

Stability and Porosity Enhancement through Concurrent Ligand Extension and Secondary Building Unit Stabilization

Daofeng Sun, Yanxiong Ke, Tracy M. Mattox, Sean Parkin, and Hong-Cai Zhou*

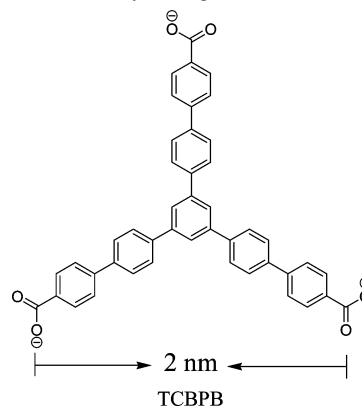
Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056

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A trigonal nanosized carboxylate ligand, 1,3,5-tris[4'-carboxy(1,1'-biphenyl-4-yl)]benzene (TCBPB), has been synthesized and applied in the construction of porous metal–organic frameworks (MOFs). A solvothermal reaction of TCBPB and a zinc salt in the presence of pyridine produces **1**, an unstable MOF consisting of a tetrazinc secondary building unit (SBU) with labile terminal ligands. Changing pyridine to a noncoordinating base in the assembly procedure affords **2**, a stable MOF with permanent porosity containing an octazinc SBU without labile terminal ligands.

Open metal–organic frameworks (MOFs) have received a great deal of attention because of their fascinating structures and intriguing potential in applications.^{1–8} Most of their applications hinge on the porosity and framework stability.^{2,4,5,7,8} One way to increase the porosity of an MOF is to extend the size of the ligand sustaining the framework. However, MOFs formed based on large ligands tend to be less stable.⁹ To improve the stability of MOFs with a larger

Chart 1. Nanosized Carboxylate Ligand



ligand, one may employ secondary building unit (SBU) stabilization,¹⁰ or framework catenation.¹¹ Despite a few successful examples¹² in making MOFs with permanent porosity, utilizing nanosized ligands to construct stable, open MOFs still poses a great challenge. Herein we report one of the first examples of stability and porosity enhancement through simultaneous ligand extension and SBU stabilization.

In continuing our MOF studies using large carboxylate ligands,^{12c–e,13} we have designed a trigonal nanosized carboxylate ligand, 1,3,5-tris[4'-carboxy(1,1'-biphenyl-4-yl)]benzene (TCBPB; Chart 1), synthesized in a two-step Suzuki coupling reaction.^{14,15} The distance between two carboxylate groups is about 2 nm, and the distance between a carboxylate group and the central benzene ring is 1.2 nm. Solvothermal

* To whom correspondence should be addressed. E-mail: zhouh@muohio.edu.

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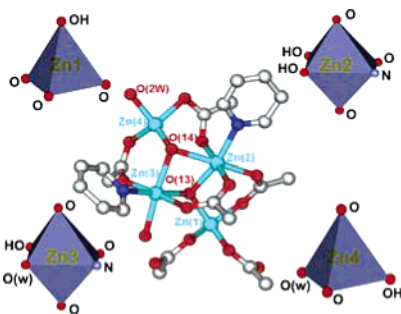


Figure 1. Coordination environment of Zn atoms in **1**: O = O atom from the TCBPB ligand; OH = μ_3 -OH group; O(w) = water molecule; N = pyridine.

reactions of TCBPB and $\text{Zn}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ in the presence of two different bases have resulted in the formation of two porous MOFs with novel SBUs: $\text{Zn}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{py})_2(\text{TCBPB})_2 \cdot 3\text{DMF} \cdot \text{py} \cdot 3\text{H}_2\text{O}$ (**1**; DMF = *N,N'*-dimethylformamide, py = pyridine) and $\text{Zn}_8(\text{OH})_4(\text{TCBPB})_4 \cdot 2\text{DMF} \cdot \text{EtOH} \cdot 3\text{H}_2\text{O}$ (**2**).

