Four Cu(II)/Co(II) coordination polymers based on N,N′-di(3-pyridyl)sebacidciamide: influence of different carboxylate ancillary ligands on structures and properties

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ABSTRACT
Four Cu(II)/Co(II) coordination polymers, [Cu(L)(BDC)(H₂O)]·3H₂O (1), [Cu(L)(DNBA)], (2), [Co(L)(DNBA)], (3), and [Co(L)(NIPH)(H₂O)]·H₂O (4) (H₂BDC = 1,4-benzenedicarboxylic acid, HDNBA = 3,5-dinitrobenzoic acid, H₂NIPH = 5-nitroisophthalic acid, L = N,N′-di(3-pyridyl)sebacidciamide), have been synthesized under hydrothermal conditions. The structures of 1–4 have been determined by single-crystal X-ray diffraction analyses and 1–4 were further characterized by infrared spectroscopy and thermogravimetric analyses. Complex 1 is a 2-D polymeric layer with a 4-connected sql topology. Complex 2 displays a 1-D zigzag chain. Complex 3 possesses a 1-D double-chain structure. Complex 4 exhibits a ribbon chain based on the 1-D [Co–L]ₙ meso-helical chain. Adjacent layers for 1 and adjacent chains for 2–4 are further linked by hydrogen bonding or π–π stacking interactions to form 3-D supramolecular networks. The differences of carboxylates and metal ions show significant effect on the ultimate architectures of the four complexes. Thermal stabilities, fluorescent properties and photocatalytic activities of 1–4 were also studied.

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1. Introduction

Coordination polymers have attracted interest for interesting structures and potential applications in photoluminescence, magnetism, catalysis, molecular recognition, gas storage, and separation [1–4]. Construction of coordination polymers can be realized by applying an effective method involving a mixed-ligand assembly system, where deliberate structural changes of organic ligands can dramatically change final structures [5–8]. Coordination polymers including 1-D, 2-D, or 3-D coordination framework based on the mixed-ligand systems containing N-donor heterocyclic ligands and O-donor carboxylates ligands have been obtained [9–12]. For example, Wang et al. have reported two threefold interpenetrating Co(II) coordination polymers based on 1,4-benzenedicarboxylic acid and length-modulated bisimidazole ligands ([Co(BDC)(bib)(H₂O)]n and [Co(BDC)(bibp)])n (H₂BDC = 1,4-benzenedicarboxylic acid, bib = 1,4-bis(1-imidazolyl)benzene, and bibp = 4,4′-bis(imidazolyl)biphenyl) [13]. Wen et al. obtained two Cu(II) coordination polymers derived from a multidentate N-donor ligand and two different dicarboxylates, [Cu(3,3′-tmbpt)(m-BDC)]·H₂O and [Cu(3,3′-tmbpt)(BDC)]·2H₂O, (3,3′-tmbpt = 1-((1H-1,2,4-triazol-1-yl)methyl)-3,5-bis(3-pyridyl)-1,2,4-triazole, m-H₂BDC = 1,3-benzenedicarboxylic acid) [14]. According to previous reports, the flexible bis(pyridyl)-bis(amide) ligands with diverse spacers –(CH₂)ₙ– (n = 0, 1, 2, ⋯, 8, 10, scheme S1), with relatively flexible conformations and amides able to form hydrogen bonds, have proven to be outstanding bridging linkers to construct coordination polymers [15–17]. For example, by introducing the flexible ligand N,N′-di(4-pyridyl)adipoamide (n = 4) into the Zn(II)-2,6-H₂ndc (2,6-naphthalene-dicarboxylic acid) system, Cao’s group prepared a framework of 2-D → 3-D inclined polycatenation based on 4₄-sql layer, which shows good thermal stability and photoluminescence [18]. Chen’s group has synthesized a variety of transition metal Zn(II)/Cd(II)/Ni(II) coordination polymers by combining the flexible bis(pyridyl)-bis(amide) ligands with different –(CH₂)ₙ– (n = 4, 6, 10) spacers and aromatic dicarboxylic acids [19, 20]. More recently, our group has reported a series of Cu(II)/Co(II) complexes derived from the flexible bis(pyridyl)-bis(amide) ligands with various spacer lengths (n = 0, 1, 2, 4, 5, 6, 8) and different aromatic polycarboxylates, which exhibit good photocatalytic activities or electrochemical behavior [16, 21–23]. However, coordination polymers constructed from flexible N,N′-di(3-pyridyl)sebacidiamide (L, n = 8) are quite rare [16, 23, 24] with only three Cu(II) complexes and one Co(II) complex based on L and aromatic carboxylic acids reported [16, 23]. Based on our previous studies, metal–organic complexes derived from the mixed ligands of flexible bis(pyridyl)-bis(amide) ligands and aromatic carboxylates are anticipated to possess significant photocatalytic ability to degrade organic dyes, which also prompts us to initiate this study.

