



# Zero-, one-, two- and three-dimensional coordination polymers based on tetracarboxylic acid: Syntheses, structures, magnetic and luminescent properties



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## ABSTRACT

A series of coordination polymers, namely,  $[\text{Co}(\text{H}_2\text{ttac})(\text{phen})_2] \cdot 4\text{H}_2\text{O}$  (**1**),  $[\text{Zn}(\text{H}_2\text{ttac})(\text{phen})_2] \cdot 4\text{H}_2\text{O}$  (**2**),  $[\text{Cu}(\text{H}_2\text{ttac})(\text{phen})]_n$  (**3**),  $[\text{Zn}_2(\text{ttac})(\text{DMZ})\text{H}_2\text{O}]_n$  (**4**), and  $[\text{Cd}(\text{ttac})(\text{phen})\text{H}_2\text{O}]_n$  (**5**) ( $\text{H}_4\text{ttac} = 4,5\text{-di}(3'\text{-carboxylphenyl})\text{-phthalic acid}$ ,  $\text{phen} = 1,10\text{-phenanthroline}$ ,  $\text{DMZ} = \text{Dimidazole}$ ) have been prepared under hydrothermal conditions and characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction. Structural analysis reveals that the as-synthesized coordination polymers have different structures, ranging from zero-(**1** and **2**), one-(**3**), two-(**4**) to three-(**5**) dimensions, which are mainly due to the different metal ions, the degree of deprotonation and coordination modes of the  $\text{H}_4\text{ttac}$  ligands. It is worth mentioning that, based on the diversified  $\pi\text{-}\pi$  stacking and/or  $\text{C-H}\cdots\pi$  interactions between  $\text{H}_4\text{ttac}$  ligands and/or nitrogen-containing auxiliary ligands, **1-4** are assembled form low-dimensional structures into three-dimensional (3D) frameworks. Especially, Jahn-Teller effect occurs in **3** and its magnetic study confirms that it presents antiferromagnetic coupling through the  $(\text{O}_2\text{C-Ar-Ar-CO}_2)_2$  bridges. Significantly, luminescent emission of **3** displays selective recognition towards L-Arginin. Thermogravimetric (TG) analyses of the coordination polymers have also been investigated.

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## 1. Introduction

As well as we know, the design and syntheses of coordination polymers (CPs) has been attracting enormous interest of synthetic chemists not only due to their networks made up of organic linkers and metal cations, often forming diversity of architectures and fascinating topologies, but also for their potentially industrial applications in gas storage and separation, heterogeneous catalysis, drug delivery, magnetic properties, molecular recognition and selective luminescent probes and so on [1–14].

Obviously, coordination mode of organic linkers and the geometry of metal cations have a major impact on the topological structures of the coordination polymers. Usually, multi-dentate organic ligands like multi-carboxylic acids are recommended to polymerize into extended open frameworks, because these ligands

may potentially provide various coordination modes and favor the construction of multi-dimensional coordination polymers [15–23]. The transition metal (TM) ions such as Co(II), Cu(II), Zn(II), and Cd(II) have been used in structure coordination polymers on account of specific geometry and excellent chemical properties [24–31]. In the meantime, nitrogen-containing auxiliary ligands containing pyridine and imidazole rings are superior in terms of hydrogen-bonding formation and  $\pi\text{-}\pi$  stacking interactions that are significant for affording extended open frameworks via polymerization [32–35]. Furthermore, the reaction conditions such as pH value, temperature, reaction time, and material ratio, etc. can be utilized to adjust and functionalize the preassembled structures of coordination polymers.

