Construction of copper metal–organic systems based on paddlewheel SBU through altering the substituent positions of new flexible carboxylate ligands†

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Received 6th March 2009, Accepted 16th July 2009
First published as an Advance Article on the web 7th August 2009
DOI: 10.1039/b904671b

Three flexible dicarboxylate ligands 2,2′-(1,2-phenylenebis(methylene))bis(sulfanediyl)dibenzoic acid ($H_2\mathbf{L}^6$), 2,2′-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)bis(oxy)dibenzoic acid ($H_2\mathbf{L}^7$) and 2,2′-(1,4-phenylenebis(methylene))bis-(sulfanediyl)dinicotinic acid ($H_2\mathbf{L}^8$), have been designed and synthesized. All ligands can adopt *syn* or *anti* conformations and the positions of the functional substituents in the central benzene ring change gradually from 1,2-, 1,3- to 1,4-position. By applying these flexible ligands to assemble with copper ions, four metal–organic complexes based on paddlewheel SBU have been isolated. Complexes **1** and **2** are discrete molecular chairs. Complex **3** is a 1D molecular-chair-based coordination polymer. The molecular chairs, similar to that found in **1** and **2**, are infinitely connected by the bridging 4,4′-bipy ligands to result in the formation of the 1D chain structure. Complex **4** is a two-dimensional wavelike layer structure containing a 68-member ring. Both $\mathbf{L}^6$ and $\mathbf{L}^7$ in **1** and **2** adopt *syn* conformation, while $\mathbf{L}^8$ adopts *anti* conformation, which results in the formation of the 2D layer structure of complex **4**.

Introduction

Metal–organic frameworks (MOFs) have attracted much interest from many chemists due to their amazing structural topologies[1] and potential applications.[2–8] The construction of low dimensional MOFs, such as 0D discrete molecules, 1D coordination polymer and 2D layer metal–organic frameworks, is highly influenced by the ligand geometry and the coordination geometry of the metal ions. Thus, selecting a suitable organic ligand with versatile binding modes to coordinate to a metal ion with plastic coordination geometry is crucial to the construction of metal–organic systems with desired topologies.

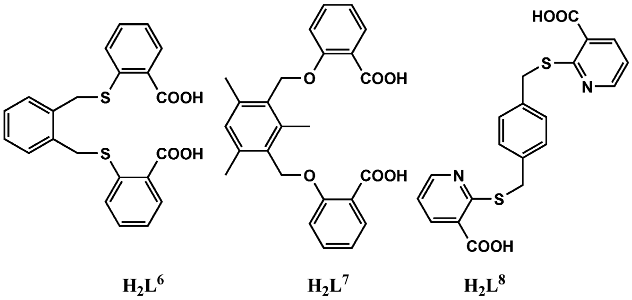
In the past decades, much research has been focused on the construction of metal–organic systems based on a rigid pyridine-based ligand and carboxylate ligands with functional groups.[9] However, the systemic research of flexible carboxylate ligand in the construction of metal–organic systems is somewhat rare.[10] Recently, Sun and coworkers have reported a series of metal–organic frameworks based on several flexible tripodal ligands such as benzene-1,3,5-triacetate, 1,3,5-tris(imidazol-1-ylmethyl)-2,4,6-trimethylbenzene and their derivatives.[11] In these complexes, the flexible tripodal ligands can adopt *cis*, *trans*, *trans* or *cis*, *cis*, *cis* conformation based on the requirement of the metal ions or the 3D packing.

In this paper, we focus our attention on the construction of metal–organic systems based on flexible dicarboxylate ligands and studying the effect of their conformation on the final structures of the products. By altering the positions of the functional substituents in the central benzene ring, three new flexible dicarboxylate ligands have been synthesized, 2,2′-(1,2-phenylenebis(methylene))bis(sulfanediyl)dibenzoic acid ($H_2\mathbf{L}^6$), 2,2′-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)bis(oxy)dibenzoic acid ($H_2\mathbf{L}^7$) and 2,2′-(1,4-phenylenebis(methylene))bis(sulfanediyl)dinicotinic acid ($H_2\mathbf{L}^8$) (Scheme 1), in which the positions of the functional substituents in the central benzene ring change gradually from 1,2-, 1,3- to 1,4-position, resulting in the different linking directions of the ligands when they coordinate to metal ions or cluster. Herein, reported are four novel metal–organic complexes, $Cu_2(\mathbf{L}^6)_2(dmf)_2\cdot 2dmf\cdot H_2O$ (**1**), $Cu_2(\mathbf{L}^7)_2(dmf)_2\cdot 2dmf$ (**2**), $Cu_2(\mathbf{L}^7)_2(bpy)\cdot 2dmf\cdot H_2O$ (**3**), $Cu_2(\mathbf{L}^8)_2(dmf)_2\cdot dmf\cdot H_2O$ (**4**), based on copper paddlewheel SBU.