In this article, we focus on assembly reactions of the flexible L with copper(II) or cobalt(II) via hydrothermal synthetic methods with three different benzene carboxylic ligands (H₂BDC, HDNBA = 3,5-dinitrobenzoic acid, H₂NIPH = 5-nitroisophthalic acid), and prepared four coordination polymers, [Cu(L)(BDC)(H₂O)]·3H₂O (1), [Cu(L)(DNBA)]₂ (2), [Co(L)₂(DNBA)]₂ (3), and [Co(L)(NIPH)(H₂O)]·H₂O (4). Influences of carboxylic acid and metal ion on the structural diversities of 1–4 are discussed. Fluorescence properties and photocatalytic activities of these complexes have also been investigated.

2. Experimental

2.1. Materials and methods

L was prepared by the literature method [25]. All other chemical reagents were commercially obtained and used without purification. The elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C elemental analyzer. FT-IR spectra (KBr pellets) were measured on a Varian FT-IR 640 spectrometer with KBr pellets from 500 to 4000 cm⁻¹. Thermogravimetric analyses were taken on a Pyris Diamond TG–DTA instrument. The fluorescence spectra were taken on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. UV–vis absorption spectra were obtained using an SP-1900 UV–vis spectrophotometer.
2.2. Preparation of the complexes

2.2.1. Synthesis of [Cu(L)(BDC)(H₂O)]·3H₂O (1)
A mixture of CuCl₂·2H₂O (0.034 g, 0.2 mmol), H₂BDC (0.025 g, 0.15 mmol), L (0.036 g, 0.10 mmol), H₂O (12 mL), and NaOH (0.018 g, 0.45 mmol) was stirred for 30 min, then transferred and sealed in a 25-mL Teflon reactor, which was heated at 120 °C for 4 days leading to blue block crystals, which were washed by water and dried in air. Yield: −27% (based on Cu). Anal. Calcd for C₂₈H₃₈CuN₄O₁₀: C, 51.41; H, 5.85; N, 8.57%. Found: C, 51.62; H, 5.65; N, 8.42%. IR (KBr, cm⁻¹): 3548m, 3476m, 3412s, 3243w, 2927w, 2849w, 2364w, 2332w, 1667w, 1615s, 1557s, 1473m, 1427s, 1376s, 1279m, 1118s, 936w, 878w, 756m, 697w, 616s, 535w.

2.2.2. Synthesis of [Cu(L)(DNBA)₂] (2)
The synthesis of 2 is similar to that for 1 except for HDNBA (0.035 g, 0.15 mmol) substituted for H₂BDC, and a different amount of NaOH (0.014 g, 0.35 mmol) was added to adjust the pH. Yield: −34% (based on Cu). Anal. Calcd for C₃₄H₃₂CuN₈O₁₄: C, 48.60; H, 3.84; N, 13.34%. Found: C, 48.47; H, 3.95; N, 13.52%. IR (KBr, cm⁻¹): 3554m, 3470m, 3406s, 3101w, 2927w, 2849w, 2358m, 2332w, 1695m, 1615s, 1537s, 1485m, 1460w, 1421w, 1389m, 1337s, 1292w, 1246w, 1110s, 917w, 878w, 813w, 723s, 620s, 509m.

