

Supporting Information

Metal-organic frameworks displaying single crystal-to-single crystal transformation through postsynthetic uptake of metal clusters

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Experimental Section

Materials and Physical Measurements. Chemicals were purchased from commercial sources and were used without further purification. Thermogravimetric analysis was performed on a NETZSCH TG 209 thermobalance in a nitrogen atmosphere, sample was placed in alumina containers and data were recorded at 10 °C/min between 20 and 800 °C. IR spectra (KBr pellet) were obtained from a Nicolet 5DX spectrometer in the region of 400–4000 cm⁻¹. X-ray powder diffraction (XRPD) was collected on Bruker D8 ADVANCE diffractometer at room temperature using Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation. Elemental analysis of carbon, hydrogen and nitrogen was carried out on a Vario EL III analyzer. The solid-state absorption spectra were measured by Vario Cary 5000 spectrometer. Electrospray ionization mass spectrometry was performed on Bruker Daltonics esquire HCT.

Synthesis of 1a: 1,3,5-benzenetribenzoate acid (H₃BTB, 0.1 mmol, 0.0438 g) was stirred in 4 ml DMF for 5 minutes, which was filtered and the resulting solution was placed in a test tube, above which 6 ml DMF-EtOH (1:1 v/v) and then 4 ml EtOH containing 0.3 mmol (0.0714 g) CoCl₂·6H₂O was layered, respectively. The test tube was sealed and put aside. Four months later, purple crystals of [Co₃O(BTB)₂(H₂O)(DMF)]·7.5DMF·12H₂O (**1a**) crystalline aggregates began to form on the wall of test tube and completed within several days. (yield: ~72% based on H₃BTB). Elemental analysis for **1a**: calcd.: C 49.76%, H 6.07%, N 6.20%; found: C 49.97%, H 5.75%, N 6.23%. IR (KBr pellet, cm⁻¹): 3408(br), 2920(sh), 1658(s), 1591(s), 1534(m), 1393(s), 1252(w), 1099(w), 1014(w), 850(w), 782(s), 669(w), 477(w).

Synthesis of 1b: A mixture of H₃BTB ligand (0.15 mmol, 0.0657 g) and CoCl₂·6H₂O (0.4 mmol, 0.0952 g) in 15 mL DMF-EtOH (1:1 v/v) was sealed in a 20 mL Pyrex glass bottle, which was heated to 45 °C at a rate of 1 °C/min and stayed at this temperature for 20 days. Then the bottle was heated to 90 °C within 9000 minutes and was directly cooled to 30 °C at a rate of 1 °C/min to give purple crystals of [Co₃O(BTB)₂(H₂O)₂]·8.5DMF·8H₂O (**1b**, yield: ~55% based on H₃BTB). Elemental

analysis for **1b**: calcd.: C 51.20%, H 5.92%, N 6.38%; found: C 51.34%, H 5.44%, N 6.50%. IR (KBr pellet, cm^{-1}): 3408(br), 2924(sh), 1652(s), 1581(s), 1538(m), 1387(s), 1250(w), 1097(w), 1017(w), 855(w), 779(m), 665(w), 478(w).

Synthesis of 1c: A mixture of H_3BTB ligand (0.10 mmol, 0.0438 g) and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.3 mmol, 0.0714 g) in 10 mL DMF-EtOH (1:1 v/v) was sealed in a 15 mL Teflon-lined stainless steel vessel, which was heated to 70 °C within 2000 minutes and stayed at this temperature for 3 days. Then the vessel was heated to 110 °C within 2000 minutes and was directly cooled to 30 °C within 2000 minutes to give purple crystals of $[\text{Co}_3\text{O}(\text{BTB})_2(\text{DMF})(\text{H}_2\text{O})_2] \cdot 7\text{DMF} \cdot 8\text{H}_2\text{O}$ (**1c**, yield: ~39% based on H_3BTB). Elemental analysis for **1c**: calcd.: C 51.24%, H 5.84%, N 6.13%; found: C 50.97%, H 5.62%, N 6.19%. IR (KBr pellet, cm^{-1}): 3416(br), 2926(sh), 1659(m), 1593(m), 1536(m), 1389(s), 1101(w), 783(m), 660(w), 485(w).

Transformation From 1a-1c to 2: Crushed crystals of **1a**, **1b** or **1c** were immersed in collective filtrate **1a-s** (freshly filtered) or **1b-s** (filtered and opened in air for at least 3 days), the solution was then sealed and **1a-1c** transformed to crystals of $[\text{Co}_6\text{O}_2(\text{OH})_4(\text{BTB})_{8/3}(\text{H}_2\text{O})_4] \cdot 14\text{DMF} \cdot 4\text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**) in one week, three weeks and two months for **1a**, **1b** and **1c**, respectively. As-synthesized un-crushed crystals of **1a** immersed in **1a-s** transformed to **2** in two months, and un-crushed crystals of **1b** or **1c** did not show obvious transformation in **1a-s**. X-ray powder diffraction studied revealed that the transformation from **1a-1c** to **2** was in 100% yield. Elemental analysis for **2**: calcd.: C 50.00%, H 6.12 %, N 6.69%; found: C 50.84%, H 6.06%, N 6.87%. IR (KBr pellet, cm^{-1}): 3422(br), 2916(sh), 1655(s), 1597(s), 1531(m), 1381(s), 1257(w), 1107(w), 1016(w), 859(w), 784(m), 660(w), 485(w).

