pH-Induced formation of metalloligand: increasing structure dimensionality by tuning number of ligand functional sites†

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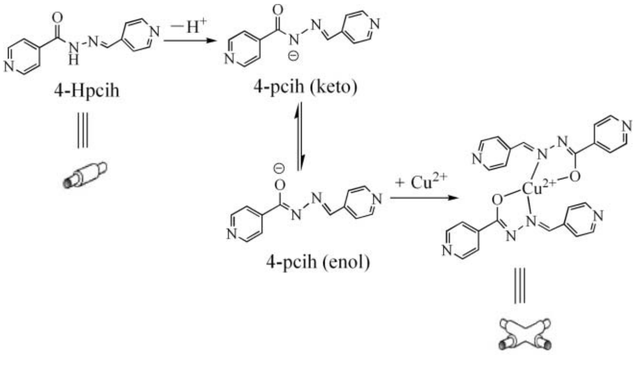
Two complexes, 2D $[Cu_2(CN)_2(4\text{-Hpcih})]_n$ and 3D $\{[Cu_2(CN)_{1.5}(4\text{-pcih})]\cdot 1.25H_2O\}_n$ (4-Hpcih = 4-pyridinecarbaldehyde isonicotinoyl hydrazone), were obtained using a synthetic approach of pH-induced formation of metalloligands, successfully demonstrating a strategy to increase structure dimensionality by tuning the number of ligand functional sites.

Current increasing interest in coordination polymers is justified not only by the potential applications of these compounds as functional materials[1,2] but also by the particular beauty and the intriguing structural diversity of the architectures.[3,4] A general principle for the construction of coordination polymers is to regard metal ions as connectors and organic ligands as linkers.[5] The design of multifunctional ligands containing appropriate coordination sites linked by a spacer with specific positional orientation is especially crucial. Besides the use of organic ligands, the metalloligand approach,[6,7] using metal complexes with vacant donor groups for further coordination, has also been developed.

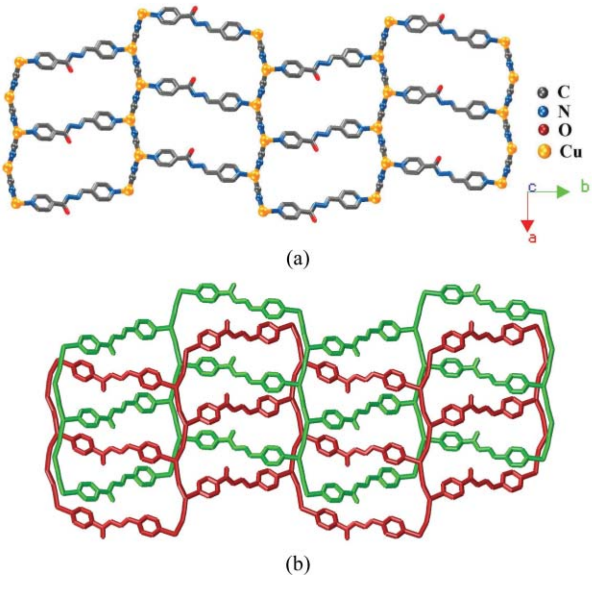
In our research on constructing coordination polymers with a Schiff-base compound 4-pyridinecarbaldehyde isonicotinoyl hydrazone (4-Hpcih) as ligand, we have noticed that 4-Hpcih is a multifunctional ligand that can either act as a linear double-coordination-site linker or be successively deprotonated, showing equilibrium between keto and enol forms. When suitable metal ions exist, 4-pcih can chelate a metal ion with two carbonyl-O and two imine-N atoms, generating a metalloligand with square-planar quadruple coordination sites (Scheme 1). We expected that the pH-induced[8] formation of the metalloligand, increasing the number of ligand functional sites, should lead to the generation of distinct polymeric coordination networks during the self-assembly process. In other words, such a strategy is based on the different ligating behaviors between the neutral and anionic forms of the Schiff-base ligand, which depends on the ligand deprotonating or not.[9]



Scheme 1 pH-induced formation of Schiff-base metalloligand.

