Porous Chiral Metal Organic Carboxylate Frameworks with a Double-interwoven $SrSi_2$ Topology: $M_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O$ (TTCA = triphenylenetricarboxylate; $M = Zn^{2+}, Cd^{2+}$)

Jae Yong Choi,[1] Jeo Kim,[1] Hiroyasu Furukawa,[2] and Hee K. Chae[1]
[1]*Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea*
[2]*Department of Chemistry and Biochemistry, University of California at Los Angeles, LA, CA90095-1569, U.S.A.*

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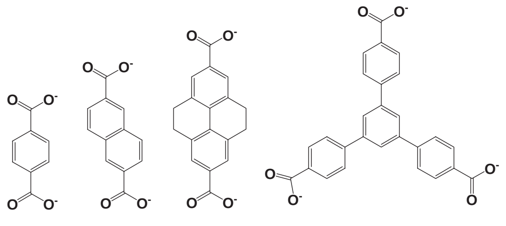
We have succeeded in assembling a new trigonal aryne ligand, triphenylene-2,6,10-tricarboxylic acid (H_3TTCA) with metal ions to give $M_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O$ ($M = Zn^{2+}$ and Cd^{2+}) (DMF = *N*,*N*-dimethylformamide), which networks show non-interpenetrated porous metal carboxylate frameworks and belong to a novel doubly-interwoven $SrSi_2$ topology.

Organic–inorganic porous coordination compounds are of great interest and importance for the novel coordination structure, relatively facile preparation, special properties and potential practical applications.[1] In particular the preparation of metal–organic frameworks (MOFs) with chiral networks has attracted potentials for asymmetric catalysis and chiral separation.[2] Much attention is drawn to geometrical approaches to chiral frameworks by using rational molecular building blocks or secondary building blocks. In general there are three synthetic ways to generate chiral networks. The first method is the coordination of a chiral ligand or building block to the metal ion or building block. Use of chiral blocks to template chiral inorganic frameworks has been relatively unsuccessful, though several chiral ligands including tartrates and binaphthalene derivatives have been known to form chiral MOFs.[3] The second method is the coordination of an achiral ligand to the metal center with an auxiliary chiral ligand. In this case chiral diols such as propane-1,2-diol have been used for auxiliary ligands.[2a,4] The last one is the assembly of an achiral ligand or a building block and the metal center or building block into chiral frameworks, where building blocks including benzene-1,3,5-tricarboxylate (BTC) have been used.[5] For example, this method is a considerable access to a helical network which default structure is a (10,3)-a net derived from a $SrSi_2$ topology.[6] Thus, it seems to be very important for practical economy to construct valuable chiral networks from cheap and achiral ligands. However, this route to chiral MOFs has been relatively unexplored.

In the formation of MOFs achiral tridentate ligands particularly give unique topologies and novel properties. For instance, BTC, triazinetricarboxylate, dicarboxylic amino acid, and pyridine-attached pyrimidine are attractive building blocks for chiral MOFs,[5,7] whereas the larger trigonal ligand 1,3,5-benzenetribenzoate (BTB) is a building block for MOF-177 that exhibits exceptionally high surface area.[8] The modification of BTB to a fused type of BTC, however, may give an opportunity to form MOFs which show chirality and highly hydrogen-capability due to specific skewed angles between COO^- groups and aromatic planes as well as the number of sharing edges among benzene rings. Some of MOFs show improving capacity of H_2 adsorption with increasing number of fused rings of the benzene in the ligand[9] (Scheme 1). Therefore, we designed the fused and trigonal ligand, triphenylene-2,6,10-tricarboxylate, and applied it to assemble MOFs.