Additional Experiment: In order to prove that **2** can only be obtained through SCSC process, more experiments have been done.

Additional exp. 1. Various metal-to-ligand ratios in the initial reaction mixture (from 3:1 to 8:1) have been adopted, and the reaction temperature was slowly increased to

90 °C within 1000 minutes, further stayed at this temperature for 1 day (Fig. S14). Then the solution was sealed in a vessel, which was heated to 130 °C within 1000 minutes and was then cooled to 30 °C within 2000 minutes. Only the metal-to-ligand ratios of 4:1 and 5:1 give little crystals of **1c** that were mixed with numerous blue crystals **3**, while large metal-to-ligand ratio (8:1) only generates large quantity of **3**. Unfortunately, we cannot determine the crystal structure of **3** because of its bad crystallinity. The color of mother solution is green (Metal:Ligand = 3:1 and 4:1) and deep blue (Metal:Ligand \geq 5:1).

Additional exp. 2. In order to find out whether dioxygen can accelerate the SCSC transformation, a DMF-EtOH (1:1 v/v) solution containing CoCl₂·6H₂O was stirred in a glass bottle for 20 days, the color of solution changed from blue-violet to red, which was used as metal-ion source. The reaction was then taken in the same conditions as synthesizing **1c** (90 and then 130 °C), larger quantity of purple crystals of **1c** (rod-like) yielded when the metal-to-ligand ratio being about 2:1. However, bulky red crystals of **4** {Co(CHOO)₃[NH₂(CH₃)₂]} (Fig. S15) crystallized out at the metal-to-ligand ratio being 3:1. When the metal-to-ligand ratio exceeded 4:1, no purple crystals of **1c** yielded and only the red crystals **4** appeared. In the above process, no crystals of **2** were found.

Crystallographic Data Collection and Structure Determination. Diffraction data for all complexes were collected on Oxford Gemini S Ultra diffractometer using Cu K α (λ = 1.54178 Å) or Mo K α (λ = 0.71073 Å) radiation. Experimental absorption corrections were performed using CrysAlisPro. The structures were solved using SHELXS-97 and refined using SHELXL-97.¹ All non-hydrogen atoms were refined anisotropically and hydrogen atoms were generated using the riding model. The contribution of highly disordered solvent molecules was treated using SQUEEZE procedure implemented in PLATON program.² Crystallographic data and structural refinement details are presented in Table 1, selected bond lengths (Å) and angles (deg) associating with bond cleavage are summarized in Table 2.

1 Sheldrick, G. M. *SHELXL-97, Program for refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

2 Spek, A. L. *Acta Cryst.* **1990**, *A46*, 194-201.






Table S1. Crystallographic data and structural refinement details of **1a-1c** and **2**.











	1a	1b	1c	2
Formula	C ₅₇ H ₃₉ Co ₃ NO ₁₅	C ₅₄ H ₃₄ Co ₃ O ₁₅	C ₅₇ H ₄₁ Co ₃ NO ₁₆	C ₃₆ H ₂₄ Co ₃ O ₁₃
T/K			173	
FW.	1154.68	1099.60	1172.70	841.34
Cryst syst		orthorhombic		cubic
Space group		<i>Pnma</i>		<i>Im</i> $\bar{3}$
<i>a</i> /Å	17.564(4)	17.561 (1)	17.446(4)	27.2496(1)
<i>b</i> /Å	25.629(5)	25.347 (2)	27.758(6)	27.2496(1)
<i>c</i> /Å	20.800(4)	20.880 (2)	18.762(4)	27.2496(1)
<i>V</i> / Å ³	9363(3)	9294.3(1)	9086(3)	20233.9(1)
<i>Z</i>		4		12
<i>D</i> (g cm ⁻³)	0.819	0.786	0.857	0.829
μ (mm ⁻¹)	0.565	0.566	0.583	6.014
<i>S</i>	1.020	0.920	1.061	1.624
<i>R</i> ₁ / <i>wR</i> ₂	0.1115/0.2909	0.1155/0.2987	0.0927/0.2575	0.1315/0.3304

Table S2. Selected bond lengths (Å) and angles (deg) associating with the bond cleavage.

	1a	1b	1c
O1-Co1-O2/deg	57.4(3)	58.7(3)	59.3(1)
Co1-O1/Å	2.186(8)	2.167(8)	2.244(4)
Co1-O2/Å	2.170(7)	2.174(7)	2.140(3)

Table S3. Crystallographic data and structural refinement details of **1c**.

	1c				
T/K	100	120	140	160	180
					
Cryst syst	orthorhombic				
Space group	<i>Pnma</i>				
<i>a</i> /Å	17.4883(6)	17.4474(3)	17.4730 (6)	17.4692(6)	17.4280(4)
<i>b</i> /Å	27.5596(19)	27.5264(10)	27.5347 (17)	27.5594(16)	27.5847(11)
<i>c</i> /Å	18.8181(15)	18.8060(9)	18.8196 (15)	18.8257(15)	18.8087(13)
<i>V</i> / Å ³	9069.8(10)	9031.8(6)	9054.4(10)	9063.5(9)	9042.2(8)
<i>S</i>	1.069	0.977	1.087	1.063	1.015

R_1/wR_2	0.0884/0.258	0.0774/0.210	0.0904/0.267	0.0901/0.258	0.0872/0.241
	4	8	1	4	0
					
