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Auxiliary ligand-assisted structural diversities of two coordination polymers with 2-hydroxyquinoline-4-carboxylic acid

Dasarath Mal [a], Rupam Sen [a], Paula Brandao [a], Fanian Shi [a], Rute A.S. Ferreira [b], Zhi Lin [a,*]

[a] *Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *Department of Physics, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal*

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ABSTRACT

The solvothermal reactions of $Cd(NO_3)_2 \cdot 6H_2O$ with 2-hydroxyquinoline-4-carboxylic acid (H_2hqc) and 4,4′-bipyridine (bpy) or trans-1,2-bi(4-pyridyl)ethylene (bpe) afforded two coordination polymers $[Cd(H\text{-}hqc)_2(bpy)(H_2O)_2]_n$ (**1**) and $[Cd(H\text{-}hqc)_2(bpe)_{0.5}]_n$ (**2**), respectively. The bipyridine based auxiliary ligands such as bpy and bpe were selected in order to analyze the effect of the length of auxiliary ligands on the formation of coordination polymers. Compounds **1** and **2** were characterized by elemental analysis, IR, and single crystal X-ray diffraction. Compound **1** shows a one-dimensional (1D) chain structure with linear topology while compound **2** shows 2D network with 3,6-c binodal net, having point symbol $\{3^2.4\}\{3^4.4^3.5^2.6^5.7\}$ and vertex symbol [3.3.6(2)][3.3.3.3.6(2).6(2).6(2).6(2).6(2).*.*.*.*.*]. The results show that the spacer lengths of N-donor ligands do effect the topological structures of cadmium(II) coordination polymers.

In the past decades, the design and construction of coordination polymers have attracted significant and sustained interest due to their fascinating range of structural topologies as well as their potential applications in catalysis, adsorption, separation, magnetism and luminescence [1–8]. However, it still remains a great challenge to control the formation and the structures of functional coordination polymers. As we knew, the formation of coordination polymers may be affected by many chemical and physical factors such as temperatures, solvents, pH values, N-donor/O-donor organic ligands, and metal ions [9–11]. A useful tactic is to design a series of reactions in similar conditions with only one factor changed. In such a case, the diversity in assembly and functionality of coordination polymer can be exclusively recognized to the change of the factor. Among them, the flexibility and rigidity of the N-donor ligands can directly influence the final structures of the resulting coordination polymers [12–16]. This is because flexible ligands can bend or rotate in some degrees, which may lead to the formation of the products with different topologies, though their reactions look fairly similar. Here, we focused our research on the auxiliary ligand-directed synthesis of the metal-carboxylate frameworks. The selection of appropriate multifunctional ligands in the design and synthesis of coordination polymers is a key step. In this study, nitrogen containing carboxylate ligand, 2-hydroxyquinoline-4-carboxylic acid (H_2hqc), is used because it has notable features as follows: (a) in which N atom is an excellent donor able to coordinate to varieties of metal ions and it is a rigid ligand which may support the formation of coordination polymer with high thermal stability; (b) the carboxyl group can offer plentiful coordination modes such as monodentate, chelating-bidentate, bridging bidentate and bridging-multidentate (Scheme 1) [17] to meet the coordination geometric requirement of metal centers and generate various structures and functional properties; and (c) H_2hqc is a multidentate N- or O-donor ligand that can be deprotonated to generate $Hhqc^-$ and hqc^{2-} with versatile metal-binding and hydrogen-bonding capabilities. Few works of the coordination polymers based on hqc have been reported [15,18,19]. For instance, Yuan et al. have reported pentanuclear Zn(II) coordination polymer based on H_2hqc ligand [18]. Feng and co-workers have reported photoluminescent properties of lanthanide coordination complexes with H_2hqc ligand [15]. Recently we have demonstrated the effect of length of N-donor auxiliary ligands on zinc coordination polymers of H_2hqc [19].

On the other hand, Cd(II)-containing coordination polymers have gained much current interest due to the capability to form bonds with different donors simultaneously, the large radius, various coordination modes, and extraordinary physical properties of Cd(II) ion. Cadmium(II) has been reported in tetrahedral, trigonal bipyramidal, octahedral, distorted pentagonal bipyramidal, and distorted dodecahedral coordination geometries [20,21]. This structural variation in Cd^{2+} coordination geometry arises from two effects: (i) the large ionic radius of Cd^{2+} allows flexibility in terms of coordination number; and (ii) the d^{10} electronic configuration of Cd^{2+} ions serves to eliminate ligand field effects and thereby permits diverse geometries. To date, researchers have reported a number of 1-D, 2-D, or 3-D Cd(II) coordination polymers and explored their prospective applications in catalysis, luminescent materials, NLO materials, phase transformation, and host–guest chemistry [22–37].

