Electronic Supporting Information

Auxiliary ligand-directed structural variation from 2D→3D polythreaded net to 3-fold interpenetrating 3D pillar-layered framework: syntheses, crystal structures and magnetic properties

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Materials and General Methods

All the solvents and reagents for syntheses were commercially available and used as received. FT-IR spectra were recorded as KBr pellets on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400 Series II analyzer. Powder X-ray diffraction (PXRD) patterns were taken on a Rigaku D/max-2500 diffractometer (Cu Kα radiation, λ = 1.5406 Å), with a scan speed of 2 °/min and a step size of 0.02° in 2θ. The calculated PXRD patterns were simulated by using the single-crystal X-ray diffraction data. Thermogravimetric (TG) curves were recorded on a NETZSCH STA 449C microanalyzer in air at a heating rate of 10 $^{o}C \cdot min^{-1}$. Variable-temperature magnetic susceptibility measurements were carried out on a Quantum Design PPMS60000 in a magnetic field of 1KOe, and the diamagnetic corrections were evaluated by using Pascal's constants.

Synthesis of [Co(H_2abtc)(4,4′-bipy)$_{0.5}$(H_2O)] (1)

A mixture of H_4abtc (0.036 g, 0.1 mmol), 4,4′-bipy(0.016 g, 0.1 mmol), $Co(ClO_4)_2 \cdot 6H_2O$(0.037 g, 0.1 mmol), NaOH (0.1 mmol) and H_2O (15mL) were placed in a Teflon-lined stainless steel vessel, heated to 120 ^{o}C for 3d, and then cooled to room temperature over 24h. Red crystals of **1** were obtained. Yield: 35% (based Co^{II}). Elemental analysis (%): calcd for $C_{21}H_{14}CoN_3O_9$: C, 49.33; H, 2.76; N 8.22 %; found: C, 49.35; H, 2.79; N, 8.30 %. IR data (KBr, cm^{-1}): 3254w, 3137w, 2878w, 1679m, 1613m, 1529m, 1413m, 1368m, 1268w, 1208s, 1139w, 964w, 764s, 680s, 660m.

Synthesis of [Co_3(H_2abtc)$_3$(btb)(H_2O)$_6$] (2)

Compound **2** was synthesized in a similar way as that for 1, except that 4,4′-bipy was replaced by btb. Yield: 45% (based Co^{II}). Elemental analysis (%): calcd for $C_{56}H_{48}Co_3N_{12}O_{30}$: C, 43.51; H, 3.13; N, 10.87 %; Found: C, 43.63; H, 3.01; N, 10.68 %. IR data (KBr, cm^{-1}): 3348w, 3130w, 2362w, 1678m, 1610m, 1547s, 1437s, 1413m, 1370s, 1224m, 1074w, 925w, 817m, 776s, 765s, 682s, 653s.

Single Crystal X-ray Crystallography

Single-crystal X-ray diffraction data for complexes **1** and **2** were collected on a Bruker APEX

II CCD diffractometer with graphite monochromated Mo Ka radiation (0.71073 Å) at 298(2) K. Empirical absorption corrections were applied using the SADABS program.[1] The structures were solved by direct methods and refined based on F^2 by the full matrix least-squares methods using SHELXTL.[2,3] All non-H atoms were refined anisotropically. The C3 and C4 atoms of btb ligand are disordered. The H-atoms of water were identified from a difference Fourier map, the other H atoms were located geometrically and refined as riding. Selected bond geometries for **1** and **2** are listed in Table S1.

References

1 Sheldrick, G M. SADABS, *Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, 1997.

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

3 Sheldrick, G. M. SHELXL, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.

Table S1 Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

		1[a]			
Co(1)-O(1)	2.016(2)	Co(1)-O(5)#1	2.048(2)	Co(1)-N(3)	2.061(3)
Co(1)-O(6)#1	2.291(2)	Co(1)-O(9)	2.003(3)	O(9)-Co(1)-O(1)	102.37(11)
O(9)-Co(1)-O(5)#1	100.71(11)	O(9)-Co(1)-N(3)	137.62(13)	O(5)#1-Co(1)-N(3)	109.56(11)
O(1)-Co(1)-O(5)#1	101.17(10)	O(1)-Co(1)-N(3)	100.10(11)	O(9)-Co(1)-O(6)#1	81.39(10)
		2[b]			
Co(1)-O(15)	2.026(3)	Co(1)-O(10)#2	2.184(3)	Co(2)-O(14)	2.172(3)
Co(1)-O(15)#1	2.026(3)	Co(1)-O(10)#3	2.184(3)	Co(2)-O(6)	2.176(3)
Co(1)-O(14)	2.158(3)	Co(2)-N(1)	2.093(3)	Co(2)-O(2)	2.204(3)
Co(1)-O(14)#1	2.158(3)	Co(2)-O(13)	2.130(4)	Co(2)-O(5)	2.262(3)
Co(2)-O(1)	2.282(3)	O(15)-Co(1)-O(15)#1	180.0	O(15)-Co(1)-O(14)	86.72(12)

