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

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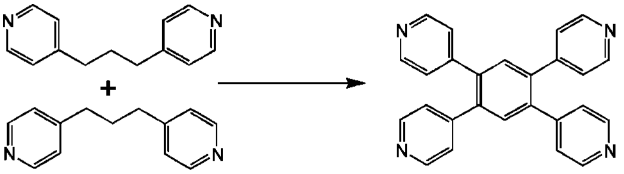
Current interest in the design of crystalline four-connected framework materials is rapidly expanding because of their intriguing architectures and large-scale industrial applications.[1−7] Of particular interest is the creation of homochiral frameworks for applications in enantioselective processes.[8−10] 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 serving as cross-linker), whereas the other ligand, often neutral amines with divergent pyridal groups, serve to cross-link metal-dicarboxylate substructures (e.g., chains or sheets) into 3D frameworks. [9a,d] 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.

Scheme 1



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 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, $[Zn_2(\text{D-cam})_2(TPB)]\cdot H_2O$ (compound **1**, $\text{D-}H_2cam$ = 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 demetalation of compound **1** through acidification allows the crystallization of TPB in the form of a crystalline dihydrate, $TPB\cdot 2H_2O$ (compound **2**). In addition to interesting synthetic, structural, and topological features of 3D homochiral $Zn_2(\text{D-cam})_2(TPB)\cdot H_2O$, 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.

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(12) Synthesis of **1** and **2**: Hydrothermal reaction of $\text{D-}H_2cam$ (0.1100 g), TMDPy (0.1118 g), $Zn(NO_3)_2\cdot 6H_2O$ (0.3487 g), GeO_2 (0.0518 g), and Na_2CO_3 (0.0595 g) in H_2O (4 mL) solution (pH 5.36) was performed at 160 °C for 6 days, and the mixture was then cooled to room-temperature. Colorless crystals of **1** were obtained (0.092 g, 35% yield). The phase purity was supported by powder X-ray diffraction (see the Supporting Information, Figure S1). To isolate the in situ formed tetradentate liagnd, we placed the powder of **1** (0.052 g) in 0.02 mol/L HCl (3 mL) solution in a vial. The vial was heated at 100 °C for 24 h and then cooled to room temperature. Colorless needlelike crystals of $TPB\cdot 2H_2O$ (**2**) were obtained in 92% yield.

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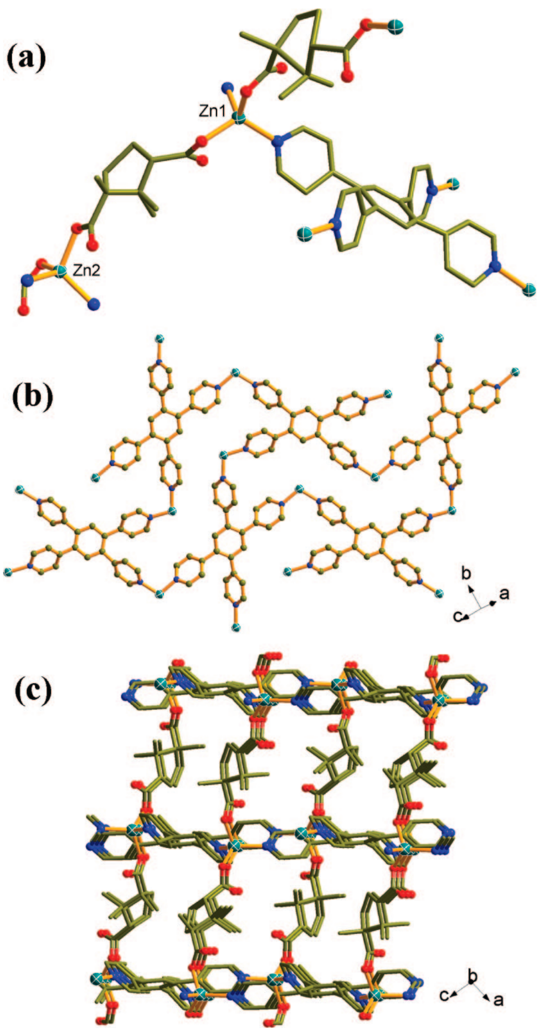

Figure 1. (a) Local coordination environment of Zn^{2+} sites in **1**; (b) 2D $[Zn_2(TPB)]_n$ sheet in **1**; (c) the 3D homochiral framework of **1**, showing the $[Zn_2(TPB)]_n$ sheets pillared by enantiopure D-cam ligands.

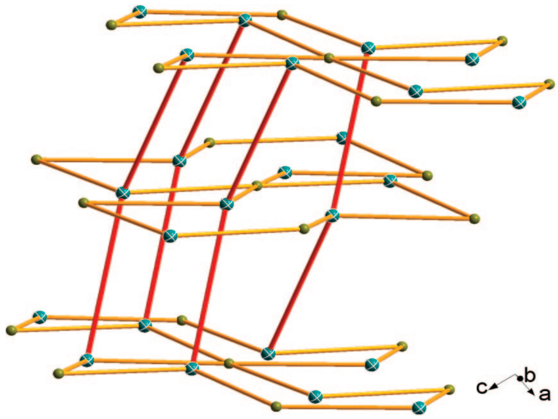

Figure 2. Topological representation of the $(6^28^4)(6^48^2)_2$ net in **1**. The D-cam ligands are shown as red lines.

