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PAPER

Controlling interpenetration in CuCN coordination polymers by size of the pendant substituents of terpyridine ligands†

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To systematically investigate the effect of the pendant groups of ligands on the assembly of coordination polymers (e.g. controlling interpenetration), four terpyridine ligands with bulky pendant groups, namely, 4'-(4-tolyl)-4,2':6',4''-terpyridine (**L1**), 4'-(4-ethylphenyl)-4,2':6',4''-terpyridine (**L2**), 4'-(4-isopropylphenyl)-4,2':6',4''-terpyridine (**L3**), and 4'-biphenyl-4,2':6',4''-terpyridine (**L4**) have been synthesized for comparative purposes. The reactions of CuCN and **L1–L4** under the same solvothermal conditions provided four CuCN coordination polymers: [(CuCN)₂**L1**]_n (**1**), [(CuCN)₂**L2**]_n (**2**), [(CuCN)₂**L3**]_n (**3**), and {[CuCN)₃**L4**]_{1.5}·H₂O}_n (**4**), respectively. Single-crystal X-ray analyses reveal that compounds **1–3** are isostructural with the same topological 4-fold interpenetrated 3D CuCN networks, and compound **4** is a non-interpenetrated CuCN network. This success demonstrates that the interpenetration is suppressed by the alteration of the size of the pendant groups of terpyridine ligands.

Introduction

Coordination polymers (or metal–organic frameworks, MOFs) have attracted great interest because of their structural diversity and potential applications as solid-state functional materials for use in gas storage,¹ sensing,² heterogeneous catalysis³ and magnetism.⁴ Compared to traditional inorganic porous materials (e.g. zeolite), one salient feature of coordination polymers is that the porous properties (e.g. pore size) can be easily tuned by rationally selecting and designing organic ligands. In principle, the high porosity of coordination polymers can be achieved by increasing the length of bridging ligands. Unfortunately, it is not always the case because the porosity is often severely compressed due to the interpenetration of multiple networks. The prevention of interpenetration in coordination polymers is extremely important, and is still a great challenge for chemists.⁵ Recently, chemists have adopted several strategies to control the degree of interpenetration, including (i) introducing guest molecules or anions as templates,⁶ (ii) changing the reaction conditions, e.g., temperature, solvents and concentration,⁷ (iii) *in situ* generation of rod shaped or high connected secondary building units,⁸ (iv) the “liquid-phase epitaxy” method,⁹ and (v) rational design of organic ligands (with steric hindrance groups, or chirality).^{6a,10} In comparison to these methods, the modification of organic ligands in controlling the interpenetration may be relatively practicable and feasible. This presumption is rooted in the fact

that the size and functional groups of organic ligands can be altered and tuned by organic synthesis.

The metal salt CuCN is very useful to assemble unique coordination polymers due to its structural diversity.¹¹ When CuCN reacts with *exo*-bidentate, or *exo*-tridentate ligands, CuCN coordination polymers with multiple interpenetration networks will probably be obtained, as with other types of coordination polymers. A series of interpenetrated CuCN coordination polymers had been reported.¹² However, a systematic study on the compression of CuCN interpenetration networks is still not available. We, and others, are interested in research on the coordination chemistry of the assembly of 4,2':6',4''-terpyridine ligands and metal ions.¹³ Herein, we report a systematic modification of the pendant substituents of 4,2':6',4''-terpyridine to control the interpenetration in CuCN coordination polymers. The idea is that the pendant groups with larger size probably cause steric hindrance in the formation of additional interpenetrated networks, and thus compress the interpenetration. A series of 4,2':6',4''-terpyridine-based ligands with alteration of the size of the pendant groups: 4'-(4-tolyl)-4,2':6',4''-terpyridine (**L1**), 4'-(4-ethylphenyl)-4,2':6',4''-terpyridine (**L2**), 4'-(4-isopropylphenyl)-4,2':6',4''-terpyridine (**L3**), and 4'-biphenyl-4,2':6',4''-terpyridine (**L4**) (Scheme 1) were synthesized and reacted with CuCN under the same conditions.

