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A three-folded interpenetrated metal-organic framework constructed by H-bonding interaction

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The polymer $[Zn(BPDPE)(NDC)(H_2O)]_n$ has been prepared and characterized using X-ray diffraction analysis.

The designed metal-organic frameworks (MOFs) from various molecular building blocks connected by coordination bonds, supramolecular contacts, are of interest due to their intriguing aesthetic structures and topological features,[1–3] as well as promising applications in photochemistry,[4,5] molecular magnetism,[6,7] heterogeneous catalysis[8,9] and molecular sorption.[10,11] Recently, a number of N-donor ligands have been widely employed to construct coordination polymers with fascinating architectures and interesting properties.[12–15] 4,4′-Bis(pyridyl) diphenyl ether (BPDPE) is a V-shaped pyridine ligand, which can be regarded as a half-flexible ligand. To test the ability of this ligand to give new architectures and topologies, we selected BPDPE, 2,6-naphthalenedicarboxylic acid (H_2NDC), and a Zn^{II} salt to solvothermally synthesize a new coordination polymer $[Zn(BPDPE)(NDC)(H_2O)]_n$ **1**.[†] The new compound was studied by X-ray crystallography.[‡]

X-ray crystallographic analysis reveals that the crystal of **1** is solved in monoclinic space group $P2_1/c$. The asymmetric unit contains an independent Zn^{II} cation, one NDC^{2-} anion, one BPDPE ligand and one coordinated water molecule. In complex **1**, only one N atom is coordinated to the Zn^{II} cation. As shown in Figure 1, the Zn^{II} centre is four-coordinated by two carboxylic O atoms from two 2,6-H_2NDC, one O atom from coordinated water and one nitrogen atom from BPDPE to form a distorted tetrahedral geometry.

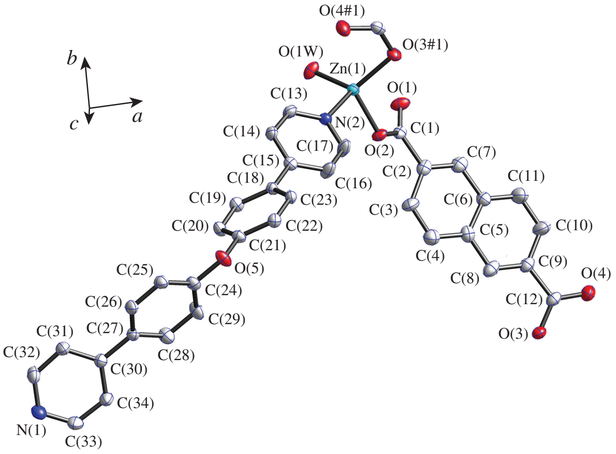

Figure 1 Coordination environment of complex **1**. The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 3 – *x*. Selected bond lengths (Å): N(2)–Zn(1) 2.063(3), O(2)–Zn(1) 1.964(2), O(3#1)–Zn(1) 1.948(2), O(1W)–Zn(1) 1.949(2); selected bond angles (°): O(3#1)–Zn(1)–O(1W) 119.44(11), O(3#1)–Zn(1)–O(2) 105.67(11), O(1W)–Zn(1)–O(2) 114.44(10), O(3#1)–Zn(1)–N(2) 116.17(11), O(1W)–Zn(1)–N(2) 103.94(11), O(2)–Zn(1)–N(2) 94.73(10).

The neighbouring Zn^{II} ions are linked by NDC^{2-} anions to form an infinite 1D helical chain, the adjacent distance of Zn···Zn is 12.994 Å. For the BPDPE ligand, only one N atom is coordinated to the Zn^{II} cation, so the BPDPE ligands connect the 1D helical chain (Figure 2). Further inspection shows that the

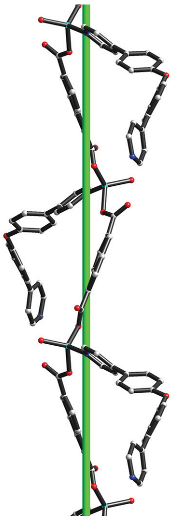

Figure 2 1D helical chain linked by Zn^{II} ions and NDC^{2-} anions.

