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In Situ Synthesis of Tetradentate Dye for Construction of Three-Dimensional Homochiral Phosphor

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Abstract

Three-dimensional assembly of enantiopure D-camphoric acid and in situ synthesized tetradentate 1,2,4,5-tetra(4-pyridyl)benzene (TPB) ligand with tetrahedral Zn^{2+} leads to a new homochiral four-connected luminescent material from which the novel TPB ligand can be isolated in the hydrated crystalline form.

Current interest in the design of crystalline four-connected framework materials is rapidly expanding because of their intriguing architectures and large-scale industrial applications.^{1–7} Of particular interest is the creation of homochiral frameworks for applications in enantioselective processes.^{8–10} However, despite intensive research on chiral framework materials, homochiral 3D frameworks with the four-connected topology remain rare.

One successful synthetic strategy for the synthesis of homochiral framework materials is the use of two functionally different ligands. One ligand, usually negatively charged enantiopure dicarboxylates, helps to charge-balance metal cations (in addition to serve as crosslinker), while the other ligand, often neutral amines with divergent pyridal groups, serve to crosslink metal-dicarboxylate substructures (e.g., chains or sheets) into 3D frameworks. 9a, 9d A number of different bipyridines such as 4,4'-bipyridine, trans-1,2-bis(4-pyridyl)-ethylene, and 4,4'-trimethylenedipyridine (TMDPy) have been employed for the construction of homochiral frameworks.

Unlike bipyridine ligands, which tend to function as spacers between framework nodes and thus play little or no roles in the framework topological type, tetradentate ligands can serve as 4-connected nodes, leading to novel 4-connected topologies. Unfortunately, in comparison

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Supporting Information Available: Additional reaction details, experimental and simulated XRD patterns and X-ray crystallographic files in CIF format is available free of charge via the Internet at <http://pubs.acs.org>.

with the wide use of bipyridine ligands, the use of tetradentate ligands with four pyridal groups in combination with chiral dicarboxylates is, to our knowledge, unknown so far. This is in part because of the lack of suitable ligands. One possible ligand is *meso*-tetra(4-pyridyl)porphyrin (TPP). However, its coordination chemistry under hydrothermal condition is rather unpredictable because of its additional coordinating capability of the central cavity.¹¹

Here we report a new homochiral luminescent framework material, $[\text{Zn}_2(\text{D-cam})_2(\text{TPB})]\cdot\text{H}_2\text{O}$ (Compound **1**, D-H₂cam = D-camphoric acid). Also reported here is the synthesis and crystal structure of an interesting tetradentate ligand, 1,2,4,5-tetra(4-pyridyl)benzene (TPB) that was in situ synthesized via dehydrogenative coupling of TMDPy under hydrothermal conditions (Scheme 1).^{12, 13} The de-metallation of compound **1** through acidification allows the crystallization of TPB in the form of a crystalline dihydrate, TPB·2H₂O (Compound **2**). In addition to interesting synthetic, structural and topological features of 3D homochiral $\text{Zn}_2(\text{D-cam})_2(\text{TPB})\cdot\text{H}_2\text{O}$, the facile synthesis of a unique tetradentate dye through a simple one-step synthetic procedure reported here may allow its use as 4-connected molecular building block for the construction of unprecedented open-framework materials. Compared to TPP, the coordination chemistry of TPB is less complicated, which provides a certain degree of predictability in the rational synthesis of coordination frameworks.

An unusual structural feature¹⁴ in **1** is its interesting network topology constructed from the square-planar (TPB) and tetrahedral (Zn^{2+}) building blocks. In general, a 3D framework containing both tetrahedral and square-planar nodes adopts the PtS-type topology. In **1**, two crystallographically independent Zn^{II} sites have the same tetrahedral coordination sphere $[\text{ZnN}_2\text{O}_2]$, which is defined by two O atoms from two individual D-cam ligands and two N atoms from two symmetry-related TPB ligands (Figure 1a). Both carboxylate groups in the D-cam ligand only monodentately coordinate to two tetrahedral Zn^{II} ions, bridging them into an infinite neutral homochiral zigzag chain, $[\text{Zn}(\text{D-cam})]_n$. The square-planar TPB ligand functions as a tetradentate ligand to connect four Zn^{II} ions through its four peripheral pyridal groups, leading to the formation of a 2D $[\text{Zn}_2(\text{TPB})]_n$ sheet (Figure 1b). Adjacent parallel sheets are pillared by the D-cam ligands, thereby generating a 3D homochiral framework based on 1D chiral connectivity and 2D achiral connectivity (Figure 1c). Using the earlier proposed classification scheme for chiral materials, compound **1** possesses the C^1A^2 type structure (C = chiral connectivity; A = achiral connectivity).^{9b}

By considering Zn sites and tetradentate TPB ligands as tetrahedral and square-planar nodes, respectively, **1** can be reduced into a four-connected net with tetrahedral and square-planar nodes in the ratio 2:1. In comparison, the ratio is 1:1 in the PtS net. In this net, two zinc sites have the same coordination sequence and also have the same Schläfli symbol 6^48^2 .¹⁵ For the square-planar TPB node, the Schläfli symbol is 6^28^4 . Thus, this four-connected network can be topologically represented as a $(6^28^4)(6^48^2)_2$ net (Figure 2).

