The first chiral 2-D molecular triangular grid†

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The two-dimensional coordination polymer, [Cu(PPh$_3$)(*N*,*N*-(2-pyridyl)(4-pyridylmethyl)amine)$_{1.5}$]·0.5CHCl$_3$·ClO$_4$ 1, with a large chiral triangular cavity and blue fluorescent emission, was synthesized by a solvothermal reaction between [Cu(MeCN)$_2$(PPh$_3$)$_2$]ClO$_4$ and *N*,*N*-(2-pyridyl)(4-pyridylmethyl)amine.

The self-assembly of chiral supramolecular entities is common *in vivo*. But to the chemist, the design and preparation of chiral artificial self-assembling systems is a most interesting and challenging task.[1,2] Metal–organic solids containing chiral cavities or helicates have drawn much attention in recent years due to their possible applications in enantioselective synthesis, catalysis, opto-electronics, magnetic materials and inclusion chemistry.[3,4] The focus of interest has been on two-dimensional polygons such as squares, rectangles and some smaller infinite assemblies, such as helices and helicates,[5–10] but chiral molecular boxes and coordination polymers with chiral cavities as well as three-dimensional polyhedra are now beginning to be explored.[11–14]

In comparison with rectangular assemblies there have been relatively few reports on triangular metallomacrocycles and most of them are molecular in nature.[15–18] To the best of our knowledge, multi-dimensional coordination polymers with trianglular cavities still remain unknown although there is an example of 3-D metal–4,4′-bipyridine (4,4′-bpy) molecular networks having triangular channels sustained by 4,4′-bpy through both hydrogen-bonding and π–π stacking interactions.[19] To our surprise, by employing the correct combination of bridging and terminal ligands, a novel two-dimensional coordination network, [Cu(PPh$_3$)(*N*,*N*-(2-pyridyl)-(4-pyridylmethyl)amine)$_{1.5}$]·0.5CHCl$_3$·ClO$_4$, **1** can be formed, which possesses an approximate triangular chiral cavity.

Coordination polymer **1** was synthesized under solvothermal reaction conditions from [Cu(MeCN)$_2$(PPh$_3$)$_2$]ClO$_4$ and *N*,*N*-(2-pyridyl)(4-pyridylmethyl)amine (L^1).‡ In its IR spectrum, there is a strong peak at 1095 cm^{-1}, clearly indicating the existence of a perchlorate anion in **1**.

The two-dimensional polymeric structure of **1** was revealed by an X-ray single crystal diffraction investigation.§ The asymmetric unit contains two crystallographically unique copper atoms having two different coordination modes in polymer **1**. That is, one Cu(I) links three 2-pyridyl nitrogen atoms and another, three 4-pyridyl nitrogen atoms from three different L^1 ligands besides which each Cu(I) atom is coordinated to one PPh$_3$. Three L^1 and one PPh$_3$ make each Cu(I) center a tetrahedral geometry. The salient features in **1** are that firstly, six copper atoms (Cu1–Cu2–Cu3–Cu4–Cu5–Cu6, Fig. 1) clearly connect into a nearly regular 2-D hexagon with Cu–Cu distances of *ca.* 8.622 Å and Cu–Cu–Cu angles of 104.9° around the circumference of the six-menbered rings. In [Cu(4,4′-bipyridine)$_{1.5}$(PPh$_3$)]BF$_4$·(THF)$_{1.33}$·(CHCl$_3$)$_{0.33}$ the connectivity of five copper atoms with five linear bipy ligands not only affords a nearly regular pentagon but also a large elliptical eight-membered ring.[20] Secondly, the PPh$_3$ ligands, all of which are pointing either up or down, and the twisted L^1 can almost completely fill the area of a triangle (Cu2–Cu6–Cu7, Fig. 1), resulting in the formation of an approximately equilateral triangle cavity with a side of 13.669 Å (Fig. 1).

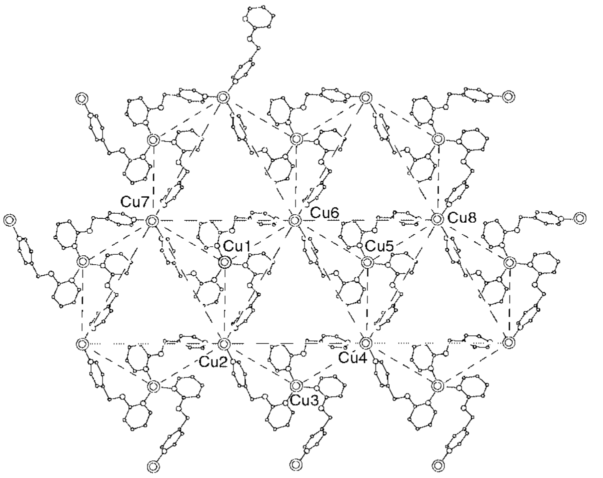

Fig. 1 A diagram showing a hexagon (Cu1–Cu2–Cu3–Cu4–Cu5–Cu6) with a triangular cavity (Cu2–Cu4–Cu6) (the open circles with increasing sizes stand for C, N, P and Cu, respectively. Solvent and perchlorates, H atoms and phenyl rings on PPh$_3$ are omitted for clarity) while a triangle area (Cu2–Cu6–Cu7) is almost space-filled by phenyl groups.