T/K	200	230	250	270	290
Cryst syst	orthorhombic				
Space group	<i>Pnma</i>				
$a/\text{Å}$	17.4516(4)	17.4940(4)	17.4362 (12)	17.426(2)	17.2514(19)
$b/\text{Å}$	27.5162(13)	27.0815(9)	25.136 (2)	25.294(6)	24.999(7)
$c/\text{Å}$	19.0369(19)	19.6022(7)	22.475 (2)	21.889(4)	21.297(5)
$V/\text{Å}^3$	9141.6(10)	9286.8(5)	9850.3(14)	9648.0(3)	9185(4)
S	1.085	1.027	0.869	0.844	0.785
R_1/wR_2	0.1081/0.308	0.0676/0.206	0.0840/0.205	0.0986/0.228	0.0942/0.223
	3	7	2	8	4
					

Additional figures

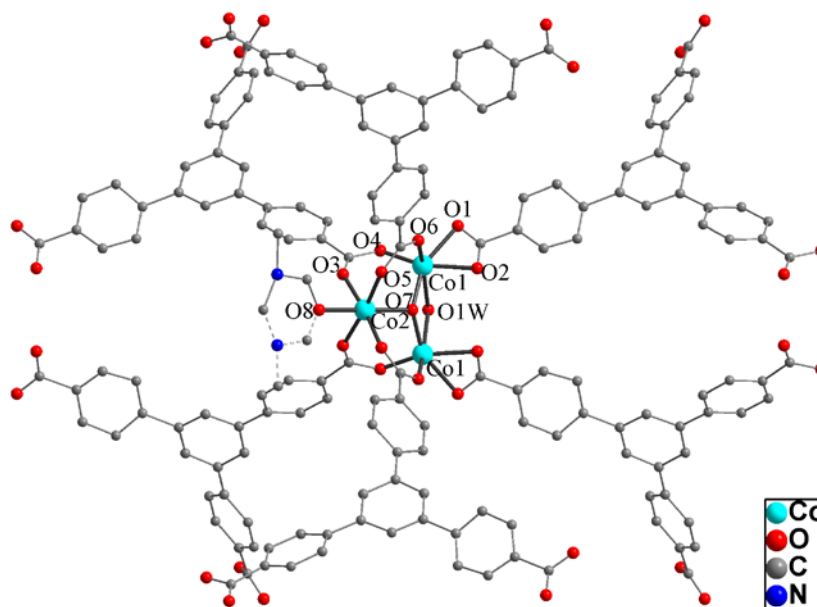


Fig. S1 Perspective view of the structural unit of **1a**.

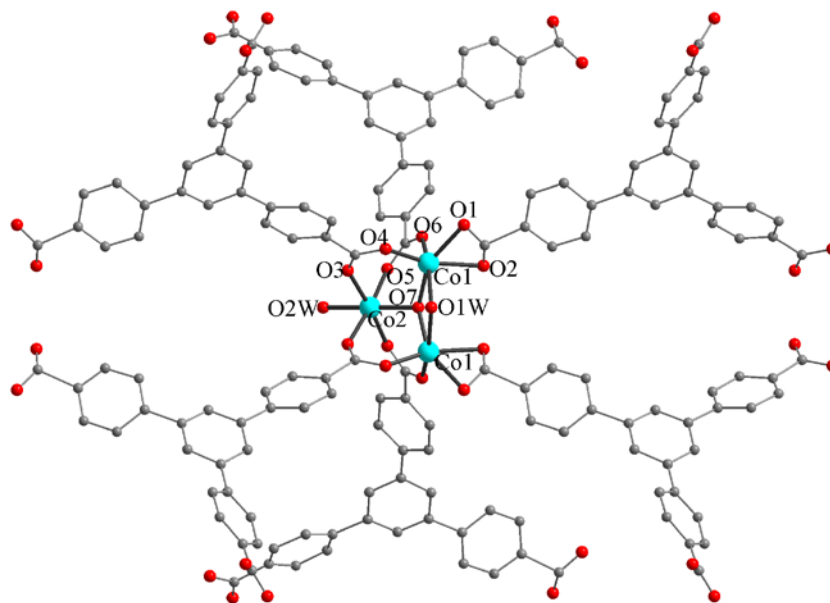


Fig. S2 Perspective view of the structural unit of **1b**.

