

# Syntheses, structures and properties of eight coordination polymers based on bis(imidazole) and biscarboxylate ligands



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## ABSTRACT

Eight coordination polymers  $\{[Co(bib)(ndc)] \cdot 0.5H_2O\}_n$  (**1**),  $\{[Co(bib)_{0.5}(aip)] \cdot H_2O\}_n$  (**2**),  $[Co(bib)(adc)]_n$  (**3**),  $\{[Co_2(bib)(adc)_2] \cdot 0.5H_2O\}_n$  (**4**),  $\{[Ni_2(bib)(adc)_2] \cdot 0.5H_2O\}_n$  (**5**),  $[Ni(bib)(hip)]_n$  (**6**),  $[Cd_2(bib)(bdc)_2]_n$  (**7**) and  $[Cd_2(bib)(bda)_2]_n$  (**8**) were synthesized by the hydrothermal reaction (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane, ndc = 1,4-naphthalenedicarboxylate, aip = 5-aminoisophthalate, adc = 1,3-adamantanedicarboxylate, hip = 5-hydroxyisophthalate, bdc = 1,2-benzenedicarboxylate, bda = 1,4-benzenediacetate). **1** consists of an unusual 4-fold interpenetrating 4-connected 3D **dia** network. **2** exhibits an unusual (3,4)-connected 2D network with the point symbol of  $(6 \cdot 8^2)(6^4 \cdot 8 \cdot 10)$ . **3** is an undulated 2D (4,4) network. **4** and **5** are isostructural showing the 1D triple-stranded chain with double adc and one bib bridges. **6** shows a special 2D (6,3) network, with six Ni(II) atoms at six corners and four hip and two double bib at six edges. **7** exhibits an unusual 6-connected self-catenated 3D network based on  $Cd_2(COO)_2$  dimer. **8** exhibits a 3-fold interpenetrating 3D **pcu** network based on  $Cd_2(COO)_2$  dimer. The diverse structures reveal that the metal centers and biscarboxylate building blocks play a significant role in the construction of the observed motifs. **1–4** exhibit good photocatalytic activity for the degradation of methyl orange. **7** and **8** exhibit the strong blue luminescence emissions.

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## 1. Introduction

The crystal engineering of coordination polymers (CPs) has been obtained great interest because of their unusual topologies and potential applications as functional materials for magnetism, gas storage, gas adsorption, gas separate, catalysis, luminescence and so on [1,2]. The center metal ions and organic bridging ligands are the key for the coordination polymers [3].

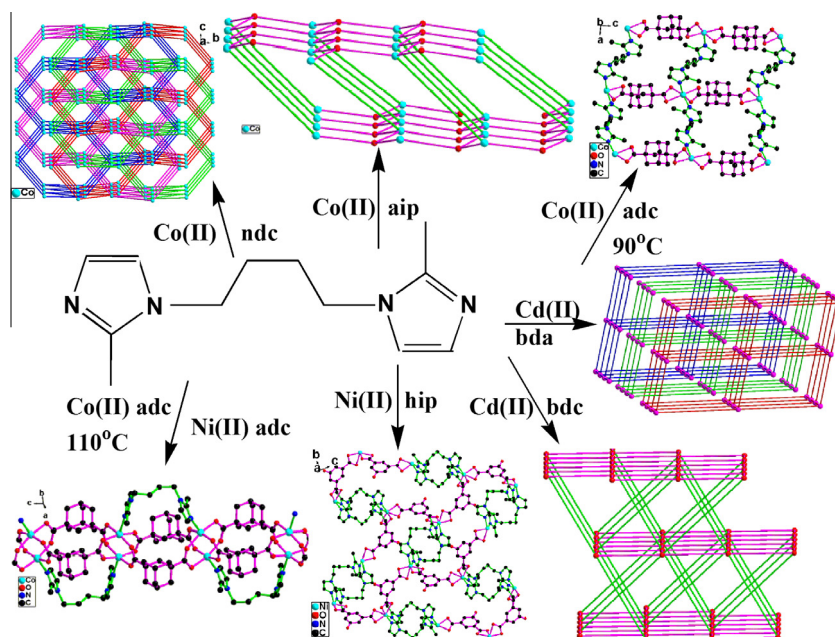
Flexible N-donor ligands such as the bis(imidazole) [4] and bis(triazole) [5] ligands are widely used to synthesis coordination polymers because flexible ligands can adopt diverse conformations according to the geometric needs of the center metal ions. Multicarboxylate ligands can influence the topologies of the coordination polymers, because that they can satisfy the charge-balance and can mediate the coordination of the metal centers, and more importantly, they can provide diverse ligands and coordination modes [6]. The coordination polymers based on flexible N-donor ligands and multicarboxylate mixed ligands can give unusual topologies and intriguing properties.