Results and discussion

Syntheses

As mentioned above, the conformation of the organic ligand and the coordination geometry of the metal ion or cluster are two determining factors and should always be carefully taken into



$H_2\mathbf{L}^6$ $H_2\mathbf{L}^7$ $H_2\mathbf{L}^8$

Scheme 1 Flexible dicarboxylate ligands involved in this work.

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† CCDC reference numbers 721690 for **1**, 714741 for **2**, 714742 for **3** and 721691 for **4**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b904671b

consideration in the design and synthesis of low-dimensional frameworks such as 0D discrete molecule, 1D supramolecular chain and 2D layer. Our strategy in the design and synthesis of low dimension frameworks is to use flexible dicarboxylate ligands with appropriate angles and conformation to coordinate to a given SBU. As known, the copper ion is apt to forming rigid paddlewheel SBU when it reacts with a carboxylate ligand.[12] Our goal in this paper is to illuminate how the ligand conformation influences the structure of the product for a given paddlewheel SBU. By a self-assembly of a flexible carboxylate ligand with the paddlewheel SBU, four copper metal–organic systems, 0D molecular chair of complexes **1** and **2**, 1D molecular-chair-based chain of complex **3** and 2D wave-like layer of complex **4** have been synthesized.

Molecular chair of $Cu_2(L^6)_2(dmf)_2\cdot dmf\cdot H_2O$ (1)

Single-crystal X-ray diffraction reveals that complex **1** is a binuclear molecule possessing "chair-like" conformation. The asymmetric unit of **1** consists of one copper ion, one **L**^{6} ligand, two dmf molecules and one H_2O molecule. The Cu∼2∼ complex lies about an inversion centre. Two copper ions are engaged by four carboxylate groups from two **L**^{6} ligands to generate the binuclear paddlewheel SBU with an average Cu–O distance of 1.977(2) Å. The axial positions of the paddlewheel are occupied by the coordinated dmf molecules with a Cu–O distance of 2.138(2) Å.

The two functional substituents (2-mercaptobenzoic acid) are located in the same side of the benzene ring and the whole **L**^{6} ligand possesses cancroid arrangement. Two such cancroid ligands bridge two copper ions to form a "chair-like" molecule, as shown in Fig. 1. The two central benzene rings of the two **L**^{6} ligands are parallel to each other, while the central benzene ring and the side benzene rings in the same ligand are not in a plane with the average dihedral angle of 82.65°.

The π···π interactions between the side benzene ring of **L**^{6} ligand in one molecular chair and the side benzene ring in the neighbor molecule further connect the discrete molecules into a 1D supramolecular chain, as shown in Fig. 2a and b. The distance between the side benzene ring is 3.458 Å, falling into the strong π···π interaction range.[13] The nearest distance between the molecular chairs in the supramolecular chain is 11.016 Å and Fig. 2c shows the 3D packing structure of **1**.

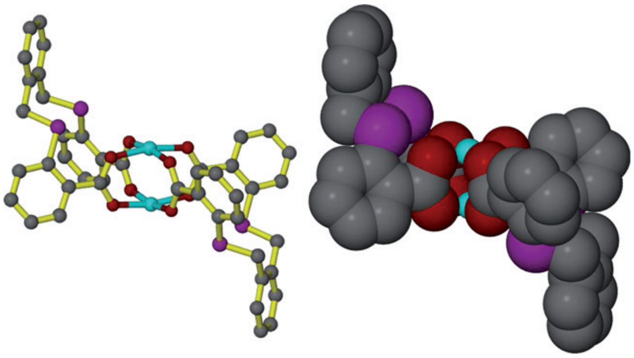


Fig. 1 The molecular chair of **1**.

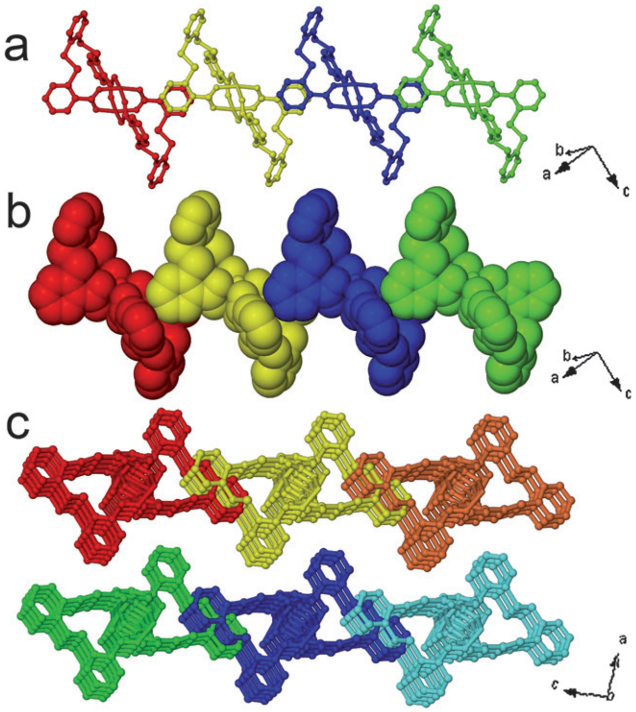


Fig. 2 (a) Ball-stick and (b) space-filling representation of the 1D chain formed by π···π interactions, (c) the 3D packing of **1**, the 1D supramolecular chain is represented in the same color.

