Metal/Carboxylate-Induced Versatile Structures of Nine 0D → 3D Complexes with Different Fluorescent and Electrochemical Behaviors

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ABSTRACT: To investigate the effect of the polycarboxylates and metal ions on the assembly and structures of complexes based on a thiophene-containing bis-pyridyl-bis-amide N,N′-bis(pyridine-3-yl)thiophene-2,5-di-carboxamide (3-bptpa) ligand, nine 0D → 3D complexes of [Ni(3-bptpa)(1,2-BDC)_2(H_2O)] (1), [Ni(3-bptpa)(IP)(H_2O)]_2(H_2O) (2), [Ni(3-bptpa)(5-MIP)(H_2O)]_2(H_2O) (3), [Ni(3-bptpa)(5-NIP)(H_2O)] (4), [Ni(3-bptpa)(5-AIP)]_2:2H_2O (5), [Ni(3-bptpa)(5-AIP)]_2(1,3,5-BTC)], DMA·SH_2O (6), [Cu(3-bptpa)(5-MIP)]_2·3H_2O (7), [Cu(3-bptpa)(5-AIP)]_2(1,3,5-AIP)(H_2O) (8), and [Cu(3-bptpa)(1,3,5-HBTC)] (9) (1,2-H_2BDC = 1,2-benzenedicarboxylic acid, H_2IP = 1,3-benzenedicarboxylic acid, 5-H_2MIP = 5-methylisophthalic acid, 5-H_2NIP = 5-nitroisophthalic acid, 5-H_2AIP = 5-aminoisophthalic acid, DMA = N,N′-dimethylacetamide, and 1,3,5-H_2BTC = 1,3,5-benzenetricarboxylic acid) have been hydrothermally/solvothermally synthesized and structurally characterized by IR, thermogravimetric, powder X-ray diffraction, and single-crystal X-ray diffraction. Complex 1 is a zero-dimensional (0D) bimetallic complex. Complexes 2 and 3 feature two similar one-dimensional ladderlike structures. Complex 4 displays a two-dimensional (2D) 4-connected network based on single-metallic nodes. Complex 5 shows a 2D double-layer structure containing a pair of 6D [Ni(5-AIP)] honeycomblike sheets. Complex 6 is a 3,5-connected three-dimensional (3D) framework derived from bimetallic nodes and 6D [Ni(3-bptpa)(1,3,5-BTC)] honeycomblike sheets. Complex 7 displays a 2D 4-connected grid based on bimetallic nodes. Complex 8 features a 2D double-layer structure based on two 4-connected [Cu(3-bptpa)(5-AIP)] sheets and bridging coordinated water molecules. Complex 9 is a 2D structure extended by incomplete deprotonation of 1,3,5-HBTC and 3-bptpa linkers. The effect of the metal ions and polycarboxylates on the structures of the title complexes was discussed, and the fluorescent properties of 1–9 were investigated. The carbon paste electrodes bulk-modified by complexes 3, 5, and 6–9 show different electrocatalytic activities for the oxidation of ascorbic acid as well as the reduction of hydrogen peroxide, nitrites, and bromates.

INTRODUCTION

Owing to the unique structural tailorability and compositional diversity, coordination polymers (CPs) have received much attention and become a hot topic due to their appealing applications as functional materials in adsorption separation, magnetism, luminescence, electrochemical sensors, and so on.1 The variety of the structures relies on the presence of suitable metal–ligand interactions and supramolecular contacts, which is directly related to the coordination characteristics of the components, such as the charge and radius of metal ions, the amount of dentate and steric hindrance of the ligands, etc.2 Although many CPs with intriguing topologies have been reported, the control of precise structures of CPs remains a great challenge in crystal engineering.3

The idea of mixed ligands can indeed obtain a great diversity of CPs.7 However, the resulting structures are somewhat unpredictable and the governing principles in this system are less ascertained and remain elusive.5 The organic polycarboxylates as mixed ligand components are considered as a kind of remarkable building blocks in the construction of CPs.6 They have the ability to balance charges, good coordination ability, and stability in acid and base.7 On the other hand, bipyridine derivatives are good neutral organic ligands, which not only have various classes but also show excellent coordination
ability and spatial expansion ability in the process of assembling with metal ions.\(^9\) Heterocyclic bridged bis-pyridine bis-amides are regarded as a kind of remarkable linking ligands.\(^10\) First, they have the coordination ability similar to other bis-pyridine ligands;\(^11\) second, they have a variable conformation and good structure-expanding ability because of the semirigid organic skeleton.\(^12\) Thus, it is meaningful to investigate the effect of the combination of polycarboxylates and heterocyclic bridged dipyridine diamide abilities with N-/O-donor ligands.\(^13\) However, compared with electrochemical active centers and excellent coordination polymers.\(^15\) In the 1,2-BDC anion, only one carboxylic group coordinates with two Ni ions to form a bimetallic complex; another carboxylic group does not coordinate with the Ni ion but deprotonates for the charge balance (Figure 1). The adjacent 0D discrete complexes are linked by hydrogen-bonding interactions between uncoordinated carboxylic group/coordinated water/amide to form a 1D chain (Figure S1). The corresponding hydrogen-bonding parameters of the complex are listed in Table S10. Generally speaking, organic dicarboxylate and bis-pyridine-bis-amide are two kinds of well-bridged ligands and are usually used to construct 1D, two-dimensional (2D), and three-dimensional (3D) coordination polymers.\(^15\) In \(\text{I}\), 3-bptpa and 1,2-BDC are both acting as terminal-type ligands to form a discrete complex, which is unusual.

