Directed formation of tri-connected Cu(I) coordination polymers†

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Two new tri-connected copper(I) coordination polymers have been synthesized, featuring a 1D staircase-like structure and an inter-penetrating 2D polycyclohexane framework. The geometries are controlled by steric factors that are generated from the terminal blocking ligand 2-diphenylphosphino-*n*-methyl pyridine (*n* = 3, 6) with the methyl group at different substituted positions.

The rational design of coordination polymers (CPs) based on transition metal ions and organic bridging ligands has received increasing interest, owing to their fascinating architectures and topologies as well as potential applications as functional materials in many fields.[1,2] Coordination preferences of metal ions and ligand geometries are essential for controlling the desired architectures and functionalities. CPs based on copper(I) complexes and bispyridyl ligands have been widely studied, and they display diverse connectivities and topologies.[3–7] The Cu(I) center is generally found in a four-coordinate tetrahedral environment, which is linked by two or four bridging ligands, leading to regular 1D chains, 2D layers, or 3D frameworks. The relatively rare examples of the Cu(I) atoms adopting a 3-coordinate trigonal geometry, afforded unprecedented structural motifs, such as interwoven honeycombs or 3D frameworks with rectangular extended channels.[5] The observations clearly indicate the important role of coordination preferences in the determination of the architectures. In this context, an elegant example was reported by Keller *et al.* who employed the combination of terminal and bridging ligands in the Cu(I) system, where one coordination site of the tetrahedral Cu(I) center is blocked by a terminal

coordinating PPh_3 ligand, leaving only three sites for external linking. A novel framework with pentagonal motifs was built in this way.[6] Subsequently, significant efforts have been made to investigate the effects of bridging ligands including spacer, flexibility, and symmetry on the final architectures;[7] nevertheless, the influence of terminal ligands in the determination of the structural motifs has not been explored.

We have recently reported a reversible process exhibiting interesting photophysical properties for Cu(I) complexes bearing hemilabile phosphine ligands, diphenylphosphino-pyridine (dppy).[8] Inspired by the mixed-ligand effects observed in the Cu(I)–PPh_3–L systems as mentioned above,[6,7] we are interested in exploring Cu(I) coordination polymers that incorporate the hemilabile dppy derivatives as the terminal ligands. We choose them as the blocking units based on the following considerations: i) the hemilabile dppy derivatives have a mixture of tightly bound and substitutionally labile functionalities, which differ distinctly from PPh_3; ii) alternating the substituents on the dppy ligand allows for studying the effects of terminal ligands on the topology of CPs. With this in mind, we introduced a pair of position isomers, 2-diphenylphosphino-*n*-methyl pyridine (*n* = 3, L_1; *n* = 6, L_2; Chart 1), and bridging ligand 4,4'-bipyridine (bipy), respectively, as mixed ligands in the Cu(I) systems. The title compounds were synthesized *via* a stepwise employment of the mixed ligands by treating bipy ligands with preformed binuclear copper(I) complexes. We reported herein the syntheses, structures, and characterization of the Cu(I) precursors $[Cu_2(L_1)_3(CH_3CN)](BF_4)_2 \cdot H_2O$ (**1**) and $[Cu_2(L_2)_3(H_2O)](BF_4)_2 \cdot 4CH_3OH$ (**2**), as well as the copper(I) CPs $[Cu_2(L_1)_2(bipy)_3](BF_4)_2$ (**3**) and $[Cu_2(L_2)_2(bipy)_3](BF_4)_2$ (**4**). **3** is a 1D staircase-like structure, and **4** features a 2-fold interpenetrating 2D framework with polycyclohexane topology.

Reaction of $[Cu(CH_3CN)_4]BF_4$ with L_1 or L_2 in a 2 : 3 ratio in acetonitrile under reflux for 1 hour led to the formation of dinuclear Cu(I) compounds **1** and **2**, respectively. Single-crystal X-ray structural analysis revealed that **1** and **2** are binuclear copper(I) complexes with a Cu···Cu separation of

