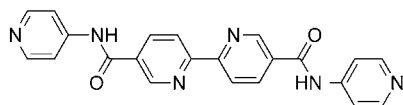


A Chiral, Self-Catenating and Porous Metal–Organic Framework and its Post-Synthetic Metal Uptake**

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The synthesis of polymeric coordination networks or metal–organic frameworks (MOFs) has evoked an immense amount of recent interest.^[1] This is due to their potential as gas storage materials,^[2] nanoscale reaction vessels,^[3] their catalytic^[4] and magnetic properties,^[5] and their ability to form intriguing architectures. Topologically complex networks can be achieved through interpenetration of two or more infinite networks,^[6] polycatenation of an indeterminate number of networks,^[7] polycatenation of cage structures,^[8] and through self-entanglement where a single network is entangled with itself.^[9,10] Pyridyl-based ligands have undoubtedly played a vital part in coordination polymer chemistry to date. The potential of 4,4'-bipyridine as a rigid bridging ligand has long ago been realized and this ligand has seen widespread use as a bridging ligand in the synthesis of two- and three-dimensional coordination polymers.^[11] We have recently reported the ligand *N,N'*-bis(pyridin-4-yl)-2,2'-bipyridine-5,5'-dicarboxamide (L) which is effectively an extended analogue of 4,4'-bipyridine with a 2,2'-bipyridine core,^[12] itself a potential metal chelating site (Scheme 1). In our previous report, 2D



Scheme 1. Ligand *N,N'*-bis(pyridin-4-yl)-2,2'-bipyridine-5,5'-dicarboxamide (L).

and 3D coordination polymers were formed with the involvement of both chelating and monodentate metal-binding sites of L.^[13] Here we report a heteroleptic metal–organic framework of L, $[\text{Zn}(\text{iso})(\text{L})]\cdot 2(\text{DMF})$ (**1** (iso = isophthalate, DMF = *N,N'*-dimethylformamide). Complex **1** has an unprecedented network topology and unmetaled 2,2'-bipyridine groups. Compound **1** can be doped with copper ions, where

Cu^{I} is bound at the ligand sites in a single-crystal-to-single-crystal post-construction modification of the material.

The reaction of L, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and isophthalic acid in a 1:1:1 ratio in DMF at elevated temperatures affords single crystals of **1** suitable for X-ray diffraction analysis.^[14] **1** crystallizes in the hexagonal space group $P6_222$.^[15] The asymmetric unit consists of half a Zn^{II} located on a 2-fold axis, and half of each L and the isophthalate anion both located around central 2-fold axes. Solvent molecules could not be located, however, thermogravimetric analysis (TGA) is consistent with two DMF molecules per formula unit (see Supporting Information). The Zn^{II} is tetrahedrally coordinated by two isophthalate anions in a monodentate interaction, and two L ligands through the pyridyl N; Zn–O 1.987(7) and Zn–N 2.062(7) Å (Figure 1a). The isophthalate anion bridges between two symmetry related Zn^{II} centers, as does L. The 2,2'-bipyridine moiety does not chelate to any metal center.

The bridging isophthalate anions and Zn^{II} centers create helical chains along a threefold screw axis (Figure 1a). The ligands L emanate out from these chains and adopt a planar conformation with their aromatic rings all perpendicular to the *ab*-plane. Each chain is closely surrounded by three other helical chains (Figure 1b). There are $\text{NH}\cdots\text{O}$ hydrogen bonds between amide groups of adjacent chains (N $\cdots$ O distance 2.76 Å), and face-to-face π – π interactions between two 4-aminopyridine moieties (ring centroid separation 3.62 Å). The L ligands in each chain bridge to another chain and the smallest circuit thus formed involves eight Zn centres (8-gon).