A space-filling representation also apparently demonstrates the formation of a triangular cavity (Fig. 2). It is noteworthy that two adjacent layers are in a staggered arrangement, as shown in Fig. 3, while the PPh$_3$ ligand sits in the hexagonal center of the adjacent layer but does not fill the triangular cavity on the adjacent sheet due to the intercalated anions and solvents separating the two adjacent layers (see ESI).† Furthermore, the formation of a chiral trianglular cavity highlights **1**, due to a combination of the achiral and dissymmetric L^1, as a flexible ligand and the sterically bulky terminal capping PPh$_3$ ligand.

The features of **1** are quite different from those found in Cu(I)–bipy coordination polymers[21] in which they only formed achiral coordination polymers, probably due to the utilization of linear, rigid ligands such as 4,4′-bipy and 3,4′-bipy. The reaction of Cd^{2+} with L^1 also, more recently reported by one of us, only afforded achiral two- and three-dimensional coordination

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† Electronic supplementary information (ESI) available: a packing representation of compound **1** showing solvent and anions intercalated between two adjacent layers. See http://www.rsc.org/suppdata/dt/b0/b007004l/

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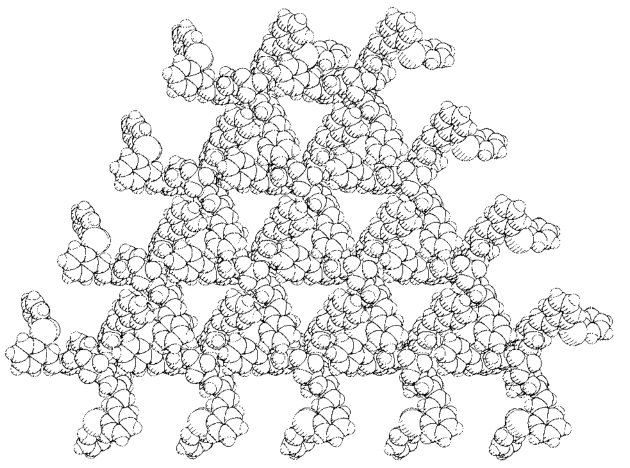

Fig. 2 A space-filling representation of compound **1** clearly showing the formation of a triangular cavity with solvent ($CHCl_3$) and anions (ClO_4^-) situated on top of the Cu atom.

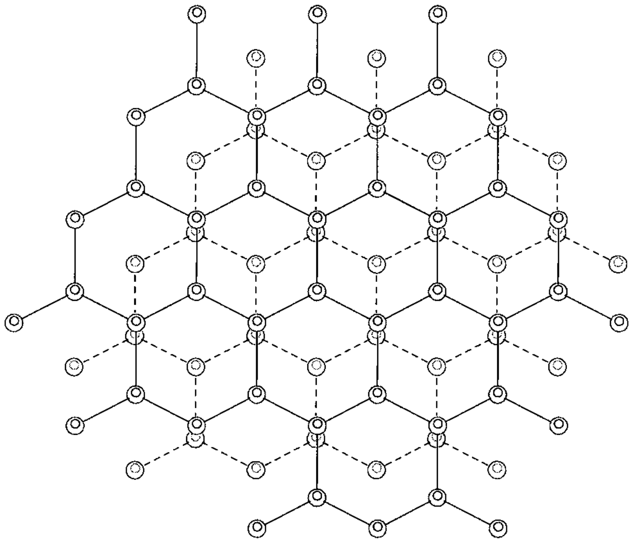

Fig. 3 A diagram showing the staggered arrangement between two adjacent layers (the dashed line represents the lower layer). The small open circles represent P atoms and the large open circles Cu atoms. The lines and dashed lines represent the free ligand. Solvent, perchlorate, H-atoms and phenyl rings on PPh_3 are omitted for clarity.

polymers, probably due to the absence of PPh_3. To this end, taking into account these facts together with the fact that the structure of polymer **1** contains both the steric bulk of the terminal group, the phosphine ligand, and the dissymmetric ligand, L^1, as flexible ligands, resulting in the formation of a twist angle of *ca.* 58.8° and the dihedral angle (124.9°) between the two pyridyl ring planes it is seen that a synergistic effect leads to the formation of chiral polymer **1**.