Complexes 2 and 3—from molecular chair (2) to 1D molecular-chair-based coordination polymer (3)

Complexes **2** and **3** are constructed from flexible 2,2′-(2,4,6-trimethyl-1,3-phenylene)bis(methylene)bis(oxy)dibenzoic acid, based on dicopper paddlewheel SBU. Single-crystal X-ray diffraction reveals that complex **2** is a binuclear molecule possessing "chair-like" conformation. The asymmetric unit of **2** consists of one copper ion, one **L**^{7} ligand, one coordinated dmf molecule and one uncoordinated dmf molecule. The Cu∼2∼ complex lies about an inversion centre. Two copper ions are engaged by four carboxylate groups from two **L**^{7} ligands to generate the binuclear paddlewheel SBU with an average Cu–O distance of 1.969(3) Å, slightly shorter than that in complex **1**. The axial positions of the paddlewheel are occupied by the coordinated dmf molecules with a Cu–O distance of 2.141(3) Å, which does not differ significantly from what was found in complex **1** (2.138(2) Å).

The two functional substituents (2-hydroxybenzoic acid) are located in the same side of the benzene ring and the whole **L**^{7} ligand possesses cancroid-like conformation. Two such cancroid-like ligands bridge two copper ions to form a molecular chair, as shown in Fig. 3. The two central benzene rings of the two **L**^{7} ligands are parallel to each other, while the central benzene ring and the side benzene rings in the same ligand are not in a plane with the average dihedral angle of 84.6°, which is slight larger than that in **L**^{6} in complex **1**.

There also exist π···π interactions between molecular chairs in **2**. However, different from complex **1**, the π···π interactions occur between the central benzene rings of **L**^{7} in different molecular chairs, which connect the discrete molecules into a 1D

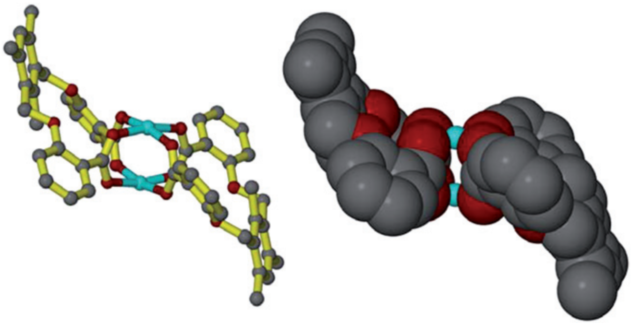


Fig. 3 The molecular chair of **2**.

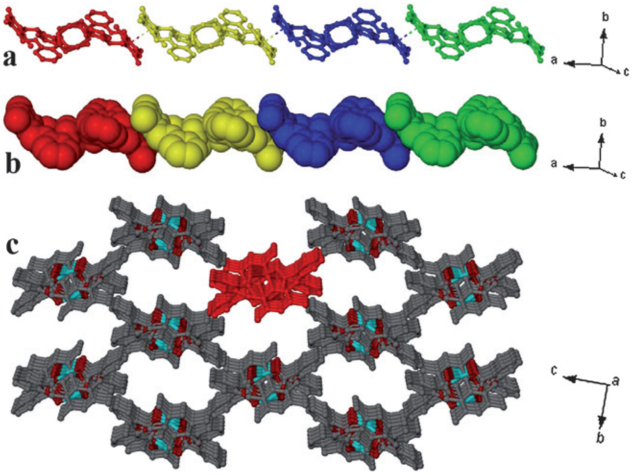


Fig. 4 (a) Ball-stick and (b) space-filling representation of the 1D chain formed by $\pi \cdots \pi$ interactions, (c) the 3D packing of **2**, the 1D supramolecular chain is shown in red color.

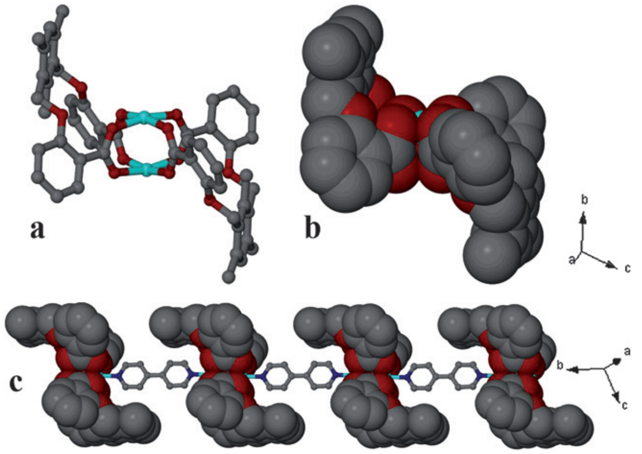


Fig. 5 (a) and (b) The chair-like unit in **3**, (c) the 1D fishbone-like chain of **3**.

