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Effect of flexible bis-pyridyl-bis-amide ligands and dicarboxylates on the assembly and properties of multifunctional Cu(II) metal–organic coordination polymers†

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A series of multifunctional Cu(II) metal-organic coordination polymers based on three flexible bis-pyridylbis-amide ligands and four aromatic dicarboxylates, namely [Cu(3-dpye)(3-NPA)(H₂O)]-3H₂O (1), [Cu(3dpye)_{0.5}(5-AIP)(H₂O)] (2), [Cu(3-dpye)(1,3-BDC)]·3H₂O (3), [Cu₃(3-dpye)(1,2-BDC)₂(µ₂-OH)₂] (4), [Cu₃(3 $dpyb)(1,2-BDC)_2(\mu_2-OH)_2]$ (5), $[Cu(3-dpyh)_{0.5}(1,2-BDC)] \cdot H_2O$ (6), $[Cu(3-dpyh)_{0.5}(5-AIP)(H_2O)]$ (7) [3-dpye = N,N'-bis(3-pyridinecarboxamide)-1,2-ethane, 3-dpyb = N,N'-bis(3-pyridinecarboxamide)-1,4-butane, 3-dpyh = $N_i N'$ -bis(3-pyridinecarboxamide)-1,6-hexane, 3-H₂NPA = 3-nitrophthalic acid, 5-H₂AIP = 5-aminoisophthalic acid, 1,3-H₂BDC = 1,3-benzenedicarboxylic acid, 1,2-H₂BDC = 1,2-benzenedicarboxylic acid], have been hydrothermally synthesized and structurally characterized by elemental analyses, IR, PXRD, TG and single crystal X-ray diffraction. X-ray analyses reveal that the seven Cu(11) complexes show three kinds of different 2D layer structures (for complexes 1, 2, 3, 6 and 7) and a 3D coordination framework (for complexes 4 and 5), exhibiting the $(4^4 \cdot 6^2)$ topology for 1, $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$ topology for isostructural complexes 2 and 7, $(4^{2} \cdot 6^{7} \cdot 8)(4^{2} \cdot 6)$ topology for complex 3, $(3 \cdot 4 \cdot 5)_{2}(3 \cdot 4^{2} \cdot 5 \cdot 8^{6})_{2}(3^{2} \cdot 8 \cdot 9^{2} \cdot 10)(4^{2} \cdot 8^{2} \cdot 10^{2})$ topology for isostructural complexes 4 and 5, and the $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$ topology for complex 6, respectively. In complexes 1–7, the bis-pyridyl-bis-amide ligands adopt a μ_2 -bridging mode in 1, 2, 3, 6 and 7 (via ligation of two pyridyl nitrogen atoms) and a μ_4 -bridging coordination mode in 4 and 5 (via ligation of two pyridyl nitrogen atoms and two carbonyl oxygen atoms), which play an important role in determining the dimensionality of the title complexes. The aromatic dicarboxylates serve as a linker (for 1) and three-connected nodes (for 2-7) to bridge the adjacent Cu(μ) ions, respectively, leading to the formation of various topological structures, which indicate both the substitute group and position of carboxyl group of the dicarboxylates play significant roles in the construction of the title complexes. The fluorescent, electrochemical and photocatalytic properties of complexes 1-7 have also been investigated.

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Introduction

Metal–organic coordination polymers have been given more research attention recently, not only for their intriguing variety of architectures and topologies,¹ but also for their potential applications as multifunctional materials with the properties of luminescence,² electrochemistry,³ magnetism,⁴ catalysis,⁵ and gas storage.⁶ Although a large amount of such polymers have been obtained by the self-assembly of metal ions and organic ligands, the influencing factors of the ultimate

structures, such as organic ligands,⁷ systematic pH value,⁸ template effect⁹ and reaction temperature,¹⁰ may play important roles in the process of the self-assembly. Therefore, significant interest has arisen in the structural tuning of coordination polymers through rational design and selection of organic building blocks, such as O-donor ligands and N-donor ligands. The dicarboxylates as multidentate O-donor ligands possess the following characteristics: firstly, the dicarboxylate ligands possess multiple potential coordination sites involving two -COOH groups and substitute group, which will be more conducive to coordinate with metal centers in the metal-organic coordination polymers and can be considered as connecting nodes or linkers to construct specific structures and topologies; secondly, they could serve as hydrogen bonding donors or acceptors to build high-dimensional supramolecular networks.¹¹ Based on the above two points, in the last decades, the dicarboxylates are usually used as the

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auxiliary ligands combining with various N-donor ligands to construct novel architectures.¹²

In the recent years, the combination of bis-pyridyl-bisamide ligands and carboxylate ligands can be regarded as an effective strategy to prepare attractive metal-organic coordination frameworks with different dimensionalities, which attracted great interest from researchers.13 Several groups have reported the assembly of rigid or semi-rigid bis-pyridyl-bisamide ligands with metal salts and some inorganic anions or various carboxylates.14 Our group also have been focusing our attention on the utilization of rigid or semi-rigid bis-pyridylbis-amide ligands combining with polycarboxylates in the construction of coordination polymers with diverse structures and multifunctional complexes.¹⁵ However, reports on the coordination complexes of flexible bis-pyridyl-bis-amide ligands are still limited.¹⁶ To the best of our knowledge, only quite a few examples based on the flexible N,N'-bis(3-pyridinecarboxamide)-1,2-ethane (3-dpye) with -(CH₂)₂- backbone or N,N'-bis-(3-pyridinecarboxamide)-1,4-butane (3-dpyb) with backbone of -(CH₂)₄- and polycarboxylates mixed ligands have been reported by us and others.¹⁷

In order to further explore the effect of flexible bis-pyridylbis-amide ligands with different spacer length and various coordination modes, as well as the dicarboxylates with different substitute group or position of carboxyl groups, on the assembly and structures of multifunctional Cu(II) metalorganic coordination polymers, in this work, three flexible bispyridyl-bis-amide ligands 3-dpye, 3-dpyb, N,N'-bis(3-pyridinecarboxamide)-1,6-hexane (3-dpyh) (Scheme 1) have been designed and used as the main ligands, four aromatic dicarboxylate ligands, 3-nitrophthalic acid (3-H₂NPA), 5-aminoisophthalic acid (5-H₂AIP), 1,3-benzenedicarboxylic acid (1,3-H₂BDC), 1,2-benzenedicarboxylic acid (1,2-H₂BDC) have been introduced to the Cu(II)/flexible bis-pyridyl-bis-amide systems. As a result, seven coordination polymers have been obtained under hydrothermal conditions (Scheme 2), namely [Cu(3-dpye)- $(3-NPA)(H_2O)]\cdot 3H_2O$ (1), $[Cu(3-dpye)_{0.5}(5-AIP)(H_2O)]$ (2), $[Cu(3-dpye)(1,3-BDC)] \cdot 3H_2O$ (3), $[Cu_3(3-dpye)(1,2-BDC)_2(\mu_2 - \mu_2)] \cdot 3H_2O$ (3), $[Cu_3(3-dpye)(1,2-BDC)_2(\mu_2 -$ OH_{2} (4), $[Cu_{3}(3-dpyb)(1,2-BDC)_{2}(\mu_{2}-OH)_{2}]$ (5), [Cu(3 $dpyh_{0.5}(1,2-BDC)] \cdot H_2O$ (6), $[Cu(3-dpyh)_{0.5}(5-AIP)(H_2O)]$ (7). To our knowledge, metal-organic coordination complexes constructed by the 3-dpyh and organic carboxylates mixed ligands have not been found up to now. The crystal structures and



Scheme 1 The structures of ligands 3-dpye, 3-dpyb and 3-dpyh.





topological analyses of these polymers have been represented and discussed. In addition, the fluorescent, electrochemical, and photocatalytic properties of 1–7 have also been investigated below in detail.