The ligand 4-pyridinecarbaldehyde isonicotinoyl hydrazone (4-Hpcih) was prepared conveniently in a high yield by the reaction of 4-pyridinecarboxaldehyde and isonicotinic acid hydrazide in ethanol. Solvothermal reactions of CuCN and 4-Hpcih (molar ratio 2 : 1) in acetonitrile under acidic and neutral conditions yielded two different complexes: $[Cu_2(CN)_2(4\text{-Hpcih})]_n$ (**1**) and $\{[Cu_2(CN)_{1.5}(4\text{-pcih})]\cdot 1.25H_2O\}_n$ (**2**) (see the ESI for synthetic and crystallographic details).†‡

X-ray crystallography reveals that **1** is a 2D double-interpenetrated structure containing two undulating sheets (Fig. 1). In each sheet, each copper(I) atom is bound by two C/N atoms [Cu–C/N 1.849(4)–1.958(4) Å] from two CN^- anions and one N atom from a Schiff-base ligand [Cu–N 2.069(3)–2.128(3) Å], adopting a T-shape three-coordination geometry (Fig. 1a). The adjacent $[CuCN]_n$ chains are linked by the neutral ligands through pyridyl-N atoms in a linear *exo*-bidentate coordination mode. Six copper(I) atoms, four cyanides and two 4-Hpcih ligands compose



(a)

(b)

Fig. 1 Structure of **1**: (a) a 2D undulating sheet; (b) two identical interpenetrating 2D undulating sheets shown in red and green. All hydrogen atoms are omitted for clarity.

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a twelve-membered ring with the cavity about 15.6 × 9.4 Å. Each ring is fused to six other rings forming the 2D undulating sheet with a dihedral angle of 157.9° between the up and down planes along the *b*-axis. As a whole, two undulating sheets entangle with each other, forming a two-fold interpenetrating structure (Fig. 1b).

As expected, the structure of **2** is more complicated because of the formation of the metalloligand and thus the increasing ligand functional sites. The asymmetric unit of **2** contains three crystallographically independent copper atoms (Fig. 2 and S3†). The necessity of charge balance indicates that the copper atoms adopt mixed-valence fashion with one Cu(II) and two Cu(I) ions. Divalent Cu(1), adopting a square-planar coordination sphere, is coordinated by two carbonyl-O atoms [Cu–O 1.916(2) Å] and two imine-N atoms [Cu–N 1.962(3) Å] from two deprotonated ligands with a *trans*-N_2O_2 geometry. The O1–Cu1–O1A and N3–Cu1–N3A bonds are strictly linear with a bond angle of 180°; therefore the $[Cu^{II}(4\text{-pcih})_2]$ metalloligand moiety bearing four pendant pyridyl-N atoms resembles a square-planar linker for further coordination. Both Cu(2) and Cu(3) are monovalent. Cu(2), which lies on a two-fold axis, coordinates two pyridyl-N atoms [Cu–N 2.185(3) Å] and two C atoms from cyanide groups [Cu–C 1.895(3) Å] with a distorted tetrahedral geometry, while Cu(3) adopts a trigonal-planar geometry surrounded by one pyridyl-N atom [Cu–N 2.063(3) Å] and two C/N atoms [Cu–C/N 1.891(4)–1.895(3) Å] from cyanide groups.

Careful examination reveals that **2** exhibits a 3D two-fold interpenetrated structure, and interestingly, each 3D identical framework is composed of 2D self-penetrating nets connected by the tetrahedral Cu(I) atoms. As shown in Fig. 3a, each 2D self-penetrated[4c,10] sheet is based on 4-connected metalloligand $[Cu(4\text{-pcih})_2]$ centers forming self-catenated 4-membered circuits. Further, the adjacent 2D self-penetrated sheets are connected by Cu(2) atoms to form a unique 3D network (Fig. 3b). Along the *a* direction, the alternate linkage of Cu(I) and cyanide ions generate *pseudo*-helical $[CuCN]_n$ chains, and the adjacent chains are linked by metalloligands $[Cu^{II}(4\text{-pcih})_2]$ to form the 3D network. Moreover, two independent 3D networks interpenetrate with each other in a parallel fashion with offset face-to-face distances of 3.436 Å between pyridyl rings (Fig. 4). The whole structure contains voids (17.8% of the cell volume) occupied by water molecules (Fig. S4†). To the best of our knowledge, this is the first entanglement system of a 3D doubly-interpenetrated network constructed from 2D self-penetrated sheets.