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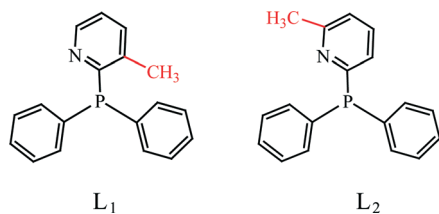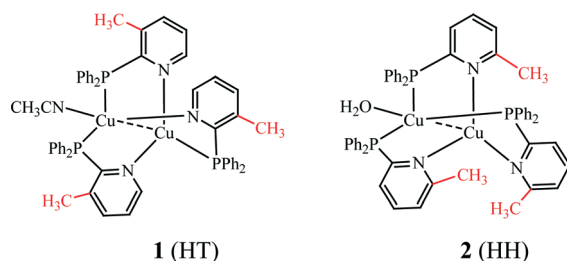
Chart 1 Structures of position isomerisms of 2-diphenylphosphino-n-methyl pyridines (n = 3, L$_1$; n = 6, L$_2$).

Scheme 1 The structures of **1** and **2**.

2.537(1) Å and 2.750(1) Å, respectively (Fig. S1 and S2).† Each structure contains three L ligands arranged in different configurations. **1** has a head-to-tail (HT) arrangement of L$_1$ with two P donors located at one Cu and the third P atom on the other one, whereas a head-to-head (HH) arrangement of L$_2$ with three phosphorus donors located at the same copper atom was observed in **2** as shown in Scheme 1.

Reaction of **1** with bipy in a mixture of CH$_2$Cl$_2$ and CH$_3$OH afforded a yellow solution, which was evaporated slowly at room temperature. Yellow-greenish crystals of **3** were obtained after 1 day in 51.3% yield. The purity of the product was confirmed by powder X-ray diffraction (PXRD). The measured XRD pattern of **3** matches the simulated one (Fig. S10).†

The X-ray crystallography revealed that **3** crystallized in an orthorhombic system with the Cmca space group, which features a staircase-like 1D coordination polymer.[2]‡ As shown in Fig. 1, each Cu(I) center is coordinated to three bipy ligands and one P atom from L$_1$ ligand in a distorted tetrahedral geometry. Some of the hemilabile L$_1$ ligands with N,P chelation to Cu(I) in **1** were replaced by the bipy ligands, leaving only one P atom coordinated to the Cu(I) center in **3**. The N–Cu–N angles are within the range of 99.9(2)–101.4(2)°, which are significantly smaller than the typical tetrahedral angles due to the steric hindrance of L$_1$. As shown in Fig. 2,
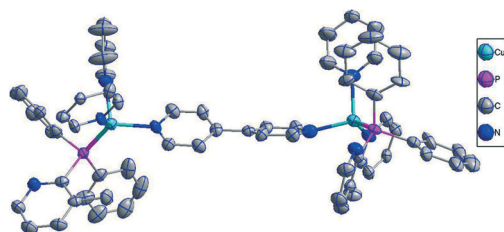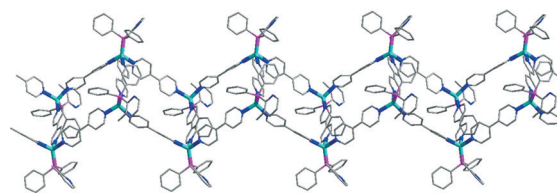

Fig. 2 The staircase-like networks in **3**.

the basic unit of **3** comprises four copper(I) atoms and four bipy ligands assembling into a regular tetragon. The tetragons are perpendicularly fused together by a third bipy ligand bridging Cu(I) centers (Cu–Cu–Cu angles are 90.0°), leading to a staircase-like 1D polymer, which can also be described as a 2-fold zigzag chain along the a axis. The width and height of each "footstep" are indicated by the distances between the adjacent copper atoms in the range of 11.145(1)–11.255(1) Å. Each "footstep" possesses a large channel which contained the disordered solvated molecules. Several types of 1D copper polymer framework patterns including linear chain, zigzag chain, or ladderlike chain have been reported.[9] The staircase-like motif described here comprises a new 1D pattern different from the one mentioned above.

While a similar synthetic procedure for **3** was carried out with **2** as the starting material, yellow block crystals of **4** were obtained in 58.5% yield. The phase purity was also confirmed by PXRD (Fig. S11).† The X-ray crystal structure analysis revealed that it crystallizes in the monoclinic space group C2/c with the formula [Cu$_2$(L$_2$)$_2$(bipy)$_3$](BF$_4$)$_2$. Interestingly, compounds **3** and **4** have the same framework stoichiometry (Cu : L : bipy = 2 : 2 : 3); however, **4** exhibits a 2D framework with polycyclohexane motifs instead of the staircase-like 1D structure in **3**.

