

Designed double layer assembly: a three-dimensional open framework with two types of cavities by connection of infinite two-dimensional bilayer†

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A photoluminescent three-dimensional coordination polymer containing two types of cavities is prepared by the covalent linkage of 2D bilayer motif with linear connecting ligand.

The rational design of porous materials has attracted much attention because the potential applications of these materials range from gas storage, ion exchange to heterogeneous catalysis.^{1–5} To date the construction of open metal-organic framework can be achieved *via* two kinds of interactions, *i.e.* coordinate covalent bonds and weaker intermolecular forces. Although many covalent 3D hybrid complexes have been reported, few of them are really porous.^{6–7} Furthermore, controlling the assembly and solid state structure of the target compound in three dimensions is still a challenge to chemists. Fortunately, recently the concept of the second building unit (SBU) has been widely used for understanding and predicting topologies of structure by Yaghi, Williams, Kitagawa, and their co-workers, and it has been proved to be helpful in directing the construction of a given structure.^{8–13} Having studied the literature, we noticed that although bilayer structure, a new motif, was reported several years ago,¹⁴ study on extending it into 3D covalent open framework remained unexplored. In addition, the excellent merits of a pillared-layer, such as controlling the cavity size and the chemical functionality *via* modification of the pillar module, inspire our research interest.¹⁵ Hence, our synthetic strategy starts first by finding a new SBU to build up a 2D bilayer motif, and then utilizes linear bidentate ligands (for example, 4,4'-bpy) as a connector in an attempt to assemble the sheet into a three-dimensional network. Such a way is available to lead to new compounds exhibiting original physical properties by confinement effects, as elucidated in a recent paper.¹⁶ Herein the rational synthesis of a three-dimensional porous complex [Zn₂(PDB)₂(4,4'-bpy)·H₂O]_n (**1**) (PDB = pyridine-3,4-dicarboxylate) by this route and its photoluminescence property are described.

In this experiment, we chose H₂PDB as the organic ligand of the SBU, based on the following considerations: (i) The use of carboxylate-bridged metal clusters as metal-organic SBUs to build extended self-assembly structure is relatively mature,^{17–18} furthermore, a reported bilayer structure has been constructed from a ternary bridging ligand,¹⁹ which suggests that H₂PDB may have the ability of forming bilayers. (ii) It has an asymmetric geometry that may lead to unprecedented structures with novel topological features.

The hydrothermal reaction of Zn(II) salt with the H₂PDB, 4,4'-bpy and triethylamine‡ in molar ratio 1:1:1:2 at 160 °C (120 h) led to the formation of light-yellow **1**. As expected, X-ray diffraction§ reveals that **1** possesses a 3D open framework constructed from bilayer and pillared 4,4'-bpy building blocks. The SBU for **1** can be considered as a dizinc carboxylate moiety, where the 2 Zn atoms are bridged by 4 carboxylate groups of two different PDB ligands. Such SBUs are connected by PDB ligands, forming a 2D sheet (Fig. 1). Interestingly, the zinc atoms distributed in the sheet, are not coplanar. Rather, half fall in one plane, and half in an adjacent

plane, resulting in the generation of distinct 2D bilayer architecture with a distance of 5.2 Å between the two single layers. As far as each PDB ligand in the bilayer is concerned, its adjacent carboxyl groups are just like an open pincer, nipping two Zn atoms located in adjacent single layers. Such a regular crossing-plane coordination fashion is still rare in the system of multi-carboxylates, and it plays an important role in the formation of a bilayer structure. More interestingly, a smaller rectangular cavity with the dimensions of 8.126 × 9.846 × 5.222 Å (based on *d*_{Zn...Zn}) is formed in the region surrounded by four SBUs.

The zinc ions have an affinity for a four-coordinate environment, three of which having been occupied by PDB ligands inter the bilayer, therefore the remaining one provides an additional binding site. This arrangement makes it possible to link bilayers *via* bpy ligands forming a 3D framework (Fig. 2). The detailed linkages of building units in the 3D framework are shown in Fig. 3a. Such a novel 3D open framework can be regarded as a unique molecular “double-floor” directly linked by pillars (bpy) through covalent bonds (Fig. 3b). Due to the participation of bpy ligands, another larger rectangular cavity emerges between the double layers with the dimensions of 8.126 × 9.846 × 11.132 Å. Differing from the above smaller cavity, it is constructed by Zn atoms, PDB and bpy building units. So far, the examples of two types of cavities coexisting in one system are still few.²⁰ Worth mentioning here is that the adjacent bilayers are parallel and stacked without

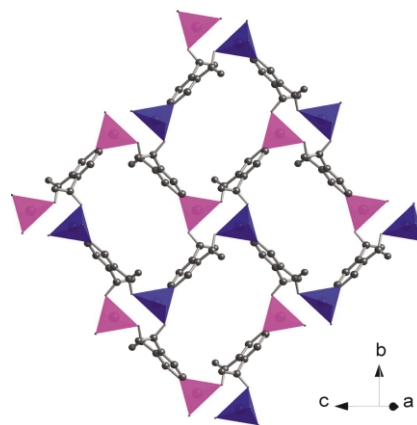


Fig. 1 Perspective view of the two-dimensional bilayer framework in **1**, different color Zn atoms lying in two layers.

