Synthesis, Structure and Properties of Two Novel 2D Zinc(II) Coordination Polymers based on Fluconazole and Benzene Carboxylic Acid

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Nowadays, the design and synthesis of coordination polymers have aroused great interest owing to their intriguing aesthetic structures and potential applications in nonlinear optics, gas storage, ion exchange, luminescence, magnetism and catalysis.1 Self-assembly of bridging organic ligands (connectors) and multi-connected metal ions can give rise to various types of interesting coordination polymers.2 Since metal ion Zn(II) with d10 electronic configuration permits a variety of coordination numbers and geometries which are not dependent on ligand field stabilization but on ligand size and charge, it is well suited for the construction of various coordination polymers. Its borderline hardness allows the coordination of N, O and S donor atoms. Moreover, the Lewis acid character of the Zn(II) complexes is useful to coordinate substrates and also allows anions such as OH−, OR− and SR− to retain their nucleophilic character.1 Fluconazole (Scheme 1) is known as an antifungal drug which was first synthesized and reported in the scientific literature by Richardson et al. as the outcome of their research initiated in 1970.4 We have found that fluconazole as ligand shows interesting coordinating characteristics to afford extended networks with good flexibility through rotating and twisting the C–C and C–N bonds when coordinating to metal ions.5–7 Besides, fluconazole could chelate to metal ions with endodentate nitrogen atoms (N2) and alkoxo atom to form binuclear complex.8 Furthermore, the HFlu ligand has been proved to be a good candidate to construct polymeric networks because it has several available donors/acceptors to form various weak interactions.5,6 Here, we report two novel 2D-network zinc(II) coordination polymer in this literature, [Zn(HFlu)(IPA)]n (1), [Zn(HFlu)-(Hbtc)]n (2). (HFlu = fluconazole, 2-(2,4-difluoro-phenyl)-1,3-bis(1,2,4-triazol-1-yl)-propan-2-ol; H2IPA = isophthalic acid; H3btc = 1,3,5-benzenetricarboxylate). The optical diffuse reflectance, thermal stability and fluorescence properties of these complexes have also been studied.

Complexes 1 and 2 are confirmed by the single crystal X-ray crystallographic (Table 1 and Supporting Information) and the selected bond lengths are list in Table S1. Complex 1 crystallizes in the Triclinic system, P-1 space group. The Zn metal centers are four coordinated by two carboxylate oxygen atoms (O2 and O5A) from two IPA− ligands, and two nitrogen atoms (N5 and N1A) from two fluconazoles. The bond distances of Zn(1)-O(2) and Zn(1)-O(5)A are 1.958(3) Å and 1.960(3) Å, as well as 2.095(4) Å and 2.017(4) Å for Zn(1)-N(5) and Zn(1)-N(1)A. These bond distances are comparable to the reported values of Zn-based complexes.5,10 The band angle for O(2)-Zn(1)-O(5)A is 103.23(15)° as well as 102.16(16)° for N(1)A-Zn(1)-N(5). The two planes based on O2/Zn1/O5 and N1/Zn1/N5 intersect at right angles. In Complex 1, the Zn ions are connected by fluconazole and IPA− ligands leading to the formation of a (4,4) coordination 2D-network with parallelogram grids (Fig. 1(b)). However, unlike most of the 2D (4,4) grid...
networks, it is not co-planar but undulated, resulting from the inherent bent conformations of the fluconazole molecules. The Zn-Zn distance connected two adjacent zinc atoms by IPA ligands is 10.219(2) Å and the Zn-Zn distance connected two adjacent zinc atoms by fluconazole ligands is 11.106(2) Å. The intersection angles for the parallelogram grid are 69.79(1)º and 110.21(1)º. Another outstanding feature is that these adjacent two 2D layers are in a face-to-face manner (Fig. 2) which may devote to the structure to be more stable. Although the single-layered network contains a 10.219(2) × 11.106(2) Å2 (based on Zn-Zn) window, the effective channels in the actual crystal structure of 1 are further reduced due to the significant offset stacking of adjacent two 2D single layers. There are π-π stacking interactions between the benzene rings of IPA ligands from these adjacent two 2D layers. The centroid-to-centroid distance between the benzene rings is 3.875(1) Å. In addition, it is worthy of note that the hydroxyl group from fluconazole forms a tricentered hydrogen bonds11 [O(1)-H(1B)···N(6) 2.847(6) Å, O(1)-H(1B)···N(4) 2.908(6) Å] with triazolyl group from fluconazole intramolecular (Fig. 3, Table S2). The triazolyl group gives two acceptors (N6, N4) for the hydroxyl group. The hydrogen band angle for O(1)-H(1B)···N(6) is 152.7°. However, the hydrogen band angle for O(1)-H(1B)···N(4) is 118.1° which show significant deviation from the O(1)-H(1B)···N(6) bond hydrogen angle. Although some tricentered hydrogen bonds have been reported,12 to our knowledge, such unusual tricentered hydrogen bond between oxygen atom and nitrogen atom are seldom.