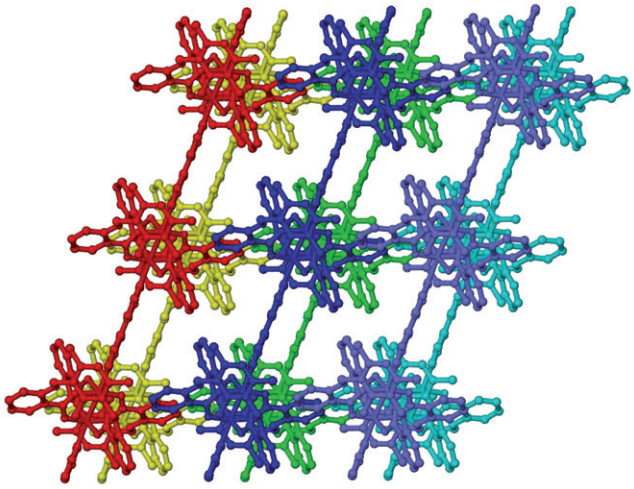


Fig. 6 The 3D packing structure of **3**. Different chains are shown in different colors.

supramolecular chain, as shown in Fig. 4a and b. The distance between the central benzene rings is 3.615 Å, much longer than that in **1**. The nearest distance between the molecular chair in the supramolecular chain is 10.055 Å and Fig. 4c shows the 3D packing structure of **2**.

Recently, it has been reported that the complicated structure can be hierarchically organized by a simple structural unit.[14] As mentioned above, the two axial positions of the dicopper paddlewheel SBU are occupied by two dmf molecules in **2**. If the two dmf molecules are replaced by a bridging organic ligand, then the molecular chair will be connected to give rise to a one-dimensional coordination polymer.[15] When the bridging 4,4′-bipy was added to the reaction system as synthesis of **2**, complex **3** was isolated as blue crystals.

Single-crystal X-ray diffraction reveals that complex **3** is a one-dimensional fishbone-like chain. There is one copper ion, one $\mathbf{L}^7$ ligand, half bpy ligand, two uncoordinated dmf molecules and one uncoordinated water molecule in the asymmetric unit. The Cu∼2∼ complex lies about an inversion centre. As expected, the axial dmf molecules were replaced by the bpy ligands and the molecular chair was connected along the *c* axis to form a one-dimensional coordination polymer (Fig. 5). The chair-like unit in **3** is quite similar to that in **2**, except that the average Cu–O distance changes to 1.967(4) Å and the average dihedral angle between the central benzene ring and the side benzene ring of $\mathbf{L}^7$ ligand changes to 48.5°. The nearest distance between two paddlewheel SBUs in the chain is 14.124 Å. Fig. 6 shows the 3D packing of **3**.

2D wave-like layer of 4

In complexes **1–3**, all carboxylate ligands adopt *syn* conformation to coordinate to metal ions, providing a molecular chair or 1D molecular-chair-based coordination polymer. However, if the flexible carboxylate ligand adopts *anti* conformation, what kind of structure will it result in? Fortunately, when we used $\mathbf{L}^8$ as ligand to assemble with the copper ion, complex **4** containing *anti* conformation of $\mathbf{L}^8$ was isolated as a blue block crystal.

Complex **4** is a two-dimensional layer structure containing 68-member ring. The asymmetric unit consists of one copper ion, one $\mathbf{L}^8$ ligand, one uncoordinated water molecule and two dmf molecules. The Cu∼2∼ complex lies about an inversion centre. Fig. 7 shows the coordination environment of the copper ion and the conformation of $\mathbf{L}^8$ ligand in complex **4**. The axial positions of the paddlewheel SBU are occupied by dmf molecules with a Cu–O

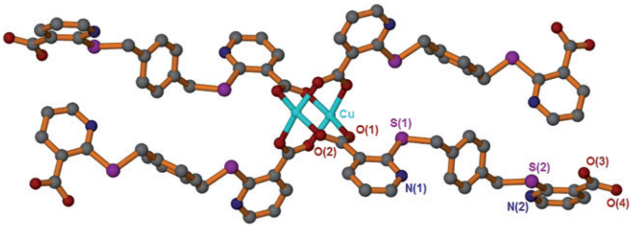


Fig. 7 The paddlewheel SBU showing the conformation of **L**^{8} ligand.

distance of 2.129(2) Å. Different from the ligands in complexes **1–3**, the **L**^{8} ligand in **4** is adopting an *anti* conformation with an average dihedral angle between the central benzene ring and the side benzene ring of 66.95°, and linking two paddlewheel SBUs to give rise to a two-dimensional wave-like layer (Fig. 8) with the nearest Cu–Cu distance between the SBUs being 14.462 Å.

