

Two CuCN hybrid networks with unusual topology tuned by terpyridine ligands†

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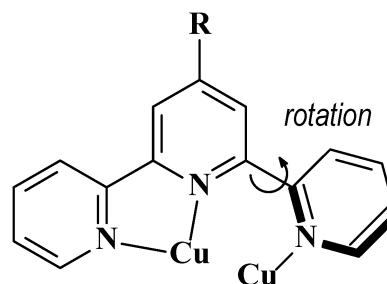
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This paper reports two structurally unique CuCN-terpyridine hybrid networks of 4'-*p*-tolyl-2, 2' : 6', 2''-terpyridine (tpty) prepared under solvothermal conditions: [(CuCN)₅(tpty)]_n (**1**), [(CuCN)₃(tpty)]_n (**2**). Complex **1** features a tri-layer structure with 3-connected binodal (8²10)·(8²10) topology, while complex **2** features unusual honeycomb-like layer structures. The adjacent honeycomb-like layers consist of the opposite handed helical CuCN-tpty chains. In both complexes, each tpty coordinates two copper(I) atoms with short Cu–Cu distances, and the side pyridyl group rotates in a certain angle from the central pyridyl plane directing the formation of the diversified networks.

Introduction

Copper(I) cyanide has received great interest by solid chemists, not only for studying its subtle structure of different phases,¹ but also for its applications in organic,² supramolecular,³ and materials chemistry.⁴ The crystal structure of solid copper(I) cyanide consists of simple –Cu–CN–Cu–CN– chains, however, the Cu(I) atoms with varied coordination geometries (line, triangle, tetrahedron) can be linked by cyanide to form complicated and multifarious charged or neutral infinite CuCN networks.⁵ For synthesizing new and novel CuCN hybrid materials, the neutral coordination organic components, organic cations or metal complex cations are usually incorporated into the systems as co-coordination ligands or templates. For example, recently, we used varied metal complexes or organic cations as templates to fabricate a series of unique CuCN or CuCN–CuSCN infinite networks with unusual topology and helical properties.⁶ Zubieta and coworkers have employed different organodiiimine ligands including exo-bis-bidentate ligands (e.g. 4, 4'-bipy) and chelating ligands (e.g. 2, 2'-bipy) to construct CuCN–organodiiimine systems with varied and interesting structures.^{5c–d, 7} Although CuCN-bis-bidentate organodiiimine systems are well documented, terpyridine ligands with three nitrogen tri-chelating sites are rarely explored.

The bis-chelating organodiiimine ligands commonly direct the formation of the simple one-dimensional CuCN chains by chelating the additional coordination sites of Cu(I) atoms of the origin CuCN chains.^{7b,8} In contrast, the tri-chelating terpyridine ligand chelates one Cu(I) atom with lower coordination numbers and coordinates one more Cu(I) atom using the freely rotating side pyridyl group, as shown in Scheme 1. Therefore, the terpyridine ligands may also direct the formation of interesting CuCN infinite hybrid networks. In fact, previous works have



Scheme 1 The possible coordination mode of terpyridine ligand with Cu(I) atoms.

documented that one terpyridine ligand can chelate two coin metal ions [Ag(I) and Cu(I)] and form metal complexes with interesting helical structures.⁹ In these compounds, the side pyridyl group of the ligand rotates at a certain angle from the central pyridyl plane due to the steric reason (the terpyridine coordinates with two metal ions), which probably induces the formation of the helical structure. Herein, we introduced a terpyridine ligand 4'-*p*-tolyl-2, 2' : 6', 2''-terpyridine (tpty) into the CuCN hybrid systems, and obtained two interesting CuCN-terpyridine networks with unique topology and helical structure under solvothermal conditions, formulated as [(CuCN)₅(tpty)]_n (**1**) and [(CuCN)₃(tpty)]_n (**2**), respectively.

Experimental

All reagents were commercially available and used as received. The solvents and chemicals were analytical grade and used without further purification. Infrared spectra were obtained in KBr disks on a Nicolet Avatar 360 FTIR spectrometer in the range of 4000–400 cm⁻¹. Elemental analyses of C, H, and N were determined with a Perkin-Elmer 2400C elemental analyzer.

