Metal–Organic Frameworks

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

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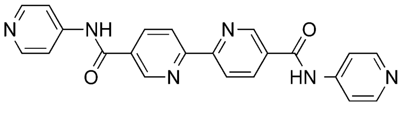
The synthesis of polymeric coordination networks or metal–organic frameworks (MOFs) has evoked an immense amount of recent interest.[1] This is due to their potential as gas storage materials,[2] nanoscale reaction vessels,[3] their catalytic[4] and magnetic properties,[5] and their ability to form intriguing 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 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, [Zn(iso)(L)]·2(DMF) **1** (iso = isophthalate, DMF = *N*,*N*′-dimethylformamide). Complex **1** has an unprecendented 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.



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

The reaction of L, $Zn(NO_3)_2·6H_2O$ 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 NH···O hydrogen bonds between amide groups of adjacent chains (N···O distance 2.76 Å), and face-to-face π–π interactions between two 4-aminopyridine moieties (ring centroid seperation 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 $\{8^5·10\}$ (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 reminescent of β-quartz, and like quartz this structure is enantiomorphic,[17] however, quartz is a $\{6^48^2\}$ net.

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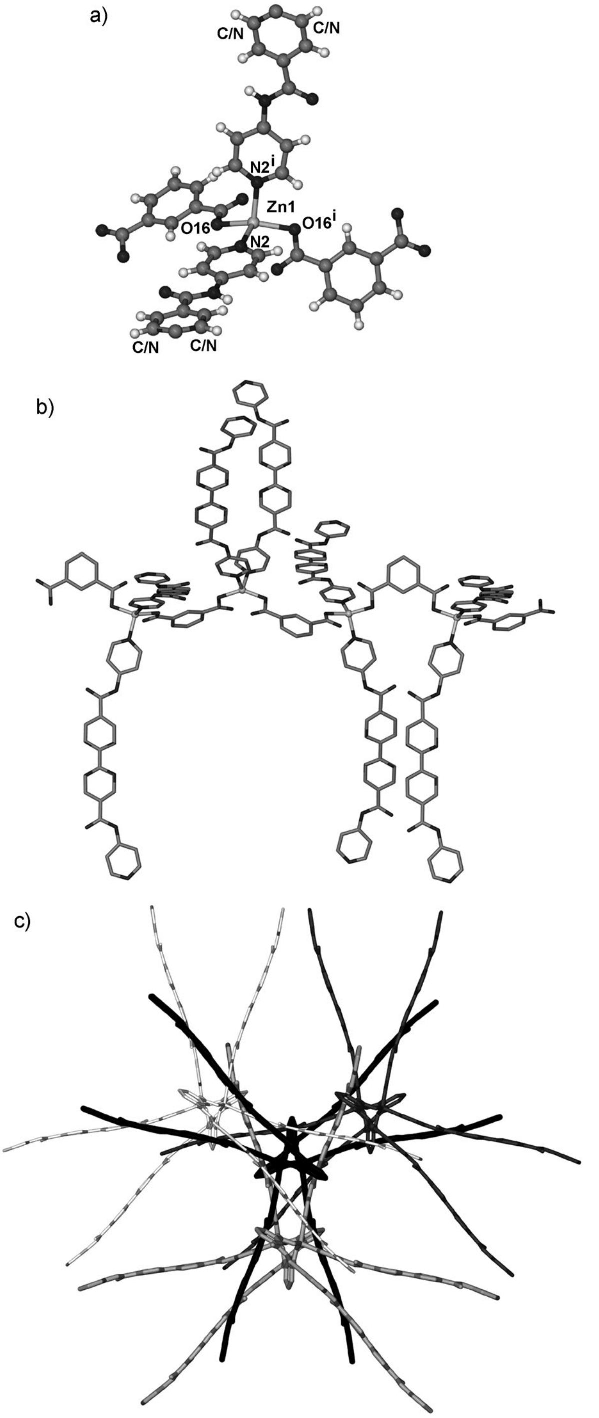

***Figure 1.*** From the X-ray structure of **1**. a) Tetrahedral Zn coordination; b) helical chain bridged by isophthalate anions; c) four such chains viewed down their 3-fold screw axes. *x*, 1+*x*−*y*, 1/3−*z*.