In the 2D layer, four **L**^{8} ligands connect four paddlewheel SBUs to constitute a 68-member quadrate metallamacrocycle (28.8 × 3.9 Å) (Fig. 8a and b). Thus, the wavelike layer can also be considered as formed by infinitely sharing the 68-member metallamacrocycles. Although several 2D layer frameworks containing macrocycles have been reported,[16] examples such as in **4** containing large 68-member metallamacrocycles are still rare. If the paddlewheel SBU can be considered as a single node and **L**^{8} as a linear linker, then complex **4** has a (4,4) net, as shown in Fig. 8c. The 2D wavelike layers stack each other to generate a 3D supramolecular architecture (Fig. 9).

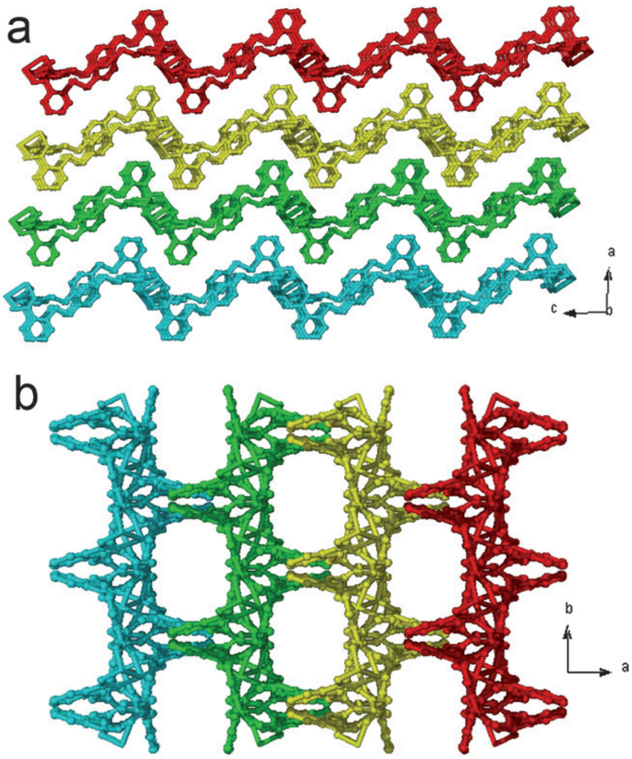


Fig. 9 The 3D packing structure of **4**. The different layers were shown in different colors.

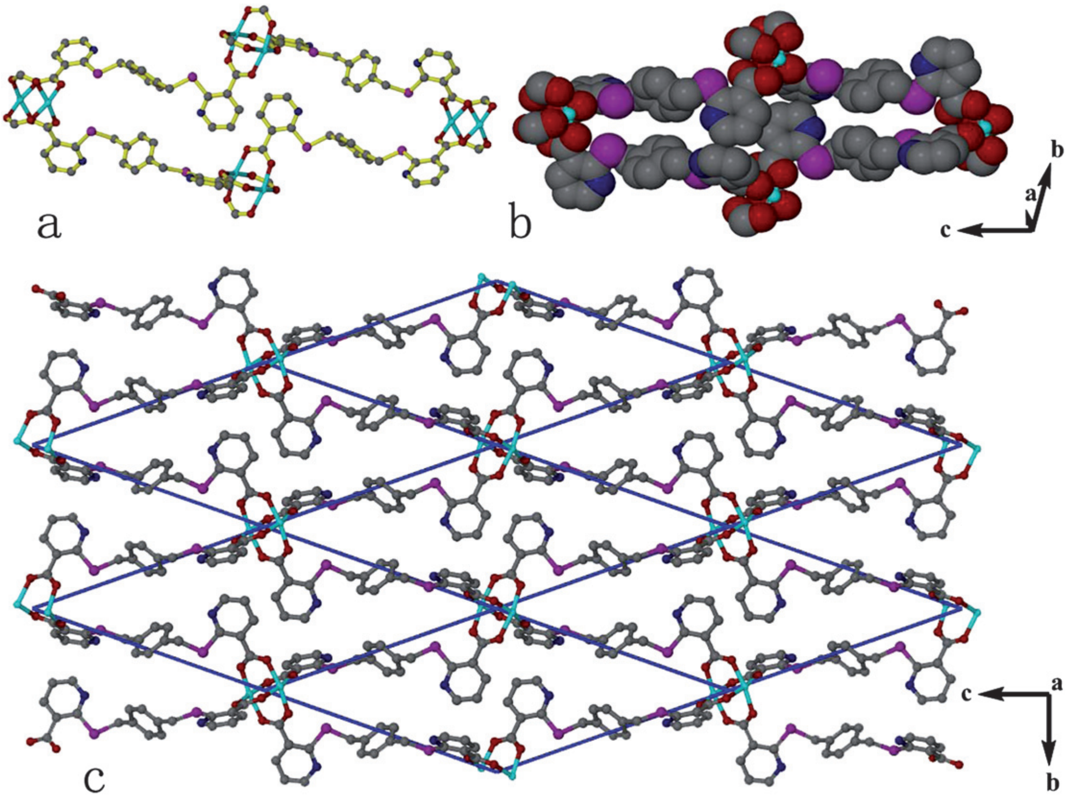


Fig. 8 (a) and (b) The 68-member metallamacrocycle in **4**, (c) the 2D layer of **4**.