Actually, complex 2 is great similar to complex 1 except the IPA replaced by Hbtc (Fig. 4). The Zn metal centers of complex 2 are also four coordinated by two carboxylate oxygen atoms (O3 and O5A) from two Hbtc, and two nitrogen atoms (N6 and N1A) from two fluconazoles. The bond distances of Zn(1)-O(3), Zn(1)-O(5)A, Zn(1)-N(1)A, Zn(1)-N(6) are respectively 1.960(4) Å, 1.966(4), 2.019(4), 2.033(5) Å and the bond angles of O(3)-Zn(1)-O(5)A and N(1)A-Zn(1)-N(6) are 104.73(16)° and 112.1(2)°. The Zn-Zn distance connected two adjacent zinc atoms by Hbtc ligands is 10.278(1) Å and the Zn-Zn distance connected two adjacent zinc atoms by fluconazole ligands is 11.041(1) Å. All these values are comparable to those of complex 1. The intersection angles for the parallelogram grid in complex 2 are 77.35(1)º and 102.65(1)º where there are 7º vary compared with complex 1. Although the offset stacking of adjacent two 2D single layers still exist in complex 2, the offset is much less than complex 1 (Figure 1S). In complex 2, the π-π stacking interactions occur between the benzene rings of Hbtc ligands from these adjacent two 2D layers. The centroid-to-centroid distance between the benzene rings is 3.776(1) Å which is 0.1 Å shorter than complex 1. All

Figure 1. (a) Coordination environment of Zn(II) ions in 1 with thermal ellipsoids at 30% probability (hydrogen atoms except O–H are omitted for clarity). Symmetry code: (O5)A −1+x, y, z; (N1)A x, 1+y, z. (b) A side view of the 2-D network in 1 (Hydrogen atoms are omitted for clarity).

Figure 2. (a) Two independent adjacent “wavy” layers in a face-to-face manner and the π-π stacking interactions of compound 1. (b) Schematic illustration of offset stacking of adjacent two 2D single layers in compound 1.

Figure 3. A perspective view of tricentered hydrogen bond in compound 1.

Figure 4. (a) Coordination environment of Zn(II) ions in 2 with thermal ellipsoids at 30% probability (hydrogen atoms except O–H are omitted for clarity). Symmetry code: B x, −1+y, z; A 1+x, y, z. (b) A side view of the 2-D network in 2 (Hydrogen atoms are omitted for clarity).
the behavior of Zn(II) complexes containing HFlu have various bands of carboxylate groups at 1611 cm⁻¹ into 3D supramolecular architecture via these hydrogen bonds (Figure 2S).

The IR spectrum of compound 1 displays characteristic bands of carboxylate groups at 1611 cm⁻¹ for the antisymmetric stretching and at 1359 cm⁻¹ for the symmetric stretching. For 2, the characteristic bands of the carboxylate groups are shown at 1627 cm⁻¹ and 1366 cm⁻¹ for asymmetric and symmetric vibrations. The separations (Δ) between νasym(CO₂) and νsym(CO₂) bands show that the carboxylate groups coordinate to the metal atoms. The absorption at 3500-3000 cm⁻¹ corresponds to the O-H group of HFlu. The presence of a strong band at 1703 cm⁻¹ proves the existence of uncoordinated carboxylic groups in 2.¹³

In order to confirm the phase purity of these polymers, the X-ray powder diffraction patterns of polymer 1 and 2 are measured and shown in Figure S3. It is clearly seen that the peak positions in the experimental PXRD patterns are in good agreement with the correspondingly simulated ones except the differences in intensity, which indicate a pure phase of each bulk sample. The difference in reflection intensity between the simulated and experimental patterns is due to preferred orientation of the powder samples during data collection.