2.2.3. Synthesis of [Co(L)₂(DNBA)₂] (3)
Synthesis of 3 is similar to that for 2 except that CuCl₂·2H₂O was replaced by Co(NO₃)₂·3H₂O (0.048 g, 0.20 mmol). Yield: −40% (based on Co). Anal. Calcd for C₅₄H₅₈CoN₁₂O₁₆: C, 54.50; H, 4.91; N, 14.12%. Found: C, 54.39; H, 4.78; N, 14.30%. IR (KBr, cm⁻¹): 3463m, 3418s, 3314w, 3270w, 2927m, 2850m, 2362m, 1679s, 1621s, 1551s, 1485s, 1421s, 1349s, 1162m, 1110m, 1027w, 956m, 917w, 781s, 723s, 704w, 613m, 561w, 517w.

2.2.4. Synthesis of [Co(L)(NIPH)(H₂O)]·H₂O (4)
Synthesis of 4 is similar to that for 3 except for H₂NIPH (0.032 g, 0.15 mmol) substituted for HDNBA and a different amount of NaOH (0.016 g, 0.40 mmol) added to adjust the pH. Yield: −33% (based on Co). Anal. Calcd for C₂₈H₃₃CoN₅O₁₀: C, 51.07; H, 5.05; N, 10.63%. Found: C, 51.23; H, 5.19; N, 10.42%. IR (KBr, cm⁻¹): 3405s, 3243m, 3069s, 2927m, 2849m, 2364m, 2326w, 1678s, 1608s, 1557s, 1486m, 1414s, 1350s, 1298m, 1220w, 1194m, 1162m, 1110m, 1020w, 930m, 801s, 729s, 639m, 554m.

2.3. X-ray crystallography
Crystallographic data for 1–4 were collected using a Bruker Apex CCD diffractometer (Mo-Kα radiation, graphite monochromator, λ = 0.71073 Å for 1–3, λ = 0.71069 Å for 4) by ω scan mode. The structures for 1–4 were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares with SHELXL [26]. Metal ions in the compounds were located from the E-maps, and all non-hydrogen atoms were refined with anisotropic thermal parameters on F². The hydrogens of the organic ligands were placed in geometrically idealized positions and refined isotropically. The hydrogens of lattice water and coordinated water in 1–4 were added by difference Fourier maps. All relevant crystallographic data for 1–4 are presented in table 1. The coordination modes of metal ions and organic ligands in 1–4 are listed in table 2. Selected bond distances and angles are listed in tables S1–S4. The related hydrogen bonding geometries of 1–4 are given in table S5. For 1–4, their crystallographic data for the structures have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1041875–1041878. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.
3. Results and discussion

3.1. Description of the structure

3.1.1. \([\text{Cu(L)(BDC)}(\text{H}_2\text{O})]\)·3\(\text{H}_2\text{O}\) (1)

