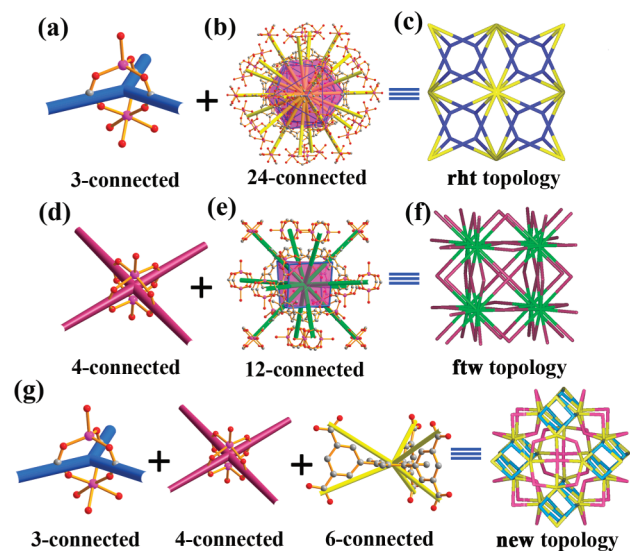


Figure 2. (a) 3-Connected $[\text{Zn}_2(\text{COO})_3]$ node. (b) 24-Connected trisoctahedral SBB node. (c) Schematic representation of a simplified 3D network with **rht** topology. (d) 4-Connected $[\text{Zn}_2(\text{COO})_4]$ node. (e) 12-Connected cubic SBB node. (f) Schematic representation of an alternatively simplified 3D network with **ftw** topology. (g) Schematic representation of a new (3,4,6)-connected topology.

resulting 3D framework, which belongs to a 2-nodal (3,24)-connected network with a common **rht** topology (Figure 2c). The short Schläfli vertex notation of the net can be represented as $\{4^3\}_8\{4^{72}\cdot 6^{132}\cdot 8^{72}\}$, indicated by TOPOS software.¹⁶ Second, if the $[\text{Zn}_2(\text{COO})_4]$ SBU and cubic SBB are treated as 4- (Figure 2d) and 12-connected (Figure 2e) nodes, respectively, the present framework can also be interpreted topologically as a novel 2-nodal (4,12)-connected **ftw** network (Figure 2f) with Schläfli symbol $\{4^{36}\cdot 6^{30}\}\{4^4\cdot 6^2\}_3$. Compared to the commonly encountered MOFs with common **rht** topology,¹⁷ MOFs with **ftw** topology were limitedly reported.¹⁸ It is worthy to note that if two kinds of SBUs and TMBHB ligand are treated as 3-, 4-, and 6-connected nodes, respectively, this framework can be topologically simplified to a low-connected 3-nodal (3,4,6)-connected network with Schläfli symbol $\{4^3\}_4\{4^4\cdot 6^2\}_3\{4^6\cdot 8^9\}_4$ (Figure 2g). This simplified net defines a completely new topology for three-periodic nets that not only is unobserved in MOFs but also is unenumerated in the electronic databases EPINET, RCSR, and TTD.¹⁹

Recently, Chen and co-workers reported two Zn^{II} MOFs (MOF-1 and MOF-2) based on 3,3',3'',5,5',5''-benzene-1,3,5-triylhexabenzic acid (H_6TMBHB) showing NaCl-type and (4,6)-connected **cor** topologies, respectively.²⁰ A comparison of **SDU-1** with MOF-1 and MOF-2 suggests that the conformation of hexacarboxylate ligand (Scheme S1 in the SI) dictates the resulting structures. In **SDU-1**, the steric hindrance of three methyl groups drives the three isophthalate units of each TMBHB to be perfectly perpendicular to the central phenyl ring with a dihedral angle of 90° . However, in the absence of three methyl groups, the steric hindrance effect was alleviated and the resulting dihedral angles between the isophthalate unit and the central phenyl ring in MOF-1 and MOF-2 are 32.6 and 40.9° , respectively.

The solid-state luminescent emission spectra of **SDU-1** and H_6TMBHB were studied at room temperature. As shown in Figure 3, H_6TMBHB and **SDU-1** have slightly different

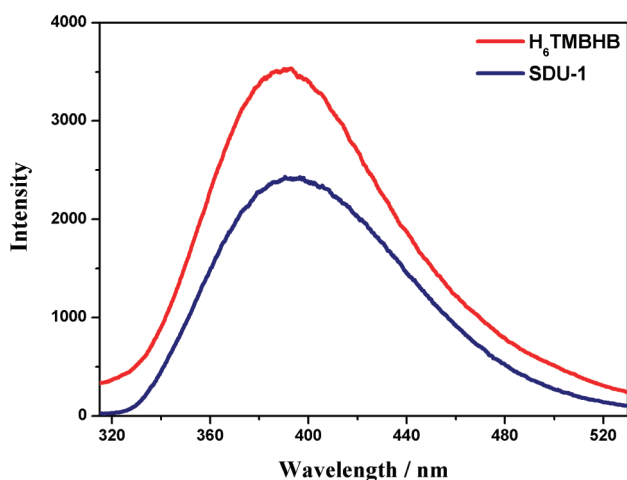


Figure 3. Photoluminescence of **SDU-1** and free ligand in the solid state.

emissions at 391 and 393 nm upon 300 nm excitation, respectively. The emission of H_6TMBHB is ascribed to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ electronic transitions. Because the Zn^{II} ion is difficult to oxidize or to reduce due to its d^{10} electronic configuration, the emissions of these complexes are neither metal-to-ligand charge transfer nor ligand-to-metal charge

transfer.²¹ The emission of **SDU-1** can probably be assigned to the intraligand or ligand-to-ligand charge transition as a result of the resemblance of the emission spectra in comparison with those of the free ligand.²²

In summary, we have successfully prepared a 3D Zn^{II} MOF based on cubic and rare trisoctahedral SBBs incorporating $[\text{Zn}_2(\text{COO})_3]$ and $[\text{Zn}_2(\text{COO})_4]$ as SBUs. This MOF reveals an uncommon (4,12)-connected **ftw** topology from the assembly of cubic SBBs and $[\text{Zn}_2(\text{COO})_4]$ SBUs. The steric hindrance from methyl groups of TMBHB ligands plays an important role in the assembly process to determine the resulting high symmetric MOF.

■ ASSOCIATED CONTENT

Supporting Information

Preparation of ligand and **SDU-1**, tables of crystal data and bond distances and angles, IR spectra, TG curves, and powder XRD patterns. X-ray crystallographic files in cif format for **SDU-1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dsun@sdu.edu.cn; dfsun@sdu.edu.cn. Fax: +86-531-88364218.

Notes

The authors declare no competing financial interest.

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