\[
\text{[Ni}_\text{2}(\text{3-bptpa})_4\text{(1,2-BDC})_2\text{(H}_2\text{O})_2\text{]} (\text{1}).
\]

The single-crystal X-ray study reveals that complex \(\text{I}\) is a one-dimensional (1D) supramolecular structure based on a zero-dimensional (0D) bimetallic complex. There are two crystallographically independent Ni(II) cations, four 3-bptpa ligands, two 1,2-BDC anions, and two coordinated water molecules, as displayed in Figure 1. The central Ni\(_1\)/Ni\(_2\) cations are six-coordinated by two nitrogen atoms from two 3-bptpa ligands, two carboxylic oxygen atoms of two 1,2-BDC anions, and two oxygen atoms from two coordinated water molecules. The Ni–N bond distances are in the range of 2.053(5)–2.071(5) Å, and the Ni–O bond lengths lie in the range of 2.037(3)–2.148(4) Å. The bond angles around Ni(II) cations vary from 83.37(14) to 177.15(16), indicating that the octahedrons are slightly distorted.

In complex \(\text{I}\), 3-bptpa shows a single-dentate coordination mode, which is unusual in the pyridine-amide-based complexes.\(^14\) In the 1,2-BDC anion, only one carboxylic group coordinates with two Ni ions to form a bimetallic complex; another carboxylic group does not coordinate with the Ni ion but deprotonates for the charge balance (Figure 1). The adjacent 0D discrete complexes are linked by hydrogen-bonding interactions between uncoordinated carboxylic group/coordinated water/amide to form a 1D chain (Figure S1). The corresponding hydrogen-bonding parameters of the complex are listed in Table S10. Generally speaking, organic dicarboxylate and bis-pyridine-bis-amide are two kinds of well-bridged ligands and are usually used to construct 1D, two-dimensional (2D), and three-dimensional (3D) coordination polymers.\(^15\) In \(\text{I}\), 3-bptpa and 1,2-BDC are both acting as terminal-type ligands to form a discrete complex, which is unusual.

\[
\text{[Ni}_\text{2}(\text{3-bptpa})\text{(IP)}\text{(H}_2\text{O})_\text{2}\text{]}\text{(H}_2\text{O})_\text{2}\text{]} (\text{2})
\]

and \[
\text{[Ni}_\text{2}(\text{3-bptpa})\text{(5-MIP)}\text{(H}_2\text{O})_\text{2}\text{]}\text{(H}_2\text{O})_\text{2}\text{]} (\text{3}).
\]

H\(_2\)IP and S-H\(_2\)MIP were selected instead of 1,2-BDC in the synthetic process. As a result, two similar 1D ladderlike structures of 2–3 with different structural details were obtained. Herein, only complex 2 is selected as a representative example for a detailed structural description. Complex 2 contains one Ni(II) center, an IP anion, one 3-bptpa ligand, two coordinated water molecules, and one lattice water molecule. As shown in Figure 2a, the Ni(II) center is six-coordinated with octahedral coordination geometry: two N

![Figure 1](image-url). Coordination environment of Ni(II) ions and the binuclear structure in I.
atoms belonging to two 3-bptpa ligands, four O atoms from two IP anions, and two coordinated water molecules. The Ni−O bond lengths are in the range of 2.046(2)−2.084(2) Å, and the Ni−N bond lengths are 2.092(2) and 2.146(2) Å. The bond angles around the Ni(II) cation are in the range of 85.39(7)−178.59(7)°, which agree with those previously reported for Ni(II) complexes.13a In complex 2, the 3D supramolecular arrays derived from 1D tubular coordination polymers show a cross arrangement, which is unusual in amide-based complexes.

\[[\text{Ni}(3\text{-bptpa})(5\text{-NIP})(\text{H}_2\text{O})]\] (4). To further investigate the effect of the uncoordinated groups of "V"-type dicarboxylates, 5-H$_2$NIP with nitro was selected instead of 5-H$_2$MIP with methyl in the synthetic process. As a result, a wavelike 2D network of complex 4 based on [Ni(5-NIP)] linear chains and [Ni(3-bptpa)] helixes is obtained. As illustrated in Figure 3a, a crystallographically independent Ni(II) ion is octahedrally coordinated by two nitrogen atoms from two 3-bptpa, three oxygen atoms from two 5-NIP, and one coordination water molecule. The Ni−O bond lengths lie in the range of 2.067(3)−2.240(3) Å, and the Ni−N bond lengths are

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**Figure 2.** (a) Coordination environment of a Ni(II) ion in 2. (b) [Ni(3-bptpa)(IP)(H$_2$O)$_2$] ladderlike chain and the schematic view. (c) 3D supramolecular stacking structure based on 1D chains. (d) Schematic view of the 3D supramolecular structure.

**Figure 3.** (a) Coordination environment of a Ni(II) ion in 4. (b) 2D network based on [Ni(3-bptpa)] helixes and [Ni(5-NIP)] linear chains. (c) Schematic view of the 2D (4,4)-connected network.
2.056(4) and 2.067(4) Å. The bond angles around the Ni(II) cation change from 61.07(11) to 177.58(13)°.