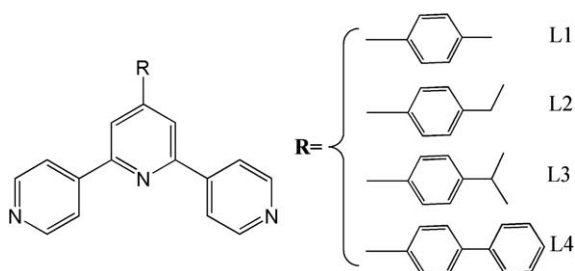
Experimental section

Materials and measurements

All starting materials were commercially available and used as received without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR

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Scheme 1

spectrometer in the range 4000–400 cm^{-1} . Elemental analyses of C, H, and N were determined with a Perkin-Elmer 2400C elemental analyzer. Thermogravimetric analysis (TGA) was carried out under an argon atmosphere with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ from room temperature to 800 $^{\circ}\text{C}$, on Seiko Extar 6000 TG/DTA equipment.

Synthesis of ligands

4'-(4-Tolyl)-4,2':6',4''-terpyridine (L1). A mixture of *p*-tolualdehyde (2.4 g, 20 mmol), 4-acetylpyridine (4.84 g, 40.0 mmol) and NaOH (s, 96%) (1.67 g, 41.75 mmol) was ground using a mortar and pestle. The viscosity rapidly strengthened to produce a tacky solid after *ca.* 5 min of constant mixing, then the yellow medium was aggregated until a yellow powder was formed (*ca.* 5 min) and further ground for 20 min. The powder was transferred to a suspension of ammonium acetate (13 g, excess) in glacial acetic acid (40 ml, *ca.* 100%) and refluxed for 5 h. The resulting solution was cooled, the solvent was reduced and treated with a mixture of ethanol (20 mL) and water (30 mL) to give a pale yellow precipitate, which was recrystallized from ethanol to yield colorless crystals. Yield: 29%, (1.87 g, 5.8 mmol). Elemental analysis calcd (%) for **L1** $\text{C}_{22}\text{H}_{17}\text{N}_3$: C 81.71, H 5.30, N 12.99; found: C 81.54, H 5.25, N 13.21. IR data (KBr, cm^{-1}) for **L1**: 3032 w, 2974 w, 2913 w, 2852 w, 1593 s, 1540 m, 1516 m, 1393 m, 1213 w, 1066 w, 997 w, 809 s.

4'-(4-Ethylphenyl)-4,2':6',4''-terpyridine (L2). 4'-(4-Ethylphenyl)-4,2':6',4''-terpyridine was prepared analogously to **L1**, but with 4-ethylbenzaldehyde (2.68 g, 20.0 mmol) in place of *p*-tolualdehyde. Yield: 24.5%, (1.65 g, 4.9 mmol). Elemental analysis calcd (%) for **L2** $\text{C}_{23}\text{H}_{19}\text{N}_3$: C 81.87, H 5.68, N 12.45; found: C 81.99, H 5.75, N 12.26. IR data (KBr, cm^{-1}) for **L2**: 3032 w, 2974 w, 2917 m, 2852 w, 1593 s, 1540 m, 1426 w, 1393 s, 1213 w, 1062 w, 997 w, 817 s.

4'-(4-Isopropylphenyl)-4,2':6',4''-terpyridine (L3). 4'-(4-Isopropylphenyl)-4,2':6',4''-terpyridine was prepared analogously to **L1**, but with 4-isopropylbenzaldehyde (2.96 g, 20.0 mmol) in place of *p*-tolualdehyde. Yield: 32%, (2.25 g, 6.4 mmol). Elemental analysis calcd (%) for **L3** $\text{C}_{24}\text{H}_{21}\text{N}_3$: C 82.02, H 6.02, N 11.96; found: C 82.37, H 5.51, N 12.12. IR data (KBr, cm^{-1}) for **L3**: 3023 w, 2958 m, 2925 w, 1593 s, 1536 m, 1426 w, 1397 m, 1217 w, 1058 w, 993 w, 821 s.

4'-Biphenyl-4,2':6',4''-terpyridine (L4). 4'-Biphenyl-4,2':6',4''-terpyridine was prepared analogously to **L1**, but with

4-biphenylcarboxaldehyde (3.64 g, 20.0 mmol) in place of *p*-tolualdehyde. Yield: 24%, (1.85 g, 4.8 mmol). Elemental analysis calcd (%) for **L4** $\text{C}_{27}\text{H}_{19}\text{N}_3$: C 84.13, H 4.97, N 10.90; found: C 84.37, H 4.51, N 11.12. IR data (KBr, cm^{-1}) for **L4**: 3027 w, 1593 s, 1544 s, 1483 m, 1409 s, 1217 w, 1062 w, 1005 w, 820 s, 764 m.