Results and discussion

Structural description

description of [Cu(3-dpye)(3-NPA) Crystal structure (H₂O)]·3H₂O (1). X-ray crystallography reveals that complex 1 crystallizes in the monoclinic system with space group $P2_1/c$. There is one $Cu(\pi)$ ion, one 3-dpye ligand, one 3-NPA anion, one coordinated water molecule, and three lattice water molecules in the asymmetric unit of complex 1. The crystallographically independent Cu(II) ion showing a distorted pyramid geometry $\{CuN_2O_3\}$, is coordinated by two nitrogen atoms from two 3-dpye ligands [Cu1–N2 = 2.014(2) Å, Cu1–N4 = 2.027(2) Å], three oxygen atoms from two 3-NPA anions and one coordinated water molecule [Cu1-O1 = 1.9751(18), Cu1-O5 = 1.9768(19), Cu1-O1W = 2.4513(25) Å] (Fig. 1a). In complex 1, The ligand 3-dpye adopts a μ_2 -bridging coordination mode connecting the neighbouring $Cu(\pi)$ ions to form a meso-helical $[Cu-3-dpye]_n$ chain (Fig. 1b). Furthermore, the adjacent [Cu-3 $dpye_n$ chains are linked by the 3-NPA anions with a bis(monodentate) coordination mode to form a 2D network (Fig. 1d), in which the 3-NPA also connect Cu(II) ions through its two carboxyl oxygen atoms in the opposite direction to build 1D [Cu-3-NPA] left- and right-helix chains (Fig. 1c and Scheme S1a[†]). For perspicuous representation, it is necessary to simplify the building blocks from the 2D metal-organic network. Each Cu(II) is surrounded by two 3-dpye ligands and two 3-NPA ligands, which can be defined as a 4-connected node. The 3-dpye and 3-NPA serve as a simple linear linker and a 'V'-like linker, respectively. Topological analysis reveals that the 2D layer of complex 1 represents a 4-connected network with $(4^4 \cdot 6^2)$ topology (Fig. 1e), in which two kinds of hexagon $[Cu_4(3-dpye)_2(3-NPA)_2]$ loops with dimensions of *ca.* 13.79 × 17.58 \AA^2 (loop A) and 15.33 × 16.26 \AA^2 (loop B) can be found. Additionally, the 2D layers are linked by the O-H…O hydrogen bonding interactions between O1W of the coordinated water

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Fig. 1 (a) ORTEP drawing of complex **1** with thermal ellipsoids at 50% probability (the H atoms and lattice water molecules have been omitted for clarity.); (b) the *meso*-helical [Cu-3-dpye] chain along the *a*-axis; (c) the [Cu-3-NPA] left-and right-handed helical chains along the *a*-axis; (d) view of the 2D layer in complex **1**; (e) the simplified representation of 2D layer in complex **1**.

molecule and O7 of the carbonyl group from 3-dpye ligand $[O(1W)-H(1WA)\cdots O(7), 2.7486 \text{ Å}, 166^\circ]$, generating a 3D supramolecular structure (Fig. S1[†]). The hydrogen bonding data are summarized in Table S1.[†]

Crystal structure description of $[Cu(3-dpye)_{0.5}(5-AIP)(H_2O)]$ (2). Crystal structure analyses reveal that complexes 2 and 7 are isostructural, so complex 2 is discussed here as the representative example. Single crystal X-ray diffraction analysis reveals that 2 is in triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit of 2 contains one Cu(π) ion, half of 3-dpye ligand, one 5-AIP anion and one coordinated water

molecule. Each Cu(II) ion is five-coordinated by two nitrogen atoms from the amino group of 5-AIP ligand [Cu1-N1 = 2.056(3)]Å] and pyridyl group of the 3-dpye ligand [Cu1-N2 = 2.027(3) Å], one oxygen atom from the coordinated water molecule [Cu1-O1W = 2.327(3) Å], and two carboxyl oxygen atoms [Cu1-O1 = 1.944(2) Å, Cu1-O4 = 2.001(2) Å] belonging to two different 5-AIP anions to furnish a distorted pyramid geometry (Fig. 2a for 2 and Fig. S8⁺ for 7). The nitrogen atoms from 3-dpye ligand and 5-AIP anion occupy the apexes and the other three coordinated oxygen atoms are located in the equatorial plane. As depicted in Fig. 2b and Scheme S1b, S1g,[†] each 5-AIP anions adopting a tri(monodentate) coordination mode links three Cu(II) ions to construct a 1D [Cu-5-AIP] ladder-like structure. Such adjacent [Cu-5-AIP] ladders are connected by the μ_2 -bridging 3-dpye ligands to form a 2D layer motif, which is shown in Fig. 2c. Furthermore, each Cu(II) ion can be considered as a four-connected node and 5-AIP can be regarded as a three-connected node, and the 3-dpye can be regarded as a linear linker, thus the resultant structure of 2 is a binodal 3,4connected 2D network with the point symbol of $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$, in which the large hexagonal $[Cu_4(3-dpye)_2(5-AIP)_2]$ loop is approximately 13.70 × 20.84 Å² in complex 2 (15.57 × 26.46 Å² in complex 7) (Fig. 2d for 2 and Fig. S9⁺ for 7). The 2D layers are further connected by hydrogen bonding interactions to form the 3D supramolecular structure, as shown in Fig. S2.⁺ The N-H…O hydrogen bonding interaction is formed between



Fig. 2 (a) ORTEP drawing of complex **2** with thermal ellipsoids at 50% probability (the H atoms have been omitted for clarity.); (b) view of the 1D [Cu-5-AIP] ladder-like chain in complex **2**; (c) view of the 2D layer in complex **2**; (d) the simplified representation of 2D layer in complex **2**.

the nitrogen atom (N3) from amino of 3-dpye and the oxygen atom O3 from carboxyl group of 5-AIP with N(3)–H(3B) \cdots O(3), 3.3684 Å, 169°. The hydrogen bonding data are summarized in Table S3.[†]

