Electronic Supplementary Information

The first one-fold inclined 1D→3D polycatenation assembled from unique interweaving triple-stranded helices

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Materials. Bib was prepared by 2-methylimidazole with 1,4-dichlorobutane [1].The other chemicals were obtained commercially and used without further purification.

General Characterization and Physical Measurements.The powder X-ray diffraction pattern was collected on a Rigaku D/Max 3III diffractometer. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C thermogravimetric analyzer with a heating rate of 10 °C·min^{-1} under a flow of N_2 atmosphere. Elemental analyses of C, H, and N were performed on a Perkin–Elmer 240C automatic analyzer. IR spectrum was recorded on a FT-IR 170 SX (Nicolet) spectrophotometer (4000–400 cm^{-1} region) using KBr pellets.

***Experimental data* for 1**: A mixture of 1,4-bis(2-methyl-imidazol-1-yl(bib)(0.0218 g, 0.1 mmol)，*5-Hydroxy*isophthalic acid (5-OIPA)(0.0182g, 0.1 mmol) in 5 mL CH_3OH was layered onto a solution of $Co(NO_3)_2·6H_2O$ (0.0291 g, 0.1 mmol) in 5 mL H_2O. The resulting mixture was kept peacefully at room temperature. Purple strip crystals of **1** were obtained after two week. Yield: 55%. Anal. calcd for $C_{20}H_{38}N_4O_{11}Co$(569.37): C,42.15; H, 6.67; N, 9.84%. Found:C, 42.33; H, 6.52; N, 9.71%. IR (KBr,cm^{-1}): 3432(s), 3134(s), 1663(m), 1619(m), 1555(m), 1452(m), 1401(s), 1279(w), 1159(w), 1004(w), 746(w), 678(w), 587(w).

***Crystal data* for 1**: The crystallographic data for **1** was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-Kα radiation (λ=0.71073 Å) at 293 K. The structure was solved by direct methods and refined by the full-matrix least-square techniques using the SHELXL program [2-3]. Semi-empirical absorption correction was applied using multi-scan techniques by the SADABS program[4]. All non-hydrogen atoms were located from the difference Fourier syntheses.All hydrogen atoms attached to the organic ligands were placed geometrically with riding model. In complex **1**, the C6 and C11 atoms are disordered and refined into two positions with multiplicities of 0.5/0.5. The H atoms of disordered carbon atoms and lattice water molecules could not be located reasonably, but were included in the formula. CCDC number of compound **1** is

895871.The crystallographic data is summarized in Table S1 and the selected bond lengths and angles is listed in Table S2.

Table S1. Crystal data and structure refinement for **1**.

Complex	**1**
formula	$C_{20}H_{25}N_4O_{11}Co$
formula wt	556.37
crystal system	Tetragonal
space group	*I-42d*
a (Å)	11.8179(10)
b (Å)	11.8179(10)
c (Å)	37.714(5)
α(°)	90
β(°)	90
γ(°)	90
V (Å^3)	5267.2(9)
Z	8
ρ (g cm^{-3})	1.403
μ(mm^{-1})	0.713
F(000)	2304
collected reflns	13953
unique reflns	2604
R_1 [I>2σ(I)]	0.0659
wR_2 (all data)	0.2097

Table S2. Selected bond distances (Å) and angles (º) for **1**.

Complex **1**			
Co(1)-N(1)	2.035(6)	O(2)#1-Co(1)-O(2)	138.5(2)
Co(1)-N(1)#1	2.035(6)	N(1)-Co(1)-O(1)#1	162.5(2)