Synthesis

1: A mixture of CuCN (0.0358 g, 0.4 mmol), tpty¹⁰ (0.0323 g, 0.1 mmol), and acetonitrile (8.0 mL) was stirred for 1 min in air, then transferred and sealed in a 15 mL Teflon-lined reactor, which was

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heated in an oven for 72 h at 180 °C and then slowly cooled to room temperature at a rate of 10 °C h⁻¹. Yellow stick-like crystals were obtained and washed with acetonitrile in 65% yield based on ttpy. There are some grey precipitates in concomitance with the origin product, therefore the crystals for characterization are mechanically sought out. Elemental analysis (%) calcd for C₂₇H₁₇Cu₅N₈: H 2.22, C 42.05, N 14.53%; found H 2.20 C 42.05, 14.52%; IR (KBr, cm⁻¹): 3109w, 3068w, 3022w, 2911w, 2845w, 2119s, 2094s, 1595s, 1534w, 1476s, 1418w, 1397w, 1298w, 1245w, 1187w, 1162w, 1014w, 890w, 816w, 787s, 742w, 655w, 569w.

2: The preparation was carried out with a method similar to that of **1**, except for the addition of CdCO₃ (equal mol of ttpy). Red block crystals were obtained and washed with acetonitrile in 71% yield based on ttpy. The origin product was an admixture with insoluble CdCO₃ and minor yellow crystals of compound **1**. Therefore the crystals for characterization are mechanically sought out. Elemental analysis (%) calcd for C₂₅H₁₇Cu₃N₆: H 2.89 C 50.71, 14.19%; found H 2.92, C 50.65, N 14.26%; IR (KBr, cm⁻¹): 3064w, 3031w, 3022w, 2917w, 2855w, 2120s, 1601s, 1568w, 1540w, 1476m, 1421w, 1401w, 1241w, 1187w, 1160w, 1094w, 1012w, 890w, 824w, 784m, 735w, 687ww, 653w, 563w.

Crystal structure determination

Single-crystal X-ray diffraction data collection for **1** and **2** was performed on a Bruker Smart Apex CCD diffractometer (Mo K α radiation, $\lambda = 0.71073$ Å). The structures were solved by direct methods, and all non hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares methods on F^2 by using the SHELXTL program.¹¹ The hydrogen atoms were located from difference maps and allowed for as riding atoms with isotropic temperature factors. To determine which atom is C or N for the CN⁻ group in the two complexes, all CN⁻ ligand

ions were supposedly assigned as nitrogen atoms, and then their occupancies were refined. For the two supposed N atoms in each CN⁻ ligand, the atom with higher occupancy (usually, 90–100%) is assigned to N, the other one with lower occupancy (usually lower than 90%) is assigned to C.^{5b} The crystal parameters and experimental details of the data collection are summarized in Table 1.

Results and discussion

The synthesis of both **1** and **2** was carried out with similar solvothermal methods and conditions, except for the adding of additive CdCO₃ in the preparation of **2**. Noticeably, the additive CdCO₃ plays an important role in affecting the supramolecular self-assembly of **2**, even though it does not exist in the final product. The CdCO₃ can not dissolve in acetonitrile at room temperature, but the solubility may be improved under extreme hydrothermal conditions with high temperature and high pressure. Then the dissolved CdCO₃ may positively affect the assembling for the formation of **2**. Under the same conditions, we also try using ZnCO₃ and CdSO₄ as additives; both additives lead to yielding an unknown yellow microcrystalline phase (CdSO₄ also induces the yielding minor phase of **1**, see powder X-ray diffractions in ESI†), unfortunately, it was not successfully determined by single-crystal diffraction. Therefore the CdCO₃ is significant for preparing **2**. In fact, the use of additive is now a powerful tool for supramolecular self-assembly in hydro-(solvo)thermal reactions, however, the mechanism is hardly understood for the black-box-like behavior of hydro-(solvo)thermal synthesis.¹²