Crystal structure description of [Cu(3-dpye)(1,3-BDC)]·3H₂O (3). Complex 3 was obtained by the similar procedure used for complex 2, except that 1,3-H₂BDC was used instead of 5-H₂AIP. It crystallizes in triclinic crystal system with $P\bar{1}$ space group. The asymmetric unit of 3 consists of one $Cu(\pi)$ ion, one 3-dpye ligand, one 1,3-BDC anion, and three lattice water molecules. Each $Cu(\pi)$ ion is five-coordinated and displays a distorted pyramid geometry supplied by three carboxyl oxygen atoms from three different 1,3-BDC anions [Cu1-O2 = 2.0272(18) Å, Cu1-O3 = 1.9692(18) Å, Cu1-O6 = 2.220(2) Å], and two pyridyl nitrogen atoms from two 3-dpye ligands [Cu1-N1 = 2.035(2) Å, Cu1-N3 = 2.027(2) Å] (Fig. 3a). In 3, the Cu(π) ions are connected by 1,3-BDC ligands with a bi(monodentate) bridging mode to form a 1D [Cu-1,3-BDC] ladder-like structure (Fig. 3b and Scheme S1c[†]). In addition, the adjacent metal Cu(II) ions are connected by two μ_2 -bridging 3-dpye ligands to construct a 1D [Cu-3-dpye] polymer chain (Fig. S3[†]). The neighboring [Cu-1,3-BDC] ladder-like chains are linked by 3-dpye ligands to form a 2D layer, as shown in Fig. 3c. Each 1,3-BDC can be considered as a three-connected node and Cu(II) ion can be



Fig. 3 (a) ORTEP drawing of complex **3** with thermal ellipsoids at 50% probability (the lattice water molecules and H atoms have been omitted for clarity); (b) view of the 1D Cu-1,3-BDC ladder-like chain in complex **3**; (c) view of the 2D layer of complex **3**; (d) the simplified representation of 2D layer for complex **3**.

considered as a five-connected node, whilst 3-dpye is regarded as a linker, and the final structure of 3 is a binodal 3,5-connected network with the point symbol of $(4^2 \cdot 6^7 \cdot 8)(4^2 \cdot 6)$ (Fig. 3d). The 2D network of 3 contains two types of hexagon $[Cu_4(3-dpye)_2(1,3-BDC)_2]$ loops with dimensions ca. 15.24 × 15.75 \AA^2 (loop A) and 11.46 × 20.82 \AA^2 (loop B). Although two similar Cu(II) polymers based on the 3-dpye and 1,3-BDC mixed ligands have been reported, their crystal structures are different.¹⁷ Biradha et al.^{17a} reported the complex [Cu(3 $dpye_{2}(1,3-BDC)_{2}]\cdot 6H_{2}O$, which represented a 0D species with a protonated carboxyl group and a monodentate 3-dpye ligand. More recently, our group^{17b} also obtained a 3D polymer [Cu(3dpye)(1,3-BDC)(H₂O)]·H₂O exhibiting a 3-fold interpenetrating structure. The formation of the 0D species may be ascribed to the solvothermal synthetic method, whilst the 3D and 2D frameworks may be caused by the systematic pH in the same reactant.

Crystal structure description of $[Cu_3(3-dpye)(1,2-BDC)_2(\mu_2 OH_{2}$ (4). Crystal structure analyses reveal that complexes 4 and 5 are isostructural, so complex 4 is discussed here as an example. Single crystal X-ray diffraction analysis reveals that complex 4 is a 3D coordination polymer constructed from Cu(π) ions, μ_2 -OH groups, 3-dpye ligands and 1,2-BDC anions. There are two crystallographically independent $Cu(\pi)$ ions in 4. The Cu1 ion is four-coordinated by two carboxyl oxygen atoms from two different 1,2-BDC anions [Cu1-O1 and Cu1-O1#1, 1.941(3) Å], and two oxygen atoms from two coordinated μ_2 -OH [Cu1–O6 and Cu1–O6#1, 1.895(2) Å], showing a distorted tetrahedron coordination geometry. While the Cu2 ion is fivecoordinated by two carboxyl oxygen atoms from two different 1,2-BDC ligands [Cu2-O2 = 1.973(2) Å, Cu2-O3 = 1.964(2) Å], one carbonyl oxygen atom from a 3-dpye ligand [Cu2-O5 = 2.4613(29) Å], one pyridyl nitrogen atom from another 3-dpye ligand [Cu2–N1 = 2.070(3) Å], and one oxygen atom from a coordinated μ_2 -OH group [Cu2–O6 = 1.895(2) Å], exhibiting a distorted tetragonal pyramid coordination geometry (Fig. 4a for 4 and Fig. S4[†] for 5). The 1,2-BDC components adopting a bidentate-monodentate coordination mode alternately link the Cu1 and Cu2, resulting in a 1D [Cu-1,2-BDC] zigzag chain (Fig. 4b and Scheme S1d-e[†]) with the non-bonding Cu1…Cu2 distance of 3.5070(5) Å, Cu2…Cu2A distance of 3.5434(6) Å, and Cu1…Cu1A distance of 8.3526(10) Å (distances: 3.3499(4) Å, 3.4145(5) Å, and 8.0878(8) Å in complex 5). As shown in Fig. 4c, the 3-dpye ligand displays a μ_4 -bridging coordination mode via ligation of two pyridyl nitrogen atoms and two carbonyl oxygen atoms, which is different from the μ_2 -bridging 3-dpye in complexes 1–3. Therefore, μ_4 -bridging 3-dpye ligands and μ_2 -OH connected the Cu(II) ions to form a 2D layer, in which the large square-shape loops $[Cu_6(3-dpye)_2(\mu_2-OH)_4]$ are approximately 13.80 × 13.92 Å² in complex 4 (13.95 × 14.92 Å² in complex 5) (Fig. $S5^{\dagger}$). Furthermore, the 1D [Cu(1,2-BDC)] zigzag chains link these adjacent 2D layers to form an intriguing 3D net (Fig. S6[†]). It is necessary to simplify the building blocks from the 3D metal-organic framework. Each Cu1 is surrounded by two 1,2-BDC ligands and two μ_2 -OH, which can be regarded as a four-connected node, and Cu2 is linked by two

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Fig. 4 (a) ORTEP drawing of complex **4** with thermal ellipsoids at 50% probability. The H atoms have been omitted for clarity. Symmetry code: #1 - x + 1, -y, -z; (b) view of the 1D Cu-1,2-BDC chain in complex **4**; (c) view of the 2D layer in complex **4**; (d) the simplified representation of 3D net in complex **4**.

1,2-BDC ligands, two 3-dpye ligands and one μ_2 -OH, which can be considered as a five-connected node. The 3-dpye ligand acts as a 4-connector to bridge four Cu2 ions, and the 1,2-BDC ligand serves as a 3-connector to link three Cu(II) ions (one Cu1 ion and two Cu2 ions), thus the resulting structure of **4** is a novel 3,4,4,5-connected net with point symbol of $(3\cdot4\cdot5)_2(3\cdot4^2\cdot5\cdot8^6)_2(3^2\cdot8\cdot9^2\cdot10)(4^2\cdot8^2\cdot10^2)$ (Fig. 4d).

