Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Unprecedented three-level hierarchical entanglement in a coordination polymer

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Materials and Methods: All chemicals were reagent grade and used as purchased without further purification. Elemental analysis for C, H and N was carried out on a German Elementar Vario EL III instrument. The FT-IR spectroscopy was performed on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000─400 cm^{-1}. Thermogravimetric analyses was recorded on a NETZSCH STA 449C unit at a heating rate of 10 °C·min^{-1} under nitrogen atmosphere. The power X-ray diffractometer using Cu Kα radiation (λ = 0.154 nm).

Synthesis of $[Co_3(btc)_2(bimb)_3]_n \cdot 7nH_2O$. A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.058g, 0.2mmol), H_3btc (0.042g, 0.2mmol), bimb (0.031g, 0.2mmol), and water (10mL) was placed in a 30 mL teflon reactor. After adjusting the pH value to 6 ─ 7 by addition of $NH_3 \cdot H_2O$, the mixture was heated at 150 °C for 3days, and then it was slowly cooled to 30 °C for 24 h. Bule violet prism crystals were obtained by filtration in 35% yield based on $Co(NO_3)_2 \cdot 6H_2O$. Anal Calcd $C_{78}N_{12}O_{19}H_{74}Co_3$ (M_r = 1660.29): C, 56.76; H, 4.32; N, 10.20. Found: C, 56.43; H, 4.49; N, 10.12.

Thermogravimetric Analysis

To investigate the exact number of the free water molecules and thermal stability of complex **1**, the thermogravimetric analysis (TGA) was carried out in the temperature range of 20─1000 °C under a flow of nitrogen with a heating rate of 10 °C·min^{-1}

(Figure S1). The weight loss in the range of 20─165 °C corresponds to the departure of free water molecules (calcd, 7.60%; found, 7.78%). No weight loss was observed from 165 to 255 °C, and the framework undergoes decomposition in the range of 255 to 765 °C.

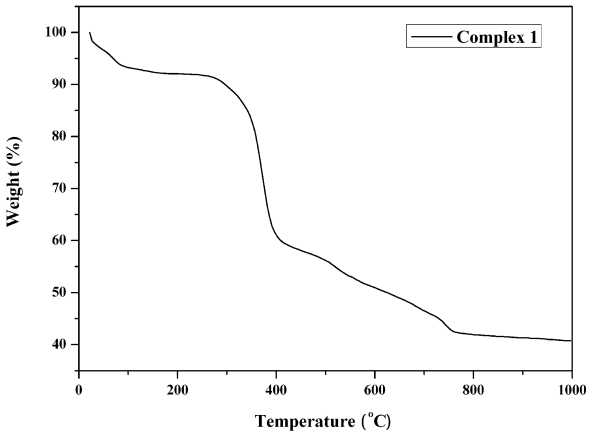

Fig. S1 TAG curve of complex **1**.

XRPD Patterns

As shown in Fig. S2, the positions of the experimental diffraction peaks are consistent with the simulated XRD patterns well, indicating the phase purity of the as-synthesized simple.

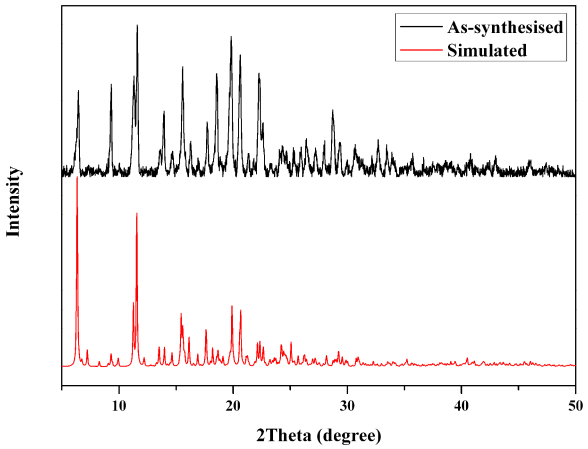

Fig. S2 Stimulated and experimental XRPD patterns of complex **1**.

FT-IR Spectroscopy

FT-IR spectroscopy was recorded on a Perkin-Elmer Spectrum using KBr pallets. FT-IR (KBr, 4000-400cm-1): 3448(m), 3118(w), 1568(s), 1454(m), 1348(s), 1092(m), 750(m).

