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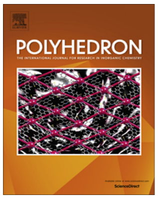

# Synthesis and characterization of new coordination polymers based on 2,3-/3,4-pyridinedicarboxylates and bispyridine ligands with structural diversity

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## ABSTRACT

New coordination polymers, formulated as $\{bpaH_2[Cu(\mu\text{-}2,3\text{-}pydc)_2]\}_n$ (**1**), $[Cd(\mu\text{-}2,3\text{-}pydc)(\mu\text{-}bpa)_{0.5}(H_2O)_2]_n$ (**2**), $\{[Co_2(\mu_4\text{-}3,4\text{-}pydc)_2(\mu\text{-}bpe)(H_2O)_2]\cdot H_2O\}_n$ (**3**) and $[Cu_2(pic)_4(\mu\text{-}4,4'\text{-}bipy)]\cdot(4,4'\text{-}bipy)\cdot 2H_2O$ (**4**) have been synthesized based on the bispyridine ligands; 1,2-bis(4-pyridyl)ethane (bpa), 1,2-bis(4-pyridyl)ethylene (bpe) and 4,4′-bipyridine (4,4′-bipy) along with dianionic 2,3- and 3,4-pyridinedicarboxylate (2,3-pydc and 3,4-pydc) and mono anionic picolinate (pic) ligands, respectively. All the complexes have been characterized by elemental and IR spectroscopy and single-crystal X-ray diffraction studies. **1** has proton transfer products of $bpaH_2$ cations and shows 1D double chain. Using of the 2,3-pydc and 3,4-pydc ligands in **2** and **3** in the presence of Cd(II) and Co(II) ions generate 1D → 2D inclined polycatenated structure in **2** and 4,5 connected $\{4^4\cdot6^2\cdot10^4\}\{4^4\cdot6^2\}$ 4,5T6 topology in **3**, respectively. The picolinate ligand in dinuclear structure of **4** was occurred by partial decarboxylation of 2,3-$pydcH_2$ in the process of the solvothermal reaction. 4,4′-Bipyridine molecules act as both a template *via* rare weak C–H···N interaction and a bridge between Cu(II) centers in the self-assembly process of supramolecular structure of **4**. Thermal decomposition behavior of complexes and luminescent property of **2** are also presented herein.

## 1. Introduction

Coordination polymers represent one of the most rapidly expanding field of material science during the last two decade owing to the diversity of structures with interesting topologies and their potential applications in gas storage, catalysis, magnetism and so on [1–8]. The structures of coordination polymers have a close relationship with their properties [9]. Nevertheless, when it comes to crystal engineering perspective, the structures with desired properties still remains a big challenge because of the abundance of intermolecular forces. Entangled networks are one of the most exotic type of coordination polymer architectures [10–12]. Coordination polymers having a 1D or 2D structure with bridging ligands tend to have large cavities. Often large cavities in the 1D ladder structures tend to polycatenate each other. Polycatenation of 1D ladder chains either in inclined or parallel fashion have been shown to generate higher dimensional coordination polymers, such as 1D → 2D and 1D → 3D [13,14].

2,3 and 3,4-Pyridinedicarboxylic acids (2,3-$pydcH_2$ and 3,4-$pydcH_2$) have proved to be interesting and versatile ligands and exhibit various coordination modes to furnish various structures with higher dimensionality [15–25]. Particularly, 2,3-pydc is able to chelating and suitable for metalloligand approach [26,27]. Moreover, it is strongly tend to form the kinetic products of 1D double-chain polymers through its coordination ability [17,21]. Picolinate ligand, which is a derivative of 2,3-pydc with absent of a carboxylic acid substituent at the 3-position, often acts as a bidentate chelating ligand through the nitrogen atom and one oxygen atom of the carboxylic group to form self-assembled metal–organic structures [28–36]. Moreover, $[Cu(pic)_2]$ complexes have been suggested as a potent antidiabetic agent [37].

It is known that bispyridine derivatives such as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane are multifunctional ligands largely used in the assembly of metal organic networks [38–41]. They act as bridging ligands to connect metal ions to form coordination

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polymers. Moreover, they can serve as template filling in the channel to stabilize the supramolecular networks [42]. The solvothermal method has been an encouraging technique in preparing highly stable, infinite coordination polymers. To date, several sort of in situ reactions have occurred under the solvothermal conditions including substitution of aromatic groups [43] and partial decarboxylation of aromatic dicarboxylates [44]. Although the carboxyl groups of carboxylate containing linkers may have been freed during the harsh solvothermal conditions, decarboxylation degree of ligands is compelling to be controlled [45].