One of the most striking features in this work is that the formation of compound **1** involves the in situ synthesis of the TPB ligand through dehydrogenative coupling. It is worth noting that this reaction is unlikely to occur by conventional organic reactions because the simultaneous activation of six inert C–H bonds would require considerable activation energy. On the other hand, under hydrothermal conditions performed here, TMDPy readily undergoes the coupling reaction to form TPB.

The coupling of TMDPy into TPB was observed only once before under a totally different reaction condition used to prepare the sulfide-cluster based framework.¹³ Still, the in situ formation of TPB from TMDPy reported here is extraordinary. This is because TMDPy has been used numerous times (in the preparation of metal-organic frameworks) without

undergoing the coupling reaction reported here, indicating that a very delicate set of reaction conditions is required for the formation of TPB.

In the synthesis of **1**, the addition of GeO₂ (or H₃BO₃) is essential for the formation of TPB and compound **1** even though GeO₂ or H₃BO₃ is not incorporated into the crystal structure. In the absence of GeO₂ (or H₃BO₃), a previously reported crystal, [Zn(D-Cam)(TMDPy)]•H₂O, is obtained.^{9a} With other oxides such as TiO₂, V₂O₅, and MoO₃, resulting polycrystalline samples could not be identified. It is clear that GeO₂ or H₃BO₃ played a critical role in the formation of TPB and **1**.

We have also attempted without success many experiments aimed at the synthesis of TPB without the concurrent formation of **1** (Scheme S1) by removing the Zn²⁺ source from the starting mixture. So it appears that the formation of TPB occurs through the "template synthesis" mechanism (also called the coordination template effect) that was originally developed for the macrocycle synthesis. More specifically, the formation of TPB is likely related to the organizational effect of Zn²⁺ that helps to bring two TMDPy molecules adjacent to each other. Unfortunately, the precise mechanism and roles of GeO₂ and H₃BO₃ have not been determined.

Because of the potential use of the TPB ligand in the synthesis of framework materials and more generally in coordination chemistry, it is desirable to isolate it and to fully characterize it by X-ray diffraction. This was achieved by the acidification-based de-metallation procedure. The crystalline solid TPB·2H₂O (**2**) features a 1D hydrogen-bonding belt through the O—H...N bond between water molecules and the peripheral pyridal groups of the TPB molecules (Figure 3). Such a relatively simple procedure for the isolation of this molecule will help to promote its application as a unique molecular building block for the construction of new open-framework materials.

The photoluminescent properties of two compounds (**1** and **2**) in the solid state have also been studied at room temperature (Figure 4). Upon excitation at 418 nm, **1** has a maximum emission at 495 nm while **2** has a maximum emission at 525 nm. The emission spectrum of **1** is similar to that of **2** with a small blue shift, which suggest that the emission of **1** is likely derived from the electronic transition of the TPB ligand.

In conclusion, we report here a homochiral luminescent framework material with a four-connected framework topology. Added to the novelty of this work is the in situ dehydrogenative coupling of TMDPy ligand into a novel tetradentate dye molecule that serves as the 4-connected node within the homochiral framework. The facile in situ formation of TMDPy into TPB is unusual and its dependence on the presence of GeO₂ or H₃BO₃ is particularly intriguing. The observed construction of homochiral framework based on tetrahedral and square-planar nodes represents a new synthetic pathway for the synthesis of 4-connected homochiral materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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- Crystal data for **1**: C₄₆H₅₀N₄O₁₀Zn₂, *M_r* = 958.65, Monoclinic, space group *P*2₁, *a* = 12.8678(7) Å, *b* = 11.6950(5) Å, *c* = 15.7404(8) Å, β = 97.791(4)°, *V* = 2346.9(2) Å³, *Z* = 2, *D_c* = 1.357 g/cm³, Flack parameter = 0.10(3), *R*1(*wR*2) = 0.0697 (0.1702) and *S* = 1.086 for 4912 reflections with *I* > 2σ(*I*). Crystal data for **2**: C₂₆H₂₂N₄O₂, *M_r* = 422.48, Monoclinic, space group *P*2₁/n, *a* = 12.6296 (17) Å, *b* = 6.1333(8) Å, *c* = 15.708(2) Å, β = 113.70(1)°, *V* = 1114.1(3) Å³, *Z* = 2, *D_c* = 1.259 g/cm³, *R*1(*wR*2) = 0.0460 (0.1215) and *S* = 0.979 for 1229 reflections with *I* > 2σ(*I*). CCDC-676026 (1) and 676027 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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Figure 1.

(a) The local coordination environment of Zn^{2+} sites in **1**; (b) the 2D $[Zn_2(TPB)]_n$ sheet in **1**; (c) the 3D homochiral framework of **1**, showing the $[Zn_2(TPB)]_n$ sheets pillared by enantiopure D-cam ligands.

Figure 2.
Topological representation of the $(6^2 8^4)(6^4 8^2)_2$ net in **1**. The D-cam ligands are shown as red lines.

Figure 3. The molecular structure of TPB·2H₂O (2), showing the hydrogen bonding interactions (dashed lines) between TPB and H₂O.

Figure 4.
The emission spectra of compounds **1** and **2** in the solid state at room temperature.

Scheme 1.