Single-crystal X-ray diffraction reveals that **1** is composed of 2D CuCN networks and ttpy ligands which stop the CuCN network extending to three dimensions by chelating the Cu(I) atoms. The asymmetric unit of **1** contains six independent copper(I) atoms, with the Cu1, Cu2 on the inversion centers in the *P*-1 space group, as shown in Fig. 1a. Three frequently observed types of cuprous coordination geometry are all found in compound **1**, including linear, triangle and tetrahedron (Cu1, Cu2, and Cu4, linear; Cu3, Cu6 triangle; Cu5 tetrahedron, respectively). The bond lengths of Cu–C/N and CN⁻ groups appear reasonable [Cu–C/N (CN⁻ group) 1.836(6)–2.190(5) Å, Cu–N (pyridyl group) 1.989(5)–2.191(4) Å C≡N 1.119(7)–1.163(10) Å]. The relatively long Cu6–C4 distance is probably due to the C4 coordination with two copper(I) atoms (Cu5 and Cu6). Like those in the above mentioned Cu(I)/Ag(I)-terpyridine complexes, one ttpy ligand coordinates with two Cu(I) atoms (Cu5, Cu6) with the distance between the two copper(I) atoms of 2.546 Å. On the other hand, after ttpy chelates two copper(I) atoms, the side pyridine ring which coordinated with Cu6 rotates about 34.2° from the central pyridyl due to a steric reason. Interestingly, the Cu(I) atoms are linked by CN⁻ anions forming unusual tri-layer 2-D networks, which probably profit from the dual Cu(I) chelating functions of the ttpy ligand (Fig. 1b and Fig. 1d). The unusual tri-layer was constructed by linking the rung of the wider ladder chain of CuCN and terpyridine (Fig. 1c) with CN–Cu–CN linkers in the opposite directions (as shown in Fig. 1b). The widths of the ladder chain of CuCN and terpyridine formed are *ca* 4.7 nm, therefore there are large grooves in the tri-layer. The grooves are filled by the adjacent layers. It leads to

Table 1 Crystal data for complexes **1** and **2**

Parameters	1	2
Empirical formula	C ₂₇ H ₁₇ Cu ₅ N ₈	C ₂₅ H ₁₇ Cu ₃ N ₆
M_r	771.19	592.07
Temp/K	293(2)	293(2)
Cryst. system	Triclinic	Monoclinic
Space group	<i>P</i> -1	<i>P</i> 2(1) <i>c</i>
$a/\text{Å}$	7.089(2)	10.586(19)
$b/\text{Å}$	12.139(4)	13.259(17)
$c/\text{Å}$	16.790(5)	17.180(3)
$\alpha/^\circ$	72.450(5)	90
$\beta/^\circ$	80.504(5)	113.73(10)
$\gamma/^\circ$	82.270(5)	90
$V/\text{Å}^3$	1353.2(7)	2208.0(6)
Z	2	4
$D_{\text{calcd}}/\text{g cm}^{-3}$	1.893	1.781
μ/mm^{-1}	3.898	2.891
Reflens colld	7039	3827
Indep reflens	4690	2561
R_{int}	0.0387	0.0360
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.0578$ $wR_2 = 0.1468$	$R_1 = 0.0593$ $wR_2 = 0.1606$
Final R indices (all data)	$R_1 = 0.0718$ $wR_2 = 0.1586$	$R_1 = 0.0682$ $wR_2 = 0.1713$
$\rho_{\text{fin}}(\text{max}/\text{min})/\text{e Å}^{-3}$	1.612/–0.893	1.224/–0.783