The asymmetric unit of **4** contains two Cu(I) atoms, three bipy ligands, and two L$_2$ ligands. As shown in Fig. 3, each Cu(I) center is coordinated to three N atoms from three bipy ligands and one P atom from dppy ligand in a distorted tetrahedral geometry. The Cu–N and Cu–P bond distances range from 2.050(3) to 2.156(4) Å and 2.183(1) to 2.186(1) Å, respectively.
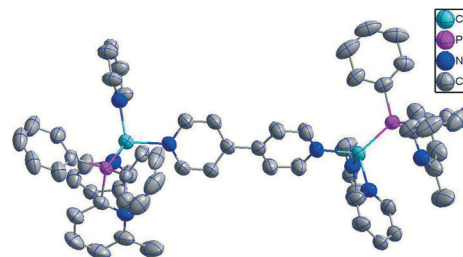

Fig. 1 Coordination environment of Cu(I) in **3**.

Fig. 3 Coordination environment of Cu(I) in **4**.

Each bipy bridges adjacent copper centers, while the bulky L_2 ligand alternately directed 'up' and 'down' along the plane comprised of three N atoms at the same Cu(I) center. The slightly distorted tetrahedral geometry of the copper atom caused by the bulky L_2 is also reflected by angles of P–Cu–N (102.8(1)–132.0(1)°) and N–Cu–N (97.2(1)–104.6(1)°). As shown in Fig. 4a, Cu(I) atoms are connected to each other through bridging bipy ligands in three directions to produce a polycyclohexane structural motif, in which each 54-membered macrometallacyclic ring consists of six bipy ligands and six copper ions. The unit can be simplified by representing the bipy ligands as simple lines with the copper atoms as the nodes (the separation of Cu⋯Cu is in the range of 11.150(1)–11.323(1) Å). In this way, one obtains a "cyclohexane ring" that adopts a "chair" configuration. Two sets of "cyclohexane rings" run along the same direction, which are fused with another two sets in roughly 90°. The alternating arrangement is repeated to form a 2D corrugated layer (Fig. 4b). The cyclohexane-based extended structural motifs adopting a chair conformation have been found in inorganic–organic hybrid compounds.[10] However, the arrangement pattern of the cyclohexane motifs in **4** was unprecedented in copper(I) CPs. Very similar motifs were observed in $[Cu(bpe)_{1.5}(PPh_3)]PF_6$ (bpe = *trans*-1,2-bis (4-pyridyl)ethylene)[7d] and $[Ca(H_2O)_4Cu_2(\mu_2\text{-bipy})_2L_2]$ ($H_3L = N$-[(3-carboxyphenyl)-sulfonyl]glycine).[11]

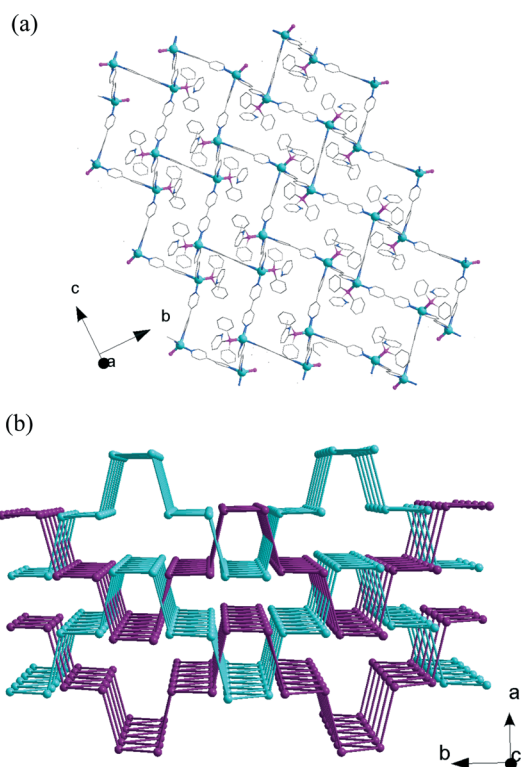Another notable feature of **4** is that 2D networks with polycyclohexane motifs are interpenetrated in a 2-fold fashion as shown in Fig. 4b. Two corrugated layers are interlocked in a regular way, leaving the skeleton to behave like a bookshelf. It should be noted that three types of microporous square channels are retained along the *c* axis. The aperture cross sections of the three channels have dimensions of approximately 11.1×11.5, 11.2×12.3, and 11.2×13.5 Å^2, respectively (Fig. 5). A PLATON analysis performed on the cationic $[Cu_2(L_2)_2(bipy)_3]^{2+}$ framework suggests a solvent- or counterion-accessible volume of approximately 3619 Å^3 per unit cell (14 082 Å^3), amounting to 25.7% of the crystal lattice. However, the void space in the channels is significantly reduced due to the interpenetration of nets and the occupation by BF_4^- counteranions.