Synthesis of complexes

$\{(\text{CuCN})_3\text{L1}_{1.5}\}_n$ (1). A mixture of CuCN (0.009 g, 0.1 mmol), **L1** (0.0323 g, 0.1 mmol) and acetonitrile (8.0 mL) was sealed in a 15 mL Teflon-lined stainless-steel autoclave, which was heated to 160 $^{\circ}\text{C}$ and held for 72 h. After cooling to room temperature at a rate of 5 $^{\circ}\text{C h}^{-1}$ and filtering, X-ray quality yellow block crystals of compound **1** were obtained. Yield: 48%. Elemental analysis calcd (%) for **1** $\text{C}_{36}\text{H}_{25.5}\text{Cu}_3\text{N}_{7.5}$: C 57.36, H 3.40, N 13.94. Found: C 56.97, H 3.17, N 14.43. IR data (KBr, cm^{-1}): 3027 w, 2913 w, 2847 w, 2124 s, 1597 s, 1556 w, 1535 m, 1515 w, 1393 m, 1061 w, 1009 w, 816 s.

$\{(\text{CuCN})_3\text{L2}_{1.5}\}_n$ (2). The procedure for preparing **2** was identical to that for preparing **1**, except **L1** was replaced with **L2** (0.0337 g, 0.1 mmol). Yellow block crystals of compound **2** were obtained. Yield: 54%. Elemental analysis calcd (%) for **2** $\text{C}_{37.5}\text{H}_{28.5}\text{Cu}_3\text{N}_{7.5}$: C 58.13, H 3.71, N 13.56. Found: C 58.39, H 3.84, N 13.31. IR data (KBr, cm^{-1}): 3040 w, 2958 w, 2925 w, 2872 w, 2120 s, 1597 s, 1532 m, 1454 w, 1393 m, 1217 w, 1066 m, 1009 m, 825 s.

$\{(\text{CuCN})_6\text{L3}_3\}_n$ (3). The procedure for preparing **3** was identical to that for preparing **1**, except **L1** was replaced with **L3** (0.0351 g, 0.1 mmol). Yellow block crystals of compound **3** were obtained. Yield: 54%. Elemental analysis calcd (%) for **3** $\text{C}_{78}\text{H}_{63}\text{Cu}_6\text{N}_{15}$: C 58.86, H 3.99, N 13.20. Found: C 58.42, H 4.11, N 13.36. IR data (KBr, cm^{-1}): 2953 w, 2921 w, 2864 w, 2120 m, 1601 s, 1535 w, 1450 w, 1393 m, 1217 w, 1062 w, 1012 w, 825 s.

$\{(\text{CuCN})_3\text{L4}_{1.5}\cdot\text{H}_2\text{O}\}_n$ (4). The procedure for preparing **4** was identical to that for preparing **1**, except **L1** was replaced with **L4** (0.0385 g, 0.1 mmol), and yellow block crystals of compound **4** were obtained. Yield: 49%. Elemental analysis calcd (%) for **4** $\text{C}_{43.5}\text{H}_{30.5}\text{Cu}_3\text{N}_{7.5}\text{O}$: C 60.41, H 3.55, N 12.15. Found: C 60.65, H 3.32, N 13.69. IR data (KBr, cm^{-1}): 3027 w, 2913 w, 2116 s, 1593 s, 1536 m, 1486 m, 1389 m, 1217 w, 1062 w, 1013 w, 825 s, 772 s.

X-ray crystallography

Suitable crystals of **1–4** were mounted with glue at the end of a glass fiber. Data collections were performed on a Bruker-AXS SMART CCD area detector diffractometer at 298(2) K using rotation scans with a scan width of 0.3 $^{\circ}$ and Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). A summary of the crystallography data and structure refinement is given in Table 1. Empirical absorption corrections were carried out utilizing the SADABS routine. The structures were solved by direct methods and refined by full-matrix least squares refinements on the basis of F^2 . All non-hydrogen atoms were anisotropically refined. Hydrogen atoms

Table 1 Summary of the crystal data and structure refinement parameters for **1–4**