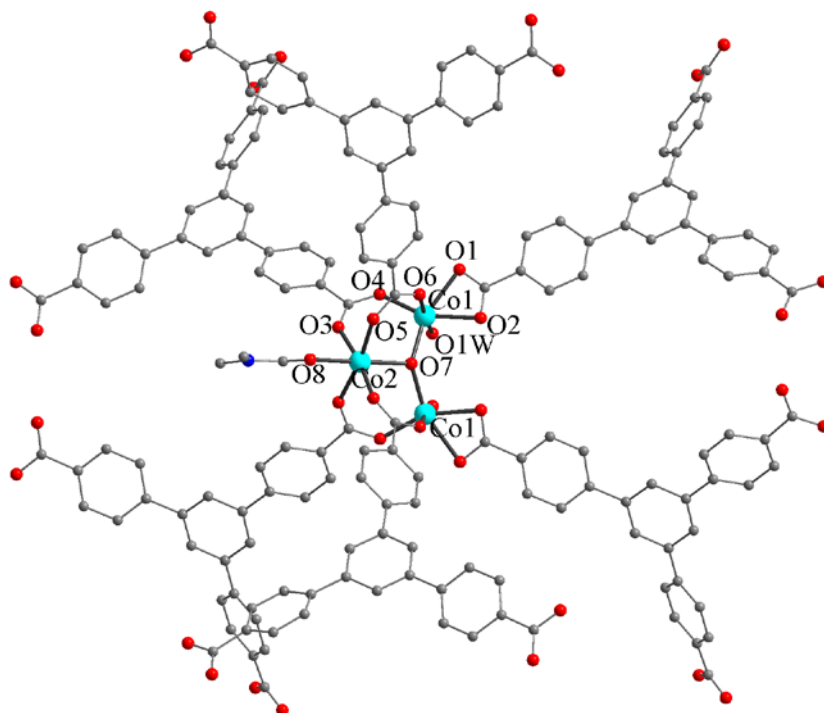


Fig. S3 Perspective view of the structural unit of **1c**.

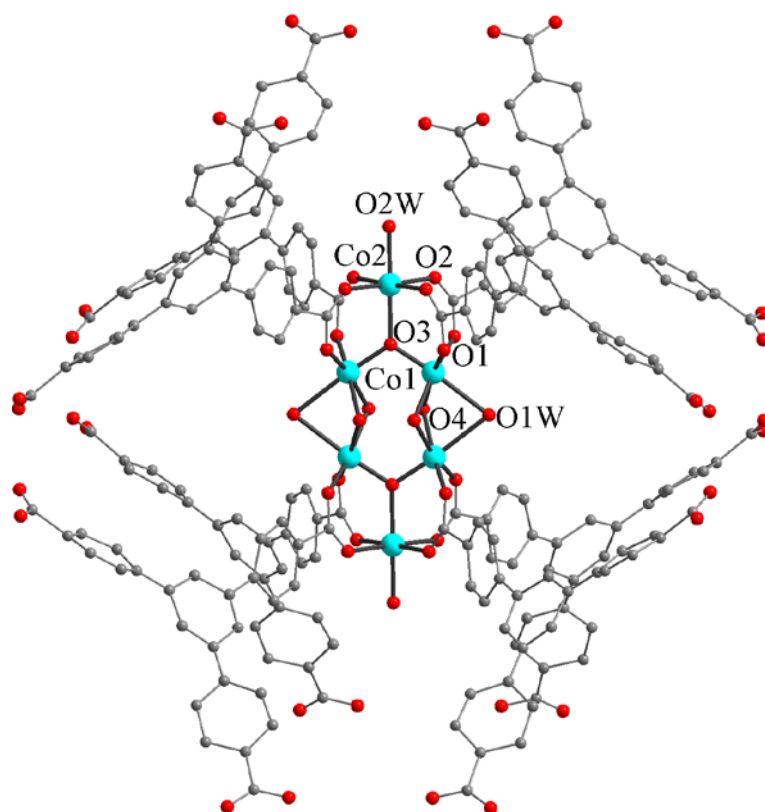
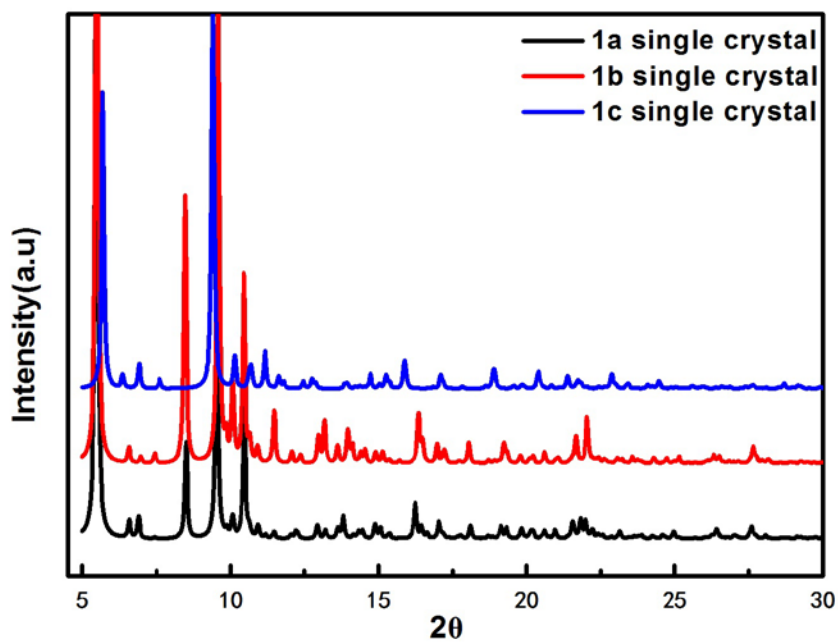


Fig. S4 Perspective view of the structural unit of 2.