In the assembling strategies of the coordination polymers, aromatic–aromatic or  $\pi\text{-}\pi$  stacking as well as  $\text{C-H}\cdots\pi$  interactions are important non-covalent intermolecular forces and may play a role in the connection process of the frameworks. Better understanding and utilizing, these intermolecular forces are of fundamental significance for the further development of arrangement

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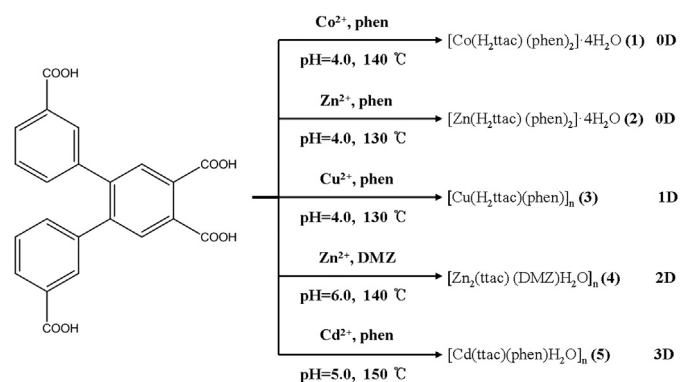
and tuning of high-dimensional crystal structures, especially when strong hydrogen bonds are absent. Nitrogen-containing in the aromatic rings may show preferences of crystal structures with stacking. Heteroatoms in an aromatic system induce differentiation of  $\pi$  (and  $\sigma$ ) electron distributions. As is well-known, nitrogen-containing aromatic rings show smaller stacking separation because the van der Waals radius for nitrogen is smaller than that for carbon atom. In the present work, nitrogen-containing ligand such as phenanthroline and dimidazole were chosen as the auxiliary ligands together with a flexible tetrahydric acid to construct a series of complexes utilizing the diversified  $\pi$ - $\pi$  stacking and C-H $\cdots\pi$  interactions [36–38].

Hydro(solvo)thermal synthesis has been proven to be an effective method in preparing functional coordination polymers and growing single crystals for structural studies. Taking into account the geometry and its degree of protonation of the title tetracarboxylic acid, as well as the flexibility of carboxy groups, different coordination conformations of the ligand may occur due to its coordination versatility and capability to build various secondary building units (SBUs). Furthermore, the introduction of nitrogen-containing co-linkers is beneficial to the fabrication of different dimensionalities of the coordination polymers. In this report, we selected a flexible tetracarboxylic acid, namely, 4,5-di(3'-carboxylphenyl)-phthalic acid ( $H_4ttac$ ), a symmetric multidentate ligand, together with different metal centers by adjusting pH value, temperature, and auxiliary ligands, then, five coordination polymers have been prepared successfully,  $\{[Co(H_2ttac)(phen)_2] \cdot 4H_2O\}_n$  (**1**),  $\{[Zn(H_2ttac)(phen)_2] \cdot 4H_2O\}_n$  (**2**),  $[Cu(H_2ttac)(phen)]_n$  (**3**),  $[Zn_2(ttac)(DMZ)H_2O]_n$  (**4**), and  $[Cd(ttac)(phen)H_2O]_n$  (**5**), the synthetic route is shown in Scheme 1. Peculiarly, there are four coordination modes in the coordination polymers **1–5**, detailed information are illustrated in Scheme 2.

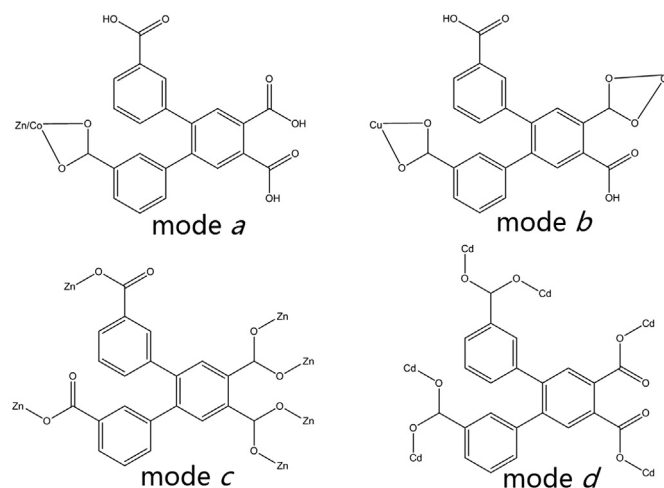
## 2. Experimental section

### 2.1. Materials and physical measurements

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240 CHN Elemental Analyzer. IR spectra in the range of 400–4000  $cm^{-1}$  were recorded with an AVATAR 360 FT-IR spectrometer (KBr pellets were used). The crystal structure was determined with a Bruker Smart CCD X-ray single-crystal diffractometer. Excitation and emission spectra were obtained with an F-7000 FL spectrofluorometer at room temperature. Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses were conducted with a Perkin–Elmer TGA7 system under flowing  $N_2$  stream (flow rate 40 mL/min) from room temperature to



Scheme 1. Experimental routes for coordination polymers **1–5**.