Can the spacer lengths of N-donor auxiliary ligands affect the coordination modes of hqc and the structures of the final coordination polymers when they work in the same system? With this question in mind, we employed two N donor auxiliary ligands with different spacer

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[*] Corresponding author. Tel.: +351 234370368; fax: +351 234370084.
E-mail address: zlin@ua.pt (Z. Lin).

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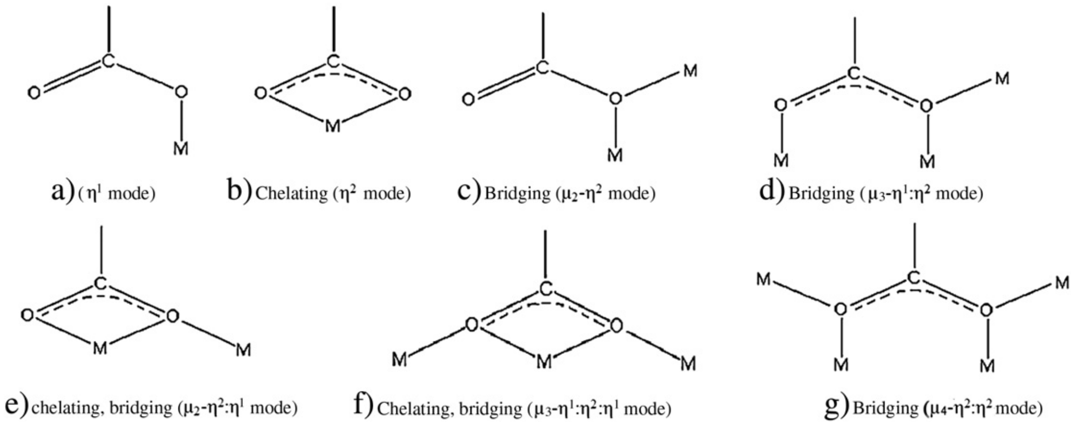

a) (η^1 mode) b) Chelating (η^2 mode) c) Bridging (μ_2-η^2 mode) d) Bridging (μ_3-η^1:η^2 mode)

e) chelating, bridging (μ_2-η^2:η^1 mode) f) Chelating, bridging (μ_3-η^1:η^2:η^1 mode) g) Bridging (μ_4-η^2:η^2 mode)

Scheme 1. Different coordination modes of carboxyl group.

lengths, bpy and bpe, and carried out the reactions with $Cd(NO_3)_2$ and hqc under solvothermal conditions.

In this contribution, two new cadmium-ion-based coordination polymers, $[Cd(H\text{-}hqc)_2(bpy)(H_2O)_2]_n$ (**1**) and $[Cd(H\text{-}hqc)_2(bpe)_{0.5}]_n$ (**2**), have been successfully prepared from the hydroxyl quinoline carboxylic acid in the presence of two different length-controllable auxiliary ligands, respectively.

Solvothermal reaction of a mixture of $Cd(NO_3)_2$, H_2hqc, bpy (molar ratio 1:1:1) in H_2O and DMF at 130 °C in a sealed Teflon-lined autoclave (inner Teflon beaker volume ca. 25 mL), for 3 day afforded colorless blocks of **1** in 30% yield based on the Cd [38]. Similar reaction of $Cd(NO_3)_2$, H_2hqc, bpe generated plate shape colorless crystals of **2** in 20% yield based on the Cd [38]. The different outcomes of the two similar reactions may be ascribed to the spacer lengths of bpy and bpe ligands, which will be described later in this article. Compounds **1** and **2** are air and moisture stable and insoluble in common organic solvents such as $CHCl_3$, MeCN, DMF and DMSO. The elemental analyses were consistent with their chemical formula.

A comparative study of the IR spectra (Figs. S1, S2 and S3) of compounds **1** and **2** with that of the free ligands gives some positive information regarding the binding sites of the 2-hydroxyquinoline-4-carboxylic ligand. The absence of strong IR bands around 1730 cm^{-1} in the spectra of compounds **1** and **2** indicates that the carboxylic group is deprotonated [39]. The Δ values, defined by Deacon and Phillips [40] for $\upsilon_{as}(COO-) - \upsilon_s(COO-)$, give some qualitative information which allows the correlation of the data of the infrared spectra with the coordination modes of metal carboxylates. The Δ values (ca. 235 cm^{-1}, Table S1) are consistent with the presence of bridging carboxylate. For non-bridging carboxylato coordination, this Δ separation is usually larger (ca. 350 cm^{-1}) [41].