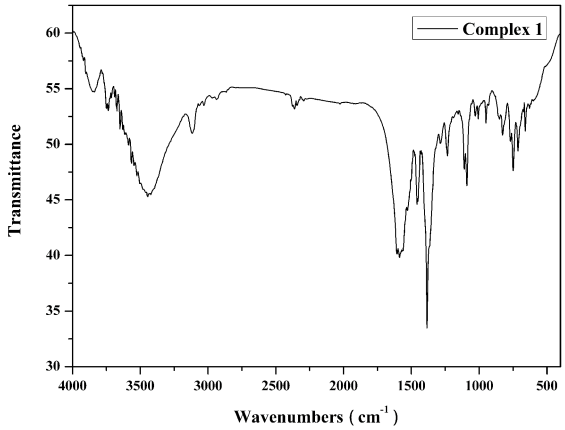

Fig. S3 FT-IR spectroscopy of complex **1**.

X-ray Crystallography

Data collection for complex **1** was performed on Rigaku CCD diffractometer with

graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073Å) by using the ω-scan mode at 123K. The structures was solved by direct methods and refined by full-matrix least-squares fitting on F^2 using the SHELX-97.[1] All non-hydrogen atoms except O15 were refined with anisotropic thermal parameters. The free water molecule O15 could not be refined with anisotropic thermal parameters because of its high thermal disorder. The position of hydrogen atoms were located at geometrically calculated positions and refined by riding. Some free water molecules (O13, O13'; O14, O14'; O15, O15'; O16, O16'; O17, O17') in **1** is disordered and refined using O atoms split over two sites with a total occupancy of 1.

(1) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, **1997**.

Table S1 Summary of the Crystal Data and Structure Refinement Parameters for **1**

complexes	**1**
empirical formula	$C_{78}H_{74}N_{12}Co_3O_{19}$
formula weight	1660.29
crystal system	Orthorhombic
T (K)	123(2)
space group	*P*bcn
a (Å)	37.985 (7)
b (Å)	14.570 (3)
c (Å)	27.895 (5)
α (°)	90
β(°)	90
γ(°)	90
V(Å^3)	15438 (5)
Z	8
D_C (g cm^{-3})	1.416
μ(mm^{-1})	0.716
F(000)	6760

θ range (°)	2.09–25.0°
Collected reflections	83559
unique reflections	13350
parameters	1043
R_{int}	0.0489
Gof on F^2	1.013
R_1[a] ($I > 2\sigma(I)$)	0.0940
wR_2[b] ($I > 2\sigma(I)$)	0.2765
R_1 (all data)	0.0991
wR_2 (all data)	0.2843

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_0)^2]^{1/2}$.

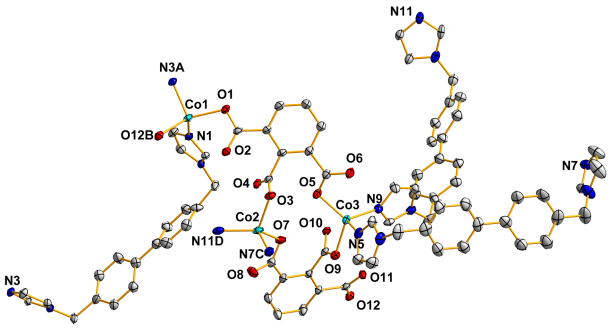

Fig. S4 The coordination environment of Co(II) atoms in complex **1** with the thermal ellipsoid at the 30% probabiltity level (hydrogen atoms and free water molecules have been omitted for clarity). Symmetry transformations used to generate equivalent atoms: *A* = 1/2 − *x*, 1/2 − *y*, *z* − 1/2, *B* = *x*, *y* − 1, *z*, *C* = *x*, 2 − *y*, 1/2 + *z*, *D* = 1/2 − *x*, 3/2 − *y*, 1/2 + *z*.