	1	2	3	4
Formula	C ₇₂ H ₅₁ Cu ₆ N ₁₅	C ₇₅ H ₅₇ Cu ₆ N ₁₅	C ₇₈ H ₆₃ Cu ₆ N ₁₅	C ₈₇ H ₆₁ Cu ₆ N ₁₅ O ₂
<i>M</i> _r	1507.58	1549.59	1591.68	1729.74
Cryst syst	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>P2₁/c</i>	<i>Pnna</i>
<i>a</i> /Å	22.4693(15)	22.7172(10)	23.568(3)	32.9876(14)
<i>b</i> /Å	14.3685(9)	14.5191(7)	14.2616(16)	15.2044(6)
<i>c</i> /Å	21.7069(16)	21.7987(10)	24.342(4)	15.3966(6)
α /°	90	90	90	90
β /°	109.1680(10)	108.7880(10)	118.922(2)	90
γ /°	90	90	90	90
<i>V</i> /Å ³	6619.5(8)	6806.8(5)	7161.2(16)	7722.3(5)
<i>Z</i>	4	4	4	4
<i>D</i> _c /g cm ⁻³	1.513	1.512	1.476	1.488
μ /mm ⁻¹	1.948	1.896	1.805	1.682
no. of refls collected	17070	17510	36875	37252
no. of unique refls	5812	5983	12592	6811
<i>R</i> _{int}	0.0394	0.0278	0.0418	0.0477
GOF	1.006	1.002	1.001	0.985
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0473	0.0400	0.0604	0.0477
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.0930	0.0996	0.1462	0.1225
<i>R</i> ₁ [all data]	0.0887	0.0631	0.1133	0.0885
<i>wR</i> ₂ [all data]	0.1099	0.1157	0.1886	0.1390

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|; ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

were added geometrically and refined with a riding model; structure solutions, refinements, and graphics were performed with the SHELXTL-97 software package.¹⁴ Selected bond lengths and angles for all complexes are given in Table S1.† The bridge C/N atoms of CN⁻ are undistinguished, and were assigned randomly as C or N atom in compounds **1–3**. The C1/N1 and C4/N4 atoms in compound **4** were refined as occupying the same site, both the C and N atoms were refined with 0.5 site occupation.

Results and discussion

Synthesis

Solvent-free synthesis is a useful approach to reduce environmental pollution, in addition to its simplicity and mild conditions. The efficient synthesis of pyridines *via* a sequential solventless aldol condensation and Michael addition had been developed by Raston and co-workers.¹⁵ Herein, a similar solvent-free method is also adopted in preparing **L1–L4**. Two equivalents of the ketone to the aldehyde were ground together in the presence of a catalytic quantity of base to proceed to the 1,5-diketone directly without any solvent. This procedure involves aldol condensation followed by a Michael addition stage. Then, reaction of the 1,5-diketone with ammonium acetate in the solvent acetic acid gave rise to the formation of the pyridine ring.

All CuCN coordination polymers were synthesized with a solvothermal method. To eliminate the influence of synthesizing conditions (*e.g.* temperature, solvent, mole ratio) to the resulting networks, the compounds **1–4** were synthesized under the same solvothermal conditions (*e.g.* temperature, 160 °C; solvent, acetonitrile; the mole ratio of metal to ligand, 1 : 1; see experimental section for more details). Therefore, the ligands here are the only variable for the self-assembly of networks **1–4**. For ligands **L1–L4**, the differences localize on the pendant R groups (Scheme 1), which will probably play important role in the assembly of the coordination polymers **1–4**.

Thermogravimetric analyses of compounds **1–4** in argon reveal the mass loss as shown in Fig. S1 in the ESI,† indicating the complexes are thermally stable up to 300–400 °C.

Crystal structures of **1** and **2**

X-ray crystallography studies reveal that both **1** and **2** crystallize in the monoclinic space group *C2/c* with similar unit cells and feature identical linkage of metal to ligand. Compounds **1** and **2** are isomorphous, therefore only compound **1** is described in detail. The crystal data, and bond distances and angles of **2** are listed in Table 1 and Table S1 (in the ESI†), respectively. The asymmetric unit of **1** contains three independent copper(i) atoms, three cyanide anions, and 1.5 **L1** ligands (the half **L1** ligand lies on the twofold axis). All copper(i) centers adopt distorted triangular geometry, and are coordinated by two CN⁻ and one ligand **L1** (Fig. 1a). Except for the central N atoms in **L1**, the other two N atoms of 4-pyridyl groups coordinate to copper centers, and **L1** adopts a μ -2 bridging mode (Cu–N: 2.031(3)–2.122(3) Å). Like the **L1**, all CN⁻ anions adopt the μ -2 bridging mode, and the Cu–C/N (CN⁻) bond distances range from 1.837(4)–1.936(4) Å, and the C–Cu–N angles in the CuCN chains range from 131.70(15)–152.22(17)°. The CN⁻ anions link the copper centers to form a *meso*-helical 1D chain, in which the helical pitch is 25.68 Å (Fig. 1b). The CuCN chains are further bound by the *exo*-bidentate **L1**, and a 3D network was constructed, as shown in Fig. 1c. The network consists of large hexagonal-like channels, and is further interpenetrated by three other identical networks, as shown in Fig. 1d. Therefore, the coordination polymer **1** consists of four fold interpenetrated CuCN–**L1** 3D networks. After the 4-fold interpenetration, there is no solvent accessible void in **1** (checked by PLATON program). To understand the whole linkage between the metal and ligands of the complicated network of **1**, the topology was analyzed. The network of **1** can be simplified as a 3-connected