The two carboxylic groups of a 5-NIP anion in 4 act as single-dentate and chelating coordination modes to coordinate with Ni(II) ions forming a 1D linear chain with the Ni–Ni separation of 10.167 Å. 3-bptpa ligands link the adjacent Ni ions to generate a 1D helix with the Ni–Ni distance of 13.177 Å. The above two chains are connected by Ni ions to form a (4,4)-connected 2D wavelike network (Figure 3bc). The parallel 2D layers are extended into a 3D supramolecular architecture by hydrogen bonds between carboxylic groups, amide, and coordinated water molecules (Figure S4). The corresponding hydrogen-bonding data are given in Table S13.

\[
\text{[Ni(3-bptpa)(5-AIP)]·2H}_2\text{O (5). To further investigate the effect of the substituents of V-type dicarboxylates, amido in 5-H}_2\text{AIP was selected instead of nitro in 5-H}_2\text{NIP in the synthetic process. A 2D double-layer structure based on two [Ni(5-AIP)] honeycomblike sheets and [Ni(3-bptpa)] zigzag chains is obtained. Single-crystal X-ray analysis shows that the Ni ion in the asymmetric unit of 5 is bound with two nitrogen atoms of two 3-bptpa [Ni–N 2.059(2) and 2.194(2) Å], one nitrogen atom of 5-AIP [Ni–N 2.141(2) Å], and three carboxylic oxygen atoms of three 5-AIP anions [Ni–O 2.023(2)–2.178(2) Å] (Figure 4a). The bond angles around the Ni(II) ion are in the range of 61.55(6)–172.60(8) °.}
\]

3-bptpa ligands in complex 5 coordinate with adjacent Ni ions to generate a 1D zigzag chain with the Ni–Ni distance of 16.889 Å. S-AIP acts as a 3-connected linker to bridge three Ni(II) ions forming a honeycomblike 2D sheet (Figure 4b). The above subunits are connected to each other to form a 2D double-layer structure (Figure 4c). Finally, the parallel 2D layers are extended into a 3D supramolecular architecture by hydrogen bonds between the amide of 3-bptpa and the amino of S-AIP, carboxylic groups, and lattice water molecules (Figure S5). The corresponding hydrogen-bonding data of complex 5 are given in Table S14.

\[
\text{[Ni}_2\text{(OH)(3-bptpa)(1,3,5-BTC)]·DMA·5H}_2\text{O (6). To further study the effect of the groups of V-type dicarboxylates, carboxyl in 1,3,5-BTC was selected instead of amino in 5-H}_2\text{NIP in the synthetic process. A 3D complex for 6 based on Ni}_2\text{O(OH) clusters was obtained. The asymmetric unit of 6 consists of two Ni(II) ions, one 1,3,5-BTC anion, two 3-bptpa ligands, one }\mu_2\text{-OH, one DMA, and five lattice water molecules. As illustrated in Figure 5a, Ni}_1\text{/Ni}_2\text{ ions are six-coordinated by two nitrogen atoms of two 3-bptpa ligands [Ni–N 2.070(4)–2.093(4) Å], three carboxylic oxygen atoms from two 1,3,5-BTC anions [Ni–O 1.996(2)–2.241(3) Å], and one oxygen atom of }\mu_2\text{-OH [Ni–O 1.996(2) and 2.011(2) Å]. The bond angles around Ni(II) cations vary from 60.63(9) to 177.02(13) °.}
\]

In complex 6, one }\mu_2\text{-OH links Ni}_1\text{ and Ni}_2\text{ cations to form a bimetallic Ni}_2\text{O(OH) subunit with the Ni–Ni separation of 3.531 Å. Each 1,3,5-BTC anion acts as a 3-connected linker to bridge three Ni}_2\text{O(OH) subunits forming a 2D honeycomblike network (Figure 5b). 3-bptpa ligands link the above parallel 2D networks forming a 3D framework, which is stabilized by hydrogen bonds between the amide, carboxylic groups, and lattice water molecules (Figures 5c and 5d). The corresponding hydrogen-bonding data are given in Table S15. Topologically, 1,3,5-BTC and the bimetallic Ni}_2\text{O(OH) subunit can be regarded as 3- and 5-connected nodes. Thus, complex 6 can be classified as a (3,5)-connected bimodal hms topological net with a Schläfi symbol of }\{6^3\}{6^2}8\} (Figure 5d).
carboxylic groups, and lattice water molecules is obtained (Figure S7). The corresponding hydrogen-bonding data are given in Table S16. The structural details and the corresponding hydrogen-bonding data of complex 9 are given in Figure S8 and Table S17. 