Single-crystal diffraction studies of **1**¹⁶ reveal four crystallographically independent Zn atoms (Figure 1): Zn(1) is tetrahedrally coordinated, bound to three O atoms from three carboxylate groups and one O from a μ_3 -OH [average Zn–O = 1.944(3) Å]; Zn(2) is octahedrally coordinated, bound to three O atoms from three TCBPB, two μ_3 -OH groups, and one pyridine [average Zn–O = 2.162(3) Å; average Zn–N = 2.130(4) Å]; Zn(3) is also octahedrally coordinated, bound to two O atoms from two TCBPB, two μ_3 -OH groups, one water, and one pyridine [average Zn–O = 2.128(3) Å; average Zn–N = 2.107(4) Å]; Zn(4) is tetrahedrally coordinated, bound to two carboxylate O atoms from two TCBPB, one μ_3 -OH, and one water [average Zn–O = 1.971(3) Å]. All four Zn atoms are connected by two μ_3 -OH groups and four carboxylate groups, forming a tetranuclear SBU, different from previously reported Zn_4O basic carboxylate SBUs.¹⁷

Two crystallographically independent TCBPB ligands differing in Zn connectivity are present in **1** (Figure 2). In each ligand, two carboxylate groups adopt a μ -carboxylato- $\kappa\text{O}:\kappa\text{O}'$ coordination mode while the remaining carboxylate uses only one of its two O atoms to coordinate. The two bridging carboxylates in TCBPB1 link [Zn(1), Zn(2)] and [Zn(2), Zn(3)], while the two bridging carboxylates in TCBPB2 bind [Zn(2), Zn(4)] and [Zn(3), Zn(4)]. The unique carboxylate group in each ligand coordinates Zn(1). Thus, every TCBPB links three SBUs and every SBU connects six TCBPBs, generating a 3D noninterpenetrating 3,6-connected open framework with a graphite-like array of channels (Figure 3).

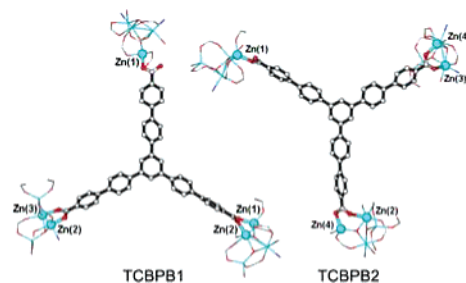


Figure 2. Two crystallographically independent ligands in **1**.

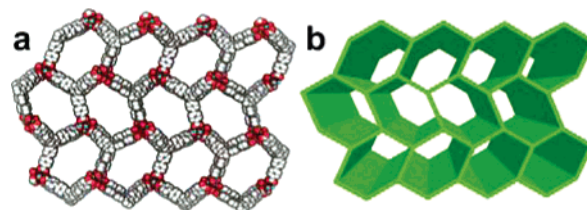


Figure 3. View of (a) the 3D nanoporous framework of **1** along the [010] direction and (b) a schematic representation of the graphite-like array of channels.

The formula of **1** was determined by elemental analysis, X-ray crystallography, and thermogravimetric analysis (TGA). TGA of **1** shows a 16.7% weight loss from 50 to 180 °C, corresponding to the loss of all free solvates (three DMF, one pyridine, and three water molecules; calcd 16.2%). Weight losses between 180 and 400 °C (8.57%) and between 400 and 550 °C (68.8%) correspond to the loss of terminal ligands (calcd 8.95%) and framework decomposition (calcd 69.1%), respectively.

Gas adsorption measurements of solvent-free **1** showed no permanent porosity, possibly because of framework collapse upon removal of coordinated water and pyridine. To improve the framework stability, coordinated small terminal molecules (pyridine and water) on four-coordinate Zn atoms in the SBU must be replaced by TCBPB or bridging oxo atoms.