Crystal structure description of $[Cu(3-dpyh)_{0.5}(1,2-BDC)]$ ·H₂O (6). Complex 6 was obtained by a similar procedure to that of 4, except that 3-dpyh was used instead of 3-dpye. X-ray structural analysis reveals that complex 6 is a 2D network in triclinic crystal system with $P\bar{1}$ space group. As shown in Fig. 5a, the asymmetric unit of complex 6 contains one Cu(π) ion, one 1,2-BDC anion, half of 3-dpyh ligand, and one lattice water molecule. Each Cu(π) is five-coordinated by one pyridyl nitrogen atom from a 3-dpyh ligand [Cu1–N1 = 1.993(3) Å],



Fig. 5 (a) ORTEP drawing of complex **6** with thermal ellipsoids at 50% probability. The lattice water molecules and H atoms have been omitted for clarity. Symmetry code: #1 - x + 2, -y, -z + 1; (b) view of the 1D Cu-1,2-BDC double chain in complex **6**; (c) view of the 2D layer in complex **6**; (d) the simplified representation of 2D layer in complex **6**.

and four carboxyl oxygen atoms from four different 1,2-BDC ligands [Cu1-O1 = 1.952(3) Å, Cu1-O2 = 1.979(2) Å, Cu1-O4 = 1.941(3) Å, Cu1–O4#1 = 1.941(3) Å], showing a tetragonal pyramid geometry. Each 1,2-BDC ligand adopts a monodentate-bidentate bridging mode to connect three Cu(II) ions, forming an infinite 1D [Cu-1,2-BDC] zigzag double chain in 6 (Fig. 5b and Scheme S1f⁺). The 1D double chains are further connected by μ_2 -bridging 3-dpyh ligands to form the 2D layer (Fig. 5c). Each $Cu(\pi)$ can be considered as a four-connected node and 1,2-BDC can be considered as a three-connected node, and the structure of 6 is a binodal 3,4-connected 2D network with the point symbol of $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$. There exist a large hexagonal $[Cu_4(3-dpyh)_2(1,2-BDC)_2]$ loop of approximately 21.46 \times 23.72 Å² in complex 6 (Fig. 5d). Furthermore, such 2D layers are further linked together by two O-H···O hydrogen bonding interactions, one is between O1W of the coordinated water molecule and O9 of the carbonyl group from 3-dpyh ligand [O(1W)-H(1WA)-O(9), 2.8592 Å, 151°], and the other is between O1W of the coordinated water molecule and O3 of the carboxyl group from 1,2-BDC ligand [O(1W)-H(1WA)····O(3), 2.7340 Å, 177°], generating a 3D supramolecular structure (Fig. S7⁺). The hydrogen bonding data are summarized in Table S4.[†]

Effect of the dicarboxylates and flexible bis-pyridyl-bis-amide ligands on the assembly and structures of the complexes

As is well-known, dicarboxylates usually play an important role in constructing the target complexes. Complexes **1–4** show the

effect of intrinsic structures for these dicarboxylates on the final topologies: the 3-NPA and 5-AIP contain two carboxyl groups and one nitro or amino group, while the 1,3-BDC and 1,2-BDC only possess two carboxyl groups in different positions. For 1, each 3-NPA anion, as a 'V'-like linker, bridges two $Cu(\pi)$ ions to generate a 1D zigzag chain, which is extended by 3-dpye to a 2D 4-connected $(4^4 \cdot 6^2)$ topology. In 2, each 5-AIP anion, as a 3-connected node, links three Cu(II) ions to generate a 1D ladder-like chain, which is further connected by 3-dpye into a 2D 3,4-connected $(4^2 \cdot 6^3 \cdot 8)(4^2 \cdot 6)$ topology. Compared with 5-AIP, the 1,2-BDC or 1,3-BDC has less coordination sites, however, both are also serving as 3-connected nodes in 3 and 4. The different angles between the two carboxyl groups in 1,3-BDC and 1,2-BDC anions (120° and 60°, respectively) result in different Cu(II)-carboxylate motifs in 3 and 4. In 3, each 1,3-BDC anion links the Cu(II) ions to yield a 1D ladderlike chain, which is further extended by the 3-dpye ligands into a 2D layer with $(4^2 \cdot 6^7 \cdot 8)(4^2 \cdot 6)$ topology. However, in 4, each 1,2-BDC anion links the Cu(II) ions to generate a 1D zigzag chain, which is further extended by the 3-dpye ligands into a 3D framework with $(3\cdot4\cdot5)_2(3\cdot4^2\cdot5\cdot8^6)_2(3^2\cdot8\cdot9^2\cdot10)$ $(4^2 \cdot 8^2 \cdot 10^2)$ topology. Comparing 3 with 4, it is clear that the positions of the carboxyl groups show an important influence on the coordination mode of 3-dpye and structures of the complexes. Comparing 1 with 4, or 2 with 3, it is not difficult to find that the substitute groups of dicarboxylates also show some effect on the final structures. In addition, complexes 6 and 7 based on the same 3-dpyh ligand and different dicarboxylates exhibit different 2D topological structures, which also indicate the effect of dicarboxylates on the final structures. Therefore, we can conclude that both the substitute group and position of carboxyl group of the dicarboxylates play significant roles in the construction of the title complexes.

It is clear that the bis-pyridyl-bis-amide ligands also show obvious effect on the final architectures. In complexes 1-4, the 3-dpye ligand adopts two kinds of coordination modes: μ_2 -bridging mode in 1–3 with 2D topological structures, and μ_4 -bridging mode in 4 with 3D topological structure, which indicate that the coordination mode of 3-dpye show a great effect on the dimensionality of complexes. Complexes 4-6 based on the same 1,2-BDC anion also exhibit the effect of coordination modes of bis-pyridyl-bis-amide ligands on the dimensionality of target complexes. As described above, 4 and 5 are isostructural 3D frameworks, in which both the 3-dpye and 3-dpyb show μ_4 -bridging mode, while in complex 6, the 3-dpyh adopts a μ_2 -bridging mode, resulting in the formation of a 2D network. Similarly, the isostructural complexes 2 and 7 based on the same dicarboxylate 5-AIP and different bis-pyridyl-bisamide ligands further show that the coordination mode of the bis-pyridyl-bis-amide play a key role in the final networks. In addition, the spacer length of bis-pyridyl-bis-amide ligands also show a subtle effect on the final structures. In the isostructural 4 and 5, the large loops $[Cu_6(3-dpye)_2(\mu_2-OH)_4]$ in 4 and $[Cu_6(3-dpyb)_2(\mu_2-OH)_4]$ in 5 are different in size. When the ligand 3-dpyh with the longest spacer $-(CH_2)_6$ - was used in

complex **6**, the largest $[Cu_4(3\text{-}dpyh)_2(1,2\text{-}BDC)_2]$ loop $(21.46 \times 23.72 \text{ Å}^2)$ was constructed. So the coordination modes and the spacer length of bis-pyridyl-bis-amide ligands also show an important effect on the dimensionalities and structures of the title complexes.

