



Structural diversity of four coordination polymers based on asymmetric dicarboxylate: Effect of metal ions and N-donor ligands



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ABSTRACT

To determine the influence of metal ion and N-donor auxiliary ligands on the formation of metal–organic frameworks, four novel metal coordination polymers, $[\text{Cd}(\text{bdam})(\text{phen})_2]_n$ (**1**), $[\text{Cd}(\text{bdam})(\text{bpy})]_n \cdot n\text{H}_2\text{O}$ (**2**), $[\text{Zn}(\text{bdam})(\text{bpy})]_n \cdot n\text{H}_2\text{O}$ (**3**) and $[\text{Ag}_4(\text{bdam})_2(\text{dpe})]_n$ (**4**) (H_2bdam = benzophenone-2,4'-dicarboxylic acid, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline, dpe = 1,2-(4-pyridyl)ethane) were synthesized and characterized. Complex **1** is 1D square-wave-like chain structure. Two phen ligands chelate to one cadmium atom in **1**. **2** shows 1D ring chain based on dinuclear cadmium unit linked by $(\text{bdam})^{2-}$ ions, while two 2,2'-bpy ligands coordinate one dinuclear cadmium unit. **3** forms a 1D right-handed helical chain. Different from the above complexes, **4** possesses a 2D network structure based on octanuclear silver clusters cross-linked by bdam^{2-} ions and dpe ligands, in which there is significantly Ag...Ag interactions. The structural differences of **1** and **2** indicate that the subtle variations on N-donor ligands can greatly affect the coordination modes of $(\text{bdam})^{2-}$ ion and the coordination geometries of Cd^{II} ion. The structural differences of **2**, **3** and **4** indicate that metal ions also have great influence on the structures of the complexes. In addition, we have investigated the luminescence of **1–4** in the solid state at room temperature, revealing that the polymers are photoluminescent and their emissions are varied with the alteration of metal ions and N-donor ligands.

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1. Introduction

The design and construction of coordination polymers have provoked great interests for not only the novel structures but also their potential technological applications [1–6]. In order to prepared coordination polymers with diverse structures and desired functionalities, judicious selection of appropriate polydentate organic ligands and metal ions is one of the most efficient strategies [7–14]. Because the former is mainly concerned with the assembly of organic molecular building blocks into well-defined crystalline structures via non-covalent bonds, while the latter relies on the utilization of stronger coordinate bonds to form extended networks by using polydentate ligands [15]. In this case, multidentate organic ligands containing O-donor or N-donor have been confirmed to play important roles in the construction of coordination polymers [16–18]. Among various organic ligands, polycarboxylate ligands are often employed as multifunctional bridging ligands to construct metal–organic coordination frameworks owing to their versatile coordination modes and their ability to act as H-bond acceptors and donors assembling supramolecular

structures [19–24], in which investigations of asymmetric dicarboxylates are fewer than symmetric dicarboxylates.

As a member of polycarboxylate ligands, the benzophenone-2,4'-dicarboxylic acid (H_2bdam) contains four potential metal binding sites and carboxyl groups can act as O-donors, which allows the formation of variable structures with different topology and dimensions constructed from different directions. A particular feature of the H_2bdam ligand is the variability in coordination modes and conformations it can display (Scheme 1). Therefore, the $(\text{bdam})^{2-}$ ligand may be an excellent candidate for the construction coordination polymers. However, to the best of our knowledge, investigations on H_2bdam ligand are scarce [25–29].

We also notice that the combination of metal ions with neutral N-donor ligands and anionic O-donor ligands can generate interestingly structures which cannot be obtained only through one type of ligand [30–33]. Structural elaboration and topological variance in these complexes can be enhanced by the incorporation of neutral ligands such as 4,4'-bipyridine (bpy), 2,2'-bipyridine (bpy), 1,2-bis(4-pyridyl)ethane (dpe) or 1,10-phenanthroline (phen) via adjustment of the carboxylate bridging mode [34–37]. They can not only interact with the metal centers through $\pi \dots \pi$ stacking interactions but also act as hydrogen bond donors and acceptors to adjust to different structures of complexes [38,39].

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With the aim of understanding the coordination chemistry of H₂bdam ligand and studying the influence on the framework structures of their complexes, we have recently engaged in the research of synthesizing the novel complexes with (bdam)²⁻ and N-donor ligands. Fortunately, four novel complexes were synthesized, namely, [Cd(bdam)(phen)₂]_n (**1**), [Cd(bdam)(bpy)]_n·nH₂O (**2**), [Zn(bdam)(bpy)]_n·nH₂O (**3**) and [Ag₄(bdam)₂(dpe)]_n (**4**). A detailed structural analysis of **1–4** proved the significance of the hydrogen bonds and π...π stacking interactions in proliferating the structures into 3D supramolecular framework. Especially, **4** possesses a 2D network structure based on octanuclear silver clusters cross-linked by H₂bdam and dpe ligands, in which there is significantly Ag...Ag interactions. The structural differences demonstrate that metal ions and N-donor auxiliary ligands have significant effects on the formation and structures of the final metal–organic coordination polymers. Herein, we report their syntheses, crystal structures and spectroscopic properties.