Single-crystal X-ray structural analysis reveals that 1 possesses a 2-D layered framework constructed by \([\text{Cu(BDC)}]_n\) linear chains and 1-D \([\text{Cu(L)}]_n\) zigzag chains, which are further extended into a 3-D supramolecular network by hydrogen bonding interactions. One \(\text{Cu(II)}\), one \(\text{L}\), one \(\text{BDC}\), one coordinated water, and three lattice waters lie in the asymmetric unit of 1. The crystallographically independent \(\text{Cu(II)}\) ion is coordinated by two pyridyl nitrogens from two \(\text{L}\) and three oxygens from two \(\text{BDC}\) anions and one coordinated water (figure 1(a)) [the distances: \(\text{Cu}1–\text{N}1 = 2.060(3)\,\text{Å}, \text{Cu}1–\text{N}2 = 2.038(3)\,\text{Å}, \text{Cu}1–\text{O}1 = 1.935(3)\,\text{Å}, \text{Cu}1–\text{O}4\#1 = 1.973(2)\,\text{Å}, \text{Cu}1–\text{O}1\text{W} = 2.312(3)\,\text{Å}]\), displaying a distorted pyramidal coordination environment. The BDC anion is bis(monodentate) bridging, connecting adjacent \(\text{Cu(II)}\) ions to give a 1-D \([\text{Cu(BDC)}]_n\) linear chain (table 2 and figure S1(a)). The bidentate \(\text{L}\) ligands show two kinds of coordination conformations: \(\text{La}\) and \(\text{Lb}\) (table 2). \(\text{La}\) and \(\text{Lb}\) alternately link \(\text{Cu(II)}\) ions to generate a 1-D \([\text{Cu–La–Cu–Lb}]_n\) zigzag chain (figure S1(b)), in which the non-bonding \(\text{Cu1}⋯\text{Cu1}\) distances are 21.970 Å (linked by \(\text{La}\)) and 21.849 Å (linked by \(\text{Lb}\)). The 1-D \([\text{Cu(BDC)}]_n\) chains and 1-D \([\text{Cu–La–Cu–Lb}]_n\) chains combine to build the 2-D coordination framework of 1 (figure 1(b)), in which there are two kinds of grids with different sizes: 16.46 × 30.30 Å² and 16.48 × 30.46 Å². In the 2-D layer, the \(\text{Cu(II)}\) ion links two \(\text{L}\) ligands and two \(\text{BDC}\) ligands as a four-connected node. The \(\text{L}\) or \(\text{BDC}\) ligands bridging two metal ions serve as linkers. Thus, the 2-D structure of 1 can be classified as a four-connected (4,4) grid layer with sql topology (figure 1(c)). The neighboring 2-D layers are extended into a 3-D supramolecular network by the hydrogen bonding interactions between \(\text{N4}\) of amide groups and the carboxyl \(\text{O2}\) of \(\text{BDC}\) \([\text{N}(4)–\text{H}(4\text{A})⋯\text{O}(2) = 3.093(5)\,\text{Å}]\), between the lattice water (\(\text{O1W}\)) and the lattice water (\(\text{O4W}\)) \([\text{O}1\text{W}–\text{H}1\text{WA}⋯\text{O}4\text{W} = 2.744(6)\,\text{Å}]\), as well as between the lattice water molecules (\(\text{O4W}\)) and the carboxyl oxygens (\(\text{O3}\) and \(\text{O5}\)) of \(\text{BDC}\) ligands \([\text{O}4\text{W}–\text{H}4\text{WA}⋯\text{O}3 = 2.902(6)\,\text{Å}, \text{O}4\text{W}–\text{H}4\text{WB}⋯\text{O}5 = 2.891(5)\,\text{Å}]\), as shown in figure 1(d).

Table 1. Crystal and refinement data for 1–4.