Compound **1** crystallizes in a triclinic crystal system with space group of *P*1 [42]. Details of the X-ray crystallography of compound **1** are discussed in Supplementary section. As shown in Fig. 1a, the crystallographically unique Cd(II) is six-coordinated, as CdN_2O_4, by two N atoms from two different 4,4′-bpys, four O atoms from two terminal coordinated water molecules and two monodentate carboxyl groups. The average Cd – O and Cd – N bond distances are 2.318 and 2.303 Å, respectively. The bond angles around the Cd(II) ion are in the range of 85.63 to 179.35°. The selected bond distances and angles are listed in Table S2 in the Supporting Information. The donor ligand bpy acts as a connector to link two Cd atoms. The crystal structure of **1** consists of infinite $[Cd(H\text{-}hqc)_2(bpy)(H_2O)_2]$ chains (Fig. 1b and c). The monomeric units are connected by bpy bridging ligands and forming the 1D rigid linear chain along the (011) direction (Fig. 1b). Two coordinated water molecules, free nitrogen atom and free oxygen atom of the hydroxyl group of the hqc ligand produce large number of hydrogen bonding interactions. 1D chains are held together by strong intermolecular hydrogen bond interactions, ultimately giving rise to 3D supramolecular framework (Fig. S4). The significant hydrogen bonding parameters are collected in Table S3 in the Supporting Information.

Under the same experimental conditions as that in **1**, compound **2** was obtained when bpy ligand was replaced by bpe. Single crystal X-ray diffraction analysis reveals that compound **2** crystallizes in a monoclinic crystal system with space group C2/c [43]. There is only one crystallographically unique Cd(II) center in compound **2**, as shown in Fig. 2a. The cadmium center in compound **2** is seven-coordinated with distorted pentagonal bipyramidal geometry by one nitrogen atom (N101) from the bpe ligand and six oxygen atoms of carboxylate groups from five different hqc ligands. The Cd – N bond length is 2.241 Å and the Cd – O bond lengths are in a range of 2.246–2.571 Å. The carboxylate group of the hqc ligand adopts two types $\mu_2 - \eta^1{:}\eta^1$ bridging mode (see Scheme 1c) and $\mu_3 - \eta^1{:}\eta^2{:}\,\eta^1$ chelating, bridging mode (see Scheme 1f) and consequently linking three Cd(II) ions. The Cd(II) ions are linked by the carboxylate groups of the hqc ligands to generate 1D infinite Cd – O – Cd chains that run along the (010) direction, which are further connected to nitrogen atoms of bpe ligands to form an overall 2D coordination polymer (Fig. 2b). The topological analysis by TOPOS [44] revealed that the structure of compound **2** is 3,6-c binodal net (Fig. 2c) with point symbol $\{3^2.4\}\{3^4.4^3.5^2.6^5.7\}$ having vertex symbol [3.3.6(2)][3.3.3.3.6(2).6(2).6(2).6(2).6(2).*.*.*.*.*]. The point symbol corresponds to the topology type 3,6L29, which is convinced via the latest TTD database (76,179 entries and updated on 25th of Aug. 2013). Free nitrogen atom and free oxygen atom of the hydroxyl group of the hqc ligand create intermolecular hydrogen bonding interaction. This hydrogen bonding force plays important role to produce 3D network (Fig. S5).

Both compounds **1** and **2** were synthesized under the same solvothermal condition using different auxiliary ligands, bpy and bpe. For comparison with compound **1**, bpy is replaced by a longer spacer ligand, bpe. As extending bridging linkage, compound **2** displays a 2D coordination network. It is well known that divalent Cd(II) ion is a d^{10} system and has no crystal field stabilization energy. Therefore, Cd(II) ion can easily attain variable coordination mode: four, five, six, seven and eight. Here, the two compounds are constructed from the same carboxylate and the same ion, Cd. Moreover, the solvent system, reaction temperature and reaction time are all the same. The only different auxiliary N-donor bridging ligand is used, which results in two compounds with different structures and topologies. Such results clearly imply that the secondary neutral nitrogen ligands play a major role in determining the structural diversity: different lengths, from short bpy to long bpe, results in different coordination polymers i.e. from rigid linear one dimensional structure to two dimensional network structure. The combination of this work and the previous work on Zn(II) [19] indicates that both metal center and flexible auxiliary N-donor ligand determine the final structure. It is worth noting that although the nitrogen atom and oxygen atom of the hydroxyl group of hqc ligand are not