IR analysis

The IR spectra of complexes 1-7 are determined in the frequency range of 500–4000 cm⁻¹, as shown in Fig. S10(a-g).[†] The strong peaks at 1625 and 1245 cm⁻¹ for 1, 1614 and 1284 cm⁻¹ for 2, 1612 and 1288 cm⁻¹ for 3, 1613 and 1207 cm⁻¹ for 4, 1641 and 1201 cm⁻¹ for 5, 1620 and 1296 cm^{-1} for **6**, 1618 and 1201 cm^{-1} for **7**, may be attributed to the asymmetric and symmetric vibrations of carboxyl groups. The bands around 1650 cm^{-1} for 1, 1678 cm^{-1} for 2, 1670 cm⁻¹ for 3, 1643 cm⁻¹ for 4, 1660 cm⁻¹ for 5, and 1651 cm⁻¹ for **6**, 1660 cm⁻¹ for **7**, are characteristic of the carbonyl groups. The presence of the characteristic bands at 1560, 1479, 1433, 1348 cm⁻¹ for **1**, 1556, 1479, 1415, 1363 cm⁻¹ for 2, 1544, 1475, 1431, 1369 cm⁻¹ for 3, 1550, 1473, 1402, 1320 cm⁻¹ for 4, 1544, 1479, 1400, 1319 cm⁻¹ for 5, 1581, 1483, 1400, 1359 cm⁻¹ for 6, 1558, 1479, 1415, 1363 cm⁻¹ for 7, suggest the $\nu_{\rm C-N}$ stretching vibrations of the pyridyl ring of the 3-dpye, 3-dpyb or 3-dpyh ligands. For complexes 1-3 and 6-7, the strong absorption peaks observed at 3344, 3439, 3487, 3433, and 3363 cm⁻¹ indicate the presence of -OH groups of water molecules. The bands at 3420 and 3404 cm⁻¹ can be assigned to stretching and bending vibrations of μ_2 -OH groups for complexes 4–5, respectively.

X-ray powder diffraction and thermogravimetric analyses

The X-ray powder diffraction (XRPD) patterns for complexes 1–7 are presented in Fig. S11.[†] The as-synthesized patterns are in good agreement with the corresponding simulated ones, indicating the phase purities of the samples.

To estimate the stability of the title complexes, thermogravimetric (TG) analyses are performed for complexes 1-7 (Fig. S12[†]). The TG curves of complexes 1–3 and 6–7 show two weight loss steps in the temperature range of 20-770 °C. The first weight loss stages start at 40 °C up to 171 °C for 1, 67 °C up to 89 °C for 2, 69 °C up to 116 °C for 3, 56 °C up to 75 °C for 6, 72 °C up to 152 °C for 7, with the weight loss of about 11.63% for 1, 4.04% for 2, 9.34% for 3, 4.51% for 6, 3.78% for 7, corresponding to the loss of the water molecules (calcd 11.71% for 1, 4.55% for 2, 9.78% for 3, 4.41% for 6, 3.91% for 7). The second weight loss occurring from 352 °C to 550 °C for 1, 148 °C to 607 °C for 2, 168 °C to 580 °C for 3, 221 °C to 512 °C for 6, 255 °C to 434 °C for 7, may suggest the decomposition of organic ligands. The weight losses are about 75.23% for 1, 74.85% for 2, 75.63% for 3, 75.76% for 6, 78.85% for 7, in correspondence with the calculated value of 75.28% for 1, 75.24% for 2, 75.73% for 3, 75.98% for 6, 78.70% for 7, respectively. The remaining weights (13.14% for 1, 21.11% for 2, 15.03% for 3, 19.73% for 6, 17.37% for 7) correspond to the percentage (13.01% for 1, 20.21% for 2, 14.49% for 3, 19.61%

for **6**, 17.39% for 7) of Cu and O components in CuO. Results of the TG analyses of complexes **4**–5 show that the two complexes possess similar thermal stabilities: the curve appears as a straight line up to 212 °C for 4 and 167 °C for 5, respectively. Beyond this temperature, the organic components (1,2-BDC and 3-dpye/or 3-dpyb) begin to decompose. When the temperature is up to 429 °C for 4 and 587 °C for 5, the weight lost about 70.26% for 4, 71.43% for 5 (calcd 70.77% for 4, 71.74% for 5), and the frameworks (29.74% for 4, 28.57% for 5) finally collapse to CuO (29.23% for 4, 28.26% for 5).

Fluorescent properties

In the recent years, the fluorescent properties of a variety of transition metal complexes have been reported. The Zn/Cd complexes are the most commonly reported fluorescent compounds, because the d¹⁰ metal ions not only possess various coordination numbers and geometries, but also exhibit luminescent properties when bound to functional ligands.¹⁸ The Cu(II) complexes do not contain d¹⁰ metal centers, but a series of fluorescent Cu(II) complexes have been reported.¹⁹ Density functional theory calculation indicates that the fluorescence may be mainly attributed to the coupling of ligand-to-metal charge transfer (LMCT) and metal-centered transitions.¹⁸ Therefore, the fluorescent properties of complexes 1-7 were investigated in the solid state at room temperature. To understand the nature of these emission bands, we also examined the fluorescent properties of the free ligands. As shown in Fig. 6a, the free 3-dpye ligand displays fluorescence with an emission maximum at 385 nm (λ_{ex} = 340 nm), while the fluorescent emission bands of complexes 1–4 are λ_{em} = 400 nm for **1**, 382 nm for **2**, 413 nm for **3**, 400 nm for **4** (λ_{ex} = 320 nm for 1–3, and λ_{ex} = 310 nm for 4), respectively. As far as we know, the polycarboxylates (3-NPA, 5-AIP, 1,3-BDC and 1,2-BDC) show very weak π^* -n transitions and contribute a little to the photoluminescence of the title complexes at room temperature.²⁰ For complex 2, the fluorescence is similar to that of the free ligand 3-dpye, which may probably be attributed to the intraligand $\pi^* \rightarrow \pi$ charge transitions.²¹ For complexes **1**, **3** and **4**, it is clear that an obvious red-shifted (15 nm for 1 and 4, 28 nm for 3) emission band has been observed comparing with the free 3-dpye. Therefore, the fluorescence behavior of 1, 3 and 4 can be attributed to the ligand-to-metal charge-transfer (LMCT), which is similar to the reported d¹⁰ metal complexes with N-donor ligands.²² The differences of fluorescence behavior for complexes 1-4 are probably caused by the different coordination environment of Cu(II) ions with N-donor ligands. In complex 1, 3, and 4, the neighboring $Cu(\pi)$ ions are linked by 3-dpye ligands building 1D chains, while in 2 the Cu(II) ions and 3-dpye ligands have not constituted a 1D chain. As shown in Fig. 6b, the free 3-dpyb ligand displays fluorescence with an emission maximum at 388 nm (λ_{ex} = 320 nm), while the fluorescent emission band of complex 5 is $\lambda_{em} = 400$ nm ($\lambda_{ex} =$ 320 nm), which also can be attributed to the ligand-to-metal charge-transfer (LMCT).²⁰ The similar fluorescent emission bands for complexes 4 and 5 may be due to their isostructural



Fig. 6 The emission spectra of complexes **1–7** and the free ligands (a) 3-dpye, (b) 3-dpyb and (c) 3-dpyh.

architectures. The results further highlight that photoluminescent behavior has a close relationship with the coordination environment of metal ions and the structures of the title complexes.²³ As shown in Fig. 6c, the free 3-dpyh ligand displays fluorescence with an emission maximum at 400 nm (λ_{ex} = 320 nm), while the strong fluorescent emission band of complexes 6 and 7 is λ_{em} = 398 nm and 396 nm (λ_{ex} = 320 nm), which may also probably be attributed to the intraligand $\pi^* \rightarrow \pi$ charge transitions. The fluorescent properties of 1–7 indicates that they may be anticipated as potential photoactive materials, especially for complex **6**.