| Complex | 1 | 2 | 3 | 4 |
|---------|---|---|---|---|
| Empirical formula | \(\text{C}_{28}\text{H}_{38}\text{Cu}_{12}\text{O}_{10}\) | \(\text{C}_{34}\text{H}_{32}\text{Cu}_{16}\text{O}_{14}\) | \(\text{C}_{54}\text{H}_{58}\text{Cu}_{24}\text{O}_{16}\) | \(\text{C}_{28}\text{H}_{33}\text{Cu}_{12}\text{O}_{10}\) |
| \(F_w\) | 654.16 | 840.22 | 1190.05 | 658.52 |
| Crystal system | Triclinic | Triclinic | Triclinic | Triclinic |
| Space group | \(P–1\) | \(P–1\) | \(P–1\) | \(P–1\) |
| \(a\) (Å) | 9.5034(9) | 6.7986(8) | 9.3496(6) | 10.000(5) |
| \(b\) (Å) | 10.8157(10) | 11.1194(14) | 11.2512(7) | 13.242(5) |
| \(c\) (Å) | 16.1791(15) | 13.3024(16) | 13.4415(9) | 13.577(5) |
| \(\alpha\) (°) | 101.717(2) | 87.729(2) | 93.3950(10) | 65.397(5) |
| \(\beta\) (°) | 101.717(2) | 87.729(2) | 93.3950(10) | 65.397(5) |
| \(\gamma\) (°) | 101.717(2) | 87.729(2) | 93.3950(10) | 65.397(5) |
| \(V\) (Å³) | 1474.7(2) | 950.7(2) | 1383.7(15) | 1574.6(11) |
| \(Z\) | 2 | 1 | 1 | 2 |
| \(T\) (K) | 296(2) | 296(2) | 296(2) | 296(2) |
| \(D_\infty\) (g cm⁻³) | 1.473 | 1.468 | 1.428 | 1.389 |
| \(F(000)\) | 686 | 433 | 621 | 686 |
| \(R_\text{p}^2\) | 1.030 | 1.029 | 1.060 | 1.077 |
| \(R_\text{R}^2\) | 1.157 | 1.157 | 1.157 | 1.157 |
| \(\mu\) | 0.0362 | 0.0362 | 0.0362 | 0.0362 |
| \(\theta\) (°) | 1.29–25.00 | 1.89–25.00 | 1.53–25.00 | 1.65–25.00 |
| \(\phi\) (°) | 0.0536 | 0.0440 | 0.0417 | 0.0383 |
| \(wR_\text{p}^2\) (all data) | 0.1443 | 0.1105 | 0.1146 | 0.1036 |

\[R_1 = \frac{\sum |F_o| − |F_c|}{\sum |F_o|},\]
\[wR_2 = \frac{\sum [w(F_o)^2 − F_c^2)]^2}{\sum [w(F_o)^2)]^2}.\]
3.1.2. \([\text{Cu(L)(DNBA)}]_{2}\) (2)

Similar to the synthesis of 1, when H$_2$BDC was replaced by HDNBA, 2 was obtained. Single-crystal X-ray diffraction analysis indicates that 2 is a simple 1-D wave-like chain, and its asymmetric unit contains one Cu(II) ion, one L, and one DNBA anion. The coordination environment around Cu(II) is shown in figure 2(a); Cu(II) is four-coordinated by two carboxyl oxygens (O3 and O7) from two DNBA anions \([\text{Cu1−O3} = 1.984(2) \text{ Å, Cu1−O3#1} = 1.984(2) \text{ Å}]\) and two pyridyl nitrogens (N1 and N3) from two L \([\text{Cu1−N1} = 1.980(2) \text{ Å, Cu1−N1#1} = 1.980(2) \text{ Å}]\), displaying a distorted square-planar geometry. In 2, L is bidentate connecting two Cu(II) ions \([\text{Cu−Cu distance: 21.713 Å}]\) to give a 1-D [Cu-L]$_n$ wave-like chain (figure S2(a)), and the dihedral angle between two pyridine rings is 0° (table 2). The DNBA anion having only one carboxyl group is monodentate; the dihedral angle between its carboxyl group and benzene ring is 4.524°. DNBA anions are connected to both sides of the 1-D [Cu-L]$_n$ chain (figure 2(b)), which cannot extend the 1-D chain into the higher dimensional framework owing to two terminal nitro groups. Adjacent 1-D chains are connected to form a 2-D supramolecular layer by N−H⋯O hydrogen bonds between the amide groups of L ligands and carboxyl oxygen of DNBA anions \([\text{N2−H2A⋯O4} = 2.939(3) \text{ Å}]\) (figure S2(b)). The neighboring 2-D layers are linked by C−H⋯O hydrogen bonding interactions to form a 3-D supramolecular architecture \([\text{C4−H4A⋯O1} = 3.144(4) \text{ Å, C21−H21A⋯O14} = 3.424(4) \text{ Å}]\) (figure 2(c)).
Single-crystal X-ray analysis reveals that 3 is a 1-D coordination chain based on [Co$_2$(L)$_2$] dinuclear loops and DNBA anions. The fundamental building unit of 3 contains one Co(II), one L, and one DNBA anion. Figure 3(a) depicts the coordination environment of Co(II) ion, which is four-coordinated by four pyridyl nitrogens of four different L ligands [Co1–N1, Co1–N1#1, 2.174(5) Å; Co1–N4#2, Co1–N4#3, 2.211(5) Å], and two carboxyl oxygens of two DNBA anions [Co1–O3, Co1–O3#1, 2.088(4) Å] to give a distorted octahedral geometry. In 3, L bridges two Co(II) ions through its two pyridyl nitrogens exhibiting a bidentate coordination with Co⋯Co distance of 20.938 Å; the dihedral angle between two pyridine rings is 82.326° (table 2). Furthermore, two L through their pyridyl nitrogens simultaneously connects two Co(II) ions to form a [Co$_2$(L)$_2$] dinuclear loop (figure S3(a)), which is different from the 1-D [Cu–L]$_n$ wave-like chain for 2. Adjacent [Co$_2$(L)$_2$] dinuclear loops are linked by sharing Co(II) ions to generate a 1-D [Co$_2$(L)$_2$]$_n$ double-chain structure (figure S3(b)). Similar to that in 2, the monodentate DNBA anion coordinates to Co(II) and hangs on both sides of the 1-D [Co$_2$(L)$_2$]$_n$ double-chain (figure 3(b) and figure S3(c)). For each DNBA anion, the dihedral angle between the carboxyl group and benzene ring is 25.533°, which

