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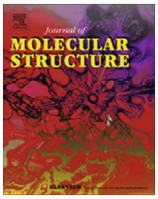

# A novel 1D → 2D interdigitated framework directed by hydrogen bonds

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## ABSTRACT

A novel Zn(II) complex, [Zn(L1)(bpe)] (**1**) ($H_2L1$ = 5-(benzyloxy) isophthalic acid, bpe = 1,2-bis(4-pyridyl)ethane) has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, IR and X-ray powder diffraction (PXRD). Compoud **1** features a one-dimensional (1D) open-ended tubular framework. These adjacent tubular frameworks are interdigitated into a two-dimensional (2D) supramolecular framework directed by hydrogen bonds. Moreover, this compound exhibits intense blue photoluminescence at room temperature.

## 1. Introduction

In recent years crystal engineering of coordination polymers has been an active research area due to their fascinating structure and potential applications as functional solid materials [1–5]. Generally, covalent interactions for the construction of coordination polymers are the most effective force. In addition, noncovalent interactions (such as hydrogen bonding interactions, $\pi$–$\pi$ stacking interactions, halogen–halogen interactions and so on) which are described as 'supramolecular glues' are often used as structural-directing tools in generating many novel supramolecular structure with promising properties [6–10]. Therefore, versatile functional organic ligands (such as N- or O-containing ligands) which have strong coordination ability as well as providing the hydrogen bond acceptors/donors and $\pi$-conjugated systems are often employed in construction of novel supramolecular framework [11–13].

5-(Benzyloxy)isophthalic acid ($H_2L1$) (Scheme 1), as a dicarboxylate ligand, has been synthesized before [14,15]. Compared to the 5-hydroxy-isophthalic acid, it not only can provides hydrogen bond acceptors/donors and $\pi$-conjugated systems, but also can exhibits a variety of conformations according to geometric requirements of metal ions due to the flexible $CH_2$–O spacer between the two phenyl rings. More interestingly, the benzyl of the $H_2L1$ ligand also can act as template in the self-assembly process [16]. To investigate its coordination chemistry and construct novel supramolecular structure with promising properties, we exploit $H_2L1$, flexible N-containing ligand (bpe) and $Zn(NO_3)_2{\cdot}6H_2O$ as reactants, and successfully obtained a novel zinc(II) complex, [Zn(L1)(bpe)] (**1**). In the structure of **1**, it features a 1D open-ended tubular framework, which is further interdigitated into an interesting 2D supromolecular framework directed by hydrogen bonds. Moreover, this compound exhibits intense blue photoluminescence at room temperature.

## 2. Experimental

### 2.1. Materials and methods

All chemicals were purchased commercially and used without further purification except for $H_2L1$. The $H_2L1$ was synthesized according to the previously reported procedure [14]. X-ray intensities were collected on Oxford Xcalibur E diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Elemental analyses (C, H and N) were performed on an EA1110 CHNS-0 CE Elemental Analyzer. IR spectra (KBr pellet) was recorded on a Nicollet Magna 750FT-IR spectrometer. Fluorescence spectra of the solid samples were performed on an Edinburgh Analytical instrument FLS920.

### 2.2. Synthesis

A mixture of $Zn(NO_3)_2{\cdot}6H_2O$ (0.297 g, 1.0 mmol), $H_2L1$ (0.136 g, 0.5 mmol), bpe (0.092 g, 0.5 mmol), and $NaHCO_3$ (0.084, 1.0 mmol)

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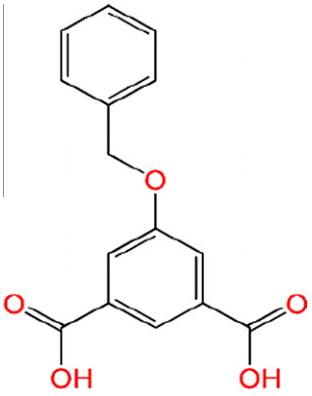

**Scheme 1.** The structure of the $H_2L1$ ligand.

in molar ratio 2:1:1:2 and 15 ml $H_2O$ was placed in a Parr Teflon-lined stainless steel vessel (25 $cm^3$), then the vessel was sealed and heated to 160 °C. The temperature was hold for 60 h, then the vessel was cooled to room temperature over 60 h to lead to the formation of colorless crystals of **1** (yield: 65% based on Zn). Anal. Calc. for **1**, $C_{27}H_{22}N_2O_5Zn$: C, 62.32; H, 4.23; N, 5. 39%. Found: C, 62.38; H, 4.18, N, 5.38%. IR (solid KBr pellet, $v/cm^{-1}$) for compound **1**: 3127(m), 2891(m), 1642(s), 1612(s), 1561(s), 1448(s), 1367(m), 1258(m), 1131(m), 1062(w); 852(vw), 775(w), 711(vw), 612(w), 554(m), 429(vw).

