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A New Approach to Synthesize Zinc(II) Coordination Polymer

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A new Zn(II) coordination polymer with benzophenone-4,4'-dicarboxylic acid (H_2bpdc) and 1,4-*bis*(imidazol-1-yl)benzene (bib) has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction, infrared and elemental analysis. Complex, $\{[Zn(bpdc)(bib)]\cdot 2H_2O\}_n$ (**1**), is triclinic, space group P-1 with a = 8.958(5), b = 11.336(5), c = 14.150(5) Å, α = 111.109(5), β = 95.077 (5)°, γ = 98.504(5), V = 1310.0 (10) $Å^3$, Z = 2, M_r = 579.86, D_c = 1.470 g/cm^3, F(000) = 596 and μ = 0.991 mm^{-1}. The final refinement gave R = 0.0352 and wR = 0.0964 for 5191 reflections with $I > 2\sigma(I)$. X-ray diffraction analysis reveals that complex **1** displays a 2D + 2D → 3D polycatenated structure.

Keywords: Zinc(II), Coordination polymer, Luminescence.

INTRODUCTION

The design and construction of new coordination polymers is currently of great interest not only because of their potential applications as functional materials in gas storage, magnetism, luminescence, *etc*. [1-6] but also due to their intriguing variety of architectural features and fascinating new topologies [7,8]. Until now, although a number of coordination polymers have been reported, the construction of new architectures and a systematic research still remain a large challenge. In order to construct coordination polymers, the crucial step is to choose multifunctional organic ligands [9]. According to literature, organic aromatic polycarboxylate ligands have been proven to be excellent structural constructors due to their various coordination modes to metal ions, which often generate multi-dimensional networks and interesting topologies [10]. Another aspect, the rigid *bis*(imidazole) shows the good ability to coordinated to the metal center and can adopt two type coordination modes: *cis*-configuration and *trans*-configuration [11].

Taking all of the above discussion into account, we used the flexible benzophenone-4,4'-dicarboxylic acid (H_2bpdc) and rigid 1,4-*bis*(imidazol-1-yl)benzene (bib) to construct a new coordination polymer $\{[Zn(bpdc)(bib)]\cdot 2H_2O\}_n$, which displays a 2D + 2D → 3D poly catenated framework.

EXPERIMENTAL

All reagents and solvents employed were commercially available and used without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer. Solid-state fluorescence spectra were recorded on a Hitachi F-4600 equipped with a xenon lamp and a quartz carrier at room temperature. The powder X-ray powder diffraction (XRPD) measurements were performed on a Bruker D8 diffractometer operated at 40 kV and 40 mA using Cu-K_α radiation.

Synthesis of $\{[Zn(bpdc)(bib)]\cdot 2H_2O\}_n$ (1): A mixture of $Zn(NO_3)_2\cdot 4H_2O$(0.099 g, 0.5 mmol), H_2bpdc (0.135g, 0.5 mmol), bib (0.105 g, 0.5 mmol), NaOH (0.04 g, 1 mmol) and deionized water (18 mL) was sealed in a 25 mL Teflon-lined stainless steel vessel and heated at 160 °C for 72 h. After cooling to room temperature, the purple block crystals were obtained and washed with alcohol for several times (Yield: 43 % based on Zn). Elemental Anal. calcd. (%) for $C_{27}H_{22}O_7N_4Zn$: C, 55.92; H, 3.82; N, 9.66. Found: C, 55.94; H, 3.82; N, 9.65. IR (KBr pellet, ν_{max}, cm^{-1}): 3438(br), 1610(s), 1381(s), 1148(m), 1020 (m), 841(m), 767(m), 679(m), 547(m).

Structure determination: Suitable colourless block crystal with dimensions of 0.30 mm × 0.25 mm × 0.21 mm was mounted on a glass fiber and the data were collected on a Bruker APEX2 CCD area-detector diffractometer with a Mo-K_α radiation (λ = 0.71073 Å) at 293(2) K by using a ω-scan mode in the range of $1.56 < \theta < 27.46°$. For the title complex **1**, a total of 9304 reflections with 5981 unique ones (R_{int} = 0.017) were measured, of which 5191 were observed with $I > 2\sigma(I)$ to the final R = 0.0352 and wR = 0.0964 ($w = 1/[\sigma^2(F_o)^2 + (0.0545P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$, S = 1.189 and $(\Delta/\sigma)_{max}$ = 0.001. All non-hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The highest and lowest residual peaks in the final difference Fourier map are 0.586 and -0.237 e/Å^3, respectively. The structure was solved by direct method with SHELXS 97 and Fourier techniques and refined by the full-matrix least squares method on F^2 with SHELXL 97 program [12].