| Complex | Metal(II) ion(s) | The flexible bis(pyridyl)-bis(amide) ligand | Dihedral angle (°) | Carboxylate |
|---------|-----------------|------------------------------------------|-------------------|-------------|
| 1       | Cu         | L$^a$                                    | 0                 | Cu⋯Cu distance: 21.970 Å |
| 2       | Cu         | L$^b$                                    | 0                 | Cu⋯Cu distance: 21.849 Å |
| 3       | Co         | L$^a$                                    | 82.326            | Co⋯Co distance: 20.938 Å |
| 4       | Co         | L$^b$                                    | 0                 | Co⋯Co distance: 19.153 Å |

3.1.3. [Co(L)$_2$(DNBA)$_2$] (3)

Table 2. Coordination modes of Cu(II)/Co(II) ions, the flexible bis(pyridyl)-bis(amide) ligand, and carboxylates in 1–4.
is markedly different from that in \(\text{2}\). The 1-D chains of \(\text{3}\) are linked by hydrogen bonding interactions between the amide nitrogen of \(L\) and carboxyl oxygen of DNBA anions \([\text{N3–H3B⋯O4} = 2.844(7) \text{ Å}]\) to build a 2-D supramolecular layer (figure S3(d)). Then, the 2-D supramolecular layers are further extended.
into a 3-D supramolecular architecture by C–H⋯O hydrogen bonding interactions between the C1 of L and oxygen of nitro groups from DNBA anions [C1–H1A⋯O6 = 3.259(4) Å], between C8 of L and the amide oxygens of L [C8–H8B⋯O1 = 3.335(18) Å], as shown in figure 3(c).

Figure 4. (a) The coordination environment for Co(II) for 4; (b) The 1-D ribbon chain of 4; (c) The 3-D supramolecular structure formed by hydrogen bonding and π–π stacking interactions in 4.
3.1.4. \([\text{Co(L)(NIPH)}(\text{H}_2\text{O})]\cdot\text{H}_2\text{O} (4)\)

