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# Tuning the structures of three coordination polymers incorporating $Zn^{II}$ and 2,2′-dichloro-4,4′-azodibenzoic acid via selective auxiliary ligands

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ABSTRACT

By tuning the auxiliary ligands in the assembling reaction, three $Zn^{II}$ coordination polymers of [Zn(Cl-adc) (phen) ($H_2O$)](DMF) (**1**), [Zn(Cl-adc) (DMA)](DMA) (**2**), and [Zn(Cl-adc) (dip)]$(DMF)_{0.5}$ (**3**) (Cl−$H_2$adc = 2,2′-dichloro-4,4′-azodibenzoic acid, phen = 1,10-phenanthroline, dip = 1,3-di(imidazole) propane) have been successfully synthesized and characterized by single-crystal X-ray diffraction study, elemental analysis, IR spectra, TGA analyses, solid-state fluorescent property, and powder X-ray diffraction (PXRD). Single crystal X-ray diffraction reveals that **1** and **2** displays a 1D polymeric chain and 2D **sql** layered net with the presence of chelated phen and terminal DMA ligands, respectively. By incorporating dip linker, **3** exhibits a 2D + 2D → 3D entangled network, with each 2D net portraying wavelike **sql** layered structure. Their structural divergences should be properly attributed to fact that, the structural topologies can be well regulated by using three auxiliary ligands incorparating different coordination function.



## 1. Introduction

Research interest on polymeric coordination networks becomes intensive, which are constructed based on diverse building tectons, including pre-designed ligands and metal ions [1–4]. These functional materials display potential application in the areas of catalysis, separation, sorption, and magnetic devices [5–11]. Therefore, the potential for creating intriguing architectures of novel materials has been recognized as a topic chemistry community. One of the most common used organic linkers is the series of bicarboxylate derivatives, including those decorated by inserting rigid or flexible spacers between the terminal carboxylates, and by adding substituent on the aromatic rings [12–14]. Especially, azo-spaced aromatic carboxylate ligands or chlorinated bicarboxylates tend to afford various coordination polymers [15–17]. Significantly, far less common has been the investigation of related chlorinated bicarboxylate linkers with azo-spacer in construction of coordination polymers. On the other hand, a large number of coordination polymers based on the mixed-ligand strategy have been reported [18]. Yue and Wang et al. reported a new coordination polymer $Zn_3(adc)_3(bib)_3$ ($H_2$adc = 4,4′-azodibenzoic acid), which exhibits a 3-fold interpenetrated framework with $3^6.4^{18}.5^3.6$ topology [19]. An unusual 2-fold interpeneatrated 3D **pts** framework of Zn(adc) ($H_2O$) has been synthesized by Li and Wang et al. [20]. In this regard, intelligent combination of azo-based bridging chlorocarboxylates with selective auxiliary ligands and metal ions is expected to afford many interesting coordination architectures.

In this work, our synthetic strategy includes that two distinct N-donor auxiliary ligands, phen (1,10-phenanthroline) and dip (1,3-di(imidazole)propane) as well as DMA (N,N-dimethylacetamide) solvent, have been employed as the chelating, bridging and terminal tectons in the assembly system of Cl−$H_2$adc (2,2′-dichloro-4,4′-azodibenzoic acid) and $Zn(NO_3)_2$. As a result, three novel $Zn^{II}$ coordination polymers are afforded, including [Zn(Cl-adc) (phen) ($H_2O$)](DMF) (**1**), [Zn(Cl-adc) (DMA)](DMA) (**2**), and [Zn(Cl-adc) (dip)]$(DMF)_{0.5}$ (**3**). Interestingly, due to the diverse coordination characteristics of auxiliary ligands, these three compounds show the 1D to 3D various polymeric structures, including a 1D comb-like chain, a 2D (4,4) rhombic layer, and a 2D + 2D → 3D interpenetrated network, respectively. In addition, thermal stability, solid-state fluorescent and sensing (nitroaromatic compound) properties of these polymeric complexes have also been explored.

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## 2. Experimental

### 2.1. Materials and general methods

All analytical grade chemicals and solvents were purchased and used as received, except that the ligand Cl-adc was synthesized according to a comparable literature procedure [16]. Fourier transform (FT) IR spectra (KBr pellets) were recorded on an AVATAR-370 (Nicolet) spectrometer. Elemental analyses of C, H, and N were taken on a CE-440 (Leemanlabs) analyzer. Thermogravimetric analysis experiments were performed on a TGA Q500 thermal analyzer in 25–800 °C (heating rate: 10 °C/min) under $N_2$ atmosphere with an empty $Al_2O_3$ crucible as the reference. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 Advance diffractometer at 40 kV and 100 mA for a Cu-target tube ($\lambda = 1.5406$ Å). The calculated PXRD patterns were obtained from the single-crystal X-ray diffraction data by using PLATON (see Fig. S1).

### 2.2. Synthesis and characterization

**[Zn(Cl-adc) (phen) ($H_2O$)](DMF) (1)**. The ligand Cl–$H_2$adc (0.1 mmol) and phen (0.1 mmol) was dissolved in DMF (5 mL), to which a aqueous solution (5 mL) of $Zn(NO_3)_2$ (0.1 mmol) was added with stirring for ca. 30 min. Then, the solution was sealed in a Teflon-linear autoclave (20 mL) and heated at 110 °C for 3 days. After cooling to room temperature at a rate of 10 °C/h, yellow block crystals of complex **1** were obtained in 55% yield. Anal. Calcd for $C_{58}H_{46}Cl_4N_{10}O_{12}Zn_2$: C, 51.69; H, 3.44; N, 10.39%. Found: C, 51.73; H, 3.36; N, 10.44%. IR (KBr, $cm^{-1}$): 3420b, 1716s, 1614vs, 1515m, 1399vs, 1259m, 1196w, 1144w, 1102w, 1037w, 893m, 847m, 820m, 792m, 725m, 692w, 669w, 620w.