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

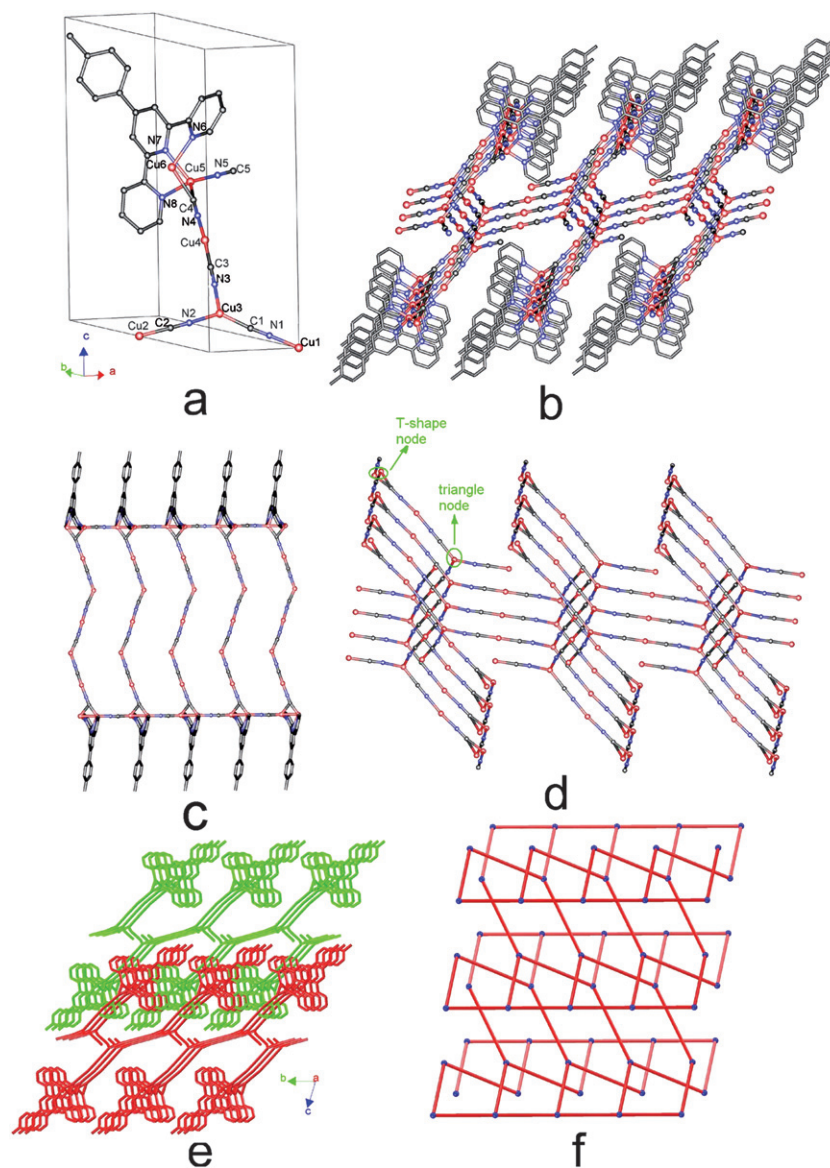


Fig. 1 The structure of **1**: Asymmetric unit (a), tri-layer hybrid network structure (b), 1-D ladder-like structure formed by ttpy and CuCN (c), CuCN layers omitting the ttpy ligands (d), a perspective view of two adjacent inter-threaded trilayer networks (e), schematic illustration of the 3-connected bimodal $(8^210) \cdot (8^210)$ network (f).

another structural feature that the tri-layers inter-thread into each other in the CuCN networks by the side pyridyl of ttpy ligands (like hook) and form a 3-D supramolecular structure (Fig. 1e). The other side pyridyl group of the ttpy ligands (not threading into the CuCN network) forms a π - π interaction (3.592 Å) with the adjacent central pyridyl ring of the terpyridine belonging to the threaded tri-layer, which makes the structure more stable.

Compared to the well documented bilayer 2-D networks which are usually constructed by bivalent metal ions and 4, 4'-bipy with a T-shape connection or Hittorf's phosphorus,¹³ the tri-layer 2-D structure of **1** is rarely characterized. Topologically, the tri-layer 2-D CuCN network can be identified as a 2-D binodal $(8^210) \cdot (8^210)$ net, when the 3-connected copper(I) atoms are treated as triangle nodes (Cu3) and two Cu(I) atoms (Cu5 and Cu6) chelated by ttpy as T-shape-like nodes (Fig.1d), and both

CN⁻ anions and 2-connected copper(I) atoms as linkers, as shown in Fig.1f. Although varied 3-connected networks have been reported, to our best knowledge, the tri-layer binodal 3-connected $(8^210) \cdot (8^210)$ CuCN network is observed for the first time.

Changing the reaction conditions of **1** by the addition of the additive agent CdCO₃, red crystals of **2** were obtained. Complex **2** features a 2-D network, which is constructed by a 1-D CuCN chain and ttpy ligands. The asymmetrical unit of **2** contains three independent copper(I) atoms (as shown in Fig. 2a), in which all Cu(I) atoms adopt triangle coordination geometry. The bond distances of Cu-C/N and CN⁻ all are reasonable [Cu-C/N (CN⁻ group) 1.819(8)–1.932(8) Å, Cu-N (pyridyl group) 1.967(7)–2.097(6) Å, C≡N⁻ 1.108(10)–1.132(9) Å]. As in **1**, the ttpy ligand in **2** also coordinates with two Cu(I) atoms (Cu2, Cu3). The distance between the two Cu(I) atoms in **2** is about 2.720 Å,