It has been widely reported that the influences of bridging ligands with different sizes, spacers, and configurations are significant on the formation, connectivity, and topology of coordination polymers in the Cu(I)–L–PPh$_3$ system.[6,7] Other factors including the type of anion and solvent are also noticeable in the determination of the crystal structures,[7d] whereas the influence of blocking units (*e.g.* PPh$_3$) has not yet been explored prior to this work. It should be noted that the previously reported example with PPh$_3$ as terminal ligand $[Cu(PPh_3)(bipy)_{1.5}]BF_4$[6] and the title compounds **3** and **4** have the same metal centers, bridging ligands, and framework stoichiometries (Cu : L : bipy = 2 : 2 : 3, L = terminal ligand). The differences of terminal ligands, however, result in the completely distinct structural motifs, *i.e.* pentagon (L = PPh$_3$), hexagon (L_2) and tetragon (L_1). Apparently, this is a consequence of the steric influence of terminal ligands. In comparison with L_1- and L_2-bearing methyl groups on the pyridine ring, the less sterically bulky PPh$_3$ allows for a wider angle around the Cu(I) center (Cu–Cu–Cu angles: 103–108°) to stabilize a larger polygonal motif.[6] Whereas the methyl group on the *ortho*-(L_1) position of the pyridine ring, which is closer to the coordinated P atom in **3**, has a more significant steric hindrance than that of the *meta*-(L_2) position in **4**, the more compressed N–Cu–N (Cu–Cu–Cu angles: 90.0°) from the tetrahedral angle is required in **3**, resulting in the tetragonal

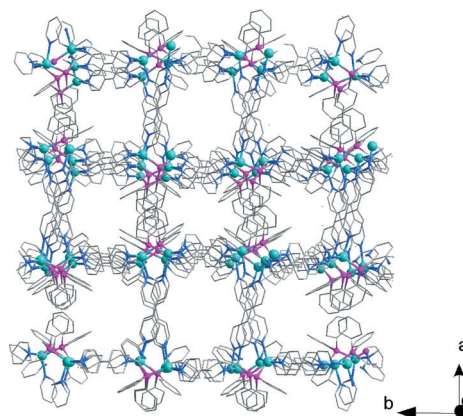

Fig. 4 (a) View of the polycyclohexane motif in **4**. (b) Schematic representation of the simplified interpenetrating layers in **4**.

Fig. 5 The representation of the microporous square channels in **4** along the *c* axis.

motif as the favorable arrangement. The *meta*-methyl in L_2 allows the angles within the "chair" configuration of the hexagon in **4** to have two kinds of Cu–Cu–Cu angles, two of the corner angles are 94.5° and 95.9°, and the other four are within the range of 99.2–104.7°.

The desolvation behavior and thermal stability of compounds **3** and **4** were investigated by thermal gravimetric analysis (TGA). A weight loss of ~2.6% was observed between 40 and 135 °C for **3**, which corresponds to the theoretical weight loss for two H_2O molecules. Decomposition of **3** occurred when the temperature went up to ~200 °C (Fig. S3†). A similar behavior was also observed in **4**. The desolvation commenced at about 50 °C and completed at ~155 °C. The observed mass loss of 6.0% was consistent with the loss of the CH_3OH and H_2O solvent molecules (6.1% calcd). **4** started to decompose at 195 °C, and the final mass residue of 12.0% at about 400 °C corresponds likely to the deposition of CuO (11.3% calcd) (Fig. S4†).