Single-crystal X-ray analysis reveals that 4 is a 1-D ribbon structure formed by Co(II), L and NIPH anions. The structure of 4 contains one crystallographically independent Co(II), as depicted in figure 4(a). The Co1 has a distorted octahedral geometry via coordinating to two pyridyl nitrogens (N1 and N3) of L, three carboxyl oxygens (O4, O7#1 and O8#1) of two NIPH anions, and one oxygen (O1W) of a coordinated water [Co–N = 2.137(2)–2.161(2) Å, Co–O = 1.9996(16)–2.2379(16) Å]. In 4, the NIPH anions have chelating-monodentate coordination and connect adjacent Co(II) ions to build a 1-D \([\text{Co(NIPH)}]\)_n linear chain with Co1⋯Co1 distance of 10.000 Å (figure S4(a)). The bidentate bridging L also exhibit two different coordination conformations (La and Lb table 2), similar to that in 1. Co(II) ions are bridged by L^a and L^b to construct a 1-D \([\text{Co–L}]\)_n meso-helical chain (figure S4(b)), in which the non-bonding Co1⋯Co1 distances are 18.950 Å (linked by L^a) and 19.153 Å (linked by L^b). By sharing the Co(II) ions, one 1-D \([\text{Co–L}]\)_n meso-helical chain and two 1-D \([\text{Co(NIPH)}]\)_n linear chains are held together to produce a 1-D ribbon structure (figure 4(b)). The hydrogen bonding interactions between the carbons of L and nitro oxygens assemble these 1-D ribbons into a 2-D supramolecular layer [C13–H13A⋯O6 = 3.269(4) Å, C17–H17B⋯O5 = 3.332(4) Å], as shown in figure S4(c). Adjacent layers are ultimately extended to a 3-D supramolecular framework by π–π stacking interactions among the benzene rings of NIPH ligands with face-to-face distance of 3.52 Å (figure 4(c)).

3.2. Effects of carboxylic acids and metal ions on structures

The flexible bis(pyridyl)-bis(amide) L was used as the main ligand and three different carboxylates were employed as ancillary ligands, giving four Cu(II)/Co(II) complexes with diverse structures. For 1 and 2 derived from Cu(II) and bridging L, they have been prepared by changing the ancillary carboxylates (H,BDC, HDNBA), which represent examples of structural changes from the 2-D layer (for 1) to 1-D polymeric chain (for 2). Compared with BDC, the DNBA only has a carboxyl group, but it possesses two extra nitro substituent groups, which usually can decrease the connection numbers of the DNBA anion and result in forming a lower dimensional structure. Similarly, by selecting two different carboxylates (HDNBA, H,NIPH), 3 and 4 with different 1-D chain structures are constructed from Co(II) and L: a 1-D double-chain for 3 and a 1-D ribbon chain containing the 1-D \([\text{Co–L}]\)_n meso-helical chain for 4. Compared to DNBA, NIPH has an extra carboxyl group and reduces a nitro substituent, which may be the main reason of forming various frameworks of 3 and 4. Similar to previous reports, Wen’s group prepared four Cd(II)/Cu(II) coordination polymers based on the same N-donor ligand and two different dicarboxylic acids, in which the dicarboxylates play key roles in determination of the structures [14].
The various structures of 1–4 reveal that the carboxylates have important influence on constructing the final frameworks, attributed to their differences in the substituent groups, positions of the carboxyl groups and numbers of the carboxyl groups.

Figure 6. Absorption spectra of the MB solution during decomposition under UV irradiation with the presence of 1–4.
For 2 and 3 based on L and DNBA, the final structures are related to the radius of the central metal ions and their coordination number. The coordination number of Cu(II) in 2 is 4, resulting in formation of a 1-D wave-like chain. The Co(II) ion in 3 possesses a slightly shorter radius compared with Cu(II), and the coordination number is 6, leading to a different 1-D double-chain of 3. Our results indicate that the metal ions play important roles in determining the final structures of the complexes.