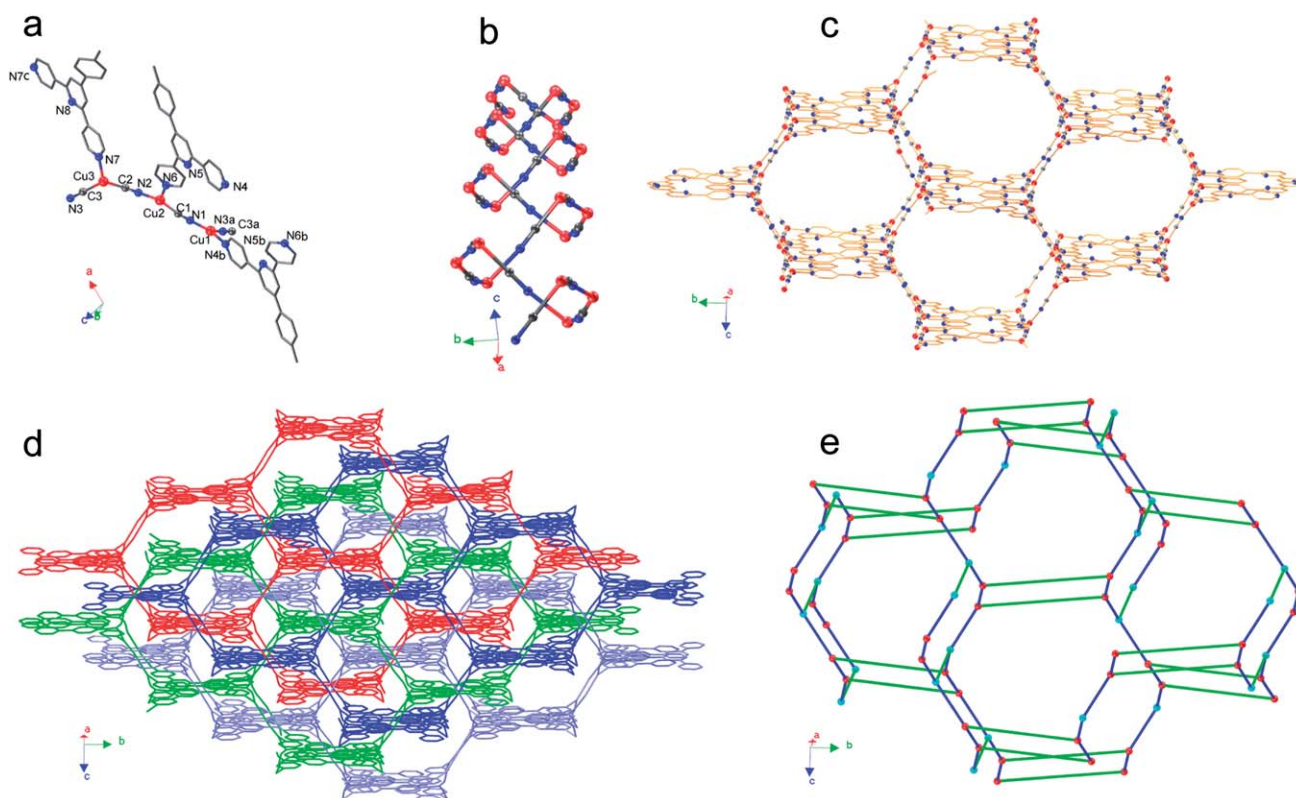


Fig. 1 Crystal structure of complex **1**: (a) coordination environment of copper(I) centers; (b) *meso*-helical CuCN chain in **1**; (c) overview of the 3D CuCN network with hexagonal channels (the tolyl groups are omitted for clarity); (d) four interpenetrating networks in **1** (the tolyl groups are omitted for clarity); and (e) topologic network representation of **1** (red sphere representing the copper nodes with $(4.8.10)$ topology, cyan sphere representing the copper nodes with $(8^2.12)$ topology, and blue and green sticks representing CN^- and **L1**, respectively). Symmetry transformations a, $x - 1/2, -y + 3/2, z - 1/2$; b, $-x - 1/2, -y + 1/2, -z$; c, $-x + 1, y, -z + 1/2$.