$[\text{Cu}(3\text{-bptpa})(5\text{-AIP})(\text{H}_2\text{O})_{0.25}] \cdot \text{H}_2\text{O}$ (8). Complex 8 is a 2D double-layer structure, which was constructed from two 4-connected single-node sheets and bridging coordinated water molecules. As illustrated in Figure 7a, the Cu(II) center is six-coordinated by two nitrogen atoms of two 3-bptpa ligands [Cu–N 2.017(3) and 2.025(3) Å], three carboxylic oxygen atoms from two 5-AIP anions [Cu–O 1.990(2)–2.438(3) Å], and one oxygen atom of the coordinated water molecule [Cu–O 2.453(2) Å]. The bond angles around Cu(II) cations vary from 58.44(9) to 161.99(12)°. The two carboxylic groups of a 5-AIP anion in 8 adopt single-dentate and chelating coordination modes to bridge Cu(II) ions forming a 1D [Cu(5-AIP)] linear chain with the Cu–Cu distance of 9.925 Å. 3-bptpa ligands link the parallel [Cu(5-AIP)] chains to generate a 2D 4-connected network based on single-metallic nodes. The parallel networks are extended into a double-layer structure by μ$_2$-coordinated water molecules (Figure 7b,c). Finally, complex 8 displays 3D supramolecular architecture extended by hydrogen bonds between the amide of 3-bptpa, the amino of 5-AIP, carboxylic groups, and coordinated/lattice water molecules (Figure S9). The corresponding hydrogen-bonding data are given in Table S18.

Figure 6. (a) Coordination environment of a Cu(II) ion in 7. (b) 2D network based on (3-bptpa)2 and (5-MIP)2 double linkers. (c) (4,4)-connected 2D network based on bimetallic Cu$_2$ subunits.

Effect of the Polycarboxylates and Metal Ions on the Structures of the Title Complexes. To investigate the effect of the coordinated angles of benzenedicarboxylic acids on the structures of the title complexes, the same center metal ion Ni(II) and linear N-donor ligand (3-bptpa) were used in 1 and 2. While the benzenedicarboxylic acids were selected from 1,2-H$_2$BDC (with the coordinated angle of 60°) and H$_2$IP (with
the coordinated angle of 120°), the title complexes of 1 and 2 display a discrete bimetallic structure and a 1D ladderlike band (Figures 1 and 2). To study the effect of the 5-site substituents of benzenecarboxylic acids on the structures of the Ni-(3-bptpa) system, –H (for H4IP in 2), –CH3 (for 5-H2MIP in 3), –NO2 (for 5-H2NIP in 4), –NH2 (for 5-H2AIP in 5), and –COOH (for 1,3,5-H3BTC in 6) were selected in the benzenecarboxylic acids in the synthetic process (Chart S1a). As a result, the structures of the corresponding complexes show 1D ladderlike bands of 2 and 3, a (4,4)-connected single-node sheet of 4, a honeycomblike 2D double layer of 5, and a (3,5)-connected 3D framework of 6 (Figure 8 and Chart S1). A further structural analysis shows that there are several differences between the complexes of 1–6. (i) Although the coordinated geometries of Ni(II) ions in 1–6 are all octahedron with two N atoms of 3-bptpa and four N/O from benzenecarboxylates, the two N atoms of 3-bptpa are in cis-modes in 1, 4, 5 and trans-modes in 2, 3, 6 (Chart S1b). (ii) The subunits of metal–polycarboxylates are discrete in 1, bimetallic loops in 2/3, a 1D linear chain in 4, and honeycomblike 2D 6° sheets in 5/6 (Chart S1c). The Ni–Ni distances linked by benzenecarboxylates are 7.75 Å for 2;
carboxylates are 8.04 Å and 10.01 Å for 7, 9, 9.3 Å for 8, 7.79 Å, and 10.02 Å for 9 (Chart S2c). The binuclear Cu–Cu distances linked by two carboxylates in 7 and 9 are 3.97 and 4.01 Å, respectively. (iii) The subunits of metal–bptpa are all 1D zigzag chains in 7–9, and the corresponding Cu–Cu distances linked by 3-bptpa are 17.02 Å for 7, 16.97 Å for 8, and 16.69 Å for 9 (Chart S2d). The corresponding configurations of the pyridine ring and amide oxygen, amide oxygen and amide oxygen, amide oxygen and the pyridine ring of 3-bptpa are all cis, cis, and trans-modes for 7–9, respectively (Chart S2d). The above structural details are different from those of 3, 5, and 6, which show that the metal ions [from Ni(II) to Cu(II)] play an important role in tuning the structures of the title complexes.

To further explore the effect of the metal ions on the structures of the 3-bptpa system, H2MIP was selected as an anion ligand and different metal ions of Co2+, Cu2+, Ni2+, Zn2+, and Cd2+ were used as research objects, as shown in Figure S10 and Chart S2. Our group has reported three complexes based on Zn2+ or Cd2+ or Co2+ and 3-bptpa and H2MIP, namely, a 2D (4,4)-connected single-metallic-node grid of [Zn(3-bptpa)(5-MIP)] (CP1), a 3D NaCl-type framework of [Cd(3-bptpa)(5-MIP)]·4H2O (CP2), and a 2D (4,4)-connected bimetallic-node sheet of [Co(3-bptpa)(5-MIP)]·2H2O (CP3) (Chart S2a). Some obvious differences of CP1–CP3, 3, and 7 are found in the further analysis. (i) With a decrease in the radius of metal ions (from Cd2+, Co2+, Ni2+, Cu2+ to Zn2+), the coordinated geometries are changed from octahedron (for CP2, CP3, and 3), triangular bipyramid (for 7) to tetrahedron (for CP1) (Chart S2b). (ii) The subunits of metal–polycarboxylates are a 1D linear chain in CP1; a bimetallic loop in 3; and 1D double chains in 7, CP2, and CP3 (Chart S2c). (iii) The subunits of metal–bptpa are all 1D chains in CP1–CP3, 3, and 7 but with the different metal–metal distances linked by 3-bptpa (14.88 Å for CP1, 16.93 Å for CP2, and 17.11 Å for CP3) (Chart S2d). The corresponding configurations of the thioephene sulfur and amide oxygen of 3-bptpa are all in cis-modes for 3, 7, CP2, and CP3 but in trans-mode for CP1 (Chart S2d). The above differences of the structural details further demonstrate the effect of metal ion on the structures of the complexes. In addition, the bimetallic nodes and (3-bptpa)2 double linkers are found in the topological structures of 6, 7, 9, CP2, and CP3, whereas the other complexes possess single-metallic nodes. In summary, the coordinated angle (from 60° of 1,2-H2BDC to 120° of H2IP), space steric hindrance (from −H of H2IP, −CH3 of 5-H2MIP to −NO2 of 5-H2NIP), and the type of coordinated dentate (from −NH2 of 5-H2AIP to −COOH of 1,3,5-H3BTC) of carboxylates, as well as the radius (from Cd2+, Co2+, Ni2+, Cu2+ to Zn2+) and coordinated characters of metal ions, all affect the structures of complexes.