Methyl orange is one of the most stable azo organic dyes, which is widely used in the textile industry and is resistant to biodegradation. Decomposition of this dye molecule (methyl orange) into simple molecules can decrease the environment pollution. One important application of coordination polymers is the photocatalysis for the degradation of organic dyes [7–9].

We synthesized a lot of coordination polymers with flexible bis(imidazole) and bis(triazole) ligands in the previous work [10,11]. The long flexible ligand 1,4-bis(2-methyl-imidazol-1-yl)butane (bib) can adopt different conformations with respect to the relative orientations of the methyl ( $CH_3$ ) groups and can obtain novel entangled coordination polymers [12]. With this background information, in the present work, eight coordination polymers  $\{[Co(bib)(ndc)] \cdot 0.5H_2O\}_n$  (**1**),  $\{[Co(bib)_{0.5}(aip)] \cdot H_2O\}_n$  (**2**),  $[Co(bib)(adc)]_n$  (**3**),  $\{[Co_2(bib)(adc)_2] \cdot 0.5H_2O\}_n$  (**4**),  $\{[Ni_2(bib)(adc)_2] \cdot 0.5H_2O\}_n$  (**5**),  $[Ni(bib)(hip)]_n$  (**6**),  $[Cd_2(bib)(bdc)_2]_n$  (**7**) and  $[Cd_2(bib)(bda)_2]_n$  (**8**) were synthesized by the hydrothermal method using flexible bib and biscarboxylate ligands (bib = 1,4-bis(2-methyl-imidazol-1-yl)butane, ndc = 1,4-naphthalenedicarboxylate, aip = 5-aminoisophthalate, adc = 1,3-adamantanedicarboxylate, hip = 5-hydroxyisophthalate, bdc = 1,2-benzenedicarboxylate, bda = 1,4-benzenediacetate) (Scheme 1). **1–8** show the diverse structures. **1–4** exhibit good photocatalytic activity for the degradation of methyl orange. The luminescence of **7** and **8** was investigated.

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**Scheme 1.** Schematic view of the syntheses and structures of eight coordination polymers.

## 2. Experimental

### 2.1. General considerations

All reagents were of analytical grade and used without further purification. Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. IR spectra were obtained for KBr pellets on a Nicolet 170SX FT-IR spectrophotometer in the 4000–400  $\text{cm}^{-1}$  region. The luminescence measurements were carried out in the solid state at room temperature and the spectra were collected with a Perkin–Elmer LS50B spectrofluorimeter. TGA was carried out using a Thermal Analyst 2100 TA Instrument and SDT 2960 Simultaneous TGA–DTA Instrument in flowing dinitrogen at a heating rate of 10  $^{\circ}\text{C}/\text{min}$ .

### 2.2. Synthesis of $\{[\text{Co}(\text{bib})(\text{ndc})] \cdot 0.5\text{H}_2\text{O}\}_n$ (**1**)

A solution of  $\text{H}_2\text{ndc}$  (0.2 mmol) in 8 mL  $\text{H}_2\text{O}$  was adjusted to pH 6 with dilute NaOH solution. Then bib (0.2 mmol) in 5 mL EtOH and  $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  (0.2 mmol) were added with stirring. The mixture was added to a 25 mL Teflon-lined stainless autoclave and this was sealed and heated to 110  $^{\circ}\text{C}$  for 2 days and then cooled to room temperature to give the red crystals **1** in 52% yield. *Anal. Calc.* for  $\text{C}_{24}\text{H}_{25}\text{CoN}_4\text{O}_{4.50}$  (**1**): C, 57.61; H, 5.03; N, 11.20. Found: C, 57.56; H, 5.01; N, 11.16%. IR( $\text{cm}^{-1}$ , KBr): 3422w, 3137w, 2941w, 1587m, 1568m, 1506w, 1481w, 1458w, 1397m, 1355s, 1280w, 1259m, 1151m, 1076w, 1001w, 830s, 787s, 738m.

