

A new enantiopure unsaturated dicarboxylate as a 4-connected unit in a flexible homochiral PtS-type framework†

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Metal cation mediated chiral ligand transformation of (*S*)-camphanic acid leads to a new enantiopure unsaturated dicarboxylate that links tetrahedral Zn^{2+} sites into 3-D homochiral 4-connected PtS-type framework structures, $Zn(tced)$ (1**, $H_2tced = 1,2,2$ -trimethyl-3-cyclopentene-1,3-dicarboxylic acid) and $Zn_4(tced)_4(4,4'$ -bipy) (**2**, $4,4'$ -bipy = $4,4'$ -bipyridine).**

Current interest in the synthesis of crystalline 4-connected zeolite-like materials is rapidly expanding owing to their intriguing architectures and potential applications.^{1–5} Of particular interest is the creation of homochiral frameworks that may have potential applications for enantioselective processes.⁶ Unfortunately, there are only a rather limited number of examples of materials with homochiral inorganic frameworks because inorganic structural building units tend to be achiral. Even if the chiral structure could be generated through the spatial organization of achiral inorganic precursors, resulting bulk materials are generally racemic. In comparison, inorganic–organic hybrid framework materials have shown greater promise for the synthetic design of homochiral framework materials because it is possible to take advantage of the chirality of organic components, in addition to the spatial organization into chiral patterns such as helices.^{7–9}

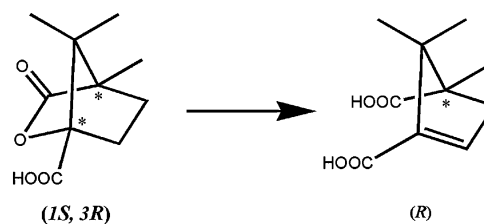
One key to the success of synthesizing homochiral inorganic–organic hybrid materials is the availability of enantiopure ligands that can serve as crosslinking ligands.^{6–8} Since rigid dicarboxylates have been shown to be highly effective in the formation of 3-D (and usually achiral) open structures,^{2a} the availability of new enantiopure rigid dicarboxylates is particularly desirable and should lead to a range of homochiral open framework materials.

In this work, (*S*)-camphanic acid, which contains an ester group and a carboxylic acid group, is used as the precursor for the synthesis of an enantiopure dicarboxylate denoted here as *tced* ($H_2tced = 1,2,2$ -trimethyl-3-cyclopentene-1,3-dicarboxylic acid, Scheme 1). (*S*)-Camphanic acid is an efficient chiral derivatizing agent for the determination of enantiomeric purity of alcohols and amines. The selection of this ligand is based on our reasoning that under hydrothermal conditions, the ester group could undergo hydrolysis reaction to produce a dicarboxylate that should be useful for creating new

homochiral open-framework materials. While hydrolysis of the ester group is well-known in organic chemistry, the transformation of (*S*)-camphanic acid into *tced* has not previously been reported. In fact, we are not aware of any earlier literature report on the synthesis of the *tced* ligand. This seems to suggest the high stability of the ester group in (*S*)-camphanic acid, because the adjacency between hydroxyl and carboxylic acid groups makes the intramolecular esterification energetically favorable. On the other hand, the free energy change during the formation of homochiral frameworks in the presence of metal cations could help to overcome such inertness of the ester group. We have found here that the hydrolysis of the ester group occurs at near-neutral pH and that the *in situ* generated enantiopure ligand can serve as 4-connected units for the construction of 4-connected framework structures.

Two homochiral zinc(II) complexes, $Zn(tced)$ (**1**) and $Zn_4(tced)_4(4,4'$ -bipy) (**2**, $4,4'$ -bipy = $4,4'$ -bipyridine), have been synthesized hydrothermally‡ and characterized by X-ray diffraction.§ Both **1** and **2** are constructed from the *tced* ligand derived from (*S*)-camphanic acid by *in situ* chiral ligand transformation (Scheme 1) and they exhibit the homochiral 4-connected pts net. However, in complex **2**, one fourth of Zn^{2+} sites are further pillared by $4,4'$ -bipy ligands, which converts these Zn^{2+} sites into octahedral coordination, and the resulting net can also be regarded as a (4,6)-connected net. The discovery of two materials with and without the pillaring $4,4'$ -bipy ligands demonstrates that the homochiral pts-type framework is highly flexible and can readily alter its conformation to accommodate the $4,4'$ -bipy ligands within its cavities.

One of the most interesting aspects of this work is the transformation of (*S*)-camphanic acid to the *tced* ligand (Scheme 1). Even though two chiral carbon centers with (1*S*,3*R*) configurations in the (*S*)-camphanic acid were reduced into one carbon center with the (*R*) configuration in the *tced* ligand with the loss of a chiral center, the resulting new chiral molecule is very interesting. Because of the remaining chiral



Scheme 1 The transformation reaction from (*S*)-camphanic acid to the *tced* ligand.