As far as we are aware, the 2-D chiral trianglular cavity in **1** is unprecedented. On the other hand, the guest molecule $CHCl_3$ and anions ClO_4^- are intercalated between adjacent layers (see ESI),† and two of these triangular cavity layers are stacked so that the Cu (such as Cu2, Cu4, Cu6, Cu8 *etc.* see Fig. 1) atoms form an AB type layer. A thermogravimetric analysis of polycrystalline samples of **1** show that a weight loss step occurred at *ca.* 138–162 °C (7.62%), corresponding to the removal of one $CHCl_3$ per formula unit (7.82%), and its structure collapses at temperatures above 162 °C, suggesting that the template ($CHCl_3$) is needed for the formation of **1**. However, preliminary experimental results show that butan-2-ol can also be intercalated between the stacked layers. Further work is still in progress.

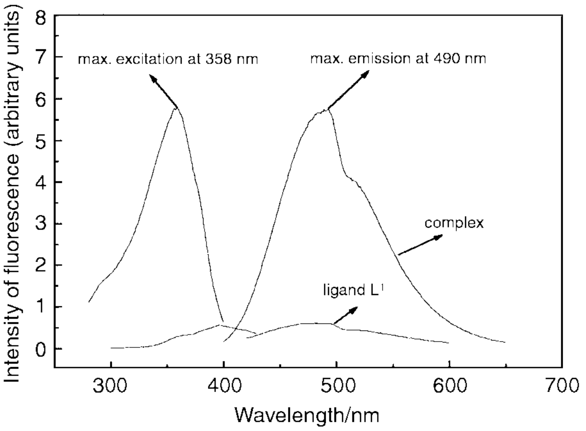

Fig. 4 A fluorescence spectrum of compound **1** in the solid state.

The free ligand L^1 has a weak emission at $\lambda = 460$ nm in the solid state when irradiated with UV light. In contrast, polymer **1** displays intense fluorescent emission ($\lambda = 490$ nm) when irradiated with UV light in the solid state (Fig. 4). The fluorescence intensity of **1** is almost 10 times larger than that of the free ligand, probably due to the rigidity enhancement in **1**. The blue fluorescent emission of **1** should originate from a $\pi \rightarrow \pi^*$ transition of intraligand L^1. On the other hand, a bathochromic shift occurred for **1**, compared to the free ligand, probably due to the enhancement of aromatic ring π–π stacking. Similarly, the solid reflectance UV-vis spectrum of **1** displays two peaks at 229.8 and 309.8 nm, respectively, most probably due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ of intraligand L^1. Owing to the blue fluorescence emission of **1**, it may be used as an advanced material for blue-light emitting diode devices.

In conclusion, we emphasize that the geometrical influence of the terminal PPh_3 group and the flexibility of ligand L^1 is vital to the formation of chiral cavities in **1**.

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Notes and references

‡ Preparation of compound **1**. L^1 was synthesized according to the method reported by Lin *et al.*[22] Solvothermal treatment of $[Cu(MeCN)_2(PPh_3)_2]ClO_4$ (0.120 g), *N*,*N*′-(2-pyridyl)(4-pyridylmethyl)-amine, $CHCl_3$ (1 ml) and THF (0.5 ml) for 5 hours at 80 °C yielded a pale-yellow polyhedral crystalline product (only one pure phase). The yield of **1** was 80% based on *N*,*N*′-(2-pyridyl)(4-pyridylmethyl)amine (found: C, 55.45; H, 4.10; N, 8.24. Calc.: C, 55.22; H, 4.04; N, 8.28%). IR (KBr, cm^{-1}): 3350vw, 3300vw, 1605vs, 1565vs, 1500vs, 1480m, 1430vs, 1420m, 1335m, 1095s, 995vw, 810m, 780m, 750vs, 695m, 630m, 530m, 505m.

§ Crystal data for **1**. $C_{70}H_{64}Cl_5Cu_2N_9O_8P_2$, trigonal, $R3$, $a = 13.6687(2)$, $b = 13.6687(2)$, $c = 32.4627(8)$ Å, $\alpha = \beta = 90$, $\gamma = 120°$, $V = 5252.54(17)$ Å^3, $Z = 3$, $M = 1525.57$, $D_c = 1.447$ Mg m^{-3}, $R_1 = 0.0563$, $wR_2 = 0.1236$ (5758 reflections), $T = 293$ K, $\mu = 0.905$ mm^{-1}. The Flack parameter was equal to 0.15(2), suggesting that **1** is probably twinned. CCDC reference number 186/2214. See http://www.rsc.org/suppdata/dt/b0/b007004l/ for crystallographic files in .cif format.

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