Electrochemical behaviors

Fig. 7 and Fig. S13[†] show the cyclic voltammograms of complexes 1-7 bulk-modified carbon paste electrodes (1-, 2-, 3-, 4-, 5-, 6-, 7-CPE) in 0.01 M H₂SO₄-0.5 M Na₂SO₄ aqueous solution. It can be seen that an obvious redox couple was observed in the potential range of +700 to 100 mV for 1-CPE, +550 to 150 mV for 2-CPE, +500 to -450 mV for 3-CPE and 6-CPE, +600 to 250 mV for 4-CPE and 5-CPE, +600 to 200 mV for 7-CPE. The mean peak potential $E_{1/2} = (E_{pa} + E_{pc})/2$ is 40 mV for 1, +45 mV for 2, -73 mV for 3, +45 mV for 4, +36 mV for 5, -25 mV for 6, +50 mV for 7 (100 mV s⁻¹), which could be attributed to the redox of Cu(II)/Cu(I).²⁴ The differences of the mean peak potentials and peak currents among the title complexes may be attributed to the different coordination environment of Cu(II) and the final composition and structures of the title complexes.²⁵ The cyclic voltammograms of all the Cu-CPEs showed reversible or quasi-reversible redox couple of Cu(II)/Cu(I). Compared with other groups' works,²⁶ the reversibility of CVs with the title complexes are better.

Scan rates effect on the electrochemical behaviors of the 1–7-CPE were investigated in the potential range of +700 to 100 mV, +550 to 150 mV, +500 to -450 mV, +600 to 250 mV, +600 to 250 mV, +500 to -450 mV, +600 to 200 mV in 0.01 M H₂SO₄-0.5 M Na₂SO₄ aqueous solution, respectively. As shown in Fig. 8 and Fig. S14,[†] with the scan rates increasing from 20 to 280 mV s⁻¹ for 1-, 2-, 3-, 6-, 7-CPE, and 20 to 200 mV s⁻¹ for 4-, 5-CPE, the peak potentials gradually shift to the negative direction and the corresponding anodic peak potentials shift to the positive direction. The insets of Fig. 8 and Fig. S14[†] show that the peak currents are proportional to the scan rates up to 280 mV s⁻¹ for 1-, 2-, 3-, 6-, 7-CPE, and to 200 mV s⁻¹ for 4-, 5-CPE, respectively, suggesting that the redox processes for 1-7-CPE are surface controlled.²⁷



Fig. 7 Cyclic voltammograms of 1-CPE (+700 to 100 mV) in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution. Scan rate: 100 mV s⁻¹.



Fig. 8 Cyclic voltammograms of the **1**-CPE in 0.1 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, 240, 260, 280 mV s⁻¹). The inset shows the plots of the anodic and cathodic peak currents against scan rates.

Fig. S15[†] shows cyclic voltammograms for the electrocatalytic reduction of nitrite at a bare CPE and the 1-, 2-, 4-, 5-, 7-CPE in 0.01 M H_2SO_4 -0.5 M Na_2SO_4 aqueous solution. There is no redox peak at the bare CPE at the presence of nitrite in the potential range of +550 to 150 mV and +600 to 250 mV. With the addition of nitrite, the reduction peak currents increase gradually while the corresponding oxidation peak currents decrease gradually at the 1-, 2-, 4-, 5-, 7-CPE. We also examined the electrocatalytic reduction of nitrite at the 3-, 6-CPE, however, there is no obvious reduction peak. Thus, the results indicate that 1-, 2-, 4-, 5-, 7-CPE exhibit electrocatalytic activity toward the reduction of nitrite.

Photocatalytic property

It is well known that some coordination polymers have been reported to be good catalysts for the photo-degradation of organic dyes in recent years. But most of these polymers are constructed from the polyoxometalates building blocks.²⁸ By contrast, the investigations on the photocatalytic activities of metal-organic coordination polymers are less.²⁹ Here the photocatalytic performance of complexes 1-7 for the degradation of methylene blue (MB) were investigated through a typical process: 150 mg powder of the title complexes was dispersed in the MB solution (10.0 mg L^{-1}), magnetically stirred in the dark for 0.5 h to ensure the equilibrium of the working solution. The solution was then exposed to UV irradiation from a 125 W Hg lamp and kept continuously stirring. 3.0 mL of sample was taken out every 30 min for analysis. The photocatalytic properties of title complexes are shown in Fig. 9 and Fig. S16.[†] It can be seen that the absorption peak of MB decreased obviously along with the reaction time for the title complexes. Moreover, the concentrations of MB (C) against reaction time (t) of the title complexes were plotted. The calculation results show that approximately 80% of MB had been decomposed after 240 min with 3 and 6 as photocatalysts and the dissociation of MB was no more than 5% without any



Fig. 9 (a–b) Absorption spectra of the MB solution during the decomposition reaction under UV irradiation with the presence of complex **3** and **6**. (c) Photocatalytic decomposition rates of MB solution under UV irradiation with the use of the title compounds and no crystal in the same conditions.

catalyst. As is known, the differences of photocatalytic activities of metal–organic coordination polymers may be attributed to the different central metals and organic ligands, as well as the final structures of the complexes.³⁰ In the presence of UV light, there is an electron transfer from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The electron of the excited state in the LUMO is usually very unstable, while the HOMO strongly demands one electron to return to its stable state. During the photocatalytic process of complexes 1-7, the central Cu(II) ions and the ligands are involved. In order to return to its stable state for HOMO, the charge transfer excited state (bis-pyridyl-bis-amide ligands and aromatic polycarboxylates) was oxygenated water molecules to generate the ·OH radicals.³¹ Thus, the ·OH active species could decompose the MB to complete the photocatalytic process. In order to investigate the stability of complexes 1-7 as photocatalysts, we repeated the IR patterns of complexes 1-7 after the photocatalytic experiments, and the IR spectra are almost identical with those of the as-prepared samples (Fig. S10[†]). Control experiments were also carried out for the complexes. The CuCl₂·2H₂O, four aromatic dicarboxylates (3-H₂NPA, 5-H₂AIP, 1,3-H₂BDC and 1,2-H₂BDC), and three flexible bis-pyridyl-bis-amide ligands (3-dpye, 3-dpyb and 3-dpyh) were added to the MB solution under UV irradiation, respectively. However, they did not show observable photocatalytic activities. In addition, it shows no obvious MB degradation in the dark. The results indicate that complexes 1-7 may be good candidates for the photocatalytic degradation of MB, which would have potential photocatalytic activity in the reduction of some other organic dyes.