Thus a uninodal network of (8,4) topology is formed with Zn^{II} as the 4-connected nodes (Figure 2). The majority of coordination networks with tetrahedral nodes have a diamondoid framework, and multiple interpenetration is common. Here, the use of two rod-like ligands of different lengths affords a single network that has, to the best of our knowledge, a unique topology denoted by Schläfli symbol $\{8^5\cdot 10\}$ (as analyzed by TOPOS)^[16] and displays rare self-entanglement. The structure is self-entangled such that three independent 8-bonded rings (i.e. sharing no mutual sides) run through each such ring (Figure 2b). Other (8,4) networks (of type $\{8^6\}$) which display self-penetration have been reported, namely a net consisting of square planar metal nodes with *trans*-3-(3-pyridyl)acrylate as linkers and a net constructed from square planar copper centres with 1,1'-(1,4-butanediyl)-bis(imidazole) and isophthalate as linkers.^[10] In contrast, complex **1** contains tetrahedral 4-connecting nodes and only consist of 8^5 circuits (not 8^6) and one 10-membered circuit. At first glance, the connectivity (tetrahedral nodes) and symmetry (they are the same space group) of the structure is reminiscent of β -quartz, and like quartz this structure is enantiomorphic,^[17] however, quartz is a $\{6^48^2\}$ net.

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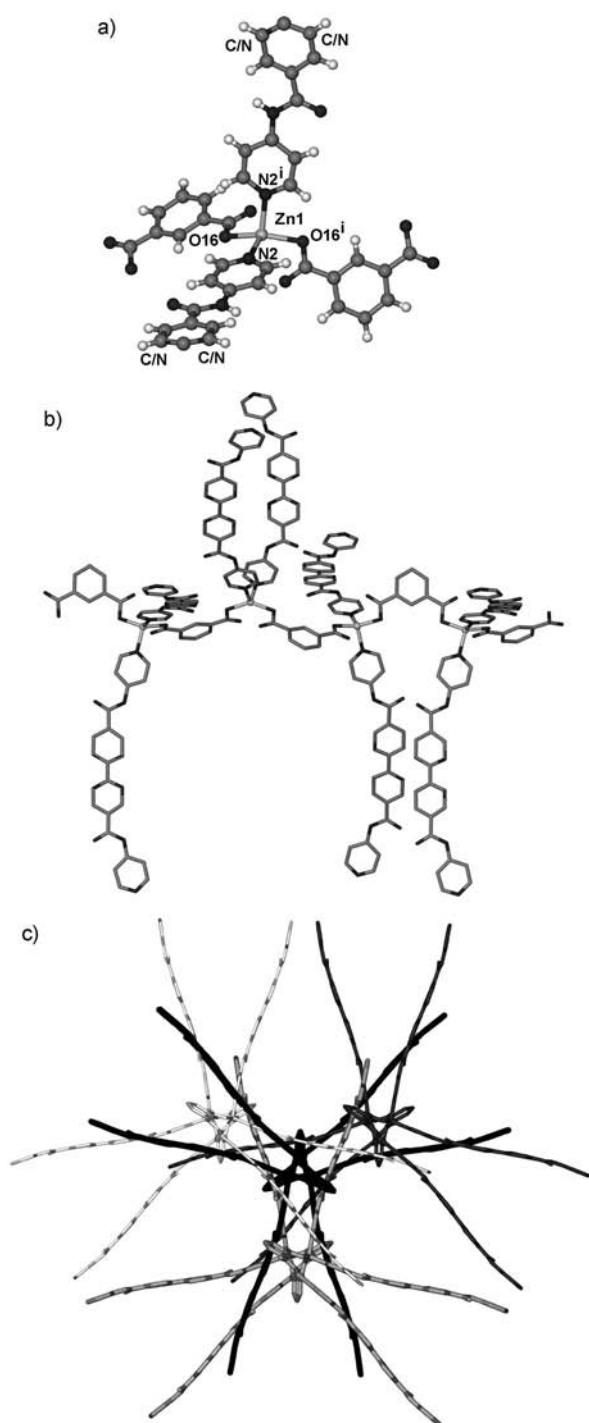


Figure 1. From the X-ray structure of **1**. a) Tetrahedral Zn coordination; b) helical chain bridged by isophthalate anions; c) four such chains viewed down their 3-fold screw axes. x , $1+x-y$, $1/3-z$.