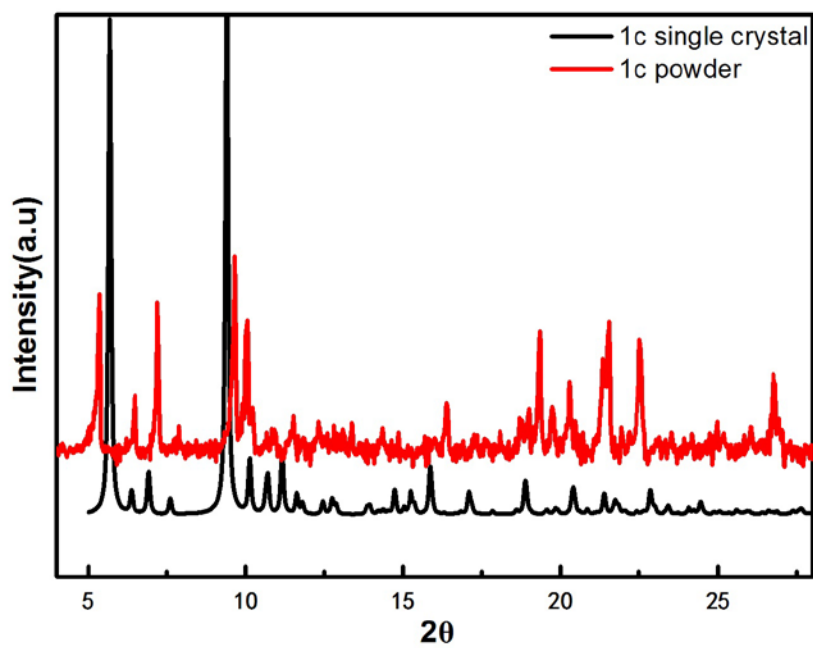
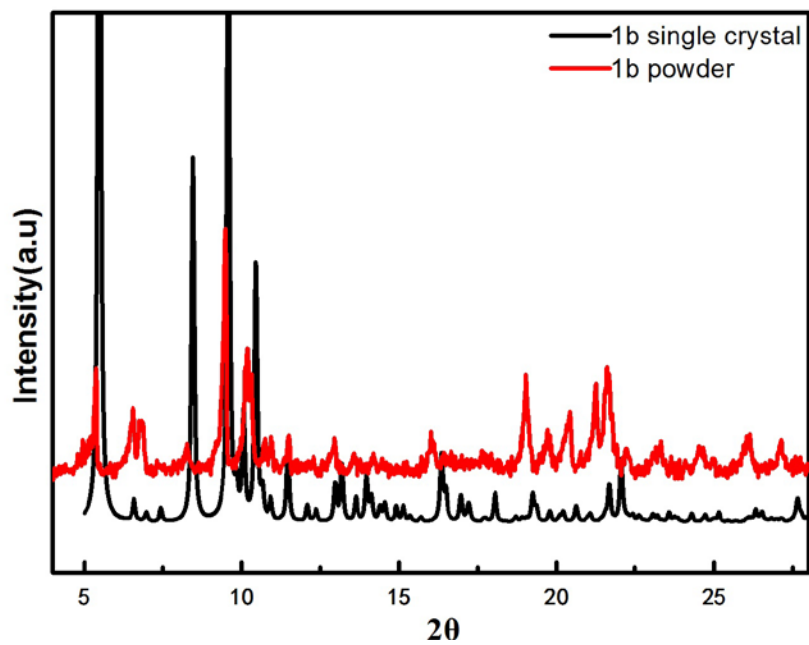


Fig. S5 XRPD pattern of **1a-1c**.

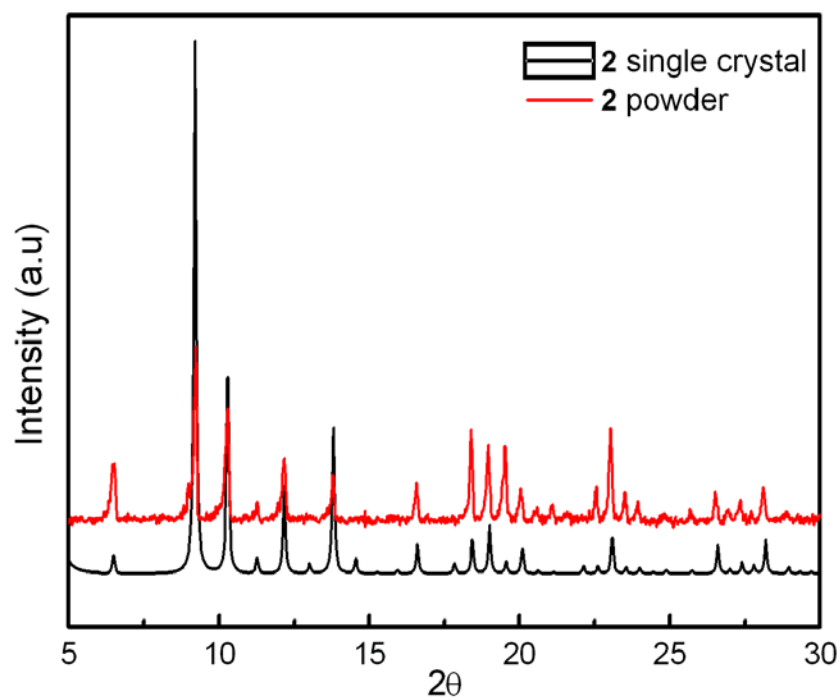


Fig. S6 XRPD pattern of 2.