In fact, pyridine plays a dual role in the formation of **1**: it acts as a base to facilitate the deprotonation of the TCBPB ligand and also acts as a terminal ligand to Zn atoms. To eliminate terminal ligands and deprotonate TCBPB, the use of a noncoordinating base is a logical choice.

Changing pyridine to triethylamine under similar reaction conditions produced **2**, a 3D network with 1D open channels. Four crystallographically independent Zn atoms are present in **2**.¹⁸ Three of the Zn atoms are four-coordinate, bound to three carboxylate O atoms from three TCBPBs and one μ_3 -OH group. The other Zn is six-coordinate, bound to six O atoms (three from carboxylate groups of three TCBPBs and three from μ_3 -OH groups).

There are two crystallographically independent TCBPB ligands in **2**, adopting a μ -carboxylato- $\kappa\text{O}:\kappa\text{O}'$ coordination

(16) Crystal structure determination of compound **1**: $\text{C}_{100}\text{H}_{70}\text{N}_2\text{O}_{16}\text{Zn}_4$, $M_r = 1817.06$; colorless rod, $0.42 \times 0.18 \times 0.12$ mm, $T = 213(2)$ K, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, orthorhombic, space group $Pna2_1$, $a = 41.041(2)$ Å, $b = 10.1287(5)$ Å, $c = 40.3822(18)$ Å, $V = 16786.5(14)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 0.719$ g cm⁻³, $2\theta_{\text{max}} = 56.64^\circ$, $\mu = 0.600$ mm⁻¹, $F(000) = 3728$, 121 223 total reflections, 38 604 unique, $R_{\text{int}} = 0.0896$, 1100 parameters, $R_1 = 0.0711$ [$I > 2\sigma(I)$], $wR_2 = 0.1460$, min/max residual electron density $-0.915/+0.682$ e Å⁻³.

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(18) Crystal structure determination of compound **2**: $\text{C}_{180}\text{H}_{112}\text{O}_{28}\text{Zn}_8$, $M_r = 3245.66$; a rod crystal ($0.16 \times 0.08 \times 0.02$ mm), $T = 90.0(2)$ K, $\lambda(\text{Cu K}\alpha) = 1.54178$ Å, monoclinic, space group $I2/a$, $a = 34.6215(9)$ Å, $b = 15.0763(3)$ Å, $c = 42.9953(3)$ Å, $V = 21298.0(8)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.012$ g cm⁻³, $2\theta_{\text{max}} = 136.18^\circ$, $\mu = 1.410$ mm⁻¹, $F(000) = 6624$, 123 280 total reflections, 19 052 unique, $R_{\text{int}} = 0.0939$, 974 parameters, $R_1 = 0.0534$ [$I > 2\sigma(I)$], $wR_2 = 0.1366$, min/max residual electron density $-0.898/+0.716$ e Å⁻³.

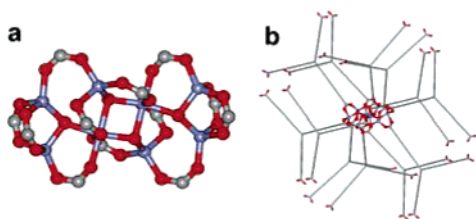


Figure 4. (a) View of the octazinc SBU in **2**. (b) Octazinc SBU connected to six pairs of TCBPB ligands.

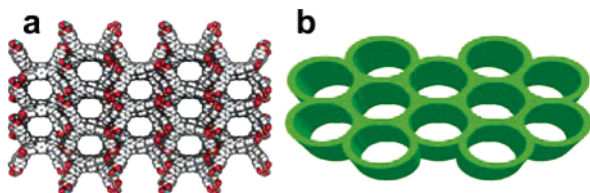


Figure 5. View of (a) 3D porous framework of **2** along the [100] direction and (b) a schematic representation of the 1D channels.

mode connecting six Zn atoms. Eight Zn atoms are bridged by 12 carboxylates from the TCBPB ligands and four μ_3 -OH groups, forming an octazinc cluster (Figure 4a). In this octanuclear SBU, two six-coordinate Zn atoms are surrounded by six four-coordinate Zn atoms. All Zn atoms are coordinated by carboxylate and μ_3 -OH groups, with no small labile terminal ligands on the SBU. No such SBU has been reported prior to this work.