Soaking crystals of $[\text{Zn}(\text{iso})(\text{L})]\cdot 2(\text{DMF})$ (**1**) in a DMF solution of CuCl_2 for 3 weeks leads to significant uptake of copper and the generation of the new heteronuclear MOF material $[\text{ZnCu}_{1/3}(\text{iso})(\text{L})]\cdot 1/3\text{Cl}\cdot [\text{CuCl}_2]_{0.3}\cdot n(\text{DMF})$ (**2**). Complex **2** retains its single crystallinity and the Cu-doping leads to a color change from very pale yellow to yellow-brown (see Supporting Information). Soaking the crystals in a similar

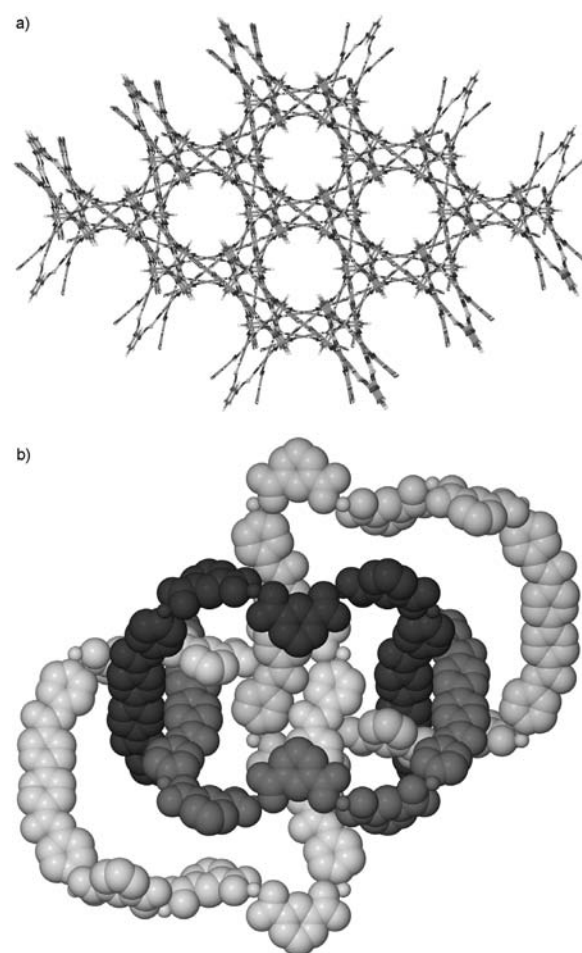


Figure 2. a) Extended structure of $[\text{Zn}(\text{iso})(\text{L})]$ viewed down the c axis; b) self-catenation within $[\text{Zn}(\text{iso})(\text{L})]$ with the entanglement of four different 8-gons shown.

$\text{Cu}(\text{BF}_4)_2$ solution gives the same color change. The single-crystal structure of **2** could be determined using synchrotron radiation with the structure solved in space group $P6_422$.^[14,15] In complex **2** the 2,2'-bipyridine moieties of ligand **L** bind copper centers, with the Cu adopting a distorted tetrahedral environment, with Cu–N distance 2.066(5) Å (Figure 3). The equivalent distance in complex **1** is 2.059 Å. This bond distance is consistent with Cu^{I} ,^[18] noting DMF is a plausible reductant.^[19] Aside from the incorporation of Cu, there is very little difference between the two structures: the unit cell volume of **2** is ca. 1% smaller than that for **1**, and the N positions of the 2,2'-bipyridine which were modeled as disordered for **1** become ordered on metal binding (Figure 3). This necessitates a solid-state rotation of the aromatic rings, a phenomenon that has been reported in other coordination network materials.^[20] The new network is also 4-connected but has smaller circuits (4-gons).

EDX analysis of the single crystals is consistent with a mixture of Cu^{I} and Cu^{II} being present, presumably due to the presence of solvated CuCl_2 in the channels. Analyses were performed after soaking the crystals in fresh DMF for a week to remove any surface contamination. The Cu:Cl % atom ratio was 2:2.8 indicating an approximately equal mixture of