Keeping these facts in mind we have used here 2,3-pydc and 3,4-pydc which have two adjacent carboxylate groups as a primary ligand and bispyridine derivatives as secondary ligands so that electron-rich anionic ligands can have supramolecular interactions with relatively electron deficient bispyridine ligands to form coordination polymers with Cu(II), Cd(II) and Co(II) ions.

Herein, we report four new coordination polymers with bispyridine ligands: $\{bpaH_2[Cu(\mu\text{-}2,3\text{-}pydc)_2]\}_n$ (**1**), $[Cd(\mu\text{-}2,3\text{-}pydc)(\mu\text{-}bpa)_{0.5}(H_2O)_2]_n$ (**2**), $\{[Co_2(\mu_4\text{-}3,4\text{-}pydc)_2(\mu\text{-}bpe)(H_2O)_2]\cdot H_2O\}n$ (**3**) and $[Cu_2(pic)_4(\mu\text{-}4,4'\text{-}bipy)]\cdot(4,4'\text{-}bipy)\cdot 2H_2O$ (**4**). Their structures have been determined by single crystal X-ray diffraction analyses. The crystal structures of these complexes, along with the effect of the bispyridine ligands, dicarboxylate and the metal ions on the topology of coordination polymers will be described and discussed in this paper. In addition, the luminescent property of complex **2** was also investigated.

## 2. Experimental

### 2.1. Measurements and materials

All starting materials were of analytical reagent grade and used as received without further purification. Elemental analyses for C, H, and N were carried out at the TÜBİTAK Marmara Research Centre. The IR absorption spectra were recorded in the range of 4000–400 $cm^{-1}$ by means of a Bruker Tensor 27 FT-IR spectrometer with KBr pellets. The photoluminescence (excitation and emission) spectrum for the solid sample of **2** was determined with a Perkin-Elmer LS-55 spectrophotometer using slit width of 8 nm excitation and 3 nm emissions at room temperature for the solid samples. Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in the static air atmosphere at a heating rate of 10 °C $min^{-1}$ in the temperature range 30–700 °C using platinum crucibles.

### 2.2. Crystallographic analyses

Suitable crystals of **1**–**4** were selected for data collection which was performed on a Bruker APEX-II diffractometer equipped with a graphite-monochromatic Mo $K_\alpha$ radiation at 296 K. The structures were solved by direct methods using SHELXS-97 [46] and refined by full-matrix least-squares methods on $F^2$ using SHELXL-97 [46] from within the WINGX [47] suite of software. All non-hydrogen atoms were refined with anisotropic parameters. The H atoms of C atoms were located from different maps and then treated as riding atoms with C–H distances of 0.93–0.97 Å. All other H atoms were located in a difference map refined subject to a DFIX restraint. Molecular diagrams were created using MERCURY [48]. Supramolecular analyses were made and the diagrams were prepared with the aid of PLATON [49]. Topological studies performed using the software package TOPOS Pro [50]. Details of data collection and crystal structure determinations are given in Table 1.

### 2.3. Preparation of the complexes

#### 2.3.1. $\{bpaH_2[Cu(\mu\text{-}2,3\text{-}pydc)_2]\}_n$ (*1*)

0.10 g $Cu(NO_3)_2\cdot 2.5H_2O$ (0.43 mmol) was mixed with an DMF-water solution (25 mL; (1:1)) of 2,3-pyd$cH_2$ (1.20 mmol, 0.20 g) and stirred for 20 min for mixing well. 1,2-Bis(4-pyridyl)ethane (0.54 mmol, 0.10 g) was dissolved in 10 mL ethanol. This ligand solution was slowly and carefully layered to the above mixed solution. The blue plate-like crystals were obtained after three weeks. The crystals were separated and washed with ethanol–water (1:1) mixture and dried. For **1**, 44% yield based on $Cu(NO_3)_2\cdot 2.5H_2O$. *Anal.* Calc. for $C_{26}H_{20}CuN_4O_8$ **1**: C, 53.84; H, 3.48; N, 9.66. Found: C, 53.93; H, 3.42; N, 9.59%. IR (KBr pellet)/$cm^{-1}$: 3076w, 3053w, 3012w, 1636vs, 1583s, 1514m, 1435m, 1358vs, 1263s, 1113m, 874m, 841s, 785w, 706m, 687m, 511m, 476m.

