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Single Crystals of a 2-Dimensional Metal Coordination Polymer Containing Pendant Carbazole Groups

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Coordination polymers consisting of metal cations and organic linkers are widely used in fundamental supramolecular approaches as well as various other practical applications.[1-4] There are various types of metal-organic coordinated structures[2,5,6] such as linear-shaped 1-dimensional (1D),[7,8] sheet-shaped 2-dimensional (2D)[9,10] and network-shaped 3-dimensional (3D)[11,12] structures.

Such coordinated structures are dependent on the substituents that are present on the organic linkers. For example, the organic linker H_2BDC (benzene-1,4-dicarboxylic acid or terephthalic acid) formed a 3D metal-organic framework (MOF) structure with a well-defined cavity, with zinc cations.[11] H_2BDC analogues that had small substituents (*e.g.*, Br, NH_2, and short alkoxy chains) with volumes that are smaller than the cavity volume, also formed similar 3D MOF structures.[13,14] In contrast, the presence of more bulky substituents results in the formation of 3D MOF or 1D coordinated structures. For example, 2,5-disubstituted H_2BDC analogues, in which the substituents were long alkoxy chains-like octyloxy chains, first formed a 3D MOF structure that then transferred to a 1D coordinated structure.[15-17] When more bulky substituents such as 3-(9*H*-carbazol-9-yl)octyloxy groups were introduced on a H_2BDC linker, only 1D coordinated structure was obtained.[18]

In this work, we studied a novel metal coordination polymer based on an organic H_2BDC analogue, in order to determine the influence of the substituents of the organic linker on metal coordinated structure. In contrast to previous reports,[15,18] the organic linker 2,5-bis(3-(9*H*-carbazol-9-yl)-propoxy)benzene-1,4-dicarboxylic acid (CZ3-acid, see Figure 1) having bulky carbazole groups formed single crystals resulting from sheet-shaped 2D metal coordinated structure. Therefore, the coordinated structure was strongly dependent on the size of the substituents on the H_2BDC linkers.

Our novel metal coordination polymer was composed of zinc cations and a H_2BDC analogue. Figure 1 shows the chemical structure of the organic linker CZ3-acid, which is a H_2BDC analogue having 2,5-disubstituted groups. The bulky non-polar carbazole groups are connected by propyloxy spacers. The metal coordination polymer of CZ3-acid with zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] was synthesized by a solvothermal reaction in dimethylformamide (DMF). As shown in

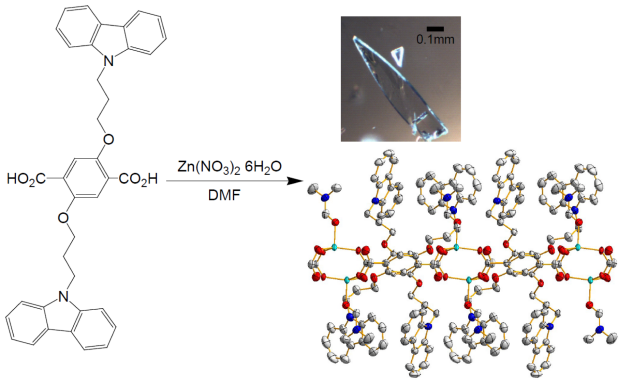


Figure 1. Schematic illustration obtaining single crystals of 2D metal coordination polymer (OTREP view with 50% probability ellipsoids).

Figure 1, transparent single crystals of the metal coordination polymer were obtained directly from the solvothermal reaction.

In order to understand the coordinated structure of the single crystals, we analyzed the crystal structure of the metal coordination polymer by X-ray single crystal structure analysis. The metal coordination polymer exhibited triclinic P-1 space group symmetry with high crystal quality as described in the Experimental section. The solvent DMF also participated in the crystal structure. These crystals are henceforth denoted as "[Zn(CZ3)(DMF)]".

In general, many metal coordination polymers that contain solvents exhibit low thermal stability, due to which solvent molecules are easily eliminated at low temperatures.[19,20] In the [Zn(CZ3)(DMF)] polymer, although solvent (DMF) molecules are coordinated with the zinc cation, the crystals exhibit high stability. As shown in Figure 2, the thermal gravimetric analysis (TGA) curve of [Zn(CZ3)(DMF)] shows a very high initial weight-loss temperature of about 240 °C. It is also noticed that non-coordinated solvent molecules were not included (*i.e.*, physisorption was not observed) in the single crystals of the [Zn(CZ3)(DMF)] polymer. This is supported by calculations using PLATON;[21] the total solvent accessible volume in the [Zn(CZ3)(DMF)] structure was only with 2.6% (47.5 Å^3) of the unit cell volume. Therefore, only DMF participated in the coordinated structure.