Co(1)-O(2)#1	2.118(4)	N(1)#1-Co(1)-O(1)#1	86.4(2)
Co(1)-O(2)	2.118(4)	O(2)#1-Co(1)-O(1)#1	60.18(18)
Co(1)-O(1)#1	2.238(4)	O(2)-Co(1)-O(1)#1	88.60(19)
Co(1)-O(1)	2.238(4)	N(1)-Co(1)-O(1)	86.4(2)
N(1)-Co(1)-N(1)#1	105.6(3)	N(1)#1-Co(1)-O(1)	162.5(2)
N(1)-Co(1)-O(2)#1	104.4(2)	O(2)#1-Co(1)-O(1)	88.60(19)
N(1)#1-Co(1)-O(2)#1	100.3(2)	O(2)-Co(1)-O(1)	60.18(18)
N(1)-Co(1)-O(2)	100.3(2)	O(1)#1-Co(1)-O(1)	85.1(3)
N(1)#1-Co(1)-O(2)	104.4(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1, z; #2 x, -y+1/2, -z+1/4; #3 -x,-y, z

1 X.Y.Huang,K.F.Yue,J.C.Jin,J.Q.Liu,C.J.Wang,Y.Y.Wang,Inorg.Chem.Commun,2010,13,338.

2 G. M. Sheldrick, SHELXS-97, Program for the Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 1997.

3 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure; University of Göttingen: Göttingen, Germany, 1997.

4 G.M.Sheldrick, SADABS, Program for Bruker Area Detector Absorption Correction; University of Göttingen: Göttingen, Germany, 1997.

Table S3 Summary of the linking modes of the 6-, 8- and 10-membered shortest ring within 3D net of **1**

Cycle 1	Cycle 2	Chain[a]	Cross[b]	Mult[c]
6a	6a	inf.	1	1
6a	8a	inf.	1	2
6a	10a	inf.	1	3
8a	6a	inf.	1	2
8a	8a	inf.	1	4
8a	10a	inf.	1	6
10a	6a	inf.	1	3
10a	8a	inf.	1	6
10a	10a	inf.	1	9

[a] Chain: the bond amount of the shortest chain that interconnected two rings.

[b] Cross: the times of each ring crossing another ring.

[c] Mult: the ring numbers of each ring crossed by other one

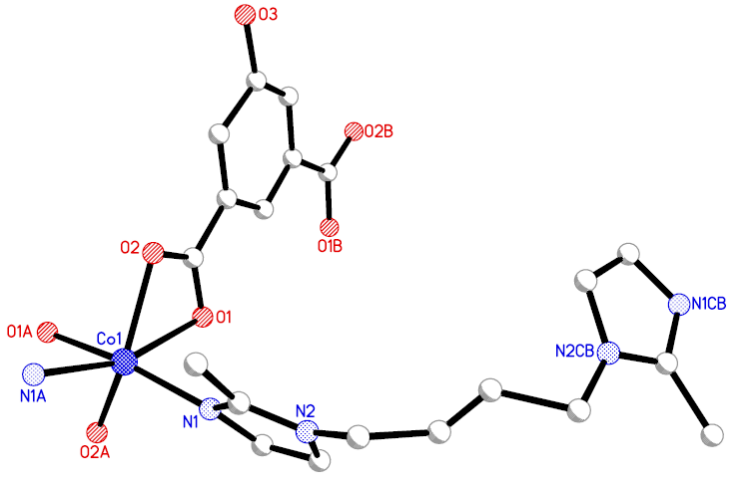


Fig. S1 The coordination environment of the Co(II) ions in **1(**Symmetry codes: A -x,-y+1, z; B x, -y+1/2, -z+1/4;**)**