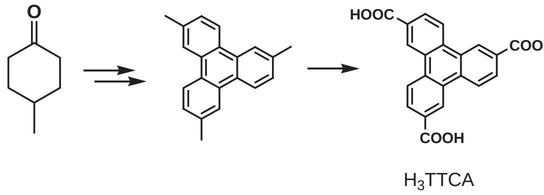
	IRMOF-1	*IRMOF-8*	*IRMOF-11*	*MOF-177*
# of Fused rings	0	1	4	0
N_2 uptake (mg/g)	965	421	548	1300
H_2 uptake (mg/g)	13.2	15.0	16.2	12.5

Scheme 1. The organic linkers and sorption data of isoreticular MOFs series and MOF-177.

Triphenylene-2,6,10-tricarboxylic acid (H_3TTCA) was synthesized by selective oxidation of trimethyl-2,6,10-triphenylene[10] as follows; a) trisannelation of 4-methylcyclohexanone with $ZrCl_4$; b) dehydrogenation with Pd/C; c) oxidation in aqueous $Na_2Cr_2O_7$; and d) acidification with hydrochloric acid as described in Scheme 2.[11]

In an attempt to prepare novel complexes by the reaction of $M(NO_3){\cdot}xH_2O$ ($Zn(NO_3)_2{\cdot}6H_2O$, 5×10^{-6} mol; $Cd(NO_3)_2{\cdot}4H_2O$, 4×10^{-6} mol) and H_3TTCA (1×10^{-6} mol) in DMF (0.3 mL) at 130 °C for 20 h, we isolated colorless cubic crystals in 53.9 and 55.8% yield, respectively. The infrared spectra of these compounds showed that the carboxylic anion has been connected to metal ions as indicated by a red shifted of $\nu_{C=O}$ stretch from $1690.1\,cm^{-1}$ in the free carboxylic acid to $1650.3\,cm^{-1}$ for Zn-bound carboxylate or $1653.1\,cm^{-1}$ for Cd-bound carboxylate. Growth of single crystal of the title compound, $M_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O$ ($M = Zn^{2+}$ **1a**, and Cd^{2+} **1b**) enables the structure determination to further understand the interwoven net.

Single-crystal X-ray diffraction studies reveal that **1a** and **1b** crystallize in a chiral space group *P*4(3)32 (No. 132) and consist of 3-D open frameworks with the (10,3)-a topology.[12] The



Scheme 2. Synthetic route for H_3TTCA.

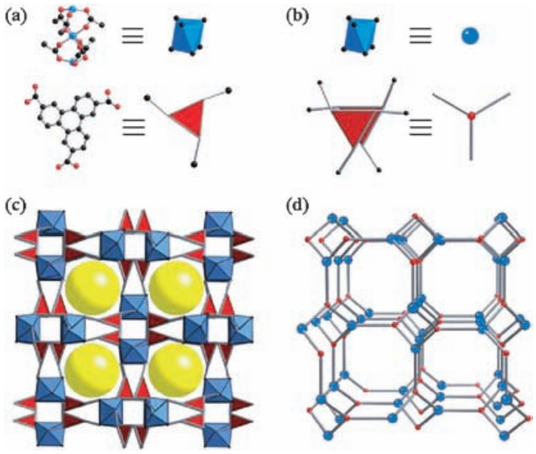


Figure 1. The crystal structure of $M_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O$ showing (a, b) $M_3(CO_2)_6$ units (blue, square SBUs), $TTCA^{3-}$ units (red, triangle SBUs), (c) $SrSi_2$ topology and yellow sphere represents the largest sphere that would occupy the cavity without contacting the interior van der Waals surface (d) (10,3)-a net along the direction of the 4-fold helices.

fundamental building unit of **1** contains three metal ions and two distorted TTCA ligands by coordination of the metal cluster to the trigonal aryne ligands in a skew.[13] (Figure 1a) Central metal atoms of the cluster are octahedrally bound to carboxylate oxygens, and each of the other metal center is tetrahedrally coordinated to carboxyate oxygens. The TTCA ligands are nearly planar, and pairing nearly staggerly by face-to-face π–π stacking with the distance of 3.3519 Å for **1a** and 3.3774 Å for **1b**, which values are comparable to the respective distances in melamine (3.20–3.40 Å), graphite (3.34 Å) and tri-*s*-triazine drivatives (3.328 Å).[7b] Trinuclear clusters are helically polymerized with TTCA to form 3-D porous frameworks. The chiral structure can be explained by consideration of stacking modes of a TTCA pair. The equal (50/50) stacking, however, generates enantiomeric pairs in the bulk.