Scheme 2. The coordination modes of  $H_4ttac$  ligand in coordination polymers **1–5**.

1000 °C at a heating rate of 10 K/min. Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance instrument with Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in the range  $2\theta = 5$ – $45^\circ$  at room temperature.

### 2.2. Synthesis of the coordination polymers **1–5**

#### 2.2.1. Synthesis of $[Co(H_2ttac)(phen)_2] \cdot 4H_2O$ (**1**)

A mixture of 4,5-di(3'-carboxylphenyl)-phthalic acid (0.05 mmol, 20.3 mg), cobalt perchlorate-hydrate (0.1 mmol, 36.6 mg) and 1,10-phenanthroline (0.1 mmol, 18.0 mg) in 10 mL of water was adjusted to pH 4.0 with 1 mol  $L^{-1}$  KOH solution. The mixture was then transferred to and sealed in a 25 mL Teflon-lined stainless autoclave, followed by heating at 140 °C for 72 h to afford pink block-shaped crystals in 24.7% yield after slowly cooling to room temperature at a rate of 5 °C/h. Elemental analysis calculated for  $C_{46}H_{36}CoN_4O_{12}$  (895.72): C 62.34%, H 4.17%, N 6.13%; Found: C 61.70%, H 4.05%, N 6.26%. Selected IR ( $cm^{-1}$ ): 3430(m), 3066(m), 2926(m), 2604(m), 1704(s), 1605(s), 1517(m), 1430(m), 1373(s), 1311(m), 1298(m), 1256(m), 1117(w), 1028(w), 816(m), 765(m), 717(m), 651(m), 560(m).

#### 2.2.2. Synthesis of $[Zn(H_2ttac)(phen)_2] \cdot 4H_2O$ (**2**)

A mixture of 4,5-di(3'-carboxylphenyl)-phthalic acid (0.05 mmol, 20.3 mg), zinc perchlorate-hydrate (0.1 mmol, 26.4 mg) and 1,10-phenanthroline (0.1 mmol, 18.0 mg) in 10 mL of water was adjusted to pH 4.0 with 1 mol  $L^{-1}$  KOH solution. The mixture was then transferred to and sealed in a 25 mL Teflon-lined stainless autoclave, followed by heating at 130 °C for 72 h to afford colorless block-shaped crystals in 35.2% yield after slowly cooling to room temperature at a rate of 5 °C/h. Elemental analysis calculated for  $C_{46}H_{36}ZnN_4O_{12}$  (902.16): C 61.77%, H 4.09%, N 6.51%; Found: C 61.24%, H 4.02%, N 6.21%. Selected IR ( $cm^{-1}$ ): 3427(m), 3066(m), 2927(m), 2607(m), 1704(s), 1582(s), 1520(m), 1430(s), 1398(w), 1361(m), 1299(m), 1256(m), 1149(w), 1110(m), 928(m), 854(s), 814(m), 770(s), 727(s), 650(w), 562(w).

#### 2.2.3. Synthesis of $[Cu(H_2ttac)(phen)]_n$ (**3**)

A mixture of 4,5-di(3'-carboxylphenyl)-phthalic acid (0.05 mmol, 20.3 mg), copper perchlorate-hydrate (0.1 mmol, 37.1 mg) and 1,10-phenanthroline (0.1 mmol, 18.0 mg) in 10 mL of water was adjusted to pH 4.0 with 1 mol  $L^{-1}$  KOH solution. The mixture was then transferred to and sealed in a 25 mL Teflon-lined stainless autoclave, followed by heating at 130 °C for 72 h to afford

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