IR, Powder X-ray Diffraction, and Thermal Stability Analyses of the Title Complexes. The IR spectra of complexes 1–9 with the frequency range of 500–4000 cm−1 are shown in Figure S11. The broad bands in the area of 3600–3250 cm−1 represent OH stretching modes within the free and coordinated water molecules or the formation of hydrogen-bonding interactions. The absorptions observed in the range 3250–3100 cm−1 in complexes 1–9 can be attributed to the ν(C–OH) stretching band of 3-bptpa ligands. The weak absorption peaks of the −CH3 group of 5-MIP in 3 and 7 are observed at 2918 and 2926 cm−1, respectively. The absorptions observed at 1693 cm−1 in 9 show that one of the carboxylic groups of 1,3,5-BTC is not deprotonated. On the other hand, there is no absorption peak between 1730 and 1670 cm−1, indicating that all carboxyl groups of the organic moieties in 1–8 are deprotonated. The absorption bands at about 1365 and 1548 cm−1 arise from the nitro groups of 5-NIP in 4. The peaks observed in the range of 1660–1600 cm−1 for these complexes are assigned to the stretching bands of ν(C=O). The skeletal vibrations of phenyl and pyridyl rings fall in the range of 1590–1430 cm−1. The strong bands in the range of 690–730 cm−1 can be attributed to the ν(C–N) stretching of the N-heterocyclic rings of the 3-bptpa ligands.

The phase purity of these nine complexes was confirmed by comparison of their experimental powder X-ray diffraction (PXRD) patterns with the reference powder diffractogram (calculated on the basis of single-crystal X-ray diffraction data) (Figure S12). The as-synthesized patterns are in good agreement with the corresponding simulated ones, indicating the good phase purity of the samples. The differences in intensity are due to the preferred orientation of the powder samples. The thermal stability of complexes 1–9 was investigated by thermogravimetry under a N2 atmosphere at 20.0 mL min−1 and 10 °C min−1 using bulk phase materials. As shown in Figure S13, the weight losses of 2.35% (calcd 2.02%) for 1, 9.19% (calcd 8.98%) for 2, 8.49% (calcd 8.78%) for 3, 2.66% (calcd 2.95%) for 4, 5.89% (calcd 6.02%) for 5, 7.98% (calcd 7.71%) for 6, 8.59% (calcd 8.71%) for 7, and 3.51% (calcd 3.82%) for 8 in the temperature ranges of 86–135 °C for 1, 105–201 °C for 2, 114–156 °C for 3, 230–267 °C for 4, 140–243 °C for 5, 103–184 °C for 6, 95–284 °C for 7, and 130–227 °C for 8, respectively, are attributed to the release of the water molecules. The weight loss of 7.14% (calcd 7.46%) for 6 at the temperature ranging from 250 to 330 °C belongs to the departure of DMA. The title complexes can be stable up to 300 °C for 1, 367 °C for 2, 365 °C for 3, 357 °C for 4, 386 °C for 5, 369 °C for 6, 285 °C for 7, 306 °C for 8, and 323 °C for 9, following the decomposition of the framework. The different decomposition temperatures may be due to the different structures and constituents of the complexes.