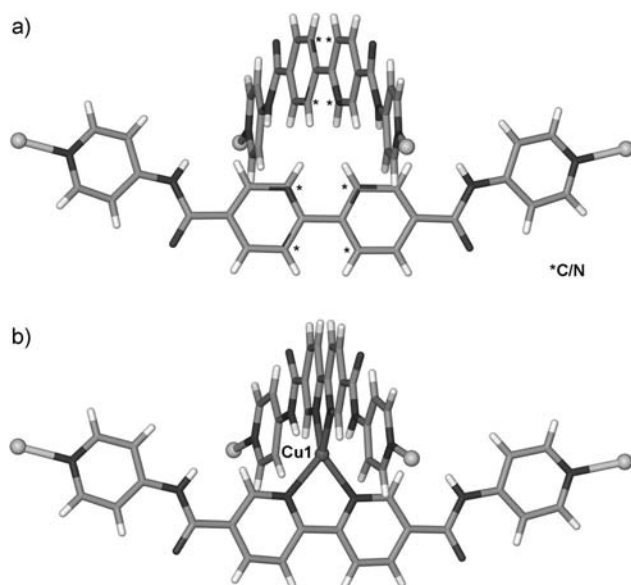


Figure 3. Crystal structures showing post-synthetic single-crystal-to-single-crystal modification; a) unmetallated bpy sites in **1** with atoms refined as disordered C/N indicated by *; b) same site in **2** showing Cu^I uptake and ordering of bpy groups.

Cu^I at the tetrahedral binding site and solvated CuCl₂ in the channels. The measured Zn:Cu ratio is 1:0.6. If the Cu^I accounts for half of this copper content the Zn^{II}:Cu^I ratio is ca. 3:1 which is in good agreement with the occupancy of the Cu position established through refinement of the X-ray data. Soaking a powdered sample of **1** in a DMF solution of CuCl₂ for only 3 days gave lower overall uptake of copper salt but maintained a similar Cu:Cl ratio of 2:3.6. Additional evidence of tetrahedral Cu^I within [ZnCu_{1/3}(iso)(L)] and solvated CuCl₂ in the channels comes from EPR analysis of the powder. There is no evidence for tetrahedral Cu^{II} and the observed EPR signal is consistent with Cu^{II} in a tetragonal ligand environment, with a measured $A_1\{^{63,65}\text{Cu}\}$ value of 160 G which is larger than the A_1 typical of tetrahedral Cu^{II}.^[21] Chloride counter-anions, solvated CuCl₂, and additional solvent were not located in the crystal structure of **2**.

The chemical transformation of **1** to **2** is an example of a post-synthetic modification (PSM) of a network material.^[22] It is a rare example of a PSM of the framework involving direct site-specific metal uptake, and the first such example that proceeds in a single-crystal-to-single-crystal fashion.^[23] Long, Yaghi and co-workers have previously reported the metalation of free 2,2'-bipyridine sites,^[24] and Humphrey and co-workers report gold uptake at a phosphine.^[25] Other examples involve metalation of a ligand site that is itself generated through a prior organic PSM.^[26] Metal ion uptake by pre-constructed coordination networks has also been reported through doping into pores or channels rather than binding at specific binding sites, often as a precursor to the generation of metal nanoparticles.^[27] Single-crystal-to-single-crystal transformations of network structures have recently been reported for metal-based redox chemistry,^[28] though are most commonly structural or chemical changes on guest

solvent desorption or uptake, or topotactic reactions such as photodimerizations.^[23,29]

The three-dimensional networks of **1** and **2** have one-dimensional channels along [001] approximately 9 Å in diameter (Figure 2a). The solvent-accessible volume is estimated to be 38 % of the unit cell volume. For both **1** and **2** the DMF can be exchanged for ethanol or chloroform without loss of structure. The solvent-exchanged material was activated by vacuum at 30 °C for 20 h, and powder XRD showed that the framework structure was retained (see Supporting Information).

Activated [Zn(iso)(L)] (**1a**) shows type I sorption behavior towards N₂ at 77 K, with a Brunauer–Emmett–Teller (BET) surface area of 404.0 m² g⁻¹. Subsequent sorption cycles exhibited a decrease in sorption ability and material that was allowed to stand in the atmosphere for a few weeks showed a marked decrease that could be only partially recovered by further ethanol activation (see Supporting Information). Similar studies on the powdered sample of **2** showed similar behavior although with a lower initial BET surface of 389.4 m² g⁻¹.

In summary, we have illustrated that a robust and porous metal–organic framework material with open chelating metal-binding sites may be constructed without having to protect the ligand chelate sites. Furthermore, these sites can be doped with additional metal cations in a single-crystal-to-single-crystal post-synthetic modification. This points to a novel approach to generating heteronuclear MOFs and hence introducing different potential functionalities.

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