

Supporting Information

A new type of entangled coordination network: coexistence of polythreading and polyknotting involved molecular braids

Zhi-Guo Gu^{a, b*}, Xin-Xin Xu,^a Wen Zhou,^a Chun-Yan Pang,^a Fei-Fei Bao^a and Zaijun Li^a

^a School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, P. R. China

^b Coordination Chemistry Institute and the State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China

Experimental section

Materials and physical measurements

5-(4-Carboxy-2-nitrophenoxy)isophthalic acid (H₃L) (98%) was purchased from Aldrich. All other chemicals were of reagent grade quality obtained from commercial sources and used without further purification.

Infrared spectra were collected over the range 650–4000 cm⁻¹ using a SensIR IlluminatIR spectrometer with a diamond ATR fitted to an Olympus microscope. The spectrum is the average of 128 scans. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. X-ray Powder Diffraction (XRPD) was carried out with a Scintag XDS 2000 powder diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), solid state detector, scan range of 5° to 50° (2 θ), step size 0.05° and scan rate 5.0°/min. All samples were ground thoroughly in a mortar and pestle prior to mounting the resultant powder in the XRPD sample holder. Thermogravimetric studies were carried out on a high-resolution Auto TGA 2950 analyzer ($T_{\text{max}} = 550 \text{ }^\circ\text{C}$, heating rate = 5 °C/s).

Synthesis of [Co(HL)(H₂O)₄]_n[Co₃(L)₂(H₂O)₁₀]_n·4nH₂O (1)

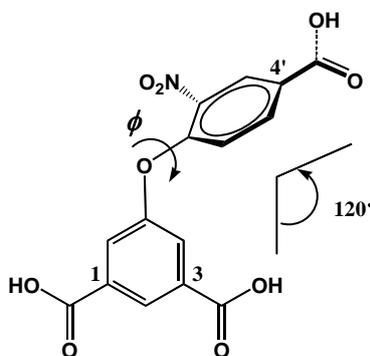
A mixture of CoCl₂·6H₂O (357 mg, 1.50 mmol), H₃L (173 mg, 0.5 mmol),

* Corresponding author: tel.: +86 510 85917090; fax: +86 510 85917763.
E-mail: zhiguogu@jiangnan.edu.cn.

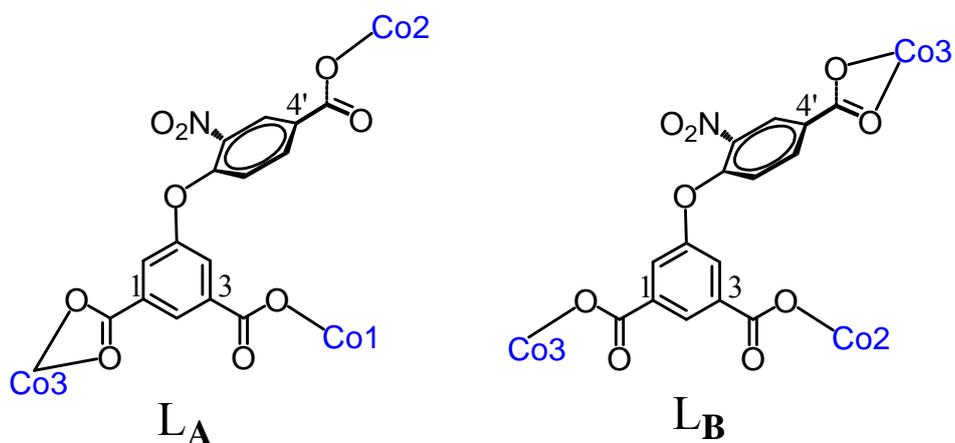
triethylamine (152 mg, 1.5 mmol), and 6 mL of H₂O was stirred in air for 0.5 h (final pH ~ 8.1). The resulting solution was heated in a stainless steel reactor with Teflon liner at 100 °C for 2 days. After a period of approximately 24 h cooling to room temperature, a orange brown solution appeared (pH ~ 6.2), which was filtered and left to stand at room temperature. Red plate-shaped crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of the solvents within one week. Yield: 40%. Anal Calcd for C₉₀H₁₀₉Co₈N₆O₉₀: C, 33.93; H, 3.45; N, 2.64. Found: C, 33.81; H, 3.58; N, 2.52.