### 2.3. X-ray crystallography

The X-ray single-crystal structure analysis of **1** was performed on a Oxford Xcalibur E diffractometer (Mo Kα radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 293(2) K. Empirical absorption corrections were applied to the data using the SADABS program [17]. The structure was solved by the direct method and refined by the full-matrix least-squares on $F^2$ using the SHELXL-97 program [18]. All of the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms attached to carbon were located at their ideal positions. Experimental details for the structure determination are presented in Table 1. Selected bond lengths and angles are listed in Table 2.

**Table 1**
Crystallographic data for compound **1**.

| | |
|---|---|
| Empirical formula | $C_{27}H_{22}N_2O_5Zn$ |
| Temperature (K) | 293(2) |
| Crystal color | Colorless |
| Crystal size | 0.20 × 0.15 × 0.10 $mm^3$ |
| Formula weight | 519.86 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| *a* (Å) | 10.1698(3) |
| *b* (Å) | 11.9741(5) |
| *c* (Å) | 20.9721(10) |
| β ° | 109.483(4) |
| Volume (Å$^3$) | 2407.63(17) |
| *Z* | 4 |
| Density (calculated) | 1.434 |
| Abs. coeff. ($mm^{-1}$) | 1.063 |
| F(000) | 1058 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Reflections collections | 8146 |
| Independent reflections | 4208 [(*R*(int) = 0.0306)] |
| $\theta$ range for data collection | 2.65–24.99 |
| *h*, *k*, *l* range | $-12 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 13$, $-24 \leqslant l \leqslant 21$ |
| Goodness-of-fit on $F^2$ | 0.974 |
| Final *R* indices [*I* 2 sigma(*I*2)] | *R* = 0.0569, *wR* = 0.1615 |
| *R* (all data) | *R* = 0.0911, *wR* = 0.1706 |
| Largest difference peak and hole | 1.206 and −0.567 e/Å$^3$ |

**Table 2**
Selected bond lengths (Å) and angles (°) of compound **1**.

| | | | |
|---|---|---|---|
| Zn(1)–O(1) | 1.953(4) | Zn(1)–O(4)[a] | 1.985(3) |
| Zn(1)–N(2) | 2.033(4) | Zn(1)–N(1) | 2.075(5) |
| O(1)–Zn(1)–O(4)[a] | 100.26(16) | O(1)–Zn(1)–N(2) | 111.67(16) |
| O(4)[a]–Zn(1)–N(2) | 113.97(16) | O(1)–Zn(1)–N(1) | 107.15(17) |
| O(1)–Zn(1)–N(1) | 107.15(17) | O(4)[a]–Zn(1)–N(1) | 108.57(16) |

[a] Symmetry codes: $x - 1$, $y$, $z$.

## 3. Results and discussion

### 3.1. Description of the structure

Single-crystal X-ray structural analysis reveals that Compound **1** exhibits a 1D open-ended tubular architecture. There are one crystallographically independent Zn(II) ion, one L1 ligand and one bpe ligand in the asymmetric unit. As shown in Fig. 1, each Zn(II) ion is in a tetrahedral $\{ZnO_2N_2\}$ coordination environment, surrounded by two N atoms from two different bpe ligands and two O atoms from two different L1 ligands. The Zn–O distance is 1.982(3) Å and the Zn–N distance is in the range of 2.032(4)–2.077(4) Å. These Zn–O/N distances are in the normal range of those observed in other Zn(II)-complexes [19]. Interestingly, rare gauche conformation of the bpe ligand, which may be benefit to construct open-ended tubular architecture, is observed in compound **1**. The two pyridyl rings from the same bpe unit twist by 53.154(1)° from each other. Such gauche conformational bpe ligands bridge two different Zn(II) ions forming a cyclic closed structure with *S*2-symmetry (Fig. 2a). Then, adjacent closed structures are bridged by the L1 ligands forming an open-ended tubular architecture propagating along crystallographical *a* axis (Fig. 2b). The dimension of the nanotube is approximately 8.1232(8) × 10.8137(6) Å. Obviously, each L1 ligand in **1** acts as a bidentate ligand with its two carboxylate groups both in monodentate mode. The phenyls of the anionic, aromatic L1 ligands in the 5-sites project out and arrange on both sides of the tube (Fig. 2b). The twist angle of L1 between the two phenyl rings is 79.355(2)°. To the best of our knowledge, such metal–organic coordination polymers containing gauche conformational bpe ligands remain rarely be reported.