To determine the topology of these crystals, each trinuclear unit can be considered as an octahedral secondary building unit (SBU), where three carbon atoms of the triphenylene ring are vertices of trigonal SBU. Linking the dots of these units with trigonal SBU of TTCA produces a chiral (10,3)-a net, which is the default three connected network (Figures 1b and 1d). This explains how assembly of achiral ligands can generate chirality, and suggests a different approach to a chiral porous network than the use of chiral linkers. As compared with BTC,[5a] the use of the TTCA ligand resulted in a porous but doubly non-interpenetrated neutral network (Figure 1c), where the solvent-accessible free volume of **1a** is 68.8% calculated by Cerius.[2] The value is comparable to 43.6% of Zn-BTC and 84.4% of Zn-HTB, respectively.[5a,7b] The measurement of porosity including N_2 and H_2 uptake will be reported in future.

It is noticeable that both of frameworks of **1a** and **1b** with double-interwoven nets allow the assembly of materials to be significantly thermostable up to 400 °C observed by thermogravimetric analysis,[14] whereas the compound $Cu_3(BTB)_2(H_2O)_3$ that has single-interwoven nets with π–π and C-H···π interactions of the benzene ring of BTB is robost to 250 °C.[15] Similar results have been also obersveded in C_3N_4 networks due to alternating arrangement of C and N atoms,[16] instead of unique layering of C and C atoms of **1**.

In summary, we have designed a new trigonal triphenylene carboxylate ligand and applied it the formation of MOFs which were found to be neutral and doubly interwoven chiral porous networks.

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11 A typical synthetic procedure of the H_3TTCA and its MOFs is described in Electronic Supporting Information.

12 Crystal Data: $\mathbf{Zn_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O}$ **(1a)**: cubic, space group $P4(3)32$, $a = 20.1401(2)$ Å, $b = 20.1401(2)$ Å, $c = 20.1401(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 8169.30(14)$ Å^3, $Z = 4$, $D_{calcd} = 0.766$ Mg/m^3, $\mu = 0.907$ mm^{-1}, $1.43° \le \theta \le 27.44°$, $-25 \le h \le 25$, $-24 \le k \le 26$, $-25 \le l \le 24$. A total of 53,100 reflections were processed of which 3029 were unique reflections. $R_1 = 0.0962$ with $I > 2\sigma(I)$, $wR2 = 0.2729$, GOF = 0.862. CCDC-607846.
$\mathbf{Cd_3(TTCA)_2{\cdot}6DMF{\cdot}7H_2O}$ **(1b)**: cubic, space group $P4(3)32$, $a = 20.487(2)$ Å, $b = 20.487(2)$ Å, $c = 20.487(2)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 8598.4(17)$ Å^3, $Z = 4$, $D_{calcd} = 0.837$ Mg/m^3, $\mu = 0.767$ mm^{-1}, $2.44° \le \theta \le 25.79°$, $-23 \le h \le 24$, $-24 \le k \le 24$, $-24 \le l \le 24$. A total of 62,566 reflections were processed of which 2622 were unique reflections. $R_1 = 0.1087$ with $I > 2\sigma(I)$, $wR2 = 0.2015$, GOF = 1.033. CCDC-607847.

13 Better descriptions of the coordination and ligand-pairing as well as chirality are shown in Figures S1 and S2.

14 TGA data are described in Figures S3 and S4. Thermal decomposition patterns of **1a** and MOF-177 are similar in air each other.

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