Conclusions

Three flexible bis-pyridyl-bis-amide ligands (3-dpye, 3-dpyb, 3-dpyh) with different spacers were introduced into the $copper(\pi)$ dicarboxylates systems and five 2D and two 3D multifunctional Cu(II) coordination polymers were obtained. In these polymers, the dicarboxylates exhibit different coordination modes or coordination capacities due to their different substitute group or position of carboxyl groups, and connect the $Cu(\pi)$ ions to form different metal-dicarboxylates chains, which reveals their great effect on the formation of the ultimate coordination architectures. In addition, three flexible bispyridyl-bis-amide ligands adopt two types of coordination modes: a μ_2 -bridging mode in 1–3 (for 3-dpye), 6 and 7 (for 3-dpyh), a μ_4 -bridging coordination mode in 4 and 5 (for 3-dpye and 3-dpyb), which plays an important role in determining the dimensionality of the title complexes. Both the four dicarboxylates and the three flexible bis-pyridyl-bis-amide ligands with different spacer length play important roles in the construction and properties of the versatile copper complexes. The title complexes exhibit intense fluorescence emissions, good electrochemical behaviors and excellent photocatalytic activities, which may make them potential candidates for luminescent, electrochemical and photocatalytic materials.

Experimental section

General considerations

All reagents and solvents for syntheses were purchased from commercial sources and used without further purification. The ligand 3-dpye, 3-dpyb and 3-dpyh were synthesized by the

reported procedure.³² Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C element analyzer. FT-IR spectra (KBr pellets) were obtained on a Shimadzu FT-IR 8400 spectrometer. Powder XRD investigations were carried out with an Ultima IV with D/teX Ultra diffractometer at 40 kV, 40 mA with Cu K α (λ = 1.5406 Å) radiation. Thermogravimetric data for complexes 1-7 were carried out on a Pyris Diamond thermal analyzer. Fluorescence spectra were recorded at room temperature on a Hitachi F-4500 fluorescence/phosphorescence spectrophotometer. A CHI 440 electrochemical workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used with an SCE as reference electrode, a platinum wire as auxiliary electrode and the modified electrodes as the working electrodes, respectively. UV-Vis absorption spectra were obtained using a SP-1900 UV-Vis spectrophotometer.

Preparation of complexes 1–7

Synthesis of $[Cu(3-dpye)(3-NPA)(H_2O)]\cdot 3H_2O$ (1). A mixture of CuCl₂·2H₂O (0.034 g, 0.2 mmol), 3-dpye (0.027 g, 0.1 mmol), 3-H₂NPA (0.032 g, 0.15 mmol), H₂O (12 mL) and NaOH (0.017 g, 0.42 mmol) was stirred for 30 min at room temperature and then transferred to a 25 mL Teflon-lined autoclave and kept at 120 °C for 4 days. After slowly cooling to room temperature, blue block crystals of 1 were obtained (yield: *ca.* 33% based on Cu). Anal. Calcd for C₂₂H₂₅CuN₅O₁₂: C 42.93, H 4.06, N 11.38. Found: C 42.95, H 4.03, N 11.36%. IR (KBr, cm⁻¹): 3803w 3732w, 3344m, 2869w, 2362m, 1651s, 1625s, 1560s, 1531s, 1479m, 1433m, 1348s, 1303m, 1245w, 1174w, 1126w, 1068w, 891w, 855m, 783m, 752m, 702s, 663w, 569w.

Synthesis of $[Cu(3-dpye)_{0.5}(5-AIP)(H_2O)]$ (2). The synthesis method of 2 is similar to that of 1 except for ligand 5-H₂AIP (0.027 g, 0.15 mmol) as the substitute of 3-H₂NPA, and the different amount of NaOH (0.016 g, 0.40 mmol) was added to adjust the systematic pH. Green block crystals of 2 were obtained (yield: *ca.* 35% based on Cu). Anal. Calcd for C₁₅H₁₄CuN₃O₆: C 45.47, H 3.54, N 10.61. Found: C 45.46, H 3.55, N 10.63%. IR (KBr, cm⁻¹): 3735w, 3357m, 3126m, 3082w, 2360m, 2333m, 1678s, 1614m, 1556s, 1475w, 1415s, 1363s, 1334m, 1284w, 1224w, 1197w, 1172w, 1112m, 1064w, 960m, 781m, 707w, 597w.

Synthesis of $[Cu(3-dpye)(1,3-BDC)]\cdot 3H_2O$ (3). The synthesis method of 3 is similar to that of 2 except for ligand $1,3-H_2BDC$ (0.025 g, 0.15 mmol) as the substitute of $5-H_2AIP$, and the different amount of NaOH (0.012 g, 0.30 mmol) was added to adjust the systematic pH. Green block crystals of 3 were obtained (yield: *ca.* 28% based on Cu). Anal. Calcd for $C_{22}H_{24}CuN_4O_9$: C 47.83, H 4.35, N 10.15. Found: C 47.81, H 4.39, N 10.17%. IR (KBr, cm⁻¹): 3876w, 3649w, 3365w, 3197w, 2333m, 1612s, 1544s, 1475m, 1431m, 1369s, 1319m, 1288w, 1272w, 1201w, 1168w, 1062w, 1035w, 825w, 742m, 721m, 700m, 655w, 520w.

Synthesis of $[Cu_3(3-dpye)(1,2-BDC)_2(\mu_2-OH)_2]$ (4). The synthesis method of 4 is similar to that of 2 except that ligand 1,2-H₂BDC (0.025 g, 0.15 mmol) was used instead of 5-H₂AIP, and the different amount of NaOH (0.014 g, 0.36 mmol) was added to

adjust the systematic pH. Green block crystals of **4** were obtained (yield: *ca.* 30% based on Cu). Anal. Calcd for $C_{30}H_{22}Cu_3N_4O_{12}$: C 43.84, H 2.68, N 6.82. Found: C 43.81, H 2.69, N 6.86%. IR (KBr, cm⁻¹): 3884w, 3743w, 3419w, 3186w, 3082w, 2356s, 1718m, 1643s, 1550m, 1473m, 1402s, 1207m, 1137w, 1091w, 1045w, 947w, 891w, 821m, 744m, 657m, 601s, 555w, 515w.

Synthesis of $[Cu_3(3-dpyb)(1,2-BDC)_2(\mu_2-OH)_2]$ (5). The synthesis method of 5 is similar to that of 4 except for ligand 3-dpyb (0.030 g, 0.1 mmol) as the substitute of 3-dpye, and the different amount of NaOH (0.016 g, 0.40 mmol) was added to adjust the systematic pH. Blue block crystals of 5 were obtained (yield: *ca.* 34% based on Cu). Anal. Calcd for $C_{32}H_{26}Cu_3N_4O_{12}$: C 45.22, H 3.06, N 6.59. Found: C 45.21, H 3.09, N 6.56%. IR (KBr, cm⁻¹): 3857w, 3801w, 3404m, 3062w, 2358m, 1641s, 1544s, 1479m, 1400s, 1319m, 1201m, 1157m, 1107m, 1033w, 827w, 806w, 752m, 700m, 651w, 584w.