It is noteworthy that the distance between the adjacent rings of the tube is 10.1698(8) Å, indicating that large space exists between the adjacent rings. CH/π hydrogen bonding is an interesting interaction and has been proved to act as a structural-directing tool

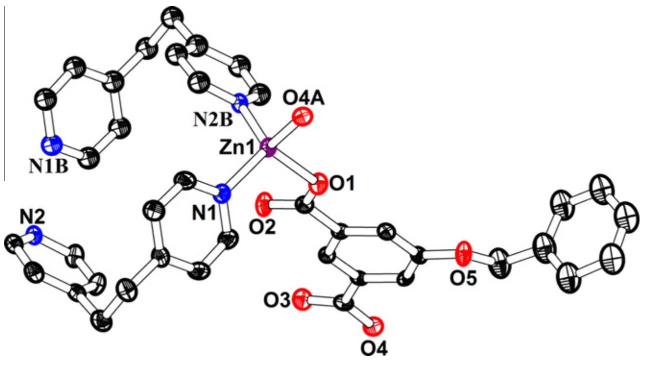

**Fig. 1.** ORTEP drawing of compound **1** (30% thermal ellipsoids). Hydrogen atoms associated with C atoms have been omitted for clarity. Symmetry codes: (A) $-1 + x$, $y$, $z$; (B) $1 - x$, $-y$, $-z$.

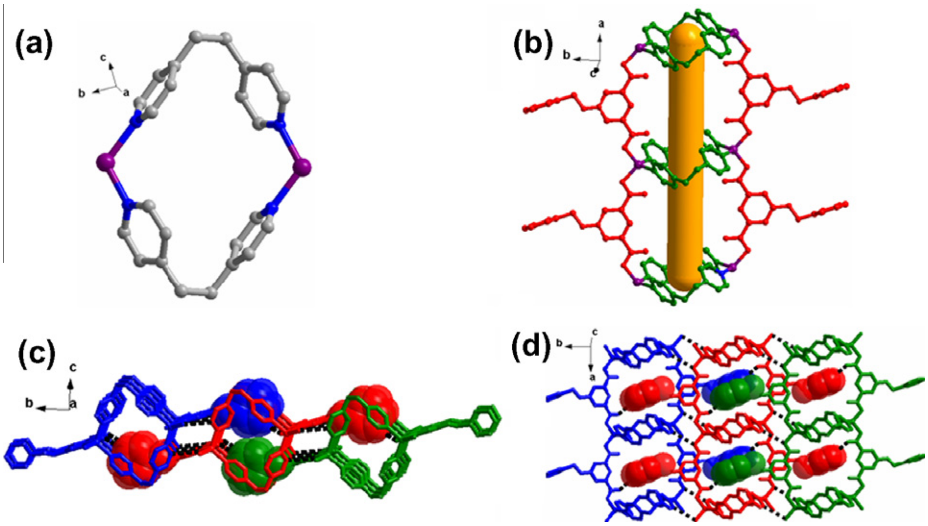

**Fig. 2.** (a) Cyclic closed structure. (b) 1D open-ended tubular framework propagating along crystallographical *a* axis (the rod represents the tube). (c) Hydrogen interactions of the framework view along *a* axis. (d) 2D interdigitated framework directed by hydrogen bonds (dashed lines represent hydrogen bonds).

[20]. Therefore, through the direction of the hydrogen bonds between the carboxylate O and C atoms (C25···O4$^b$ and C14$^a$···O2) (Fig. 2c), the large space are effectively occupied by the phenyls of the L1 ligands from adjacent tubular architecture, leading to the final 2D interdigitated framework (Fig. 2d). The detailed hydrogen bond parameters are list in Table 3. Therefore, hydrogen bonds play an important direction role in the final 2D interdigitated framework. Although supramolecular frameworks constructed by hydrogen bonds have been widely investigated [21–23], such unique 1D → 2D interdigitated framework directed by hydrogen bonds has not been reported before.