### 2.3. Synthesis of $\{[\text{Co}(\text{bib})_{0.5}(\text{aip})] \cdot \text{H}_2\text{O}\}_n$ (**2**)

The synthetic procedure of **2** was similar to that for **1**, except that  $\text{H}_2\text{aip}$  (0.2 mmol) was used instead of  $\text{H}_2\text{ndc}$ . The red crystals **2** in 37% yield was obtained. *Anal. Calc.* for  $\text{C}_{14}\text{H}_{16}\text{CoN}_3\text{O}_5$  (**2**): C, 46.04; H, 4.42; N, 11.51. Found: C, 45.88; H, 4.38; N, 11.46%. IR( $\text{cm}^{-1}$ , KBr): 3250w, 3147w, 1560s, 1498w, 1476m, 1441m, 1370w, 1342m, 1322m, 1277w, 1249w, 1130w, 1068s, 1000m, 799m, 727s, 677w.

### 2.4. Synthesis of $[\text{Co}(\text{bib})(\text{adc})]_n$ (**3**)

A solution of  $\text{H}_2\text{adc}$  (0.2 mmol) in 8 mL  $\text{H}_2\text{O}$  was adjusted to pH 6 with dilute NaOH solution. Then bib (0.2 mmol) in 5 mL EtOH and  $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$  (0.2 mmol) were added with stirring. The mixture was added to a 25 mL Teflon-lined stainless autoclave and this was sealed and heated to 90  $^{\circ}\text{C}$  for 2 days and then cooled to room temperature to give the red crystals **3** in 48% yield. *Anal. Calc.* for  $\text{C}_{24}\text{H}_{32}\text{CoN}_4\text{O}_4$  (**3**): C, 57.71; H, 6.46; N, 11.22. Found: C, 57.63; H, 6.35; N, 11.15%. IR( $\text{cm}^{-1}$ , KBr): 2925w, 1542s, 15206m, 1472w, 1417s, 1379m, 1277w, 1216w, 1153m, 1128w, 1002w, 817w, 760w, 735m, 670m.

### 2.5. Synthesis of $\{[\text{Co}_2(\text{bib})(\text{adc})_2] \cdot 0.5\text{H}_2\text{O}\}_n$ (**4**)

The synthetic procedure of **4** was similar to that for **1**, except that  $\text{H}_2\text{adc}$  (0.2 mmol) was used instead of  $\text{H}_2\text{ndc}$ . The blue crystals **4** were obtained in 41% yield. *Anal. Calc.* for  $\text{C}_{36}\text{H}_{47}\text{Co}_2\text{N}_4\text{O}_{8.50}$  (**4**): C, 54.76; H, 6.00; N, 7.10. Found: C, 54.63; H, 5.89; N, 7.04%. IR( $\text{cm}^{-1}$ , KBr): 2915w, 2854w, 1616s, 1558m, 1508m, 1456w, 1401s, 1375w, 1312w, 1282m, 1128w, 1008w, 831w, 797m, 669m.

### 2.6. Synthesis of $\{[\text{Ni}_2(\text{bib})(\text{adc})_2] \cdot 0.5\text{H}_2\text{O}\}_n$ (**5**)

The synthetic procedure of **5** was similar to that for **4**, except that  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.2 mmol) was used instead of  $\text{Co}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$ . The green crystals **5** were obtained in 38% yield. *Anal. Calc.* for  $\text{C}_{36}\text{H}_{47}\text{N}_4\text{Ni}_2\text{O}_{8.50}$  (**5**): C, 54.79; H, 6.00; N, 7.10. Found: C, 54.72; H, 5.93; N, 7.05%. IR( $\text{cm}^{-1}$ , KBr): 2889m, 2854m, 1607s, 1542m, 1509m, 1480w, 1449m, 1425s, 1401s, 1377w, 1311w, 1281w, 1127w, 1011w, 831w, 772s, 697m.

### 2.7. Synthesis of $[\text{Ni}(\text{bib})(\text{hip})]_n$ (**6**)

The synthetic procedure of **6** was similar to that for **5**, except that  $\text{H}_2\text{hip}$  (0.2 mmol) was used instead of  $\text{H}_2\text{adc}$ . The green crystals **6** were obtained in 41% yield. *Anal. Calc.* 12.18%. IR( $\text{cm}^{-1}$ , KBr): 3441w, 2815m, 1617s, 1509m, 1451m, 1420m, 1402s,

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