The optical absorption properties of **3** and **4** were studied using UV–vis diffuse reflectance spectroscopy. The onsets of absorptions are 535 nm and 510 nm for **3** and **4**, respectively, which are in good agreement with the yellow-greenish color of the crystals (Fig. S7 and S8).†

Both **3** and **4** are not soluble in common solvents. The emission properties of **3** and **4** in the solid state were studied. Upon excitation at 445 nm, the solid sample of **3** displays a bright yellow emission with λ_{em} maximum at 560 nm at room temperature (Fig. 6). Compound **4** is not emissive at room temperature but is luminescent at 77 K. The reason might be that there is energy transfer between the interpenetrating 2D networks at room temperature. At low temperature, the nonradiative pathway is limited, thus the emission occurs. The emission spectra of **3** and **4** along with those of L_1, L_2 and bipy are illustrated in Fig. 7. Compounds **3** and **4** have similar emission bands around 560 nm (λ_{ex} = 448 nm) at 77 K. This is because both compounds have quite similar coordination environments around the Cu(ɪ) centers (Fig. 1 and 2). The excited state may be generated by a metal-to-ligand (bipy) charge transfer, because ligand-based excited states should give off much higher energy light. Compound **4** is not emissive at room temperature, which is different from
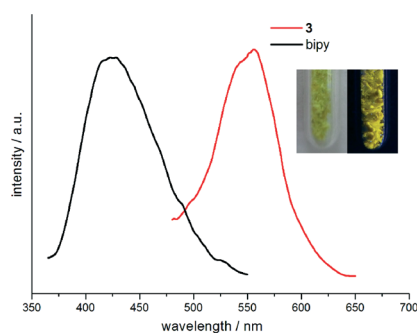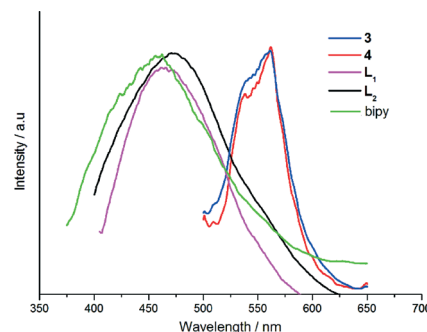

Fig. 7 Emission spectra of **3**, **4**, L_1, L_2 and bipy in the solid state at 77 K.

the case of **3**. The basic structural units in **3** and **4** are almost identical, so the different polymeric structures account for the different luminescence behaviors at room temperature.

Conclusions

The structural control of CPs is usually realized by changing reaction conditions such as temperature, reactant ratio and solvent. In many cases, synthetic methods such as solvothermal reaction, microwave-assisted reaction and even non-solution reaction are used. In this work, we show that tuning the methyl positions on the terminal phosphine ligands could lead to the formation of two distinct structural types of tri-connected copper(ɪ) CPs, a novel staircase-like 1D polymer and a 2-fold interpenetrating 2D polycyclohexane framework. Our research demonstrates that a subtle factor could have a significant influence on the formation of a final architecture, which provides more options for the structural design of coordination polymers.

Acknowledgements

Notes and references

‡ Crystal data for **3**, $C_{66}H_{56}B_2Cu_2F_8N_8P_2$, a = 42.216(2), b = 17.4513(7), c = 20.0960(9) Å, $\alpha = \beta = \gamma = 90°$, V = 14805.3(11) Å³, orthorhombic, space group *Cmca*, Z = 8, T = 173 K, 33 918 reflections measured, 10 352 unique (R_{int} = 0.1325), final R_1 = 0.0949, wR_2 = 0.2938 for 3412 observed reflections [$I >$ $2\sigma(I)$]. Crystal data for **4**, $C_{66}H_{56}B_2Cu_2F_8N_8P_2$, a = 25.4343(5), b = 39.7572(8), c = 17.0847(3) Å, β = 125.400(2)°, V = 14082.1(5) Å³, monoclinic, space group *C2/c*, Z = 8, T = 173 K, 10 970 reflections measured, 24 165 unique (R_{int} = 0.0193), final R_1 = 0.0661, wR_2 = 0.21974 for 9083 observed reflections [$I > 2\sigma(I)$].

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Fig. 6 Emission spectra of solid state **3** and bipy at room temperature. Inset: pictures of **3** under ambient light and 365 nm irradiation.

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