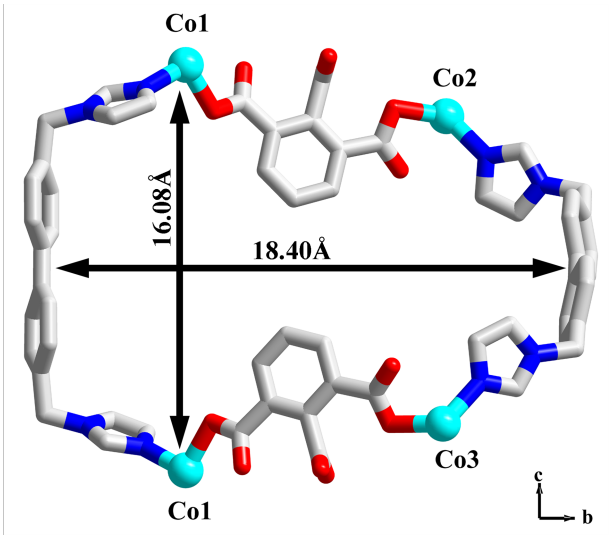

Fig. S5 The basic distorted ring [Co1(btc)Co2(bimb)Co3(btc)Co1(bimb)].

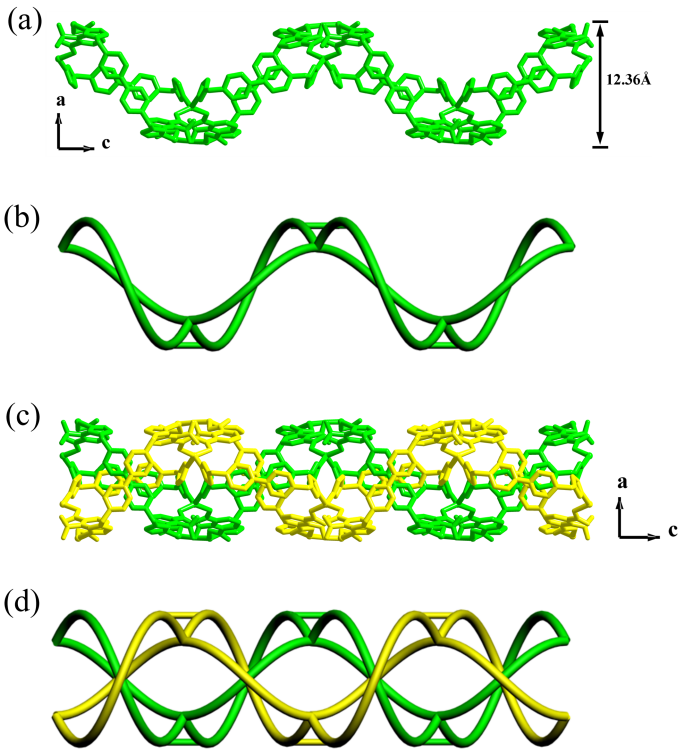

Fig. S6 A lateral view of the undulating self-penetrating layer (a) and schematic representation (b) of the layer. The interpenetration of pair of the self-penetrating layers (c). Schematic representation of the two-fold interpentration (d).

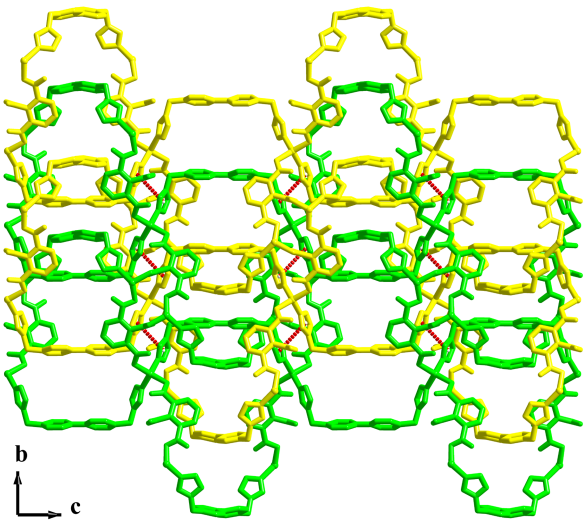

Fig. S7 The π-π interactions (red lines) between imidazole rings in the 2D self-penetrated layers.