### 3.2. PXRD patterns and photoluminescent properties

As shown in Fig. 3, the experimental PXRD pattern of **1** is in good agreement with the simulated one except for the relative intensities variations because of the preferred orientation of the crystals, indicating that compound **1** is in a pure phase.

Considering the excellent photoluminescent properties of d$^{10}$ complexes, the solide-state luminescence of compound **1** was investigated at room temperature. As shown in Fig. 4, compound **1** exhibits intense blue emission band at 460 nm when excited at 359 nm. To understand the nature of the emission band, the luminescent properties of the ligand $H_2L1$ and bpe were also investigated at room temperature. However, no obvious emission bands were observed in the range of 400–600 nm. Therefore, the emission band of the title compound may be attributed to the ligand-to-metal-charge-transfer (LMCT). These observations indicates that metal centers may play an important affection on the photoluminescent properties of the coordination polymers, and compound **1** may be an excellent candidate for potential photoactive materials.

**Table 3**
Hydrogen-bonding geometrical parameters (Å, °) of compound **1**.

| D–H···A | D–H | H···A | D···A | ∠ D–H···A |
|---|---|---|---|---|
| C14$^a$–H14A···O2 | 0.93 | 2.64 | 3.3976(8) | 139.582(5) |
| C25–H25A···O4$^b$ | 0.93 | 2.53 | 3.4063(3) | 158.743(5) |

[a] Symmetry codes:$3 - x, 0.5 + y, 0.5 - z$.
[b] Symmetry codes:$2 - x, 0.5 + y, 0.5 - z$.

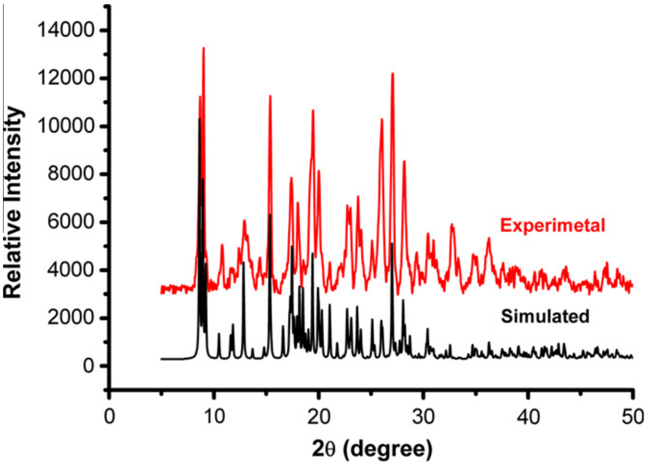

**Fig. 3.** Experimental and simulated XRD patterns for compound **1**.

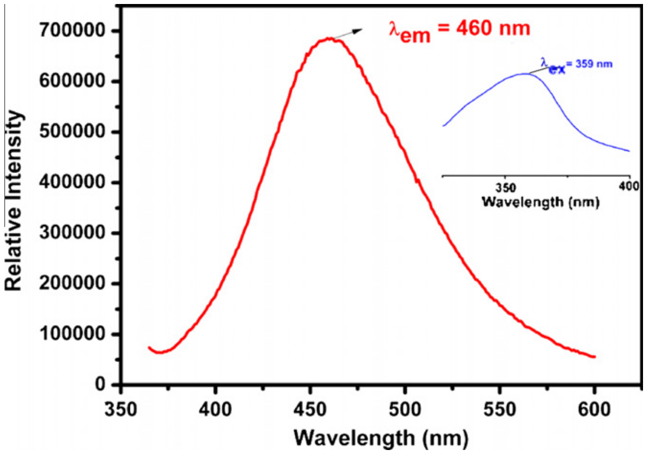

**Fig. 4.** Emission spectrum and excitation spectrum (inset) of **1** in the solid-state at room temperature.

## 4. Conclusions

In summary, a novel luminescent compound, $[Zn(L1)(bpe)]_n$, has been hydrothermally synthesized and structurally characterized, which features an open-ended tubular framework. Directing by the hydrogen bonds, the 1D tubular framework is interdigitated into a unique 2D supramolecular framework.

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## Appendix A. Supplementary material

CCDC No. 804453 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK. Fax:C44 1223336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2011.01.036.

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