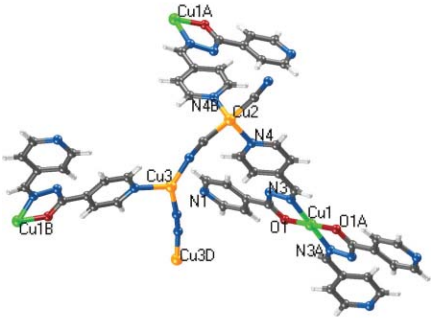

Fig. 2 View with the labeling scheme of the coordination environment of copper atoms in **2**. Symmetry codes: A: $-x + 1, -y + 1, -z + 1$. B: $-x + 1/2, -y, z$. C: $x, -y - 1, z + 1/2$. D: $x, -y - 1, z - 1/2$. E: $-x + 1, y, -z + 3/2$.

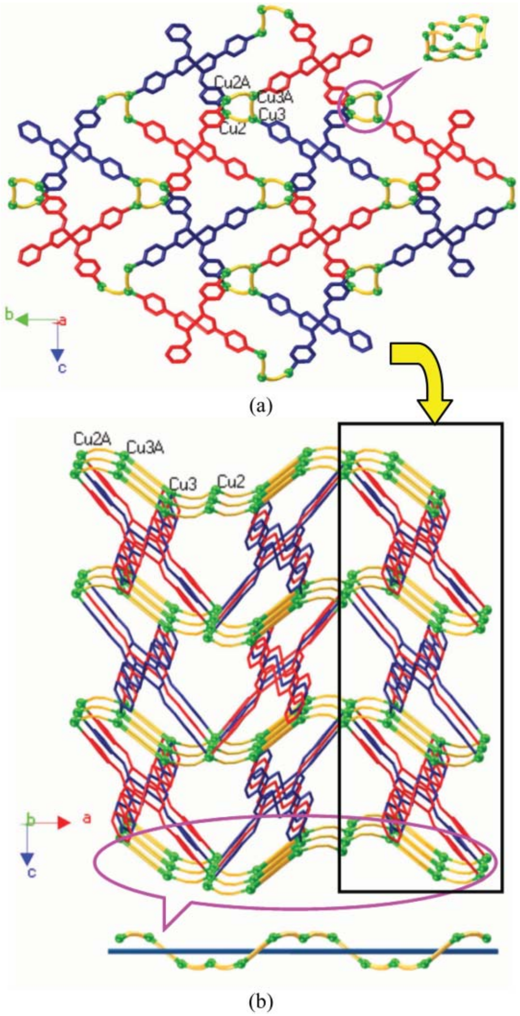

Fig. 3 Structure of **2**: (a) 2D self-penetrating net, showing different catenated circuits in blue and red; (b) one identical 3D framework. The additional images in pink highlight the *pseudo*-helical $[CuCN]_n$ chains (CN^-: yellow; Cu: green). Water molecules and all hydrogen atoms are omitted for clarity.

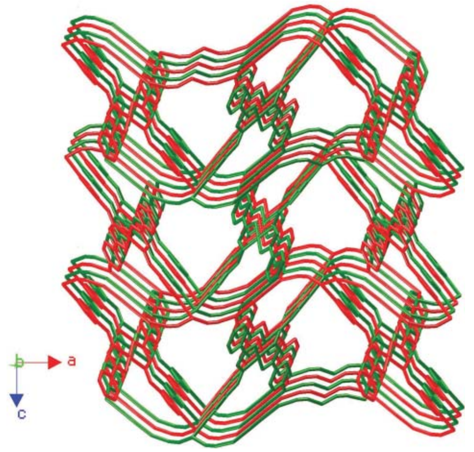

Fig. 4 3D two-fold interpenetrating framework of **2**, showing different networks in red and green.