X-ray structure determination

Data sets were collected on a Bruker APEX-II diffractometer with a CCD area detector at 100 K with Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were retrieved using SMART software and refined using SAINT¹ on all observed reflections. Data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10s/frame. The highly redundant data sets were reduced using SAINT¹ and corrected for Lorentz and polarization effects. Absorption corrections were applied using SADABS² supplied by Bruker. Structures were solved by direct methods using the program SHELXS-97.³ The positions of metal atoms and their first coordination spheres were located from direct-methods *E*-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} .



Scheme S1. Structure of H₃L ligand.



Scheme S2. Schematic representation of the coordination mode of 5-(4-Carboxy-2-nitrophenoxy)isophthalic acid in the 2D $[Co_3(L)_2(H_2O)_{10}]_n$ motif.

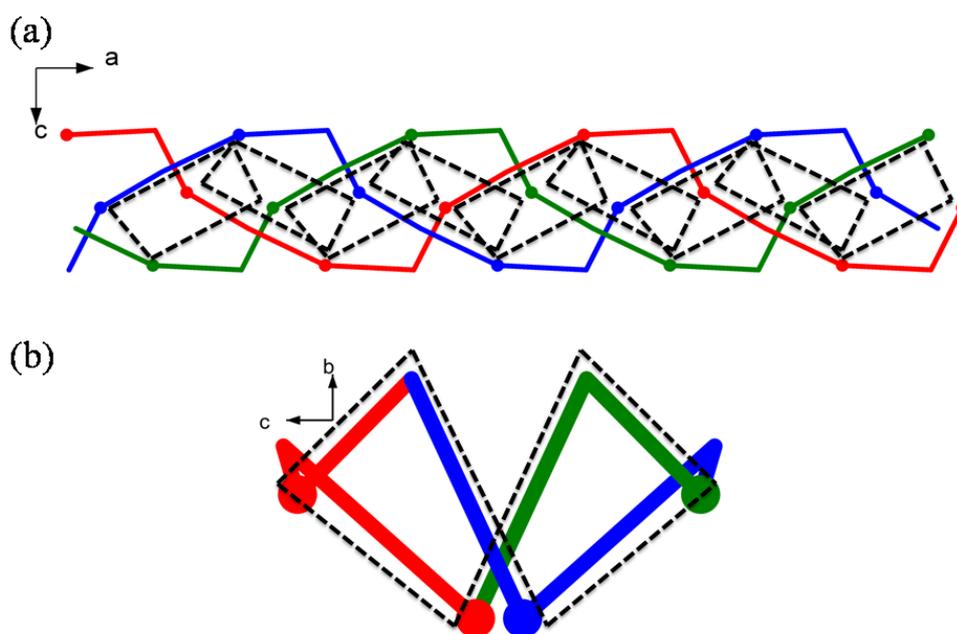


Fig. S1 (a) View of the topology of the triple-stranded braid along the helical axis. The dashed represent the pseudo four-membered loops. (b) View of the topology of the triple-stranded braid down the helical axis. The dashed represent the vertex-sharing two pseudo-quadrangles.