RESULTS AND DISCUSSION

Description of crystal structure: X-ray single-crystal diffraction analysis shows that complex **1** is a polycatenated 2D + 2D → 3D structure based on undulated 4^4-sql single sheet. It crystallizes in the triclinic system with space group of P-1 with an asymmetric unit that contains one Zn(II) ion, one bpdc^{2-} dianion and two halves of bib ligands. As shown in Fig. 1, the Zn(II) is four-coordinated by two carboxylate atoms [Zn(1)-O(1) = 1.9523 (16) Å and Zn(1)-O(4) = 1.9733 (17) Å] and two nitrogen atoms[Zn(1)-N(1) = 2.0349 (17) Å and Zn(1)-N(5) = 1.9992 (19) Å] in a tetrahedral geometry. The bib ligands connect Zn(II) to form a one-dimensional chain and the 1D chains are further connected by bpdc^{2-} ligands to construct an undulated 4^4-sql layer which contains a window of 13.502 × 14.6011 Å exhibits a undulated character with a thickness of about 7.099 Å (Fig. 2). A more impressive structural characteristic of complex **1** is that each highly undulated 2D 4^4-sql single sheet is simultaneously penetrated by the two nearest neighboring ones (one above and the other below) with density of catenation (Doc = 2) and index of separation of (Is = 1), which have parallel but one coincident mean planes (Fig. 3).

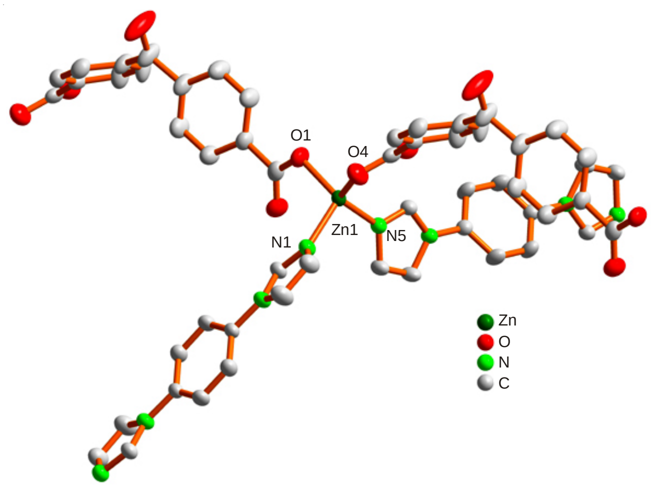

Fig. 1. Coordination environment for Zn(II) ion in complex **1** (omitted the hydrogen atoms for clarity)

Luminescent property: The solid-state photoluminescence of bib and title complex **1** at room temperature are depicted in Fig. 4. The bib ligand exhibits a broad weak fluorescent with emission centered on 456 nm. Compound **1** displays red-shifted fluorescent emission around 458 nm upon excitation at 334 nm. As we know, Zn(II) ion is difficult to oxidize or reduce due to its *d*^{10} configuration. Thus, the fluorescent emission of complex **1** is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT), it may be assigned to intraligand (π-π*) fluorescent emission [13].

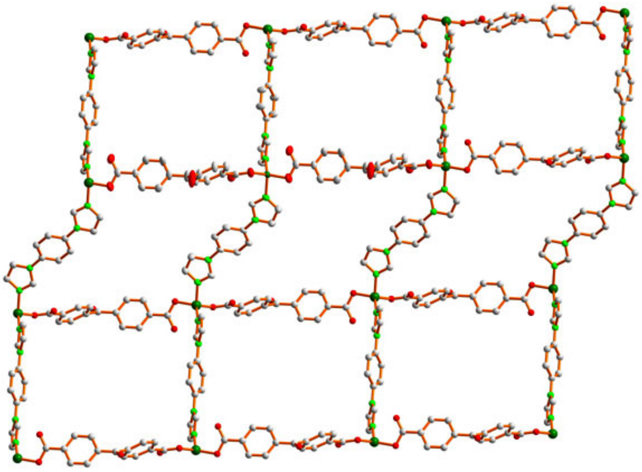

Fig. 2. 2D undulated sheet for complex **1**

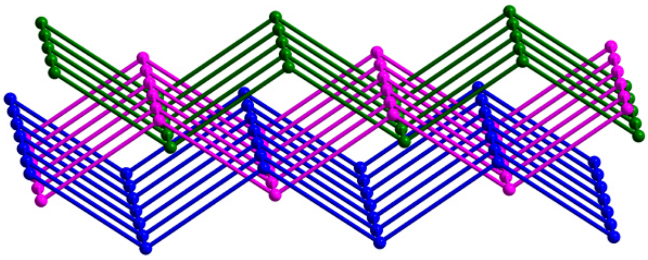

Fig. 3. 3D parallel polycatenation of sql observed for complex **1**

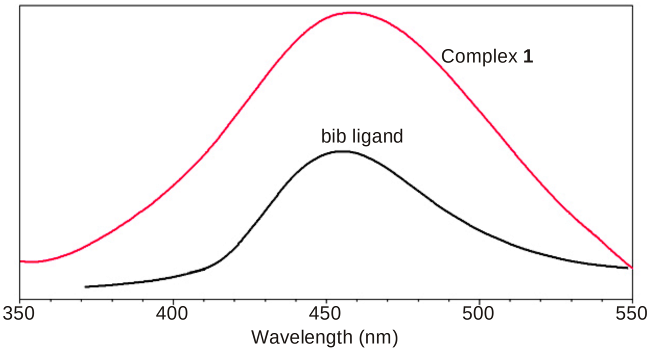

Fig. 4. Solid-state emission spectra for bib and complex **1** at room temperature

Conclusion

In summary, a new 3D Zn(II) coordination polymer which displays a 2D + 2D → 3D poly catenated structure is synthesized. The solid state luminescent emission of complex was also investigated and assigned tentatively to the ligand-to-ligand charge transfer effect.

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