Table 1 Bond lengths (Å) in the C_b=N_b–N_a(H)–C_a=O moiety of the free ligand and two complexes

	4-Hpcih	**1**	**2**
C_a=O/C_a–O	1.2117(18)	1.223(5)/1.229(5)	1.281(4)
C_a=N_a/C_a–N_a	1.355(2)	1.331(5)/1.331(5)	1.305(4)
N_b–N_a	1.3765(17)	1.383(4)/1.378(4)	1.390(4)
C_b=N_b	1.265(2)	1.279(5)/1.280(5)	1.269(4)

The enol form of 4-pcih in the metalloligand can be verified by crystallographic and spectroscopic data. The corresponding C–N, N–N and C–O bond distances in the C=N–N(H)–C=O moiety in free 4-Hpcih and the two complexes show significant differences (Table 1), which indicates that the C=N–N(H)–C=O moiety exists in the free ligand and **1**, whereas the conjugated C=N–N=C–O^- moiety is present in **2**.[9] The negative charge, arising upon the loss of the proton originally bound to the amido-N atom, is delocalized to the carbonyl-O atom. The electron delocalization enhances the coordination ability of the oxygen atom, hence the oxygen atom binds to Cu^{2+} in **2** but stays vacant in **1**. The amide N–H (*ca.* 3448 and 3443 cm^{-1}, respectively) and C=O (*ca.* 1688 and 1650 cm^{-1}, respectively) stretching vibrations are found in the IR spectra of the free ligand and **1**, but are not observed in that of **2**. An absorption band at 1614 cm^{-1} due to the enol resonance in the conjugated C=N–N=C–O^- moiety, which is absent in the spectra of the free ligand and **1**, exists in the spectrum of **2**.[9a,11]

It is noted that the formation of the metalloligand in **2** was accompanied by the oxidation of CuCN to Cu(II), likely due to the dissolved atmospheric oxygen in the solution. Because the hard base oxygen donors tend to coordinate Cu^{2+} rather than Cu^+, the deprotonation of the ligand seems to facilitate the oxidation of Cu(I) to form the metalloligand.

In summary, we have developed a synthetic approach toward higher dimensionality entangled frameworks by pH-induced formation of the metalloligand. This work successfully demonstrates that increasing the coordination sites of the ligand favors assembling a more complicated and higher-dimensional structure. The resulting 3D two-fold interpenetrating network constructed by 2D self-penetrated sheets is unique.

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Notes and references

‡ Crystal data for **Ligand**, CCDC 643873: $C_{12}H_{10}N_4O$, monoclinic, space group $P2_1/n$, M = 226.4, a = 7.7099(11) Å, b = 14.665(2) Å, c = 10.2423(15) Å, β = 109.166(3)°, V = 1093.8(3) Å^3, Z = 4, ρ_{calcd} = 1.374 g cm^{-3}, F(000) = 472, T = 293(2) K, 7486 reflections collected, 2684 unique with (R_{int} = 0.0276), $R1[I > 2\sigma(I)]$ = 0.0512, final (for all data) $R1$ = 0.0769, w$R2$ = 0.1419, GOF = 1.028; **Complex 1**, CCDC 646863: $C_{28}H_{20}Cu_4N_{12}O_2$, monoclinic, space group $P2_1/n$, M = 810.72, a = 9.4337(6) Å, b = 32.490(2) Å, c = 10.2061(7) Å, $\alpha = \gamma$ = 90°, β = 105.3930(10)°, V = 3015.9(3) Å^3, Z = 4, ρ_{calcd} = 1.785 g cm^{-3}, F(000) = 1616, T = 293(2) K, 19 172 reflections collected, 6977 unique with [R_{int} = 0.0263], $R1[I > 2\sigma(I)]$ = 0.0575, final (for all data) $R1$ = 0.0815, w$R2$ = 0.1392, GOF = 1.187; **Complex 2**, CCDC 646864: $C_{27}H_{23}Cu_4N_{11}O_{4.5}$, orthorhombic, space group $Pcca$, M = 827.72, a = 21.9969(15) Å, b = 7.3578(5) Å, c = 20.3447(14) Å, V = 3292.8(4) Å^3, Z = 4, ρ_{calcd} = 1.670 g cm^{-3}, F(000) = 1656, T = 293(2) K, 20 812 reflections collected, 4066 unique with [R_{int} = 0.0333], $R1[I > 2\sigma(I)]$ = 0.0475, final (for all data) $R1$ = 0.0673, w$R2$ = 0.1353, GOF = 1.074. Data collections of crystals were performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker Smart Apex CCD diffractometer at T = 293(2) K using SMART. See Fig. S1–S3† for XP drawings of the ligand and the complexes, respectively. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b705603f

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