[†] Crystals of **1** were prepared by a solvothermal reaction: a mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (29.7 mg, 0.1 mmol), 2,6-H_2NDC (21.6 mg, 0.1 mmol) and BPDPE (32.4 mg, 0.1 mmol) was dissolved in 9 ml of DMF/H_2O (2:1, v/v). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 ml) and heated at 90 °C for 3 days; colourless plank crystals were obtained; yield, 63% (based on BPDPE).

[‡] *Crystallographic data for* **1**: crystals of $C_{34}H_{24}N_2O_6Zn$ (M = 621.92) are monoclinic, space group $P2_1/c$, at 293 K: a = 8.0301(9), b = 21.012(2) and c = 17.3295(17) Å, β = 112.532(4)°, V = 2700.8(5) Å^3, Z = 4, d_{calc} = = 1.530 g cm^{-3}, μ(MoKα) = 0.963 mm^{-1}, F(000) = 1280. 13 255 reflections were measured and 4756 independent reflections (R_{int} = 0.0438) were used in a further refinement. The refinement converged to wR_2 = = 0.1123 and GOF = 0.948 for all independent reflections [R_1 = 0.0469 was calculated against F for 3458 observed reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on F^2.[16] The hydrogen atom positions were fixed geometrically at calculated distances and allowed them to ride on the parent atoms.

CCDC 885118 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2012.

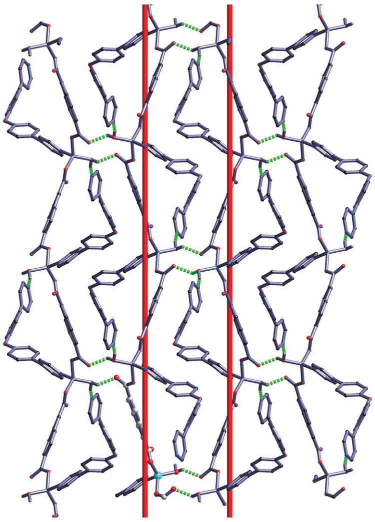

Figure 3 3D framework formed by H-bondings, the helical and opposite chirality chains are arranged alternately.

coordinated water, carboxyl group, and uncoordinated N atom from every two identical chains are actually contacting each other by strong H-bonding. These H-bonds are of two kinds, one contains coordinated water and a carboxyl group, and the O(1W)H(1A)···O(1) distance is 1.746 Å; while another is between coordinated water and uncoordinated N atom, and the O(1W)H(1B)···N(1) distance is 1.759 Å (Figure 3). Obviously, these H-bonded interactions are also available for increasing the stability of the whole crystal structure.

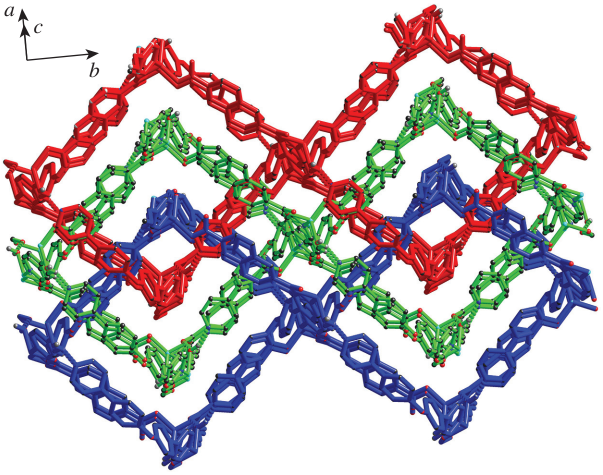

Figure 4 Three-fold interpenetrated framework in **1**.

This extension of the structure into a 3D framework is accomplished by H-bonded interactions; the helical and opposite chirality chains are arranged alternately. Because of the spacious nature of a single framework, it allows other two identical networks to interpenetrate each other leading to a threefold interpenetrated metal-organic framework (Figure 4). The results demonstrate that the uncoordinated N atom and coordinated water molecule can be well used as the structure-directing tool and can produce various H-bonding in the synthesis of unusual coordination frameworks.

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