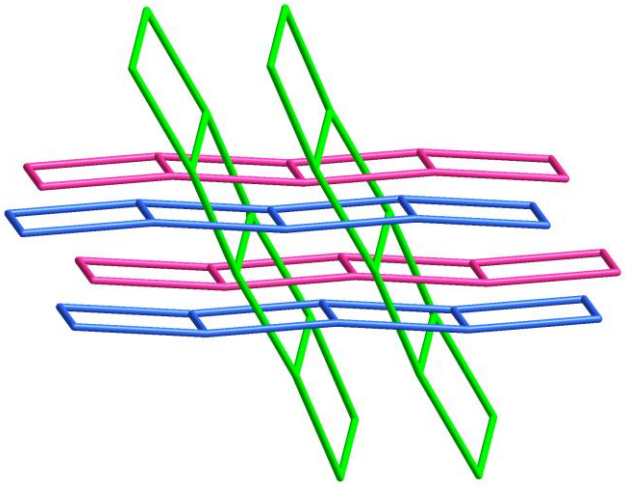


Fig.S2 Perspective view of the two-fold polycatenated ladders

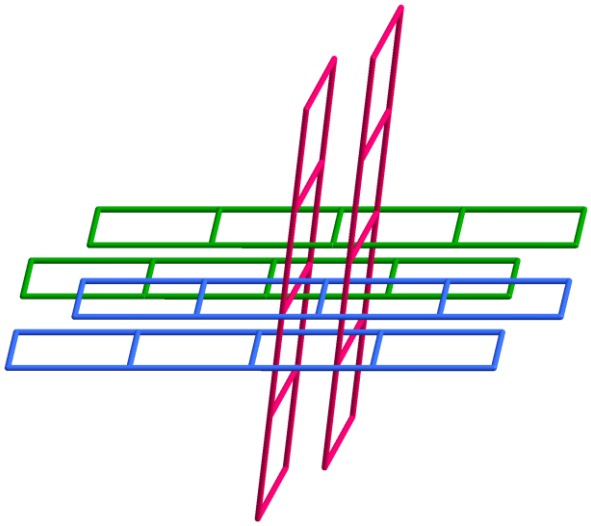


Fig.S3 Perspective view of the four-fold polycatenated ladders

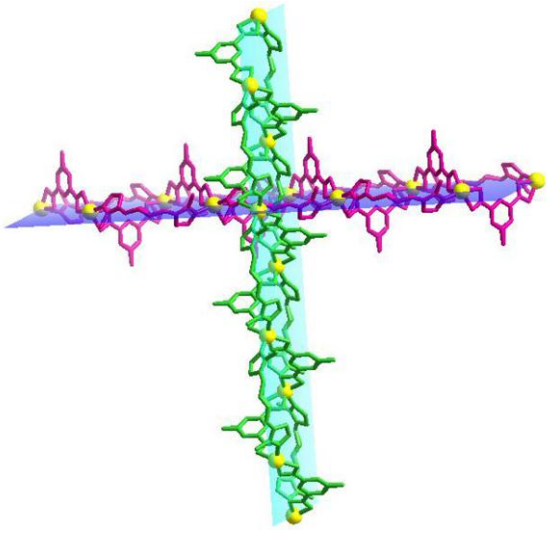
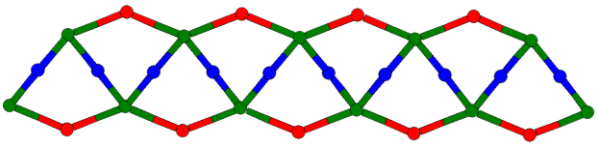
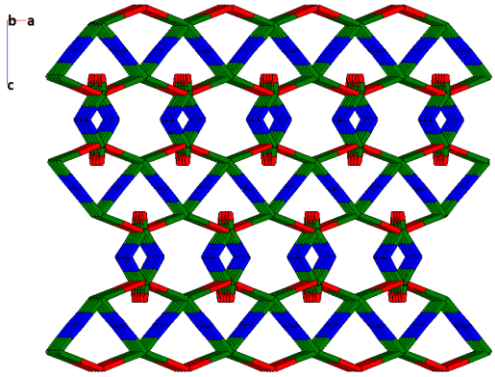


Fig. S4 A view of one left-handed interweaving triple-stranded helices (green) interlocked with adjacnt one right-handed interweaving triple-stranded helices (purple) in vertical fashion.