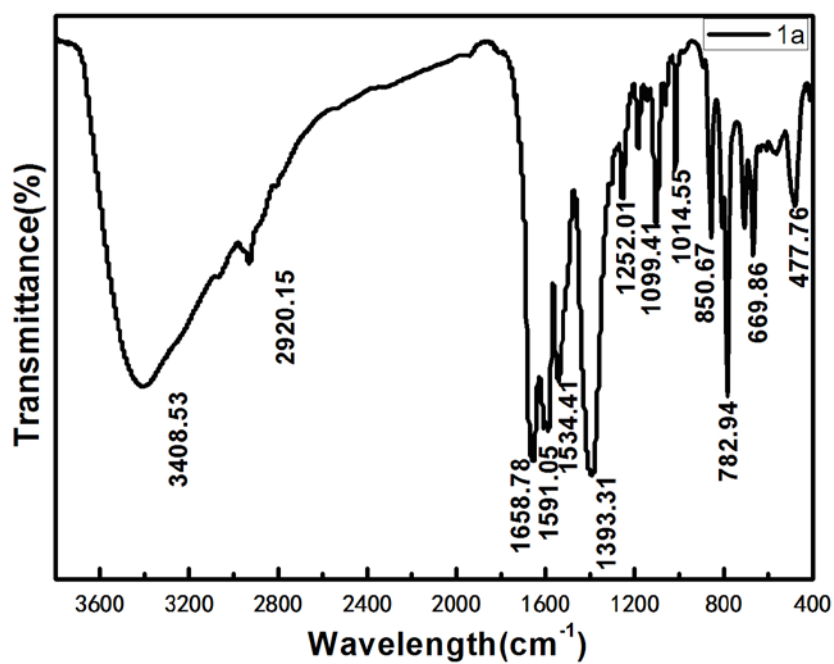


Fig. S7 IR spectra of 1a.

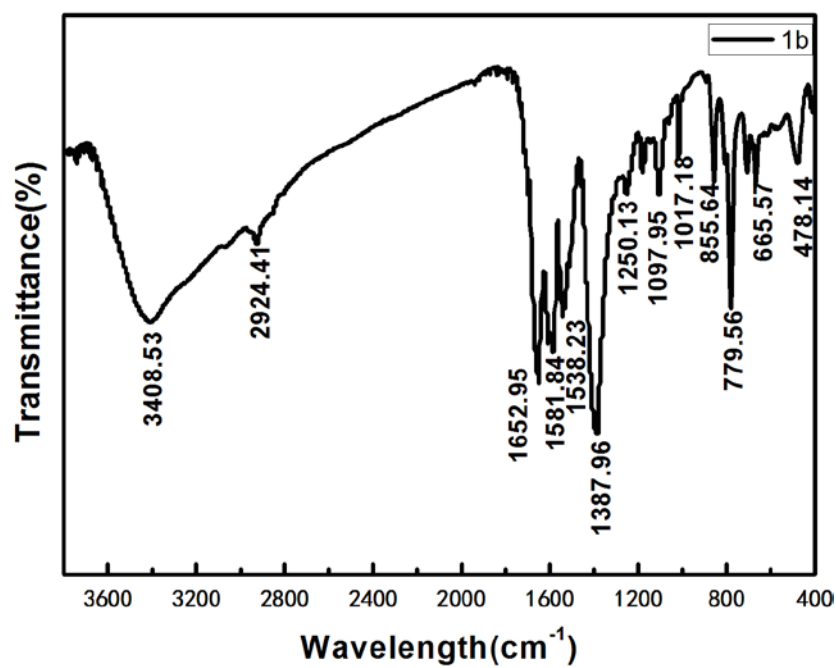


Fig. S8 IR spectra of 1b.

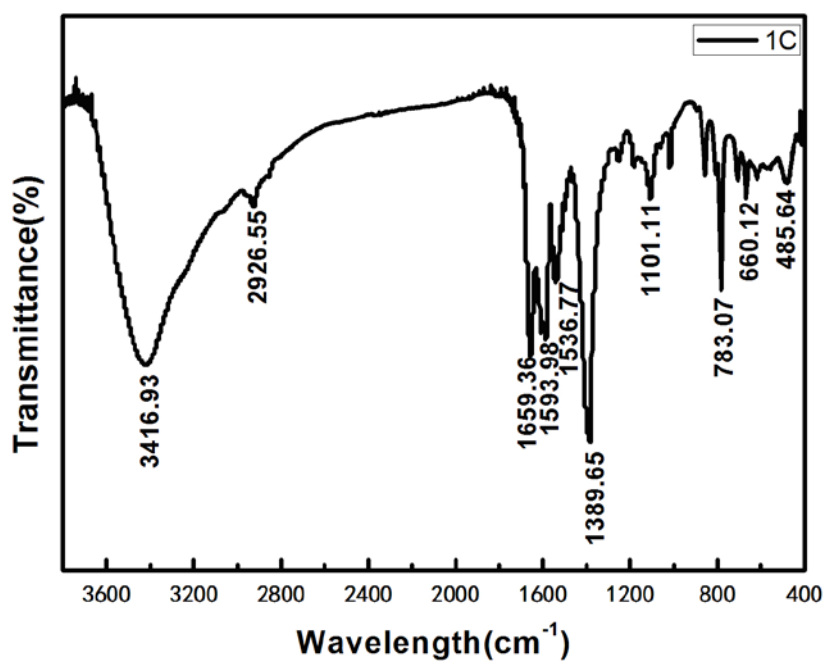


Fig. S9 IR spectra of 1c.