Effect of the ligand geometry on the supramolecular structures

It is well known that the ligand geometry has a significant influence on the structure of the final product,[17] In **L**^{6}, the two 2-mercaptobenzoic acid groups are located in the 1,2-positions of the central benzene ring, and the two flexible substituted groups are bent to make the two carboxylate groups chelate one paddlewheel SBU. The ligand adopts *syn* conformation and two such ligands chelate one paddlewheel SBU to generate a "chair-like" molecule of **1**. When the substituents are changed to the 1,3-positions of the central benzene ring as in **L**^{7} ligands, the two carboxylate groups are separated much, but as the flexible arm of the ligands can bend itself to achieve near-parallel conformation, it can still chelate the paddlewheel SBU in *syn* conformation to form molecular chair, similar to that in complex **1**. It is worth noting that the substituents in 1,3-position of the central benzene ring in **L**^{7} ligand relieve the overcrowding hindrance between the side benzene rings, which make the paddlewheel SBU more open than that in complex **1**. When 4,4-bipy was added in the reaction, it replaced the axial dmf molecules to connect the discrete molecular chairs to generate the 1D coordination polymer. When the substituents locate in 1,4-position of the central benzene ring as in **L**^{8} ligand, the two carboxylate groups are separated the farthest, which makes the flexible arms of the ligands difficult to bend itself to achieve synclastic near-parallel conformation to chelate one paddlewheel SBU, resulting in its connecting different paddlewheel SBUs in *anti* conformation to form a 2D layer framework. The comparison between complexes **1–4** is listed in Table 1.

Thermogravimetric analysis

Thermogravimetric analysis was measured for complexes **1–4**. A TGA study on an as-isolated crystalline sample of **1** shows a 14.98% weight loss from 50 to 200 °C, corresponding to the loss of two uncoordinated dmf molecules and two incoordinated water molecules (calcd: 14.34%). The second gradual weight loss of 11.6% from 200 to 240 °C corresponds to the loss of two coordinated dmf molecules (calcd: 11.5%), and after 240 °C, **1** starts to decompose. For complex **2**, there is no weight loss from 50 to 160 °C. The rapid weight loss of 21.5% between 165 and 200 °C is in accordance with the loss of two uncoordinated and two coordinated dmf molecules (calcd: 23.3%), and after that, **2** starts to decompose. For complex **3**, we did not find the loss of the uncoordinated water molecule in the lattice. A rapid weight loss of 10.5% from 225 to 250 °C corresponds to the loss of one uncoordinated dmf molecule (calcd: 9.8%), and after that, **3** starts to decompose. For complex **4**, the first weight loss of 14.8% from 50 to 150 °C corresponds to the loss of two uncoordinated water molecules and two uncoordinated dmf molecules (calcd: 14.2%), the second weight loss of 11.27% between 150 and 225 °C is in accordance with the loss of two coordinated dmf molecule. (calcd: 11.42%) and after that, **4** starts to decompose.

Conclusion

By using flexible dicarboxylate ligands to assemble with copper ions, a series of copper metal–organic systems based on paddlewheel SBU has been constructed. The positions of the functional substituents on the central benzene ring as well as the conformation of the ligands have a significant effect on the formation of the compounds. In **1–3**, the ligands adopt *syn* conformation, which is the key to forming 0D molecular chair or 1D molecular-chair-based coordination polymer. The *anti* conformation of **L**^{8} ligand in complex **4** results in the formation of a 2D layer framework. Further studies will focus on the synthesis of other metal–organic systems with **L**^{6}–**L**^{8} ligands that adopt different conformation.

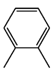
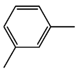
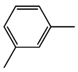
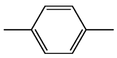
Experimental

Materials and physical measurements

All chemicals used are as purchased without purification. Thermogravimetric experiments were performed using a TGA/SDTA851 instrument (heating rate 10 °C min^{-1}, argon stream). Elementary analyses were carried out in the elementary analysis group of this institute.

Synthesis of H$_2$L^6. Sodium methoxide (1.62 g, 0.03 mol) was dissolved in absolute methanol (200 mL). The *o*-mercapto benzoic acid (4.63 g, 0.03 mmol) was then added with stirring. After the mixture had been stirred for 10 min at room temperature, 1,2-bis(bromomethyl)-benzene (2.64 g, 0.01 mmol) was added and the reaction mixture was stirred under refluxing for 6 h. The solid was filtered while still hot, and dissolved in water. After removing any undissolved substance by filtration, the filtrate was acidified with dilute hydrochloric acid. The solid was filtered and washed with water and hot methanol. Yield: 60%. ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 4.31$ (s, 2 H), 7.23 (m, 1 H), 7.31 (m, 1 H), 7.48 (m, 3 H), 7.90 (d, 1 H), 13.09 (s, 1 H). ^{13}C NMR (400 MHz, 298 K, (CD$_3$)$_2$SO): $\delta = 167.9$, 141.5, 135.3,