Synthesis of [**Cu**(3-**dpyh**)_{0.5}(1,2-**BDC**)]·**H**₂**O** (6). The synthesis method of **6** is similar to that of **4** except for ligand 3-dpyh (0.033 g, 0.1 mmol) as the substitute of 3-dpye, and the different amount of NaOH (0.016 g, 0.40 mmol) was added to adjust the systematic pH. Blue block crystals of **5** were obtained (yield: *ca.* 32% based on Cu). Anal. Calcd for $C_{17}H_{16}CuN_2O_6$: C 50.02, H 3.92, N 6.87. Found: C 50.01, H 3.90, N 6.89%. IR (KBr, cm⁻¹): 3433w, 3197w, 3064w, 2920w, 2854w, 2360m, 1620s, 1581s, 1554s, 1510w, 1483m, 1400s, 1359s, 1296w, 1203m, 1143m, 1070w, 1035w, 831m, 792m, 700m, 651w, 572w.

Synthesis of [Cu(3-dpyh)_{0.5}(5-AIP)(H₂O)] (7). The synthesis method of 7 is similar to that of 6 except for ligand 5-H₂AIP (0.027 g, 0.15 mmol) as the substitute of 1,2-H₂BDC, and the different amount of NaOH (0.014 g, 0.36 mmol) was added to adjust the systematic pH. Green block crystals of 7 were obtained (yield: *ca.* 30% based on Cu). Anal. Calcd for C₁₇H₂₂CuN₃O₈: C 44.36, H 4.78, N 9.13. Found: C 44.38, H 4.79, N 9.15%. IR (KBr, cm⁻¹): 3857w, 3364m, 3261m, 3078m, 2931m, 2333m, 1660s, 1618s, 1558s, 1479m, 1415m, 1363s, 1321m, 1201w, 1143w, 1112m, 1021w, 962w, 933w, 777m, 734s, 684m, 624m, 584w, 551w.

Preparation of complexes 1–7 bulk-modified CPEs. The complexes **1–7** bulk-modified CPEs (**1-, 2-, 3-, 4-, 5-, 6-, 7-**CPE) were fabricated by mixing 0.50 g graphite powder and 0.030 g complexes **1–7** in an agate mortar for approximately 30 min to achieve a uniform mixture; then 0.16 mL paraffin oil was added and stirred with a glass rod.³³ The homogenized mixture was packed into a 3 mm inner diameter glass tube and the tube surface was wiped with weighing paper. The electrical contact was established with the copper wire through the back of the electrode. The bare CPE was prepared by a similar process without complexes **1–7**.

X-Ray crystallography

Crystallographic data for complexes 1–7 were collected on a Bruker SMART APEX II with Mo K α (λ = 0.71073 Å) by ω and θ scan mode. All the structures were solved by direct methods SHELXS program of the SHELXTL package.³⁴ For complexes 1–7, the crystal parameters, data collection, and refinement

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Table 1 Cr	vstallographi	c data for	complexes 1–7

Complex	1	2	3	4	5	6	7		
Complex Empirical formula Formula weight Crystal system Space group a (Å) b (Å) c (Å) a (°) β (°) γ (°) V (Å ³) Z D_c (g cm ⁻³) μ (mm ⁻¹) F (000)	$\begin{array}{c} 1\\ C_{22}H_{25}CuN_5O_{12}\\ 615.01\\ Monoclinic\\ P21/c\\ 9.0931(6)\\ 13.8662(10)\\ 20.4468(15)\\ 90\\ 90\\ 92.7390(10)\\ 90\\ 2575.1(3)\\ 4\\ 1.586\\ 0.922\\ 1268\\ \end{array}$	$\begin{array}{c} 2\\ C_{15}H_{14}CuN_3O_6\\ 395.83\\ Triclinic\\ P\bar{1}\\ 6.9268(7)\\ 10.0557(11)\\ 11.1566(13)\\ 104.553(2)\\ 99.146(2)\\ 99.756(2)\\ 727.43(14)\\ 2\\ 1.807\\ 1.544\\ 404 \end{array}$	$\begin{array}{c} 3\\ \\ C_{22}H_{24}CuN_4O_9\\ 551.99\\ Triclinic\\ P\bar{1}\\ 10.004(3)\\ 10.719(3)\\ 11.754(3)\\ 106.938(5)\\ 101.838(5)\\ 92.317(4)\\ 1173.2(6)\\ 2\\ 1.563\\ 0.992\\ 570\\ \end{array}$	$\begin{array}{c} \textbf{4} \\ \hline \\ C_{30}H_{22}Cu_3N_4O_{12} \\ 821.14 \\ Triclinic \\ P\bar{1} \\ 8.3526(10) \\ 8.6543(10) \\ 10.7547(13) \\ 85.213(2) \\ 75.719(2) \\ 80.446(2) \\ 742.20(15) \\ 1 \\ 1.837 \\ 2.205 \\ 413 \end{array}$	$\begin{array}{c} 5\\ \\ C_{32}H_{26}Cu_3N_4O_{12}\\ 849.19\\ \\ Triclinic\\ P\bar{1}\\ 8.0878(7)\\ 8.8044(8)\\ 11.3643(10)\\ 85.133(2)\\ 75.9090(10)\\ 87.445(2)\\ 781.81(12)\\ 1\\ 1.804\\ 2.097\\ 429 \end{array}$	$\begin{array}{c} 6 \\ & \mathbf{C}_{17}\mathbf{H}_{16}\mathbf{CuN}_{2}\mathbf{O}_{6} \\ & 407.86 \\ & \text{Triclinic} \\ P\bar{1} \\ & 5.9159(12) \\ & 11.620(2) \\ & 12.661(3) \\ & 74.184(4) \\ & 80.552(4) \\ & 81.929(4) \\ & 821.9(3) \\ & 2 \\ & 1.648 \\ & 1.368 \\ & 418 \end{array}$	$\begin{array}{c} 7\\ C_{17}H_{22}CuN_3O_8\\ 459.92\\ Triclinic\\ P\bar{1}\\ 8.9363(10)\\ 10.1567(12)\\ 10.7519(12)\\ 80.852(2)\\ 79.235(2)\\ 74.262(2)\\ 916.69(18)\\ 2\\ 1.666\\ 1.245\\ 476\\ \end{array}$		
Reflection collected Unique reflections Parameters R_{int} GOF $R_1^{\ a} [I > 2\sigma(I)]$ $wR_2^{\ b}$ (all data)	14 512 5046 361 0.0342 1.055 0.0418 0.1106	4182 2824 232 0.0223 1.006 0.0432 0.0978	6230 4091 325 0.0165 1.048 0.0356 0.0925	3804 2586 223 0.0107 1.049 0.0306 0.0867	4135 2747 232 0.0107 1.064 0.0284 0.0822	3721 2836 241 0.0296 0.984 0.0447 0.0992	4680 3196 262 0.0166 1.040 0.0441 0.1154		
${}^{"}R_{1} = \Sigma F_{o} - F_{c} / \Sigma F_{o} . {}^{"}wR_{2} = \Sigma w(F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w(F_{o}^{2})^{2} ^{1/2}.$									

results are summarized in Table 1. Selected bond distances and bond angles are listed in Table S1.[†] Hydrogen bonding geometries of complexes **1**, **2** and **6** are summarized in Tables S2–S4.[†] CCDC 889598, 889600, 889599, 889597, 891322, 891323, and 909348 for complexes **1–7** contain the supplementary crystallographic data in this paper.

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