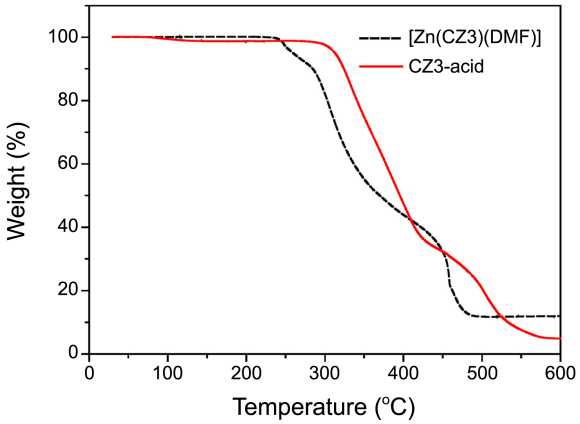


Figure 2. Thermal gravimetric analysis (TGA) curves of [Zn(CZ3)(DMF)] polymer and the organic linker CZ3-acid.

The coordinated structure and crystal packing diagram of [Zn(CZ3)(DMF)] are shown in Figures 3 and 4, respectively. The fundamental building units for [Zn(CZ3)(DMF)] are di-zinc cores, as shown in Figure 3. For clarity, the substituent 3-(9*H*-carbazol-9-yl)propoxy group is represented by a sphere. The crystal structures were composed of two Zn centers bridged by two 'μ_4-CZ3-acid' ligands through their carboxylate groups (O4, O5) (see Figure 3 and Figure 5(b)). In addition to the oxygen atoms of the bridging 'μ_4-CZ3-acid' ligands, each zinc atom was coordinated by two oxygen atoms; One (O1) from another 'μ_2-CZ3-acid' ligand in a mono-dentate fashion at the equatorial position and the other (O6) from dimethylformamide (DMF) at the axial position, forming a slightly distorted tetrahedral coordination environment, Zn-O1, O4, O5, O6. The oxygen atom O2 was at a distance of 2.912 Å from the Zn. The Zn···Zn distance was 3.735 Å. Therefore, the [Zn(CZ3)(DMF)] polymer crystal exhibited a 2D coordinated structure.

As shown in Figure 4, the 2D coordinated structure appeared as di-zinc cores that were interconnected by CZ3-acid ligands. There were two types of distinguishable CZ3-acid ligands in the coordination mode; one 'μ_2-CZ3-acid' ligand was bonded to two zinc atoms, and was of the type represented in Figure 5(a), and the other 'μ_4-CZ3-acid' ligand was bonded to four zinc atoms, and was of the type represented in Figure 5(b). Both types of CZ3-acid ligands

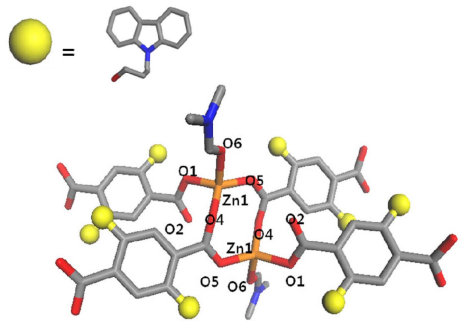


Figure 3. Fundamental building unit of [Zn(CZ3)(DMF)], which are composed of a zinc di-nuclear core.

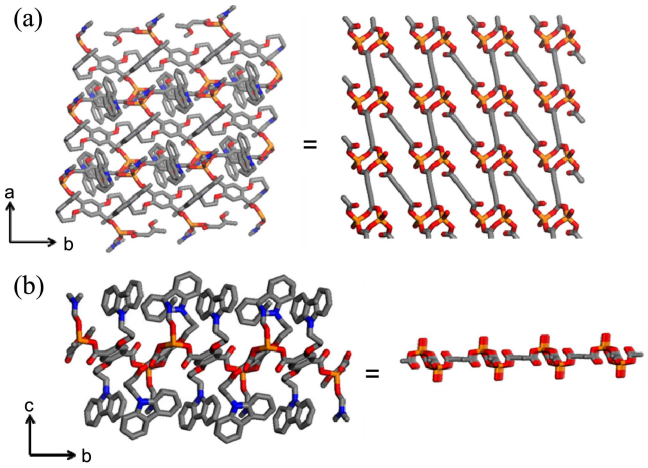


Figure 4. Crystal packing diagram projected along *c*-axis (a) and *a*-axis (b) of 2D [Zn(CZ3)(DMF)] structure.