An unusual structural feature[14] 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 $[ZnN_2O_2]$, 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, $[Zn(D\text{-cam})]_n$. 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 $[Zn_2(TPB)]_n$ 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 dehyrdogenative 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 GeO_2 (or H_3BO_3) is essential for the formation of TPB and compound **1** even though GeO_2 or H_3BO_3 is not incorporated into the crystal structure. In the absence of GeO_2 (or H_3BO_3), a previously

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(14) Crystal data for **1**: $C_{46}H_{50}N_4O_{10}Zn_2$, M_r = 958.65, monoclinic, space group $P2_1$, a = 12.8678(7) Å, b = 11.6950(5) Å, c = 15.7404(8) Å, β = 97.791(4)°, V = 2346.9(2) Å^3, Z = 2, D_c = 1.357 g/cm^3, Flack parameter = 0.10(3), R1(wR2) = 0.0697 (0.1702), and S = 1.086 for 4912 reflections with $I > 2\sigma(I)$. Crystal data for **2**: $C_{26}H_{22}N_4O_2$, M_r = 422.48, monoclinic, space group $P2_1/n$, a = 12.6296(17) Å, b = 6.1333(8) Å, c = 15.708(2) Å, β = 113.70(1)°, V = 1114.1(3) Å^3, Z = 2, D_c = 1.259 g/cm^3, R1(wR2) = 0.0460 (0.1215), and S = 0.979 for 1229 reflections with $I > 2\sigma(I)$. 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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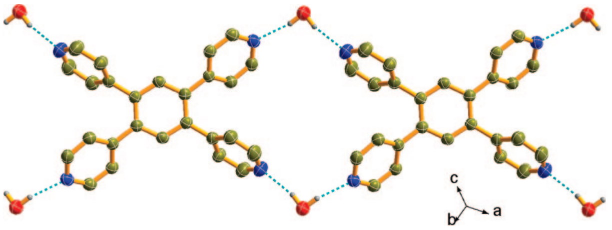

Figure 3. Molecular structure of TPB·$2H_2O$ (**2**), showing the hydrogen bonding interactions (dashed lines) between TPB and H_2O.

reported crystal, [Zn(D-Cam)(TMDPy)]·H_2O, is obtained.[9a] With other oxides such as TiO_2, V_2O_5, and MoO_3, resulting polycrystalline samples could not be identified. It is clear that GeO_2 or H_3BO_3 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** (see the Supporting Information, Scheme S1) by removing the Zn^{2+} 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 Zn^{2+} that helps to bring two TMDPy molecules adjacent to each other. Unfortunately, the precise mechanism and roles of GeO_2 and H_3BO_3 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 and fully characterize it by X-ray diffraction. This was achieved by the acidification-based demetalation procedure. The crystalline solid TPB·$2H_2O$ (**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, whereas **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 suggests that the emission of **1** is likely derived from the electronic transition of the TPB ligand.

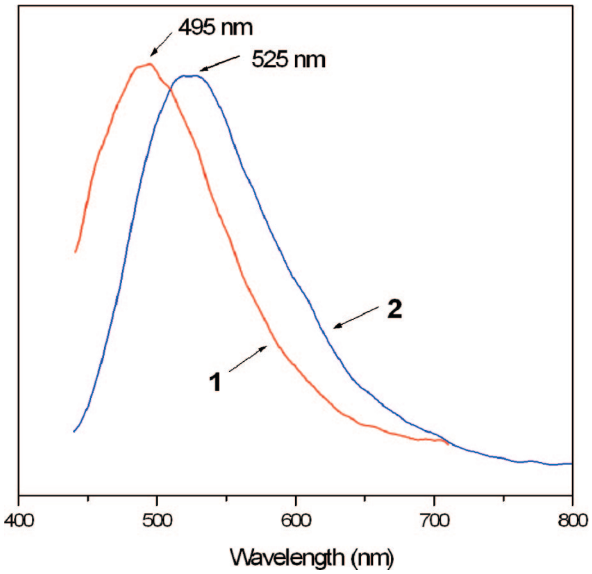

Figure 4. Emission spectra of compounds **1** and **2** in the solid state at room temperature.

In conclusion, we report here a homochiral luminescence 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 GeO_2 or H_3BO_3 is particularly intriguing. The observed construction of homochral framework based on tetrahedral and square-planer nodes represents a new synthetic pathway for the synthesis of 4-connected homochiral materials.

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Supporting Information Available: Additional reaction details and experimental and simulated XRD patterns (PDF); X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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