2. Experimental

2.1. Materials and methods

All chemicals and reagents were obtained from commercial sources without further purification. All reactions were carried out under hydrothermal conditions. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. IR spectra were recorded as KBr pellets on a Bruker EQUINOX55 spectrophotometer in the 4000–400 cm⁻¹ region. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermogravimetric analyses (TGA) were performed in a nitrogen atmosphere with a heating rate of 10 °C min⁻¹ with a NETZSCHSTA 449C thermogravimetric analyzer. The X-ray powder diffraction pattern was recorded with a Rigaku D/Max 3 III diffractometer.

2.2. Synthesis of complex **1**

A mixture of Cd(NO₃)₂·4H₂O (0.0309 g, 0.1 mmol), H₂bdam (0.0270 g, 0.1 mmol), phen (0.0396 g, 0.2 mmol) and NaOH (0.0080 g, 0.2 mmol) in molar ratio 1:1:2, in water (10 mL) was stirred for 30 min in air, then sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 160 °C for 96 h. After cooling to room temperature at a rate of 5 °C h⁻¹, the colorless block crystals were obtained in ca. 43% yield based on H₂bdam. *Anal. Calc.* for C₃₉H₂₄Cd₁N₄O₅: C, 63.21; H, 3.26; N, 7.56. Found: C, 63.25; H, 3.23; N, 7.59%. IR (KBr cm⁻¹) for **1**: 3448w, 3063w, 1656s, 1604m, 1380w, 1286m, 932w, 833s, 734m, 664w.

2.3. Synthesis of complex **2**

An identical procedure with **1** was followed to prepare **2** except that phen (0.0396 g, 0.2 mmol) was changed to 2,2'-bpy (0.0312 g, 0.2 mmol). The pale-yellow crystals were obtained in ca. 48% yield based on H₂bdam. *Anal. Calc.* for C₂₅H₁₈Cd₁N₂O₆: C, 54.12; H, 3.27; N, 5.05. Found: C, 54.17; H, 3.23; N, 5.08%. IR (KBr cm⁻¹) for **2**: 3435s, 3075w, 1680s, 1592s, 1550m, 1389s, 1289m, 1154w, 1091w, 929w, 845s, 736s, 668w.

2.4. Synthesis of complex **3**

An identical procedure with **1** was followed to prepare **3** except that Cd(NO₃)₂·4H₂O (0.0309 g, 0.1 mmol) was changed to Zn(Ac)₂·2H₂O (0.1 mmol, 0.0219 g). The pale-yellow block crystals were obtained in ca. 53% yield based on H₂bdam. *Anal. Calc.* for C₂₅H₁₈N₂O₆Zn: C, 59.13; H, 3.57; N, 5.52. Found: C, 59.11; H,

3.56; N, 5.49%. IR (KBr cm⁻¹) for **3**: 3460s, 3073w, 1661s, 1618s, 1550s, 1416m, 1289m, 1166w, 1098w, 945m, 851m, 778vs, 735s, 657w.

2.5. Synthesis of complex **4**

A mixture of AgNO₃ (0.0340 g, 0.2 mmol), H₂bdam (0.0270 g, 0.1 mmol), 1,2-dpe (0.0184 g, 0.1 mmol) and NaOH (0.0080 g, 0.2 mmol) in molar ratio 2:1:1, in water (10 mL) was stirred for 30 min in air, then sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 160 °C for 96 h. After cooling to room temperature at a rate of 5 °C h⁻¹, the colorless block crystals were obtained in ca. 46% yield based on H₂bdam. *Anal. Calc.* for C₄₂H₂₈Ag₄N₂O₁₀: C, 43.78; H, 2.45; N, 2.43. Found: C, 43.76; H, 2.46; N, 2.49%. IR (KBr cm⁻¹) for **4**: 3430w, 3055w, 1656s, 1605m, 1553s, 1384s, 1288w, 1016w, 935w, 839s, 736m, 668w.

2.6. X-ray crystallography

Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [40]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **1–4** are summarized in Table 1. Selected bond distances and bond angles are listed in Table S1.

3. Results and discussion

3.1. Synthesis

Hydrothermal synthesis has been proved to be an effective and powerful technique in the preparation of solid-state materials. In hydrothermal process, many factors may affect the formation and crystal growth of products, such as the type of initial reactants, metal center, solvent, the mole ratio of the reactants, pH value, reaction time and temperature. Complexes **1–2** were synthesized by using H₂bdam, Cd(NO₃)₂·4H₂O and NaOH with different N-donor auxiliary ligands under the same hydrothermal reaction conditions. As result, we obtain two complexes with different structures, different coordinate modes and different luminescence properties. Complexes **2** and **3** were obtained from the reactions between Cd²⁺/Zn²⁺, H₂bdam and bpy ligand under the same hydrothermal reaction conditions, which show different 1D chain structures. Complex **4** was synthesized using different metal ions and N-donor auxiliary ligands, metal ligand ratio as **2** under the same hydrothermal synthesis conditions. The results reveal that metal ions, especially their ionic radii and coordination numbers, have an obvious effect on the formation and the structures of complexes, which can induce H₂bdam ligand adjusting its coordination modes to form diverse structures. H₂bdam ligand has great ability to construct coordination architectures with different metal centers, adopting versatile coordination fashions from monodentate to chelating and bridging. Scheme 1 shows four coordination modes of (bdam)²⁻ ion observed in this work.

3.2. Crystal Structure of [Cd(bdam)(phen)₂]_n (**1**)

In the asymmetric unit of **1**, there are one Cd^{II} ion, one bdam²⁻ ion and two phen molecules. As shown in Fig. 1a, Each Cd^{II} ion is coordinated by four nitrogen atoms [Cd1–N1 = 2.516(4),

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