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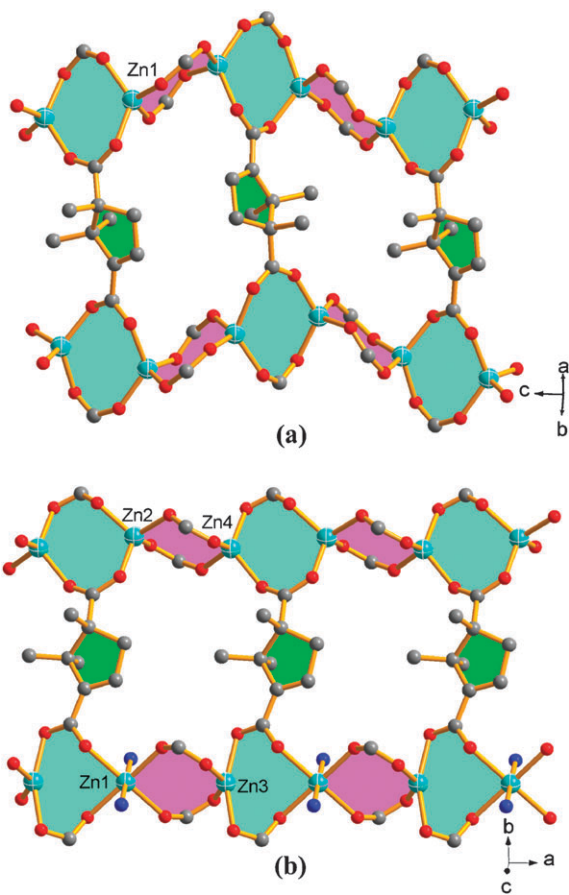


Fig. 1 (a) The connectivity between tetrahedral Zn sites and planar 4-connected tced ligands in **1**; (b) the connectivity between Zn sites (tetrahedron: Zn2, Zn3 and Zn4; octahedron: Zn1) and planar 4-connected tced ligands in **2**.

center, it may be possible to carry out enantioselective processes such as cycloaddition involving this double bond. Furthermore, it is possible that this unsaturated enantiopure dicarboxylate may be immobilized onto a silica gel host through coupling between the functional double bond and Si–OH groups, and the resulting materials may have potential applications as a stationary phase in chiral separation. In this work, however, the focus is on the synthetic and structural chemistry of this interesting ligand.

X-Ray diffraction of complex **1** indicates that it crystallizes in the enantiomorphous space group $P4_32_12$ (no. 94). The asymmetric unit contains one Zn atom and one (*R*)-tced ligand. Each Zn atom has tetrahedral geometry with four oxygen atoms from four separate tced ligands. Each tced ligand acts as a planar μ_4 -linker and each carboxylic acid group of the tced ligand bridges two tetrahedral Zn sites with a Zn...Zn separation of 3.584 Å (Fig. 1(a)). Two adjacent tetrahedral Zn atoms are doubly bridged by two carboxylic acid groups, resulting in a Zn-carboxylate chain with $Zn_2(COO)_2$ rings. Each carboxylate-bridged Zn chain is further linked to four neighboring chains by the tced ligands, to generate a 3-D homochiral framework (Fig. 2(a)). Such a framework can be described as a 4-connected pts net with Schläfli symbol of 4^28^4 by considering Zn as tetrahedral nodes

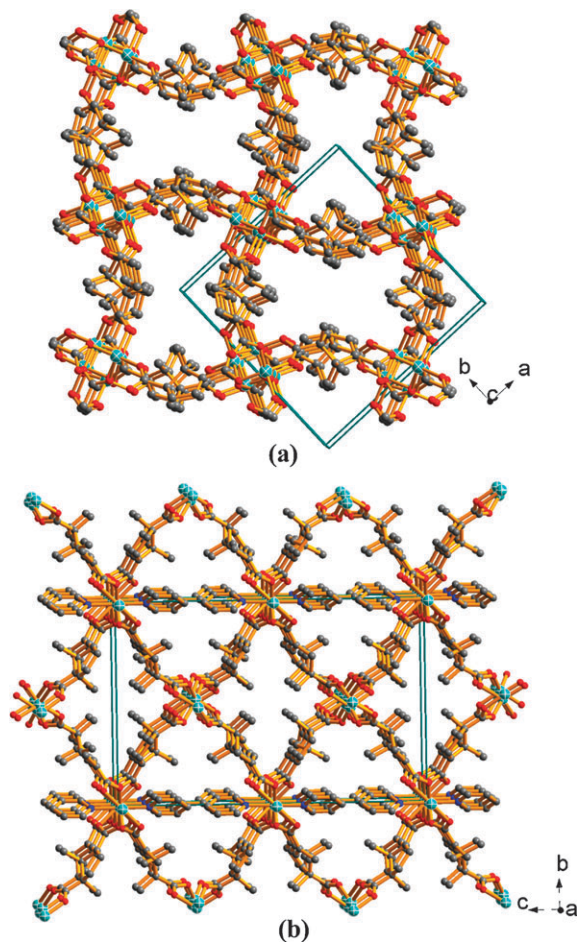


Fig. 2 (a) View of the 3D framework of **1** along the *c* axis; (b) view of the 3D framework of **2** along the *a* axis.

and (*R*)-tced as planar 4-connected nodes.¹⁰ Unlike the 4-connected zeotype topologies containing only tetrahedral nodes, the pts net has both tetrahedral and square planar nodes. Because of the protrusion of methyl groups (particularly the α -methyl group) into the channels, no solvent accessible space is present in this 4-connected PtS-type $[Zn(tced)]_n$ framework.¹¹ However, when an auxiliary 4,4'-bipy ligand was added into the reaction, a new complex **2** based on the similar PtS-type $[Zn(tced)]_n$ framework was obtained and the new structure (also with the pts net) contains sufficient space to accommodate 4,4'-bipy ligands in the $[Zn(tced)]_n$ framework.