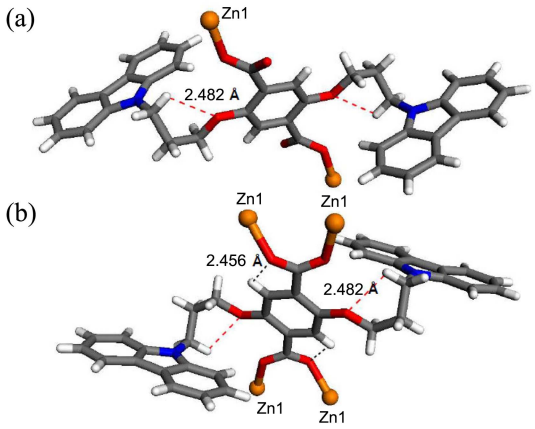


Figure 5. CZ3 ligands with two different connecting modes: (a) μ_2-CZ3-acid, coordinated with two zinc atoms, and (b) μ_4-CZ3-acid, coordinated with four zinc atoms.

had strong internal hydrogen bonding interactions (2.482 Å) due to the twisting of the carbazole rings for close packing.

As mentioned above, single crystals of [Zn(CZ3)(DMF)] that contained bulky carbazole groups and short propyloxy spacers exhibited sheet-shaped 2D coordinated structure. In contrast, in previous work[18] H_2BDC linker having identical carbazole groups but having relatively long dodecyloxy spacers exhibited linear-shaped 1D coordinated structure due to the packing tendency of long alkyloxy spacers[15] and π-π stacking force of carbazole groups.[15,18] As shown in Figure 4(b), in [Zn(CZ3)(DMF)] polymer, the carbazole groups are packed in zig-zag shape and then the π-π stacking force of carbazole groups is not strongly involved. Therefore, the coordinated structure was strongly dependent on the size of the substituents that were present on the H_2BDC linkers.

In addition, such single crystal structure in polymers with carbazole groups is unique. While many molecular crystals that contain carbazole groups have been reported,[22-26] the single crystal structure of conventional organic polymers and metal coordination polymers that contain carbazole groups

has rarely been reported. Zhang *et al*. reported the crystal structure of coordination polymers containing carbazole groups.[27] It was, however, a 1D coordinated structure wherein the carbazolylacetic acid was directly coordinated to the zinc cation.

In summary, in order to determine the influence of the substituents of organic linkers on metal coordinated structure, we investigated a novel metal coordination polymer, [Zn(CZ3)(DMF)], which consists of zinc cations and the organic linker H_2BDC analogue CZ3-acid that has two bulky propyloxy carbazole groups as substituents. Single crystals of [Zn(CZ3)(DMF)] polymer that were obtained by solvothermal reaction, exhibited 2D metal coordinated structure. Such polymer crystal structure including carbazole groups has rarely been reported.

Experimental Section

Synthesis of Monomer. The organic linker CZ3-acid was synthesized by a method that was similar to that described in Ref. [28]. ^{1}H-NMR (400 MHz, DMSO-d_6, δ relative to $(CH_3)_4Si$): ^{1}H-NMR (400 MHz, DMSO-d_6) δ 8.11 (d, 4H, J = 7.6 Hz, C_6H_4), 7.61 (d, 4H, J = 8.0 Hz, C_6H_4), 7.36 (t, 4H, J = 15.2 Hz, C_6H_4), 7.29 (s, 2H, C_6H_2), 7.15 (t, 4H, J = 14.8 Hz, C_6H_4), 4.58 (t, 4H, J = 14.0 Hz, CH_2), 3.99 (t, 4H, J = 10.8 Hz, CH_2), 2.16 (t, 4H, J = 11.2 Hz, CH_2).

Synthesis of Polymer. The metal coordination polymer was synthesized by a solvothermal reaction;[15] the organic linker CZ3-acid (0.125 mmol, 0.0766 g) and $Zn(NO_3)_2{\cdot}6H_2O$ (0.25 mmol, 0.0744 g) were added to a solvent mixture containing 2 mL of dimethylformamide (DMF) and 2 mL of ethanol, and heated to 100 °C for 1 day. Needle-like crystals were obtained. There were filtered and washed with DMF and acetone. The synthesis of metal coordination polymer was very sensitive to the ratio of solvent mixture and other experimental conditions and then easily formed another crystalline powders. The yield of [Zn(CZ3)(DMF)] phase is obtained up to 65%.

Crystal Structure Analysis: $C_{41}H_{37}N_3O_7Zn$, M_r =749.1, triclinic, space group *P-1*, a = 10.0375 (5) Å, b = 10.3460 (4) Å, c = 18.1680 (8) Å, α = 87.3327 (11)°, β = 83.8644 (12)°, γ = 77.4709 (13)°, V = 1830.70 (14) Å^3, Z = 2, T = 290 (1) K, μ (Mo Ka) = 0.73 mm^{-1}. Of 14369 reflections collected in the θ range 3.0°-25.0° using w scans on a Rigaku R-axis Rapid S diffractometer, 6423 were unique reflections (R_{int} = 0.028). The structure was solved and refined against F^2 using SHELX-97,[29] 469 variables, R_1 = 0.035 ($F_o^2 > 2\sigma(F_o^2)$), wR_2 = 0.108, GOF = 1.19, and max/min residual electron density 0.76/–0.96 eÅ^{-3}. CCDC-950341.

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