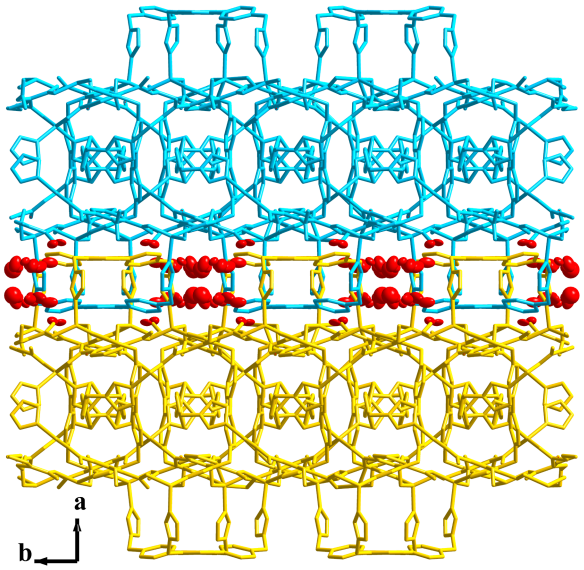

Fig. S8 The lattice water molecules (red) occupy the void spaces between the polycatenated frameworks.

Topology Analysis

In order to understand the underlying topology of the 2D network of **1** more fully, a

'node and linker' approach was undertaken, In this treatment, btc ligands, Co1 atoms, Co2 and Co3 atoms are 3-connected, 4-connected, and 4-connected nodes, respectively (Fig. S7). The resulting 3,4,4-connected trinodal network (Fig. S8) has a Point symbol of $(4\ 6^2)_2(4\ 6^2\ 8^2)_2(6^4\ 8\ 10)$ as calculated by TOPOS. It is worth to note that the aforementioned basic ring, [Co1(btc)Co2(bimb)Co3(btc)Co1(bimb)], is topological shortest six-member ring. Thus the two levels of self-penetration in complex **1** are well defined.

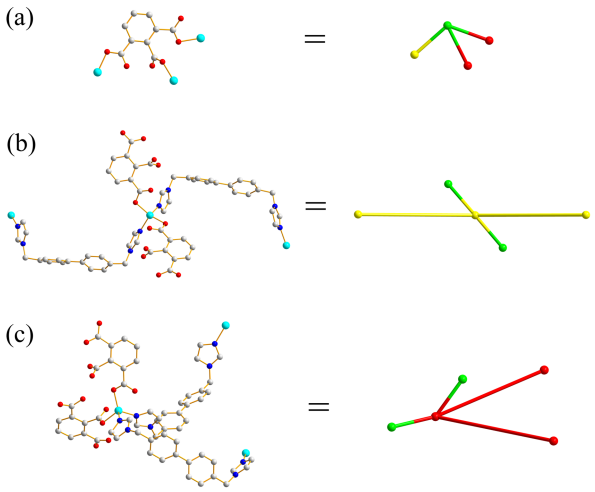

Fig. S9 Description of the structure of **1**: illustration of the btc ligand, viewed as a 3-connected node (a), illustration of the Co1 atoms, viewed as a 4-connected node (b), illustration of the Co2 and Co3 atoms, viewed as another 4-connected node.

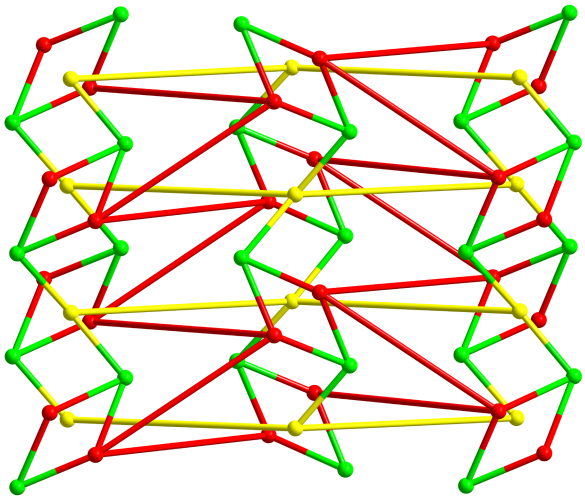

Fig. S10 Schematic illustrating the 2D (3,4,4)-connected net topological network in **1** (green balls represent the 3-connected btc ligand nodes, yellow balls represent the 4-connected Co1 atoms, red balls represent the 4-connected Co2 and Co3 atoms.