In the presence of 4,4'-bipy ligands, complex **2** crystallizes in a lower symmetry chiral space group $P222_1$ (no. 17). In **2**, 4,4'-bipy and all four independent Zn atoms lie on two-fold axes. The tced ligand exhibits the similar μ_4 -bridging coordination mode and acts as a planar 4-connected node. Unlike all tetrahedral Zn sites in **1**, one fourth of Zn atoms in **2** have distorted octahedral geometry due to the additional coordination to 4,4'-bipy ligands (Fig. 1(b)). Like in **1**, the Zn atoms are also doubly bridged by the carboxylate groups, however there are two distinct Zn-carboxylate chains with $Zn_2(COO)_2$ rings. One Zn-carboxylate chain consists of all tetrahedral Zn atoms and the other Zn-carboxylate chain consists of alternating

tetrahedral and octahedral Zn atoms. The connectivity of the resulting chains through tced and 4,4'-bipy ligands gives a homochiral 3D framework as shown in Fig. 2(b). If the pillaring function of 4,4'-bipy ligands is not considered, the [Zn(tced)]_n framework in **2** has the same 4-connected pts net as that in **1**. However, the PtS-type [Zn(tced)]_n framework in **2** possesses more open channels along the *a* axis that are filled with 4,4'-bipy ligands.

In conclusion, we have demonstrated that a previously unreported transformation from (*S*)-camphanic acid into an enantiopure unsaturated dicarboxylate. The process is believed to be promoted by the metal mediated assembly between metal cations and the product enantiopure ligand. The resulting 3-D framework structures can be regarded as 4-connected PtS-type framework topologies, which are flexible enough to accommodate two different conformations, one of which incorporates auxiliary 4,4'-bipyridine ligands within its channels. In addition to serving as a novel enantiopure ligand for the creation of new open-framework materials, the new enantiopure ligand prepared here may have useful applications in enantioselective processes.

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Notes and references

‡ *Synthesis of Zn(tced) 1*: Zn(NO₃)₂·4H₂O (0.1094 g), Na₂CO₃ (0.0303 g), (*S*)-camphanic acid (0.0487 g), and distilled water (5.0596 g) were mixed in a 23 ml Teflon cup and the mixture was stirred for 20 min (pH = 6.63). The vessel was then sealed and heated at 160 °C for 3 days. The autoclave was subsequently allowed to cool to room temperature (pH = 6.37). Transparent colorless crystals were obtained (yield: 0.0489 g, 75% based on (*S*)-camphanic acid). *Synthesis of Zn₄(tced)₄(4,4'-bipy) 2*: Zn(NO₃)₂·4H₂O (0.1063 g), Na₂CO₃ (0.0270 g), (*S*)-camphanic acid (0.0514 g), 4,4'-bipyridine (0.0633 g) and distilled water (5.0744 g) were mixed in a 23 ml Teflon cup and the mixture was stirred for 20 min (pH = 5.54). The vessel was then sealed and heated at 140 °C for 3 days. The autoclave was subsequently allowed to cool to room temperature (pH = 5.95). Transparent colorless crystals were obtained (yield: 0.0624 g, 83% based on (*S*)-camphanic acid). The thermal analysis shows that both compounds are stable until approximately 400 °C.

§ *Crystal data for 1*: C₁₀H₁₂ZnO₄, *M_r* = 261.57, tetragonal, space group *P*4₃2₁2, *a* = *b* = 13.215(1), *c* = 12.8435(1) Å, *V* = 2242.9(2)

Å³, *Z* = 8, *D_c* = 1.549 g cm⁻³, Flack parameter = -0.011(14), *R*1 (*wR*2) = 0.0289 (0.0656) and *S* = 1.033 for 2958 reflections with *I* > 2σ(*I*). *Crystal data for 2*: C₅₀H₅₆Zn₄N₂O₁₆, *M_r* = 1202.53, orthorhombic, space group *P*222₁, *a* = 7.4577(11), *b* = 14.967(3), *c* = 22.633(4) Å, *V* = 2526.3(8) Å³, *Z* = 2, *D_c* = 1.581 g cm⁻³, Flack parameter = 0.02(2), *R*1 (*wR*2) = 0.0421 (0.0964) and *S* = 1.011 for 3566 reflections with *I* > 2σ(*I*). CCDC 671276 and 671277. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b719368h

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