topologic network, when all the copper(I) centers are rationalized as the 3-connected nodes, and the CN^- anions and **L1** are treated as the linkers, as shown in Fig. 1e. The numbers of copper nodes in the shortest path of the resulting circuits is varied, including 4, 8, 10, and 12-membered. The Cu1 and Cu2 nodes have the same topological linkage (composing 4, 8, and 10-membered circuits), and Cu3 is involved in one 8, and two 12-member circuits. Therefore **1** can be treated as a 3-connected binodal network with the short vertex Schläfli symbol of $(4.8.10)_2(8^2.12)$. Lots of 3-connected networks with varied topologies have been reported (e.g. (8^3) ,¹⁶ (10^3) ,¹⁷ (12^3) ,¹⁸ (4.12^2) ¹⁹ and $(6^2.10)$ ²⁰). However, to the best of our knowledge, the topology of $(4.8.10)_2(8^2.12)$ in **1** is unprecedented.

Crystal structure of **3**

Compound **3** crystallizes in monoclinic space group $P2_1/c$ (a lower symmetry than $C2/c$ in compound **1**), and features identical topologic linkage of **1**. The asymmetric unit of **3** contains 6 copper(I) centers, 6 cyanide anions, and three **L3** ligands, which are double that in **1**. All copper(I) centers adopt the triangular geometry, and are coordinated by two CN^- and one **L3**, as shown in Fig. 2a. Both of the bond distances of Cu–N (**L3**) (2.051(4)–2.109(4) Å) and Cu–C/N (CN^-) (1.867(5)–1.938(7) Å) are comparable with the bond distances in compound **1**. The copper(I) centers are also bridged by CN^- to form the CuCN

chain in **3**. The angles around the copper centers of the CuCN chains in **3** are $137.3(2)$ – $148.5(2)^\circ$ for the chain containing Cu1–Cu3 copper centers, and $131.3(2)$ – $148.0(2)^\circ$ for the chain containing Cu4–Cu6 copper centers (Fig. 2b). Both angle values are slightly different to the angles in **1** ($131.70(15)$ – $152.22(17)^\circ$). The slight angle difference leads to a large change in the whole CuCN chain motif when compared to compound **1**, as shown in Fig. 2b. The CuCN chain seems to derive from the normal *meso*-helical chain. The pitch is about 24.34 Å, and the value is smaller than that in **1** (25.68 Å). Further comparing the 3D network of **3** to that of **1**, the network of **3** is relatively distorted (Fig. 2c), which is consistent with the relative lower symmetry in **3**. Albeit compound **3** has a larger ligand **L3** and lower symmetric space group and distorted networks when compared to **1**, it also contains 4-fold interpenetrated networks, and has the same $(4.8.10)_2(8^2.12)$ topology. Therefore, the increase of the pendant group size from tolyl in **L1** to isopropylphenyl in **L3** do not compress the interpenetration in these CuCN coordination polymers.

Crystal structure of **4**

In a further study, we employed a more bulky ligand **L4**, and obtained the non-interpenetrating CuCN coordination polymer **4**. Single crystal X-ray diffraction reveals that compound **4** crystallizes in orthorhombic space group $Pnna$, and features