**[Zn(Cl-adc) (DMA)](DMA) (2)**. The ligand Cl–$H_2$adc (0.1 mmol) was dissolved in DMA (5 mL), to which a aqueous solution (5 mL) of $Zn(NO_3)_2$ (0.1 mmol) was added with stirring for ca. 30 min. Then, the solution was sealed in a Teflon-linear autoclave (20 mL) and heated at 100 °C for 5 days. After cooling to room temperature at a rate of 10 °C/h, yellow block crystals of complex **2** were obtained in 61% yield. Anal. Calcd for $C_{22}H_{24}Cl_2N_4O_6Zn$: C, 45.82; H, 4.19; N, 9.71%. Found: C, 45.78; H, 4.16; N, 9.76%. IR (KBr, $cm^{-1}$): 1605vs, 1474w, 1403vs, 1261w, 1194w, 1126m, 1038m, 898w, 855w, 824w, 793m, 692w, 622m, 595w, 443w.

**[Zn(Cl-adc) (dip)]($DMF)_{0.5}$ (3)**. The ligand Cl–$H_2$adc (0.1 mmol) and dip (0.1 mmol) was dissolved in DMF (5 mL), to which a aqueous solution (5 mL) of $Zn(NO_3)_2$ (0.1 mmol) was added with stirring for ca. 30 min. Then, the solution was sealed in a Teflon-linear autoclave (20 mL) and heated at 120 °C for 3 days. After cooling to room temperature at a rate of 10 °C/h, yellow block crystals of complex **3** were obtained in 58% yield. Anal. Calcd for $C_{49}H_{43}Cl_4N_{13}O_9Zn_2$: C, 47.83; H, 3.52; N, 14.80%. Found: C, 47.78; H, 3.46; N, 14.86%. IR (KBr, $cm^{-1}$): 1619vs, 1526w, 1391vs, 1364s, 1287w, 1239w, 1198w, 1111m, 1038w, 824w, 794w, 655w, 626w.

### 2.3. X-ray crystallography

Single crystal X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer equipped with a graphite monochromated Mo K$\alpha$ radiation at 173(2) K for **1** and **2**, and 296(2) K for **3**. The structures were solved by direct methods and refined anisotropically on $F^2$ for all non-H atoms by full-matrix least-squares methods using SHELXTL. H atoms of the ligands were located geometrically with assigned isotropic thermal parameters. The lattice solvents in **1** and **2** were treated as the diffuse contribution to the overall scattering without specific atom sites by SQUEEZE/PLATON. The detailed crystallographic data and structure refinement parameters for four complexes are summarized in Table 1. Selected bond distances and angles are listed in Table S1.

## 3. Results and discussion

### 3.1. Description of crystal structures

#### 3.1.1. Structure description of *1*

Single crystal X-ray diffraction study shows that complex **1** has a 1D polymeric chain motif, which crystallizes in the triclinic crystal system with *P*-1 space group. The asymmetric unit consists of one $Zn^{II}$ ion, one Cl-$adc^{2-}$ ligand, one phen co-ligand, and one water molecule, as well as one DMF guests. As shown in Fig. 1a, Zn1 center is six-coordinated by four oxygen atoms from two Cl-$adc^{2-}$ ligands and one water ligand, and two nitrogen atoms from a chelating phen ligand, to complete a distorted octahedral geometry. Two carboxylates of Cl-$adc^{2-}$ ligand show the monodentate and

**Table 1**
Crystallographic data for **1**–**3**.

| Compound reference | 1 | 2 | 3 |
|---|---|---|---|
| Chemical formula | $C_{58}H_{46}Cl_4N_{10}O_{12}Zn_2$ | $C_{22}H_{24}Cl_2N_4O_6Zn$ | $C_{49}H_{43}Cl_4N_{13}O_9Zn_2$ |
| Formula mass | 1347.59 | 576.72 | 1230.50 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| *a*/Å | 8.4538(14) | 14.7437(11) | 10.0106(9) |
| *b*/Å | 12.667(2) | 24.4404(19) | 11.0553(10) |
| *c*/Å | 13.596(2) | 7.9873(6) | 15.1837(14) |
| $\alpha$/° | 95.874(3) | 90.00 | 69.814(2) |
| $\beta$/° | 96.709(3) | 103.368(2) | 82.810(2) |
| $\gamma$/° | 101.759(3) | 90.00 | 72.778(2) |
| Unit cell volume/Å$^3$ | 1403.6(4) | 2800.2(4) | 1506.0(2) |
| Temperature/K | 173(2) | 173(2) | 296(2) |
| Space group | *P*-1 | *C*2/*m* | *P*-1 |
| *Z* | 1 | 4 | 1 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 1.119 | 1.108 | 1.034 |
| No. of reflections measured | 7964 | 8180 | 8722 |
| No. of independent reflections | 4918 | 2543 | 5289 |
| $R_{int}$ | 0.0348 | 0.0340 | 0.0326 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0658 | 0.0481 | 0.0656 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1665 | 0.1388 | 0.1833 |
| Final $R_1$ values (all data) | 0.0950 | 0.0534 | 0.0872 |
| Final $wR(F^2)$ values (all data) | 0.1825 | 0.1427 | 0.2024 |
| Goodness of fit on $F^2$ | 1.089 | 1.109 | 1.053 |