#### 2.3.2. $[Cd(\mu\text{-}2,3\text{-}pydc)(\mu\text{-}bpa)_{0.5}(H_2O)_2]_n$ (*2*)

A mixture of 0.39 g $Cd(CH_3COO)_2\cdot 2H_2O$ (1.2 mmol), 0.25 g 2,3-pyd$cH_2$ (1.5 mmol), 0.27 g 1,2-bis(4-pyridyl)ethane (1.2 mmol), 0.08 g KOH (1.5 mmol) and 35 mL of $EtOH/H_2O$ (1:1) was sealed in a 47 mL vial and heated at 130 °C for 72 h. After 72 h, yellow block crystals were collected, washed with DMF, and allowed to dry on filter paper at room temperature. For **2**, 51% yield based on $Cd(CH_3COO)_2\cdot 2H_2O$. *Anal.* Calc. for $C_{13}H_{13}CdN_2O_6$ (**2**) C, 38.49; H, 3.23; N, 6.91. Found: C, 38.54; H, 3.37; N, 6.77%. IR (KBr pellet)/$cm^{-1}$: 3406s, 3080w, 1632vs, 1581s, 1450m, 1383s, 1236m, 1103m, 1045m, 773m, 698m, 461w, 424w.

#### 2.3.3. $\{[Co_2(\mu_4\text{-}3,4\text{-}pydc)_2(\mu\text{-}bpe)(H_2O)_2]\cdot H_2O\}_n$ (*3*)

A mixture of 0.37 g $Co(CH_3COO)_2\cdot 4H_2O$ (1.2 mmol), 0.25 g (1.5 mmol) pyridine-3,4-dicarboxylic acid, 0.27 g 1,2-bis(4-pyridyl)ethylene (1.2 mmol), 0.035 g (1.5 mmol) LiOH and 35 mL of $EtOH/H_2O$ (1:1) was sealed in a 45 mL vial and heated at 150 °C for 72 h. Red block crystals were collected, washed with DMF, and allowed to dry on filterpaper at room temperature. For **3**, 62% yield based on $Co(CH_3COO)_2\cdot 4H_2O$. *Anal.* Calc. for $C_{26}H_{22}Co_2N_4O_{11}$ (**3**): C, 45.63; H, 3.24; N, 8.19. Found: C, 45.74; H, 3.41; N, 7.99%. IR (KBr pellet)/$cm^{-1}$: 3381s, 3250s, 3061s, 1641vs, 1610vs, 1566s, 1485s, 1411s, 1219s, 1188m, 1171m, 1128m, 1063m, 1015m, 989m, 833s, 708m, 677w, 552w, 438w, 411w.

#### 2.3.4. $[Cu_2(pic)_4(\mu\text{-}4,4'\text{-}bipy)]\cdot(4,4'\text{-}bipy)\cdot 2H_2O$ (*4*)

A mixture of 0.24 g $Cu(CH_3COO)_2\cdot H_2O$ (1.2 mmol), 0.25 g (1.5 mmol) pyridine-2,3-dicarboxylic acid, 0.22 g 4,4′-bipy (1.2 mmol), 0.059 g (1.5 mmol) NaOH and 30 mL of $EtOH/H_2O$/DMF (1:1:1) was sealed in a 45 mL vial and heated at 140 °C for 72 h. Blue crystals were collected, washed with DMF, and allowed to dry on filterpaper at room temperature. For **4**, 34% yield based on $Cu(CH_3COO)_2\cdot H_2O$. *Anal.* Calc. for $C_{44}H_{36}Cu_2N_8O_{10}$ (**4**): C, 54.83; H, 3.76; N, 11.63. Found: C, 54.72; H, 4.40; N, 10.83%. IR (KBr pellet)/$cm^{-1}$: 3448s, 3078s, 3033s, 1649vs, 1598vs, 1348s, 1219s, 1188m, 1171m, 1129m, 1012m, 973m, 712m, 643w, 552w, 453w.

## 3. Results and discussion

### 3.1. Synthesis and spectral characterization

Solvothermal and slow diffusion methods were attempted in the synthesis of complexes. Complex **1** could be obtained *via* slow diffusion method in a test tube. To apply slow diffusion method it is desired that bottom phase of the test tube should be more concentrated than top phase in order to avoid fast reaction of the phases. Moreover it is necessary that both of the phases completely dissolve. In the synthesis of **1**, the molar ratio of $Cu(NO_3)_2\cdot 2.5H_2O$/2,3-pyd$cH_2$