Photoluminescent Properties. The luminescent properties of 1–9 in the solid state at room temperature were measured. As shown in Figure 10, the nine complexes exhibit similar blue emission with different intensities. Upon excitation at 320 nm, the emissions of these complexes are at 461, 413, 460, 424, 416, 458, 414, 404, and 413 nm, respectively. Compared with the emission of 3-bptpa (λem = 439 nm), the emissions of the title complexes exhibit red shifts of ca. 22, 21, 20, 15, 12, 10, 8, and 7 nm, respectively.
behaviors are researched in 0.01 M H2SO4 and 0.5 M Na2SO4 according to our previous report, and their electrochemical increased scan rates from 20 to 300 mV s−1 which prove that the redox of title complexes.18 The peak currents are proportional to the scan rates, to-peak separation between the corresponding cathodic and anodic peaks, the complexes 3-bptpa, and structures of the chemical sites [Ni(II) for 3, 7, 8, and 9] (Chart S3). Thus, to explore the effect of metal ions on the electrochemical behavior and electrocatalytic activity, the complexes 3-, 7-, 8-, 9-, and 9-bulk-modified carbon paste electrodes (n-CPE, n = 3, 7, 5, 8, 6, and 9) are prepared according to our previous report, and their electrochemical behaviors are researched in 0.01 M H2SO4 and 0.5 M Na2SO4 aqueous solution.19 Figure S14 shows the cyclic voltammograms of 3, 5–9-CPE at different scan rates in the same potential range of −100–700 mV for 3, 5, and 6 and −500 to 500 mV for 7–9. One pair of reversible redox peaks with the oxidation peaks at 0.195, 0.189, 0.180, −0.100, −0.105, and −0.080 V for 3, 5–9-CPE, respectively, and the corresponding reduction peaks at 0.287, 0.298, 0.290, 0.050, 0.010, and 0.020 V can be clearly observed. At the scan rate of 100 mV s−1, the relative mean peak potentials \( E_{1/2} = (E_{pa} + E_{pc})/2 \) are 241, 244, 235, −25, −47, and −30 mV, respectively, which may be attributed to the redox of NiII/NiI and CuII/CuI.13 With the increased scan rates from 20 to 300 mV s−1, although the peak-to-peak separation between the corresponding cathodic and anodic peaks increases, the mean peak potentials do not change. The peak currents are proportional to the scan rates, which prove that the redox of n-CPEs is the surface-confined process.19

In the 0.01 M H2SO4 and 0.5 M Na2SO4 aqueous solution, the electrocatalytic activities of 3, 5–9-CPEs toward oxidation of ascorbic acid (AA) and reduction of H2O2, NO2−, and BrO3− were investigated. To the best of our knowledge, there is no obvious response of the bare CPE for AA, H2O2, NO2−, and BrO3−.19 With the addition of AA, NO2−, BrO3−, and H2O2, the oxidation peak currents of 6-CPE and reduction peak currents of 3-CPE, 5-CPE, and 7-CPE increase at the corresponding peak potentials of about 320, 250, 220, and −110 mV, respectively (Figure 11). The results display that 6-, 3-, 5-, and 7-CPEs can act as effective electrocatalysts for the oxidation of AA and reduction of NO2−, BrO3−, and H2O2, respectively. The system comparisons are shown in Chart S3 and Figure S15. NO2− can be electrocatalytically reduced by all of the three Ni-based complexes (3, 5, and 6) and one Cu-complex (9). BrO3− can be electrocatalytically reduced by complexes 5 and 6. H2O2 can be electrocatalytically reduced only by three Cu-complexes (7, 8, and 9), and AA can be electrocatalytically oxidized only by one Ni-complex (6). Different electrochemical activities may be due to the different structures and constituents of the complexes.13

**CONCLUSIONS**

In summary, by tuning the polycarboxylates and metal ions, we have successfully obtained nine 0D → 3D complexes from a thiophene-containing bis-pyridyl-bis-amide ligand under hydrothermal/solvothermal reactions. The title complexes display from a 0D binuclear cluster (for 1), 1D ladderlike bands (for 2 and 3), a (4,4)-connected 2D sheet (for 4), a honeycomblike double layer (for 5), a 3,5-connected 3D framework (for 6), a bimetallic-node 2D network (for 7), a 5-connected double layer (for 8) to a (4,4)-connected 2D grid (for 9). The versatile structural features of the title complexes indicate that the polycarboxylates and metal ions play an important role in the construction of metal–organic complexes. The different fluorescent properties and electrochemical activities for ascorbic acid, hydrogen peroxide, nitrites, and bromates of the title complexes show that the
properties of the target complexes can be adjusted by the rational design of the starting materials.

**EXPERIMENTAL SECTION**

**General Remarks.** N,N’-bis(pyridine-3-yl)thiophene-2,5-dicarboxamide (3-bptpa) was prepared according to the reported method. All of the other chemicals purchased were of reagent grade and used without further purification. IR spectra (KBr pellets) and luminescence spectra were recorded on a Varian-640 spectrometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively; thermodiagramm -titration analyses (TGA), powder X-ray diffraction, and electrochemical experiments were performed with a Pyramis Diamond TG instrument, an Ultima IV diffractometer (40 kV and 40 mA, Cu Kα), and a CHI 760 electrochemical workstation, respectively.

**Synthesis of [Ni(3-bptpa)(1,2-BDC)](H2O)2 (1).** A mixture of Ni(NO3)2·6H2O (0.1 mmol), 1,2-BDC (0.1 mmol), 3-bptpa (0.1 mmol), NaOH (0.2 mmol), and H2O (8 mL) was sealed in a 25 mL Teflon-lined autoclave under autogenous pressure at 120 °C for 4 days. After cooling to room temperature, green block crystals of 1 suitable for X-ray diffraction were obtained in 7% yield based on Ni. Elem. anal. calcld for C25H24N4NiO9S: C, 48.81; H, 3.93; N, 11.71. Found: C, 48.03; H, 3.33; N, 11.55%. IR (KBr, cm−1): 3607 w, 3530 w, 3378 w, 3249 w, 2926 w, 2851 w, 1669 s, 1629 m, 1588 m, 1541 m, 1486 w, 1430 m, 1350 m, 1284 m, 1189 w, 1130 w, 1052 w, 784 w, 737 m, 700 w, 699 w.