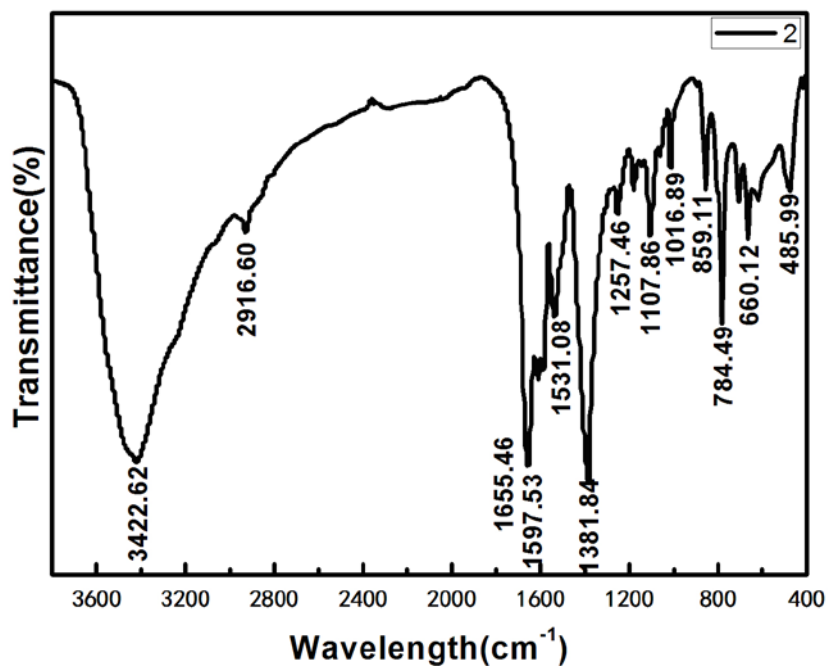


Fig. S10 IR spectra of 2.

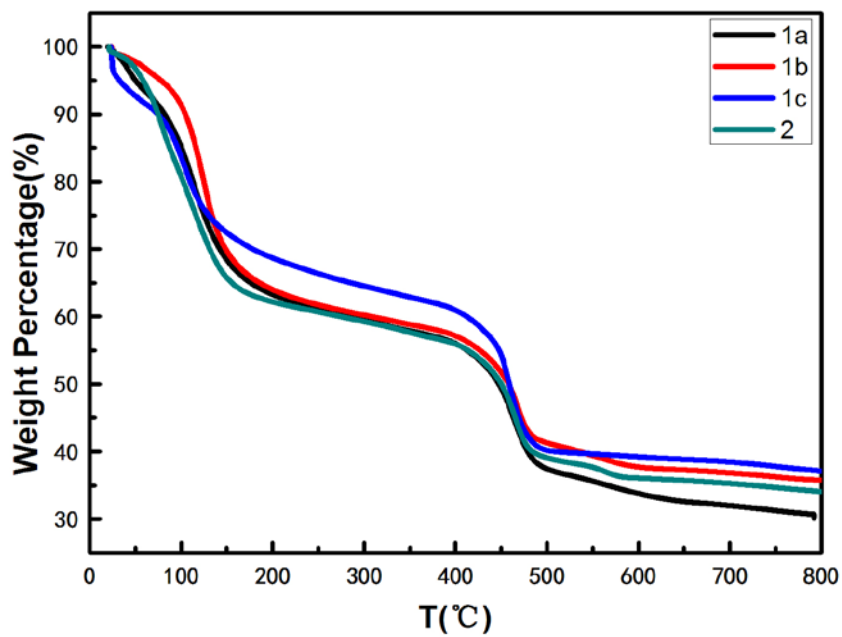


Fig. S11 TGA pattern of 1a-1c and 2.

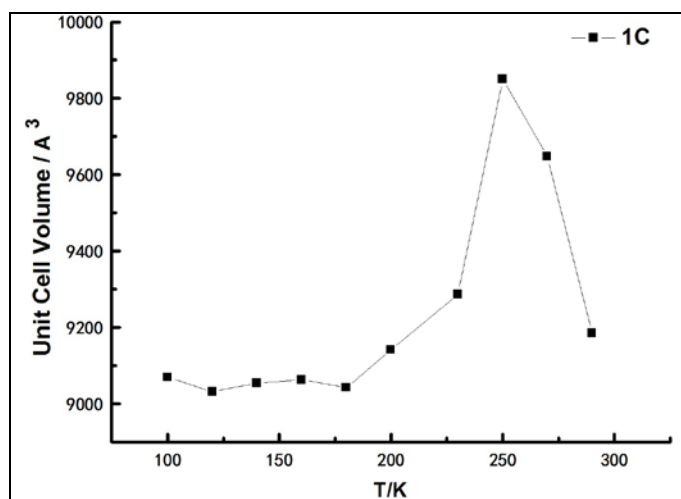


Fig. S12 Plot of the unit cell volume of **1c** evolution versus temperature.

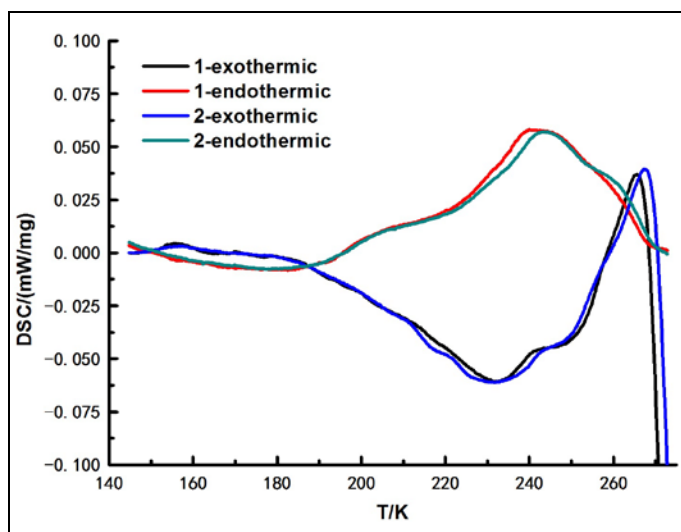


Fig. S13 DSC plot of **1c**.