(a)



(b)

Fig. S5 (a) Single (2,2,4)-connected trinodal network with the point symbol of $(6)_2(6^3.\ 8^2.10)$. (b) 1D→3D topological network with vertical interlocking pattern(red for bib, blue for $hoip^{2-}$ and green for Co^{2+}).

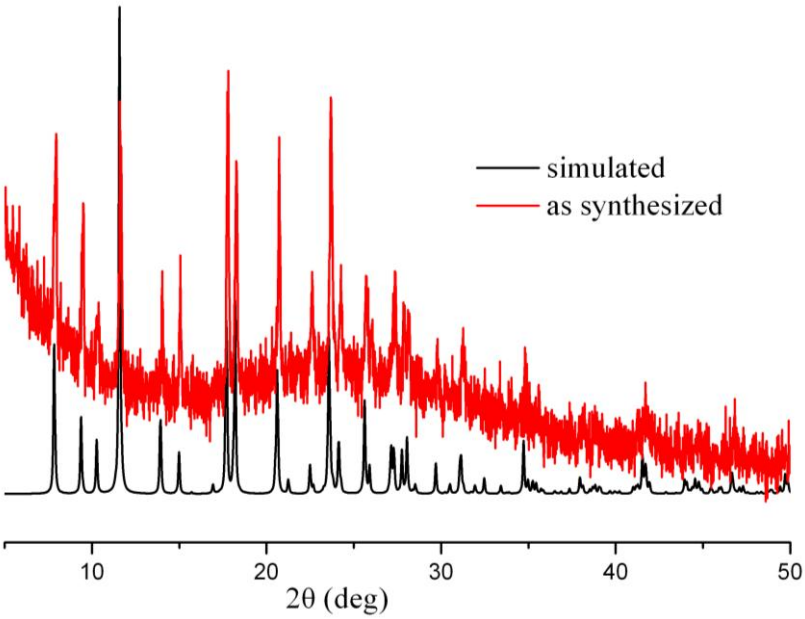


Fig. S6. Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination and the as-synthesized product

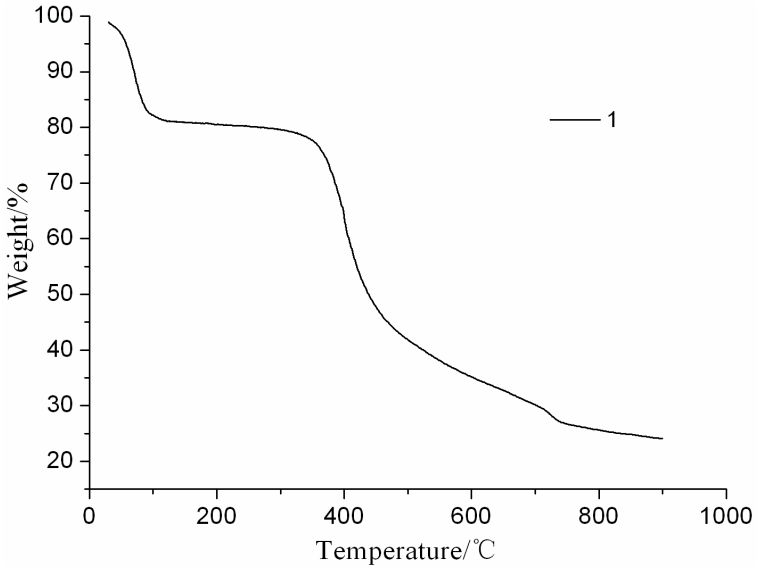


Fig. S7. TGA curves of compound 1 under N_2 atmosphere.

Thermogravimetric analysis (TGA) was performed on a heating rate of 10 °C·min^{-1} under a flow of N_2 atmosphere. The TGA indicates that the first weight loss occurs at 120 °C, weight loss rate is 18.79% ,corresponding to the removal of the three water molecules(calcd:19.41%). The collapse of the polycatenation framework occurs in the temperature range of 350–900 °C.