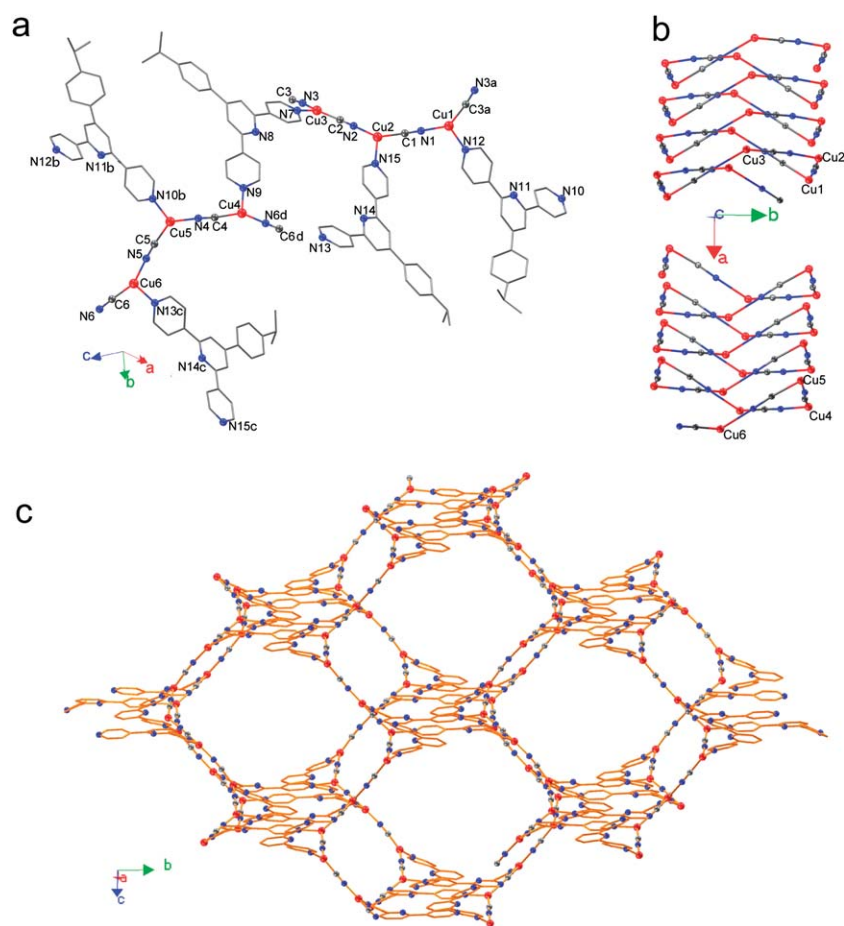


Fig. 2 Crystal structure of **3**: (a) coordination environment of copper(I) centers; (b) view of CuCN chains (top, containing Cu4–Cu6 atoms, and bottom, containing Cu1–Cu3 atoms); and (c) overview of the 3D CuCN network (the isopropylphenyl groups are omitted for clarity). Symmetry transformations a: $x, -y + 3/2, z - 1/2$; b: $x + 1, -y + 1/2, z - 1/2$; c: $x, -y - 1/2, z - 1/2$; d: $x, -y + 3/2, z + 1/2$.

a non-interpenetrated 3D coordination network. The asymmetric unit of **4** contains three independent copper(I) atoms, three cyanide anions, and 1.5 **L4** ligands (the half **L4** ligand lies on the twofold axis). Similar to compounds **1–3**, each Cu(I) atom in **2** is three-coordinated by two C/N atoms (CN[−], Cu–C/N 1.836(4)–1.919(4) Å) and one N atom (**L4**, Cu–N 2.094(5)–2.108(4) Å), as shown in Fig. 3a. The copper(I) centers are also linked by CN[−] to form a *meso*-helical CuCN chain (Fig. 3b). The C–Cu–N angles in the *meso*-helical CuCN chain range from 138.52(6)–149.77(6) Å, which is slightly different when compared with the angles of compounds **1–3**. However, the *meso*-helical chain is obviously different to those in compounds **1–3**, and the length of the helical pitch (48.63 Å) is about double that in compounds **1–3**. On the other hand, the CuCN *meso*-helices run along two different directions, with the CuCN chain extending along the same direction in **1–3**. The CuCN chains are further connected by the **L4** ligands to form a 3D network (Fig. 3c). Unlike the four-fold networks in compounds **1–3**, compound **4** only contains a mono-fold network. Therefore there is no interpenetration in **4**. Although the coordination mode of both the ligands and copper centers in compounds **1–4** are the same, the total linkage of the network in **4** is distinctly different when compared to networks in **1–3**. The CN[−] and **L4** ligands linking copper(I) centers form the uniform 10-membered circuits in **4**, as shown in

Fig. 3d. Further topological analysis found that the network of **4** can be abstracted into a (10,3)-b network¹⁷ (Fig. 3e), when both CN anions and **L4** ligands are donated as linkers and Cu(I) atoms donated as 3-connected nodes. The major voids of coordination polymer **4** are occupied by the pendant biphenyl group, a volume of about 8.9% of unit cell volume is still solvent accessible in compound **4** (calculated by PLATON program), which is occupied by disordered water molecules. Thus, by increasing the pendant group size to biphenyl, the interpenetrations were successfully compressed in CuCN coordination polymer **4**. However, the total linkage and topology of the non-interpenetrated network were also changed at the same time in comparison with those in compounds **1–3**.