**Synthesis of [Ni(3-bptpa)(5-AIP)(H2O)] (4).** The same synthetic procedure as for 1 was used, except that H2AIP (0.1 mmol) was used instead of 1,2-BDC, yielding yellow block X-ray-quality crystals of 4 in 16% yield based on Ni. Elem. anal. calcld for C24H21N5NiO8S: C, 48.19; H, 3.54; N, 11.71. Found: C, 48.03; H, 3.33; N, 11.55%. IR (KBr, cm−1): 3499 w, 3364 w, 3310 w, 3249 w, 2926 w, 1660 m, 1630 w, 1605 m, 1545 m, 1515 w, 1473 m, 1432 w, 1375 m, 1331 w, 1284 w, 1196 w, 1120 w, 1055 w, 960 w, 785 w, 729 m, 696 w.

**Synthesis of [Ni(3-bptpa)(3-bptpa)(1,3,5-BTC)]·DMA·5H2O (6).** The same synthetic procedure as for 1 was used, except that 1,3,5-H3BTC (0.1 mmol) and DMA (1 mL) were used instead of 1,2-BDC, yielding green block X-ray-quality crystals of 6 in 32% yield based on Ni. Elem. anal. calcld for C45H47N9Ni2O17S2: C, 46.30; H, 4.06; N, 10.80. Found: C, 46.20; H, 3.88; N, 10.69%. IR (KBr, cm−1): 3427 m, 3287 w, 3100 w, 2932 w, 1669 s, 1613 m, 1555 m, 1487 m, 1432 w, 1376 m, 1330 m, 1250 w, 1195 m, 1111 w, 1062 w, 1027 w, 937 w, 810 w, 769 m, 734 s, 700 w, 643 w.

**Synthesis of [Cu(3-bptpa)(5-MIP)]·3H2O (7).** The same synthetic procedure as for 3 was used, except that Cu(NO3)2·4H2O (0.1 mmol) was used instead of Ni(NO3)2·6H2O, yielding blue block X-ray-quality crystals of 7 in 26% yield based on Cu. Elem. anal. calcld for C24H21N5CuO7S: C, 48.42; H, 3.90; N, 9.04. Found: C, 48.33; H, 3.76; N, 8.96%. IR (KBr, cm−1): 3607 w, 3530 w, 3378 w, 3249 w, 2926 w, 1669 s, 1629 m, 1553 m, 1485 m, 1426 w, 1358 m, 1328 m, 1295 m, 1196 m, 1108 w, 1061 w, 933 w, 886 w, 831 m, 805 m, 777 w, 724 m, 696 m, 655 w.

**Synthesis of [Cu(3-bptpa)(5-AIP)(H2O)2] (8).** The same synthetic procedure as for 5 was used, except that Cu(NO3)2·4H2O (0.12 mmol) was used instead of Ni(NO3)2·6H2O, yielding blue block X-ray-quality crystals of 8 in 10% yield based on Cu. Elem. anal. calcld for C24H19.50CuN5O7.25S: C, 48.90; H, 3.36; N, 11.88. Found: C, 48.93; H, 3.36; N, 11.90%. IR (KBr, cm−1): 3378 w, 3330 w, 3229 w, 3080 w, 1669 s, 1610 m, 1586 m, 1541 m, 1486 w, 1430 m, 1350 m, 1330 m, 1284 m, 1189 w, 1130 w, 1052 w, 784 w, 730 m, 724 m, 690 m, 649 w.

**Synthesis of [Cu(3-bptpa)(1,3,5-HBTC)] (9).** The same synthetic procedure as for 6 was used, except that Cu(NO3)2·4H2O (0.1 mmol) was used instead of Ni(NO3)2·6H2O, yielding blue block X-ray-quality crystals of 9 in 24% yield based on Cu. Elem. anal. calcld for C24H19.50CuN5O7.25S: C, 49.58; H, 2.71; N, 9.40. Found: C, 49.53; H, 2.66; N, 9.26%. IR (KBr, cm−1): 3330 w, 3128 w, 3085 w, 2926 w, 2851 w, 1693 m, 1629 m, 1588 m, 1541 m, 1483 w, 1426 m, 1372 m, 1277 m, 1236 w, 1192 w, 1115 w, 933 w, 830 w, 798 w, 760 m, 728 m, 692 m, 669 w.

**X-Ray Crystallography.** The X-ray intensity data for 1–9 were collected on a Bruker SMART APEX II diffractometer, and the structures were solved by direct method and difference Fourier synthesis and refined by full-matrix least-squares techniques. Absorption corrections were applied using a multiscan technique. The nonhydrogen atoms were refined as anisotropic thermal parameters, and all H atoms of the organic ligands were positioned geometrically and allowed to ride on their parent atoms with isotropic displacement parameters. The H atoms of water molecules were located from difference Fourier maps and refined as riding atoms. In complex 6, the H2B and HSb atoms of water, attached to O2W and O5W, respectively, are not involved in hydrogen bonds according to the hydrogen-bonding scheme. In complex 7, a close contact [3.103(13) Å] between O3W and its symmetry-related equivalent atom (at 1−x,−y,−z) indicates a hydrogen-bonding interaction between them. Therefore, one of the H atoms of O3W should be disordered in two half-occupied sites due to the restraint of the symmetry center, one (H3B) involved in this hydrogen bond and the other (H3C) not in any hydrogen-bonding interaction. Their occupancy
Table 1. Crystal and Refinement Data for Complexes 1–9