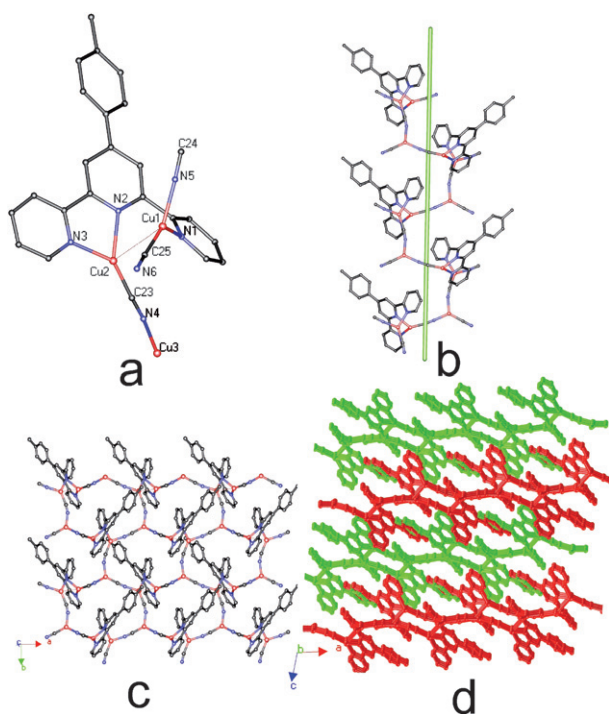


Fig. 2 The structure of **2**: asymmetric unit (a), helical CuCN-ttpty chain (left handed, b), honeycomb-like chiral layer consisting of a left-handed helical CuCN-ttpty chain (c), perspective view of ABAB stacking of the opposite-handed chiral layers (d, red: right-handed, green: left handed).

which is longer than that in **1** [2.546 Å]. On the other hand, the rotation angle between side pyridyl and centred pyridyl of **2** is about 38.7°, which is obviously larger than the angle of **1** (34.2°) and consists of the longer Cu–Cu distance between the chelated Cu(I) atoms in **2**. As mentioned above, the rotation of the side pyridyl of the terpyridine may cause helical structures, in **2**, as expected, CuCN and terpyridine form a twofold helical chain with the same handed fashion with a helical pitch of 13.259 Å, which equals the length of the *b*-axis which propagates along the 2(1) screw axis directions (Fig. 2b). The helical chains are further linked by CN[−] groups to extend into a 2-D CuCN-terpyridine hybrid network (Fig. 2c). The 2-D networks feature a honeycomb-like topology. It is common knowledge that CuCN forms anionic honeycomb-like networks balanced by varied cations or neutral honeycomb-like network with organodiiimine ligands. However, honeycomb-like CuCN networks consisting of helical chains are very rare. Careful examination found that the helical chain in the two adjacent layers has opposite handedness, which consists in **2** solved in a central space group *P2(1)/c*. As shown in Fig. 2d, the layers with oppositely handed helical chains adopt the ABAB stacking type to complete a 3-D structure.

Hybrid compounds **1** and **2** demonstrate the power of the terpyridine ligands in directing the formation of CuCN hybrid infinite networks. The structural differences between **1** and **2** are obvious. The basic reason are probably the varied linking ways of CuCN [rich coordination geometry of Cu(I)] resulting in a structurally rich potential. Another reason is probably the different rotation angles of the side pyridyl from the central pyridine in ligand ttpy in the two compounds, controlling the coordination mode and distances of the two Cu(I) atoms of

CuCN (**1** 2.546 Å, **2** 2.720 Å) and further affecting the whole structure. For example, the shorter Cu5–Cu6 distance in **1** creates a chance for C4 of CN[−] binding with the two Cu(I) atoms and forming the 2-D unusual tri-layer structure. Reversely, the relative longer Cu3–Cu2 distance in **2** probably favors the carbon atom (C2 or C3) non-binding with two Cu(I) atoms at the same time to form the honeycomb-like layers with helical chains.

Conclusion

Two 2-D CuCN hybrid networks directed by a terpyridine ligand ttpy have been successfully synthesized and characterized. The structures of **1** and **2** are a tri-layer 2-D network with 3-connected binodal (8²10)·(8²10) topology and a rare CuCN honeycomb hybrid network with opposite helical CuCN-ttpt chains, respectively. It is likely that the rotation angles of the side pyridyl from the central pyridine in the terpyridine ligand play an important role in directing the structures. The complexes represent a new research territory for structurally unique CuCN hybrid networks by introducing terpyridine ligands.

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