O(15)#1-Co(1)-O(14)	93.28(12)	O(15)-Co(1)-O(10)#2	86.87(12)	O(15)#1-Co(1)-O(10)#2	93.13(12)
O(15)-Co(1)-O(10)#3	93.13(12)	N(1)-Co(2)-O(13)	90.42(16)	N(1)-Co(2)-O(14)	178.13(13)
O(13)-Co(2)-O(14)	88.31(15)	N(1)-Co(2)-O(6)	92.59(13)	O(13)-Co(2)-O(6)	82.75(12)

[a] Symmetry codes for 1: #1: x-1/2,-y+3/2,z-1/2;

[b] Symmetry codes for 2: #1: -x+2,-y,-z; #2: -x+1,-y,-z-1; #3: x+1,y,z+1.

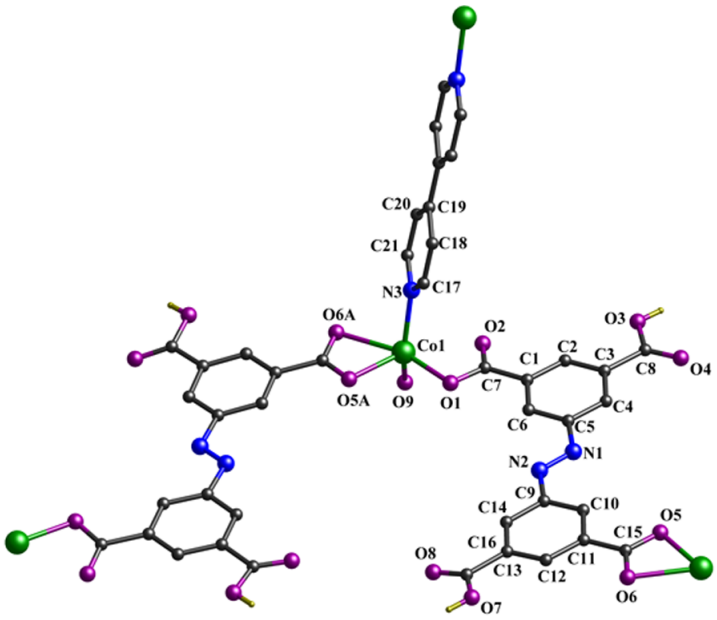

Fig. S1 The local coordination environments of Co(II) ions in **1** with atom labeling of the asymmetric unit; some hydrogen atoms are omitted for clarity. Symmetry code: A: -0.5+x, 1.5-y, -0.5+z.

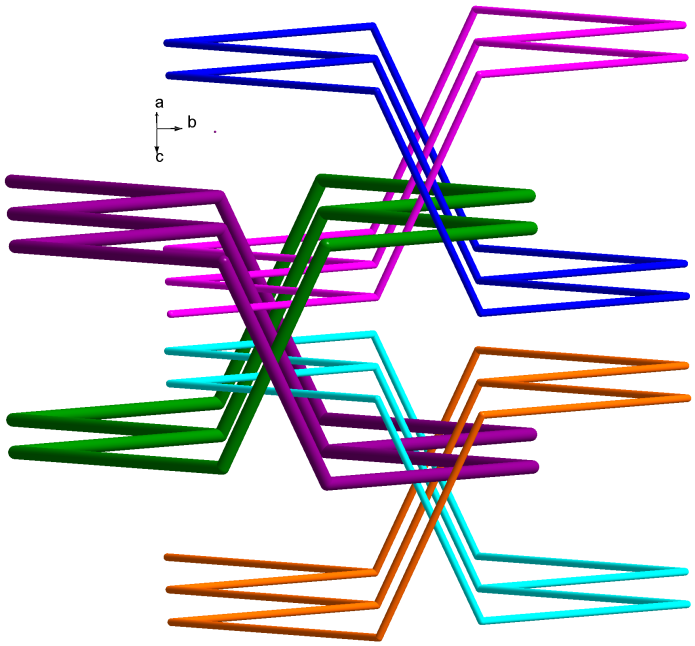

Fig. S2. Schematic representation of polythreading motif involving the sheets from the above and the below. The H4abtc and 4,4'-bipy ligands are simplified as rods for clarity.