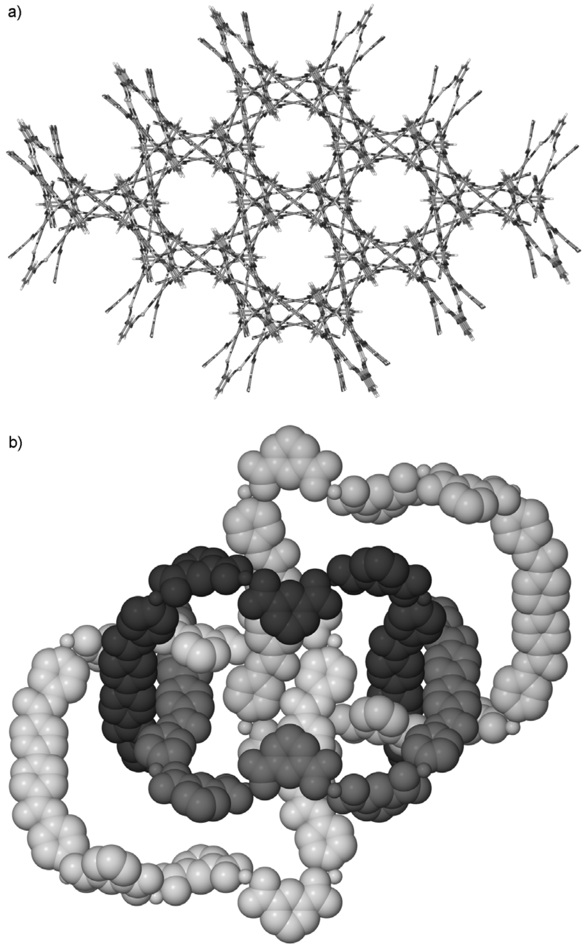

***Figure 2.*** a) Extended structure of [Zn(iso)(L)] viewed down the *c* axis; b) self-catenation within [Zn(iso)(L)] with the entanglement of four different 8-gons shown.

Soaking crystals of [Zn(iso)(L)]·2(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 $[ZnCu_{1/3}(iso)(L)]\cdot 1/3\,Cl\cdot[CuCl_2]_{0.3}\cdot n(DMF)$ (**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 $Cu(BF_4)_2$ 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

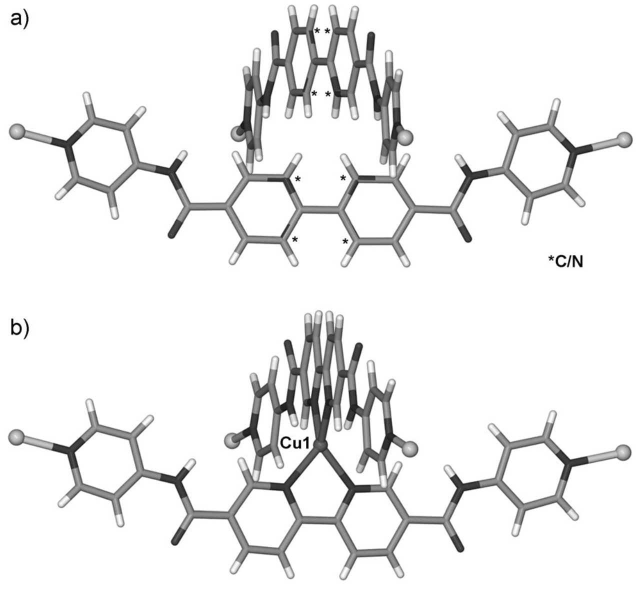

***Figure 3.*** Crystal structures showing post-synthetic single-crystal-to-single-crystal modification; a) unmetaled bpy sites in **1** with atoms refined as disordered C/N indicated by *; b) same site in **2** showing $Cu^I$ uptake and ordering of bpy groups.

$Cu^I$ at the tetrahedral binding site and solvated $CuCl_2$ 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 $CuCl_2$ 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 $CuCl_2$ 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 $A_1\{^{63,65}Cu\}$ value of 160 G which is larger than the $A_1$ typical of tetrahedral $Cu^{II}$.[21] Chloride counter-anions, solvated $CuCl_2$, 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 $N_2$ at 77 *K*, with a Brunauer–Emmett–Teller (BET) surface area of $404.0\,m^2g^{-1}$. 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 $389.4\,m^2g^{-1}$.

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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