UV-vis spectra of 1 and 2 complexes have similar bands in the UV-vis-near-IR region (Figure S4). The spectroscopic behavior of Zn(II) complexes containing HFlu have various spectroscopic transitions including ligand-centered and metal-ligand charge transfer. Bands in the UV region were attributed to the intraligand transition mainly centered in HFlu. The intraligand bands are sufficiently intense to mask a MLCT band involving dπZn(II)→π*(HFlu) observed at 253 nm as assigned in a UV-vis spectrum of [Zn(HFlu)(IPA)]µ (1) as well as 260 nm for [Zn(HFlu)(Hbtc)]µ (2).

The fluorescence properties of the fluconazole ligand and complexes 1-2 have been studied in solid state at room temperature and the results were shown in Figure 5. Under the 253 nm excitation, the fluconazole ligand emits strongly at 302 nm assigned to the π→π transition. And complex 1 gives stronger fluorescence at 346 nm under 228 nm. However complex 2 gives relatively weak fluorescence at 339 nm under 232 nm. For complexes 1 and 2, the emission peaks are red-shift, which may be caused by the metal coordination as well as the introduction of TPA ligand and Hbtc.

Thermogravimetric (TG) analyses are performed to examine the thermal stabilities of the two title complexes as shown in Figure S5. Both TG curves exhibit similar step which may be attributed to the similar frameworks. For complexes 1 and 2, the weight loss of 59.3% and 55.5% were observed in the range of 285-417 and 296-416 °C, respectively, corresponding to the decomposition of HFlu ligand (calc 57.1% for 1 and 52.8% for 2). Continuous heating brought about the pyrolysis of TPA ligand and Hbtc ligand until 1000 °C.

**Experimental**

All chemicals were commercial materials of analytical grade and used as received. The FT-IR spectrum was obtained on a Nicolet 520 FT-IR spectrophotometer Fourier transform infrared spectroscopy in the 4000-400 cm⁻¹ regions, using KBr pellets. Elemental analysis for C, H, N was carried out on a Perkin-Elmer 2400 II elemental analyzer. Powder X-ray diffraction (XRD) patterns were obtained using a pinhole camera (Anton Paar) operating with a point focused Ni-filtered Cu Kα radiation in the 2θ range from 5° to 50° with a scan rate of 0.08° per second. The optical properties were analyzed by UV-vis diffuse reflectance spectroscopy using a UV-vis spectrophotometer (Cary-500, Varian Co.), in which BaSO₄ was used as the internal standard. Fluorescence spectra were recorded with a F-2500 FL Spectrophotometer analyzer. Thermogravimetric analyzer was performed on a Perkin-Elmer TG/DTA 6300 thermal analyzer under N₂ atmosphere at a heating rate of 10 °C/min in the temperature range 30-1000 °C.

For preparation of complex 1, a mixture of fluconazole (153 mg, 0.5 mmol), isophthalic acid (83 mg, 0.5 mmol), ZnCl₂ (136 mg, 1.0 mmol), 15 mL H₂O, and 4 mL ethanol was sealed in a 30 mL Teflon-lined stainless steel container. An aqueous solution of sodium hydroxide was added dropwise with stirring to adjust the pH value of the solution being 6.0. Kept under autogenous pressure at 150 °C for 3 days before cooling to room temperature at a rate of 5 °C h⁻¹; Then the transparent crystals of 1 were obtained. The crystals were isolated, washed with alcohol three times, and dried in a vacuum desiccator using silica gel (yield 72.6%, based on Zn). Elemental analysis Calcd (%) for C₁₂H₁₀F₆N₆O₇Zn: C 47.08, H 3.01, N 15.69. Found (%): C 47.11, H 3.04, N 15.73. IR (KBr, cm⁻¹): 3430w, 3159w, 3124w, 1611s, 1565s, 1500m, 1477w, 1359s, 1276m, 1130m, 1102w, 994w, 965w, 740m, 674w, 658w.

For preparation of complex 2, the same synthetic procedure as that for 1 was used except that isophthalic acid (83 mg, 0.5 mmol) was replaced by H₃btc (105 mg, 0.5 mmol)
X-ray diffraction data for the complex were collected on a Bruker SMART CCD diffractometer equipped with Graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at 296(2) K. A high quality crystal of the complex was selected and was mounted on a glass fiber. Collect the data sets with the o scan technique. Empirical absorption corrections were applied using the SADABS program. The structure was solved by direct methods and all non-hydrogen atoms were refined with anisotropic thermal parameters by a full-matrix least-squares based on F² using SHELXTL package. All non-hydrogen atoms were refined anisotropically. Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-940683 (1) and CCDC-940684 (2)). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk

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Notes

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