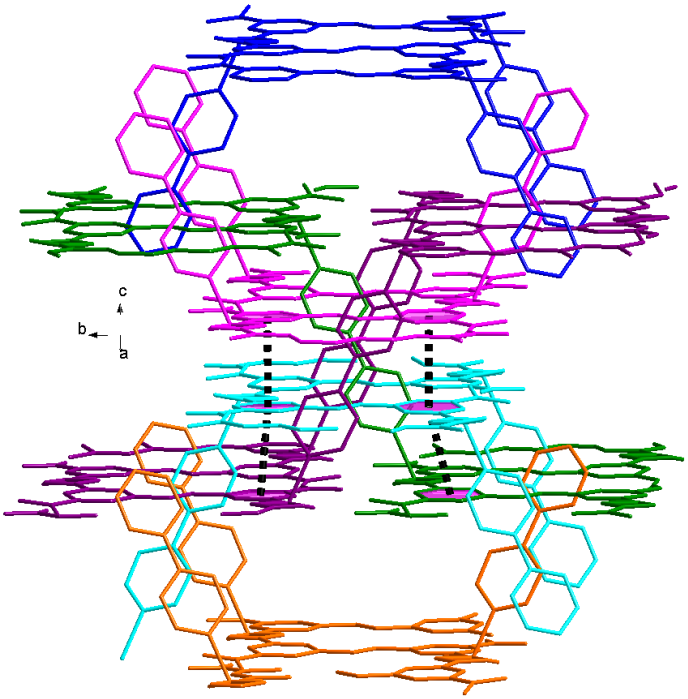

Fig. S3. The π···π stacking interactions in the adjacent layers in **1**. The centre-to-centre distances between the

phenyl rings are in the range of 3.507(4) to 3.573(7) Å.

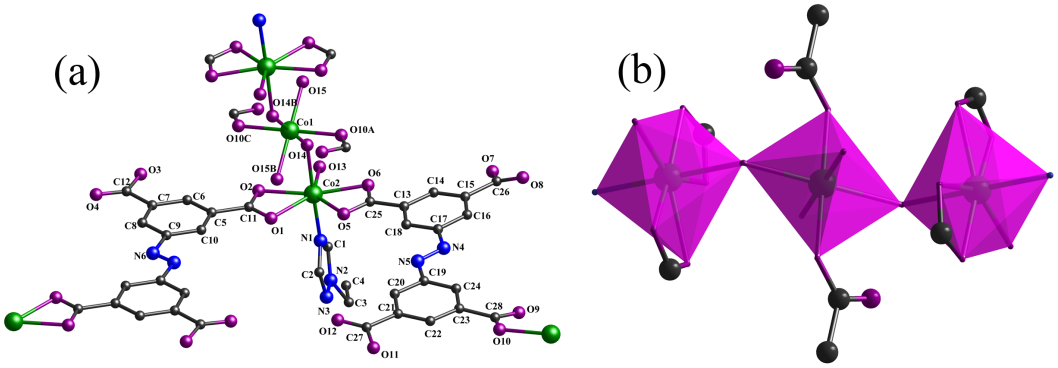

Fig. S4 (a) The local coordination environments of Co(II) ions in **2** with atom labeling of the asymmetric unit; hydrogen atoms are omitted for clarity. Symmetry code: A: 1-x, -y, -1-z; B: 2-x, -y, -z; C: 1+x, y, 1+z; (b) View of the liner trimer: The $Co(1)O_6$ octahedron and $Co(2)O_6N$ pentagonal bipyramidal geometries.

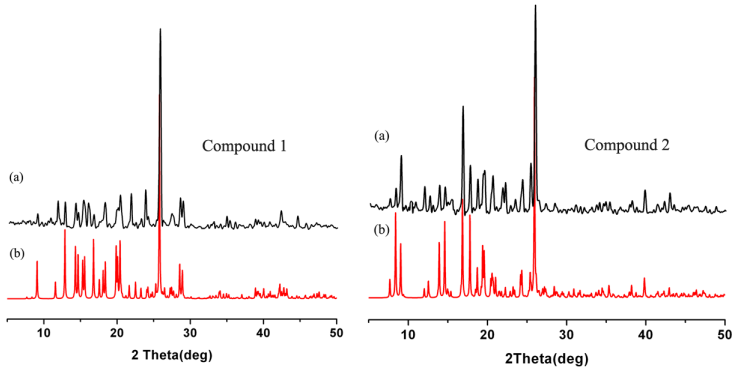

Fig. S5. The PXRD patterns of **1** and **2**. (a for experimental data, b for the simulated from the single-crystal diffraction data).

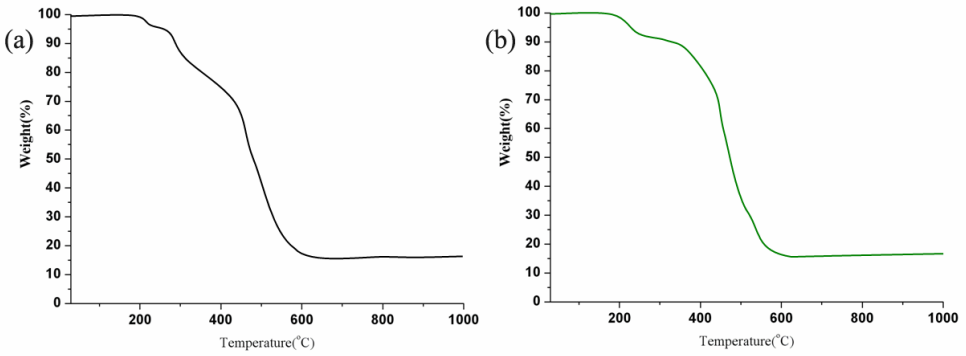

Fig. S6. TG curves of **1** (a, black line) and **2** (b,green line).