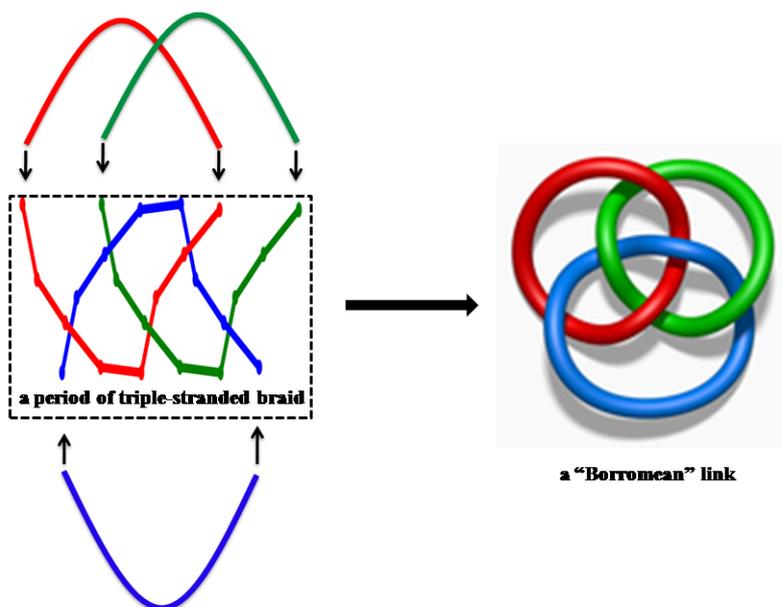


Fig. S2 Schematic view of the relationship between triple-stranded braid and “Borromean” link.

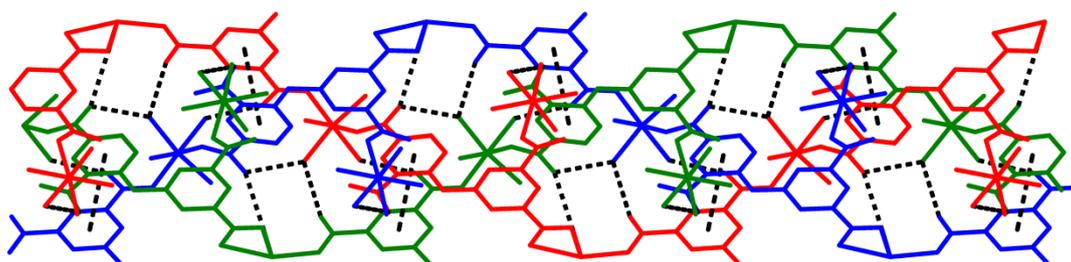


Fig. S3 Self-assembly of the triple-stranded braid through formation of π - π stacking interactions (interplanar distance of 3.68 Å) and hydrogen bonds (O10W-H10X \cdots O9^{#6} 2.686(4) Å, O6W-H6Y \cdots O11^{#1} 2.702(4) Å, O7W-H7X \cdots O12^{#1} 2.706(4) Å, O7W-H7Y \cdots O9^{#5} 2.732(4) Å, O4W-H4X \cdots O6^{#1} 2.867(4) Å; #1 $x + 1/2, y, -z + 1/2$, #5 $x - 1/2, y, -z + 1/2$, #6 $x - 1/2, -y + 1/2, -z$).

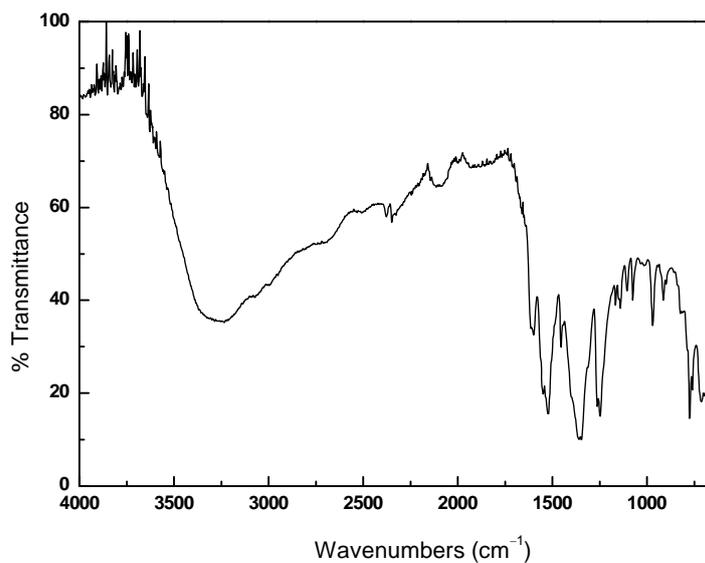


Fig. S4 FT-IR spectroscopy for as-synthesized sample of **1**. (3233 (br), 1602 (m), 1521 (s), 1454 (w), 1346 (s), 1247 (s), 1141 (m), 1106 (w), 1075 (m), 970 (m), 914 (w), 776 (s), 712 (s))