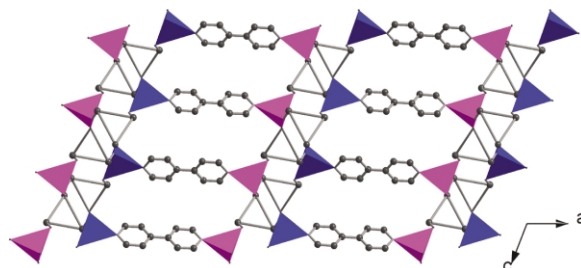


Fig. 2 View of the 3D framework of **1**, Δ represents PDB ligand.

† Electronic supplementary information (ESI) available: asymmetric unit of **1**, TGA, XRPD, fluorescence spectrum of **1**. See <http://www.rsc.org/suppdata/cc/b3/b313364h/>

interpenetrating to generate rectangular channels along [100] direction (Fig. 4); the channels possess approximate dimensions of $8.1 \times 9.8 \text{ \AA}$ and are occupied by free water molecules.

TGA study of **1** shows that there is a weight loss (found: 2.71%) from 60 to 120 °C, corresponding to the loss of free water molecules (calc. 2.83%) and leading to a framework of $[\text{Zn}_2(\text{PDB})_2(4,4'\text{-bpy})]_n$. This framework is stable up to 332 °C where the decomposition starts and ends at 590 °C. After heating the sample of **1** at 120 °C for 2 h, the guest water molecules are removed (defined as **1'**); the X-ray powder diffraction studies reveal that the pattern of **1'** is similar to that of **1**, thus indicating that the framework of **1** is retained after removal of the guests.

In the solid state **1** exhibits an intense emission at 497 nm in the blue region ($\lambda_{\text{ex}} = 399 \text{ nm}$). According to the literature²¹ and our experimental verification, it may be assigned to ligand-to-metal charge transfer (LMCT). This observation suggests that compound **1** may be an excellent candidate for potential photoactive materials.

In a word, using a suitable bridging ligand and pillaring spacer, we have synthesized to date the only structurally characterized pillared-bilayer complex with a three-dimensional open framework. The new design idea embodied in this paper, may be a promising technique in coordination polymer chemistry to gain porous materials with potential photoelectronic properties.

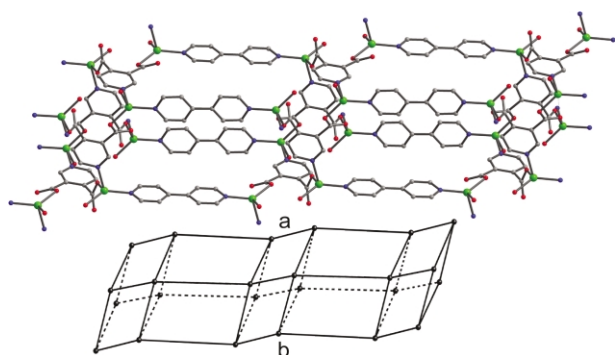


Fig. 3 (a) Detail of the linkages of building units in the 3D framework. (b) A schematic illustration of the 3D open-framework of **1**.

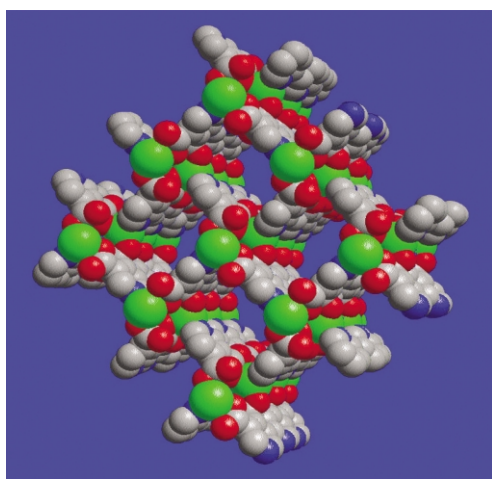


Fig. 4 Space-filling diagram of the three-dimensional framework of **1**. Guest water molecules included in the channels are omitted for clarity.

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Notes and references

† Preparation of $[\text{Zn}_2(\text{PDB})_2(4,4'\text{-bpy})\cdot\text{H}_2\text{O}]_n$ (**1**): The mixture of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.1487 g, 0.5 mmol), H_2PDB (0.0836 g, 0.5 mmol), 4,4'-bpy (0.0781 g, 0.5 mmol), triethylamine (0.1012 g, 1 mmol) and H_2O (8 mL) was placed in an 18 mL Teflon reactor, then heated at 160 °C for 5 days; light-yellow crystals of **1** were obtained in pure phase (yield: 83%). The initial pH value of the reactive solution was 5.5 and the final pH value was 4.7. Calc. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_9\text{Zn}_2$: C 45.34, H 2.52, N 8.82%; Found: C 45.18, H 2.37, N 8.71%.

‡ Crystal data for **1**: $\text{C}_{24}\text{H}_{16}\text{N}_4\text{O}_9\text{Zn}_2$, $M = 635.15$, monoclinic, $a = 16.069(3)$, $b = 13.635(3)$, $c = 11.508(2) \text{ \AA}$, $U = 2344.3(8) \text{ \AA}^3$, $T = 293 \text{ K}$, space group C_2/c , $Z = 4$, $\mu (\text{Mo-K}\alpha) = 2.112 \text{ mm}^{-1}$, 5113 reflections measured, 2673 unique ($R_{\text{int}} = 0.0273$) which were used in all calculations. $R_1 = 0.0333$ and $wR_2 = 0.1021$ for $I > 2\sigma(I)$. CCDC 222200. See <http://www.rsc.org/suppdata/cc/b3/b313364h/> for crystallographic data in .cif or other electronic format.

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