Each octazinc SBU connects 12 carboxylate groups (six pairs, Figure 4b) and every TCBPB links three SBUs, resulting in a 3D framework with 1D open channels (10×13 Å) along the *a* axis (Figure 5). The solvent-accessible volume of **2** is 42% (8901.9.2 Å³ per 21298.0 Å³) calculated using PLATON.¹⁹

TGA of **2** revealed a 7% weight loss from 40 to 200 °C, corresponding to the loss of all free solvates (two DMF, one EtOH, and three water; calcd 7.1%). There was no further weight loss from 200 to 400 °C. Above 400 °C, **2** decomposed to form ZnCO₃ (found 27.5%; calcd 28.7%). Though TGA alone cannot determine the MOF stability, the above data suggest that the thermal stability of **2** falls in the range of 200–400 °C in an inert atmosphere.

The N₂ adsorption of solvent-free **2** at 77 K showed a type I isotherm (Langmuir surface area of 942 m² g⁻¹), indicating permanent porosity (Figure 6). The strategy of using a noncoordinating base (triethylamine) in place of pyridine (in **1**) allows the formation of the octazinc SBUs containing only nonlabile ligands. Thus, the elimination of labile terminal ligands was the key to obtaining a stable MOF.

It is interesting to note that the nanosized TCBPB ligands are nonplanar. Each TCBPB has average dihedral angles

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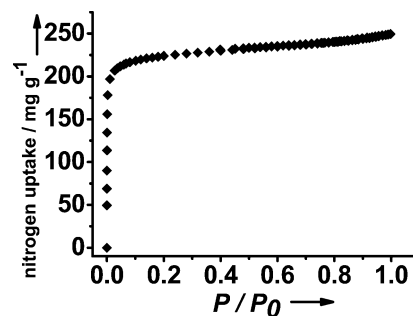


Figure 6. Brunauer–Emmett–Teller N₂ sorption isotherm of **2** at 77 K.

between the two peripheral rings of 31.5° and 26.1° for **1** and 31.3° and 34.8° for **2** and between the central and peripheral rings of 32.7° and 27.4° for **1** and 27.4° and 30.5° for **2**, respectively (compared to 37.1° in BTB).^{12b} These angles are much larger than the 4.7–10.0° angle found in TATB^{12c,13} because of the central triazine ring's lack of C–H bonds. As a result, although TCBPB ligands in **1** and **2** exist in pairs, there is no strong π – π stacking in the MOFs (see the Supporting Information).

In conclusion, the first use of a newly developed trigonal nanosized carboxylate ligand, TCBPB, resulted in **1** with a novel tetrazinc SBU and a graphite-like array of channels. However, because of coordinated pyridine and water in such a SBU, **1** cannot retain its framework integrity after solvate removal. Using a noncoordinating base (triethylamine) instead of pyridine under similar reaction conditions caused the formation of an octazinc SBU containing no labile terminal ligands, leading to **2** with permanent porosity. SBUs in **1** and **2** are the first examples of their kind found in the literature. Controlled synthesis of MOFs still poses a great challenge, but using concurrent ligand extension and SBU stabilization represents a useful synthetic strategy to obtain MOFs with enhanced stability and porosity based on ligands of nanometer size and beyond. Future studies will focus on the synthesis of new MOFs with even larger porosity using TCBPB and other more extended ligands.

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Supporting Information Available: Experimental procedures and synthetic details for compounds **1** and **2** and complete crystallographic data (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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