| complexes | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-----------|---|---|---|---|---|---|---|---|---|
| empirical formula | $C_{80}H_{60}N_{16}Ni_{2}O_{18}S_4$ | $C_{24}H_{22}N_{4}NiO_{9}SC$ | $C_{25}H_{24}N_{4}NiO_{9}SC$ | $C_{24}H_{17}N_{5}NiO_{9}SC$ | $C_{24}H_{21}N_{5}NiO_{8}SC$ | $C_{45}H_{47}N_{9}Ni_{2}O_{17}S_2$ | $C_{25}H_{24}CuN_{4}O_{9}SC$ | $C_{24}H_{19.5}CuN_{5}O_{7.25}SC$ | $C_{25}H_{16}CuN_{4}O_{8}S$ |
| $F_w$ | 1779.06 | 601.21 | 615.23 | 610.18 | 598.21 | 1167.42 | 620.09 | 589.54 | 596.03 |
| crystal system | monoclinic | orthorhombic | orthorhombic | monoclinic | monoclinic | monoclinic | triclinic | triclinic | triclinic |
| space group | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ | P $\overline{2}$ |
| $a$ (Å) | 12.5858(6) | 20.9052(14) | 21.5233(18) | 10.1670(18) | 19.5397(12) | 10.0807(4) | 10.0122(10) | 9.7850(9) | 9.5351(7) |
| $b$ (Å) | 20.9170(9) | 24.2857(17) | 24.378(2) | 15.932(3) | 7.7630(5) | 24.8681(11) | 11.9884(11) | 12.1481(12) | 13.5265(12) |
| $c$ (Å) | 14.6932(6) | 9.8558(7) | 10.1884(9) | 15.588(3) | 16.0231(10) | 20.3417(9) | 66.634(2) | 66.634(2) | 66.634(2) |
| $\alpha$ (°) | 90 | 90 | 90 | 90 | 90 | 90 | 89.688(2) | 91.391(2) | 82.070(1) |
| $\beta$ (°) | 100.695(1) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| $\gamma$ (°) | 100.695(1) | 90 | 90 | 90 | 90 | 90 | 90 | 90 | 90 |
| $V$ (Å$^3$) | 3800.9(3) | 5003.8(6) | 5345.8(8) | 2432.1(8) | 2311.2(3) | 5038.7(4) | 1334.1(2) | 1179.56(19) | 1155.76(14) |
| Z | 2 | 8 | 8 | 4 | 4 | 4 | 2 | 2 | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.554 | 1.596 | 1.529 | 1.666 | 1.719 | 1.539 | 1.544 | 1.660 | 1.713 |
| $\mu$ (mm$^{-1}$) | 0.691 | 0.921 | 0.864 | 0.950 | 0.995 | 0.911 | 0.957 | 1.074 | 1.098 |
| $F(000)$ | 1832 | 2480 | 2544 | 1248 | 1232 | 2416 | 638 | 603 | 606 |
| $R_w$ | 0.0362 | 0.0528 | 0.0312 | 0.0747 | 0.0453 | 0.0442 | 0.0534 | 0.203 | 0.0240 |
| $R_p | [I > 2\sigma(I)]$ | 0.0447 | 0.0326 | 0.0320 | 0.0583 | 0.0362 | 0.0223 | 0.0582 | 0.0436 | 0.0473 |
| $wR_p | (all data)$ | 0.0699 | 0.0788 | 0.0851 | 0.1355 | 0.0866 | 0.1525 | 0.1188 | 0.1126 | 0.1242 |
| GOF | 1.000 | 1.022 | 1.035 | 1.056 | 1.006 | 1.054 | 1.019 | 1.028 | 1.034 |
| $\Delta\rho_{max}$ (e Å$^{-3}$) | 0.330 | 0.281 | 0.835 | 0.754 | 0.324 | 1.432 | 0.681 | 0.904 | 0.977 |
| $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.330 | 0.281 | 0.835 | 0.754 | 0.324 | 1.432 | 0.681 | 0.904 | 0.977 |

$\text{R}_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum(wF_o^2)^2]^{1/2}$. 
factors are 0.5. The occupancy factor of O(2W) in 8 is 0.25. The amide of 3-bptpa in 9 is disordered (C11 and O2), and their occupancy factors are 0.6 and 0.4, respectively. The crystal data and structure refinement details for complexes 1–9 are summarized in Table 1. Selected bond lengths and angles are listed in Tables S1–S9.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02124.

Selected bond lengths and angles (Tables S1–S9), hydrogen-bonding data (Tables S10–S18), structure illustrations of complexes 1–9 (Figures S1–S9), IR for 1–9 (Figure S11), PXRD data (Figure S12), TGA (Figure S13), cyclic voltammograms of 3-CPE and 5–9-CPE (Figure S14), electrocatalytic activity (Figure S15), structural details (Charts S1 and S2), and comparison of electrocatalytic activity on the effect of metal ions (Chart S3) (PDF)

Crystallographic data of CCDC 1876596, 1876597, 1876642, 1876598, 1876599, 1876643, 1876600, 1876601, and 1876602 1–9 (CIF)

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G.-C.L. and X.L. are co-first authors.

### Notes

The authors declare no competing financial interest.

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