3.3. Thermal gravimetric analyses of 1–4

Thermal gravimetric (TG) curves of 1–4 were determined under N\textsubscript{2} with a heating rate of 10 °C min\textsuperscript{-1} from 30 to 650 °C (figure S9). For the TG curve of 1, the first weight loss step at 98–160 °C should be assigned to loss of coordinated water and lattice water (12.47%, Calcd 12.23%). The second weight loss from 332 to 510 °C demonstrates loss of BDC and L. The final residue of 12.47% is close to the calculated value of 12.23% by assuming CuO as the final residue. The TG curve of 2 (or 3) displays that there is only one obvious weight loss step from 280 to 400 °C (283 to 478 °C for 3), which can be ascribed to decomposition of DNBA and L. The remaining weight 9.42% for 2 (6.52% for 3) corresponds to the percentage 9.52% (6.30% for 3) of Cu and O components (Co and O components for 3), indicating that the final product is CuO for 2 (CoO for 3). As shown in figure S9, the first weight loss of 5.52% at 108–172 °C for 4 can be attributed to removal of water (Calcd 5.47%). The second weight loss at 310–475 °C is attributed to decomposition of NIPH and L. The remaining weight 11.15% corresponds to the percentage of Co and O components (Calcd 11.39%), implying that the final product is CoO.

3.4. Fluorescent properties of 1–4

The fluorescent properties of 1–4 and L were investigated in the solid state at room temperature. As shown in figure (5), free L shows intense emission band at 408 nm (\lambda\textsubscript{ex} = 320 nm), which may be attributed to the π* → π or π* → n transitions [27]. The aromatic carboxylate ancillary ligands (H\textsubscript{2}BDC and HDNBA) show very weak π*-n transitions and contribute little to the photoluminescence of 1–4 at room temperature [28, 29]. Thus, H\textsubscript{2}BDC and HDNBA have no significant contribution to the fluorescent emission of the coordination complexes [30]. For 1–4, the compounds, respectively, display intense emission peaks with maxima at ca. 418, 428, 414, and 412 nm upon excitation at 320 nm. Compared with the peak of 408 nm for free L (\lambda\textsubscript{ex} = 320 nm), the emission bands for 1–4 have different degree of red-shift (10 nm for 1, 20 nm for 2, 16 nm for 3, and 14 nm for 4). A series of fluorescent Cu(II)/Co(II)
complexes have been reported [31, 32]. Density functional theory calculation indicates that the fluorescent emission should be ascribed to ligand-based emission [32] and the emission band of 1–4 may be assigned to the ligand-based emission. The intensities or shapes of emission spectra are different from each other, which may be assigned to the different coordination fashions of metal centers, organic ligands, and their final different coordination structures.

3.5. Photocatalytic properties of 1–4

Photocatalysts have attracted much attention owing to potential applications in purifying water by thoroughly decomposing organic complexes [33–35]. Recent reports reveal that metal–organic coordination complexes often possess photocatalytic activities in the degradation of organic dyes under UV irradiation [36, 37]. In this article, methylene blue (MB) is used as model dye contaminant to evaluate the activities of photocatalysts in purification of wastewater [38, 39]. We investigated the photocatalytic activities of 1–4 for the photodegradation of MB under UV irradiation to evaluate the photocatalytic performances in the purification of wastewater. As shown in figure (6), absorption peaks of MB decreased gradually with reaction time. The concentrations of MB (C) versus reaction time (t) of 1–4 are plotted in figure (7). The calculations show that MB degrades only 9% without any catalyst under UV irradiation. However, the MB degrades approximately 66% for 1, 52% for 2, 46% for 3, and 64% for 4. The experimental results suggest that 1–4 may be candidates for photocatalytic degradation of MB. The differences of photocatalytic activities under UV irradiation for 1–4 may arise from different framework structures.

4. Conclusion

We have synthesized four new Cu(II)/Co(II) coordination polymers in the system of N,N’-di(3-pyridyl) sebacidiamide and carboxylate ligands. The complexes display a 2-D layer, a 1-D linear chain, a 1-D double-chain, and a 1-D ribbon, respectively, and the adjacent layers for 1 and the adjacent chains for 2–4 are further extended into 3-D supramolecular frameworks by hydrogen bonding or π–π stacking interactions. The differences of carboxylates and metal ions in coordination modes play important roles in determining the structural diversity of the complexes. Complexes 1–4 exhibit good fluorescent properties and photocatalytic activities. These preliminary results display that these complexes may be candidates for fluorescent and photocatalytic materials.

Supplementary material

X-ray crystallographic files; selected bond distances and angles, related hydrogen bonding geometries, IR spectra, TG curves for 1–3.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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