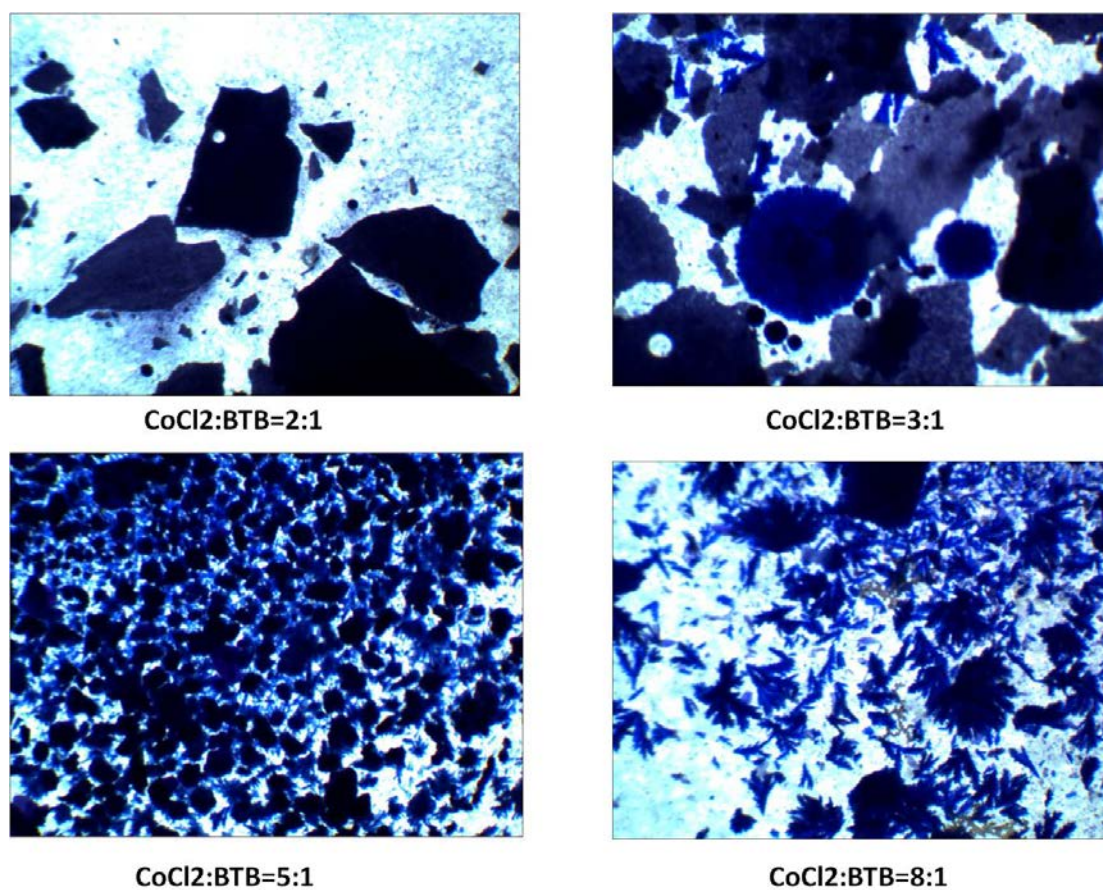


Fig. S14 Additional experiment with the CoCl₂:BTB ratio ranging from 2:1 to 8:1 (washed with DMF).

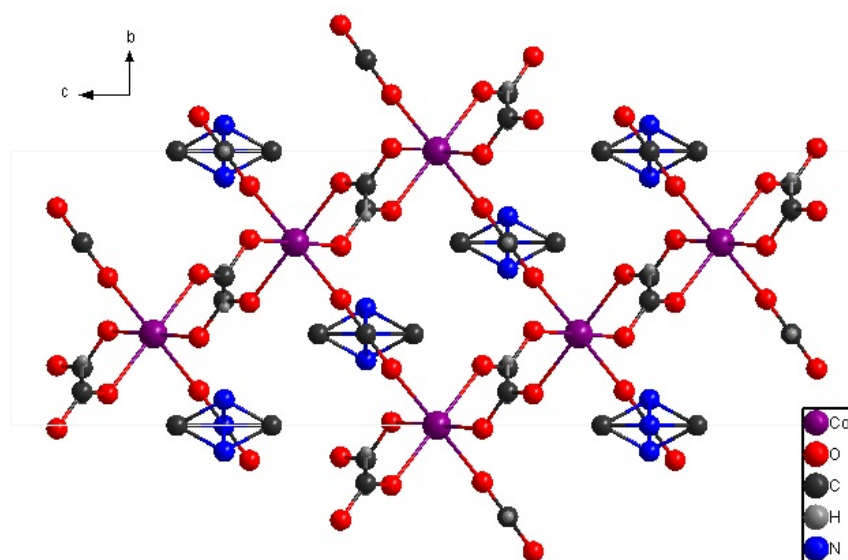


Fig. S15 Crystal packing diagram of {Co(CHOO)₃[NH₂(CH₃)₂]}. (*Inorg. Chem.*, 2004, **43**, 4615)