Table 1 Comparison between complexes **1–4**

Complexes	1	2	3	4
Ligands	**L**^{6}	**L**^{7}	**L**^{7}	**L**^{8}
Positions of substituents				
Conformation of the ligands	*syn*	*syn*	*syn*	*anti*
Separation of carboxylate groups/Å	3.44	3.804	3.627	13.868
Structures	molecular chair	molecular chair	molecular-chair-based coordination polymer	2D layer

132.9, 131.3, 131.0, 128.3, 128.2, 126.4, 124.6, 33.8. Elemental anal. Calcd for H_2L^6: C, 64.37; H, 4.42; S, 15.62%. Found: C, 64.25; H, 4.45; S, 15.46%.

Synthesis of H_2L^7. A mixture of 2,4-bis(bromomethyl)-1,3,5-trimethylbenzene (3.06 g, 10.0 mmol), methyl salicylate (3.08 g, 22.0 mmol) and K_2CO_3 (3.04 g, 22 mmol) in 40 ml acetone was refluxed for 6 h. The reaction mixture was filtered while it was still hot, then cooled to room temperature and white precipitate formed. The white solid and NaOH aqueous solution (20 ml, 2 mol L^{-1}) were mixed in 30 ml methanol and stirred for 8 h under refluxing. After cooling to room temperature, the clear solution was acidified to pH = 2 by dilute hydrochloric acid. The resulting white precipitates were washed with water and dried in air to give H_2L^7, yield: 30%. 1H NMR (300 MHz, DMSO-*d*$_6$): δ = 2.31 (s, 3 H), 2.51 (s, 6 H), 5.16 (s, 4 H), 7.01 (s, 1 H), 7.04 (t, 2 H), 7.38 (d, 2 H), 7.52 (t, 2 H), 7.60 (d, 2 H). ^{13}C NMR (400 MHz, 298 K, $(CD_3)_2SO$): δ = 168.0, 157.8, 139.0, 138.8, 133.1, 131.2, 130.7, 130.2, 122.9, 120.8, 114.4, 66.1, 19.7, 15.4. Elemental anal. Calcd for H_2L^7: C, 71.42; H, 5.752%. Found: C, 71.25; H, 5.45%.

Synthesis of H_2L^8. Sodium (1.8 g, 0.078 mmol) was dissolved in absolute ethanol (200 mL). 2-Mercaptonicotinic acid (4.7 g, 0.034 mmol) was then added under nitrogen with stirring, and the stirring was continued for 10 min. To the resulting suspension was added 1,4-bis(bromomethyl)benzene (3.3 g, 0.01 mmol) and the reaction mixture was stirred under refluxing for 6 h. The solid was filtered while still hot and dissolved in water. After removing any undissolved substance by filtration, the filtrate was acidified with dilute hydrochloric acid. The solid was filtered and washed with water and hot ethanol. Yield: 50%. ^{1}H NMR (300 MHz, DMSO-*d*$_6$): δ = 4.35 (s, 2H), 7.33 (s, 2H), 7.24 (m, 1H), 8.21 (m, 1H), 8.65 (m, 1H). ^{13}C NMR (400 MHz, 298 K, $(CD_3)_2SO$): δ = 166.7, 161.0, 152.3, 139.4, 137.0, 129.6, 123.6, 119.5, 33.9. Elemental anal. Calcd for H_2L^8: C, 58.24; H, 3.91; N, 6.79; S, 15.55%. Found: C, 58.54; H, 4.12; N, 8.05; S, 15.46%.

Preparation of $Cu_2(L^6)_2(dmf)_2\cdot 2dmf\cdot 2H_2O$ (1). $Cu(NO_3)_2\cdot 3H_2O$ (0.01 g, 0.04 mmol) and H_2L^6 (0.01 g, 0.0243 mmol) were dissolved in 8 mL mixed solvents of DMF, EtOH and H_2O (v/v = 5 : 2 : 1) in a 25 mL beaker. After stirring at room temperature for 10 min, the reaction mixture was filtered. The filtrate was left to stand at room temperature and the dark-blue crystals of **1** were obtained after two weeks (yield: 65%). Elemental anal. Calcd for **1**: C, 52.91; H, 5.08; N, 4.41; S10.07%; Found: C, 52.67; H, 4.48; N, 4.08; S, 10.41%

Preparation of $Cu_2(L^7)_2(dmf)_2\cdot 2dmf$ (2). $Cu(NO_3)_2\cdot 3H_2O$ (0.01 g, 0.04 mmol), H_2L^7 (0.01 g, 0.024 mmol) and NEt_3 (1 drop) were dissolved in 16 mL mixture of dmf, ethanol and H_2O (v/v = 5 : 2 : 1), in a 25 mL beaker. After stirring at room temperature for 10 min, the beaker was left at 60 °C for 3 d. The resulting blue block crystals were collected in 60% yield on the basis of copper. Elemental anal. Calcd for **2**: C, 59.27; H, 5.78; N, 4.46%. Found: C, 58.95; H, 5.72; N, 4.45%.