Effect of ligands on structures

The reaction of CuCN with **L1–L4** under the same solvothermal conditions yield three 4-fold interpenetrated 3D CuCN coordination polymers: [(CuCN)₂**L1**]_n (**1**), [(CuCN)₂**L2**]_n (**2**) and [(CuCN)₂**L3**]_n (**3**), and one non-interpenetrated CuCN coordination polymer {[(CuCN)₃**L4**]_n·H₂O}_n (**4**), respectively. Ligands **L1–L4** are similar except for the pendant groups. The pendant groups (tolyl to biphenyl, with non-active C–H bonds) in ligands **L1–L4** are not functionalized, and they have no

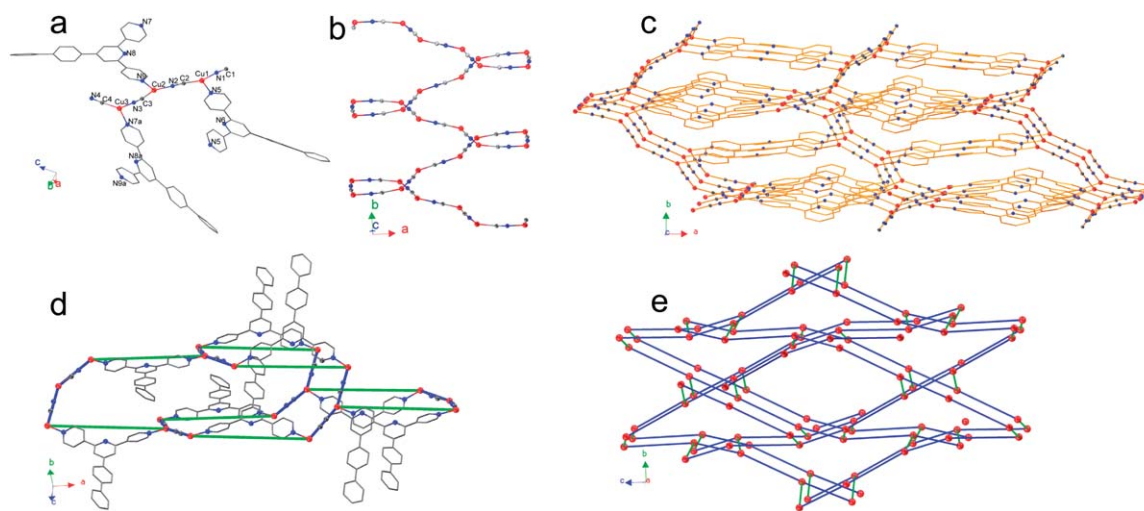


Fig. 3 Crystal structure of **4**: (a) coordination environment of copper centers, (b) *meso*-helical CuCN chain, (c) overview of three-dimensional network of **4** (the biphenyl groups are omitted for clarity), (d) view of the 10-membered circuits, and (e) the (10, 3)-b topologic network of **4** (red sphere, Cu; green sticks, L4; and blue sticks, CN⁻). Symmetry transformation a: $x - 1/2, y, -z + 1$.

hydrogen bond sites or potential coordination sites. Additional affecting factors including the inherent π - π interactions for aromatic rings and steric hindrance of ligands may play important roles in the assembly of the final structures of CuCN coordination polymers **1-4**. In the crystal structures of **1-4**, there are no obvious π - π interactions found between the pendant group and adjacent ligands. Therefore, the leftover factor of steric hindrance of pendant groups may become the sole variable in the assembly of the structures of **1-4**. As depicted above, complexes **1-3** feature identical four-fold interpenetrating 3D networks and binodal 3-connected (4.8.10)₂(8².12) topology. The networks **1-2** are almost identical, apart from the difference of tolyl and ethylphenyl groups. Due to the increase in steric hindrance (after the change to the larger isopropylphenyl), the CuCN network in **3** is beginning to distort from the normal CuCN network **1**. It makes us contemplate that coordination polymer **3** may be an intermediate state between the interpenetrated CuCN coordination polymer and non-interpenetrated CuCN coordination polymer in this system. The continuing increase of steric hindrances by employing more bulky pendant biphenyl group leads to the non-interpenetrated network **4**. The change in the linkage and topology in **4** in comparison to **1-3** may be attributed to the inherent flexible property of CuCN coordination polymers.

Conclusions

In summary, four CuCN coordination polymers based on four terpyridine ligands with various sized pendant substituents have been synthesized and characterized. The control over the interpenetration in these CuCN frameworks was systematically studied by carefully varying the size of the pendant group of the ligands. Our results showed the pendant tolyl, ethylphenyl, and isopropylphenyl groups did not compress the 4-fold interpenetrations in **1-3**, and the bulkier biphenyl group suppressed the interpenetration in **4**. In brief, the rational design of organic ligands shall prove to be a generally applicable route for control over the interpenetration in CuCN coordination polymers. The

study of the control over the interpenetration in other coordination polymer systems based on these ligands need to be extended.

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