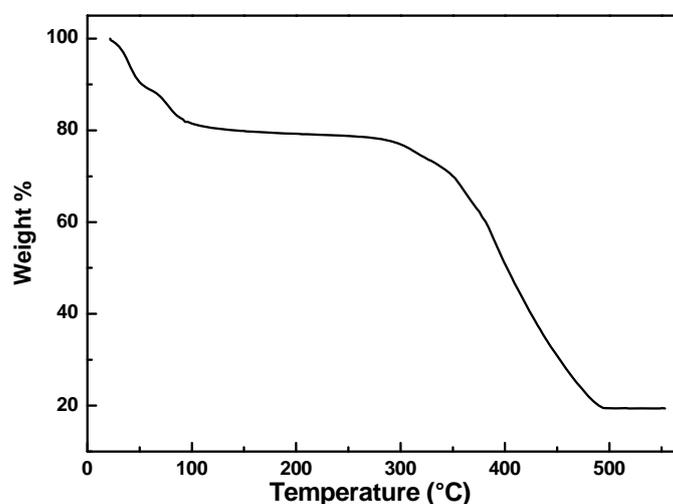


Fig. S5 Thermogravimetric analysis for as-synthesized sample of **1**. The first weight loss until 120 °C was due to the coordinated and uncoordinated water molecules (obsd. 19.52%, calcd 20.35%). The decomposition of the organic links in the anhydrous compound occurs at 280 to 500 °C. The remaining weight corresponds to the formation of Co_2O_3 (obsd 19.43%, calcd 20.82%).

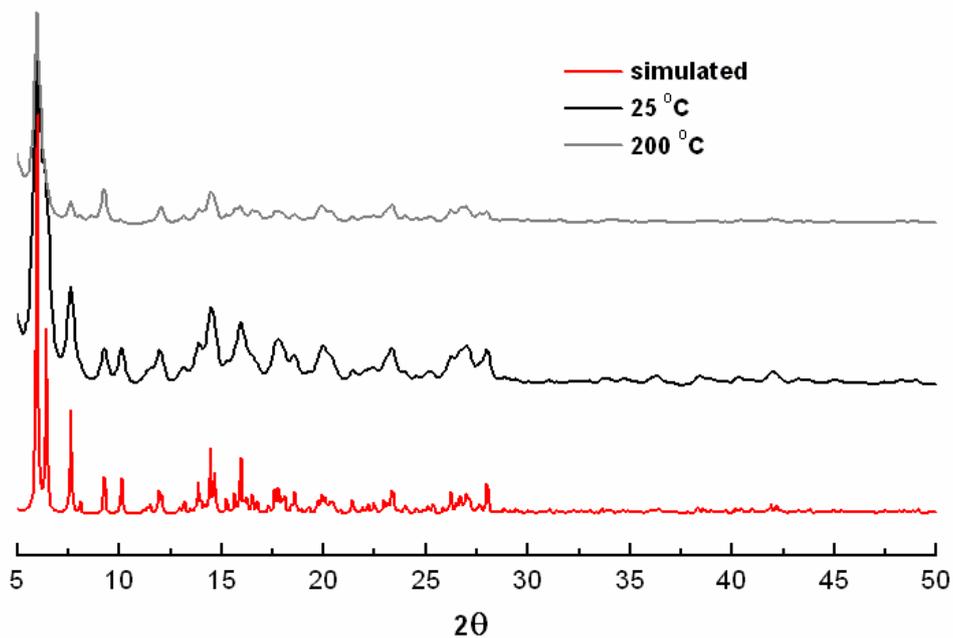


Fig. S6 The variable temperature XRPD patterns for **1**.

- 1 *SAINT-Plus*, version 6.02; Bruker Analytical X-ray System: Madison, WI, 1999.
- 2 G. M. Sheldrick, *SADABS: An Empirical Absorption Correction Program*; Bruker Analytical X-ray Systems: Madison, WI, 1996.
- 3 G. M. Sheldrick, *SHELXTL-97*; Universität of Göttingen: Göttingen, Germany, 1997.