Preparation of $Cu(L^7)(bpy)_{1/2}\cdot 2dmf\cdot H_2O$ (3). A methanol solution (5 mL) of $Cu(NO_3)_2\cdot 3H_2O$ (0.01 g, 0.04 mmol) was layered on a DMF solution (5 mL) containing H_2L^7 (0.024 mmol, 0.01 g) and 4,4′-bipy (0.01 g, 0.064 mmol) in a tube. Blue crystals of **3** suitable for X-ray analysis were obtained at the junction of the layer after a few days. Elemental anal. Calcd for **3**: C, 58.28; H, 5.98; N 5.67%. Found: C, 57.50; H, 5.642; N, 5.307%.

Preparation of $Cu_2(L^8)_2(dmf)_2\cdot 2dmf\cdot 2H_2O$ (4). $CuCl_2\cdot 2H_2O$ (0.01 g, 0.059 mmol), H_2L^8 (0.01 g, 0.0242 mmol) and pyridine (1 drop) were dissolved in 8 mL DMF in a 25 mL beaker. After stirring at room temperature for 10 min, the reaction mixture was filtered. The filtrate was left to stand at room temperature and the dark-blue crystals of **4** were obtained after one month (yield: 30%). Elemental anal. Calcd for **4**: C, 48.76; H, 4.45; N, 7.42; S, 11.30%. Found: C, 48.50; H, 4.64; N, 7.31; S, 11.45%.

Crystal structure determinations

Crystallographic data for **1–4** were collected on a Bruker Smart APEXII CCD diffractometer with Mo Kα (λ = 0.71073 Å) at room temperature. All structures were solved by the direct method using the SHELXS program of the SHELXTL package and refined by the full-matrix least-squares method with SHELXL.[18] The metal atoms in each complex were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with anisotropic thermal parameters on F^2. The organic hydrogen atoms were generated geometrically (C–H 0.96 Å).

Crystal data for 1. $C_{56}H_{60}Cu_2N_4O_{12}S_4$, M = 1236.40, triclinic, space group P–1, a = 10.4913(9), b = 11.0159(9), c = 12.4366(10) Å, α = 89.1180(10), β = 89.0410(10), γ = 79.8570(10)°, U = 1414.5(2) Å^3, Z = 1, D_c = 1.451 Mg m^{-3}, μ(Mo Kα) = 0.964 mm^{-1}, T = 293 K, 8377 reflections collected. Refinement of 6148 reflections (397 parameters) with $I > 2\sigma$(I) converged at final $R1$ = 0.0465 ($R1$ all data = 0.0600), $wR2$ = 0.1417 ($wR2$ all data = 0.1556), gof = 1.085.

Crystal data for 2. $C_{62}H_{72}Cu_2N_4O_{16}$, M = 1256.32, monoclinic, space group $P2(1)/c$, a = 15.5453(11), b = 10.0554(7), c = 21.4858(12) Å, β = 113.182(4)°, U = 3087.4(4) Å^3, Z = 2, D_c = 1.351 Mg m^{-3}, μ(Mo Kα) = 0.759 mm^{-1}, T = 293 K, 13531 reflections collected. Refinement of 4700 reflections (466 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0549 ($R1$ all data = 0.0848), $wR2$ = 0.1438 ($wR2$ all data = 0.1686), gof = 1.043.

Crystal data for 3. $C_{72}H_{84}Cu_2N_6O_{18}$, M = 1448.54, triclinic, space group P-1, a = 10.568(2), b = 14.124(3), c = 14.562(5) Å, α = 111.999(5), β = 96.899(5), γ = 111.303(4)°, U = 1793.1(8) Å^3, Z = 1, D_c = 1.341 Mg m^{-3}, μ(Mo Kα) = 0.666 mm^{-1}, T = 293 K, 6751 reflections collected. Refinement of 4337 reflections (442 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0568 ($R1$ all data = 0.0879), $wR2$ = 0.1541 ($wR2$ all data = 0.1957), gof = 1.034.

Crystal data for 4. $C_{52}H_{60}Cu_2N_8O_{13}S_4$, M = 1258.38, monoclinic, space group $C2/c$, a = 17.258(5), b = 10.889(3), c = 31.014(8) Å, α = 90.00, β = 95.417(4), γ = 90.00 °, U = 5802(3) Å^3, Z = 4, D_c = 1.441 Mg m^{-3},

μ(Mo Kα) = 0.945 mm^{-1}, T = 293 K, 16412 reflections collected. Refinement of 6437 reflections (357 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0420 ($R1$ all data = 0.0753), $wR2$ = 0.1027 ($wR2$ all data = 0.1210), gof = 1.022. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center.

Acknowledgements

We gratefully thank the financial support of the NSF of China (Grant 20701025), the NSF of Shandong Province (Grant Y2008B01), and Shandong University.

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