

Electronic Supplementary Information for MS:

An unusual 8-connected entangled coordination network: coexistence of polythreading, self-threading and interpenetration based on 3D motifs

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Experimental section

Materials and general methods

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Co was determined by a tps-7000 Plasma-Spec (I) inductively coupled plasma atomic emission spectrometer (ICP-AES). IR spectra were recorded in the range 400-4000 cm^{-1} on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. XRPD data were recorded on a XD-3 diffractometer using Cu $\text{K}\alpha$ radiation. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range of 2-300 K with an applied field of 1.0 kOe.

Synthesis of $[\text{Co}(\text{tpba})_2]$ (1**).** A mixture of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ (0.4 mmol), Htpba (0.2 mmol), NaOH solution (0.5 mL, 2 M) and distilled water (9 mL) and methanol (1 mL) was stirred for about 15 min in air, then transferred and sealed in an 18 mL Teflon-lined autoclave, which was heated at 170 $^\circ\text{C}$ for 72 h. After slow cooling to the room temperature, purple block crystals of **1** were obtained (yield: 79% based on Htpba). Elemental analysis (%) calcd for $\text{C}_{44}\text{H}_{28}\text{CoN}_6\text{O}_4$: C, 69.20, H, 3.70, Co, 7.72, N, 11.00. found: C, 68.96, H, 3.52, Co, 7.93, N, 11.24 %. IR (KBr pellet): 3314(m), 3195(m), 3070(m), 3029(m), 1591(s), 1547(s), 1406(s), 1316(w), 1231(w), 1212(w), 1181(w), 1101(w), 1062(m), 1015(m), 992(m), 888(w), 860(w), 822(s), 784(s), 747(w), 696(s), 668(w), 649(w), 621(m), 563(w), 517(m), 476(m).

Crystallographic Data Collection and Refinement

Suitable single crystals of **1** were selected for single-crystal X-ray diffraction analysis on a Bruker Smart Apex CCD diffractometer with Mo K α monochromated radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Absorption corrections were applied using the multi-scan technique. The structure of **1** was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 software.¹ All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms were generated geometrically. Selected bond lengths for compound **1** are listed in Table S1.

CCDC 935239 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

Reference

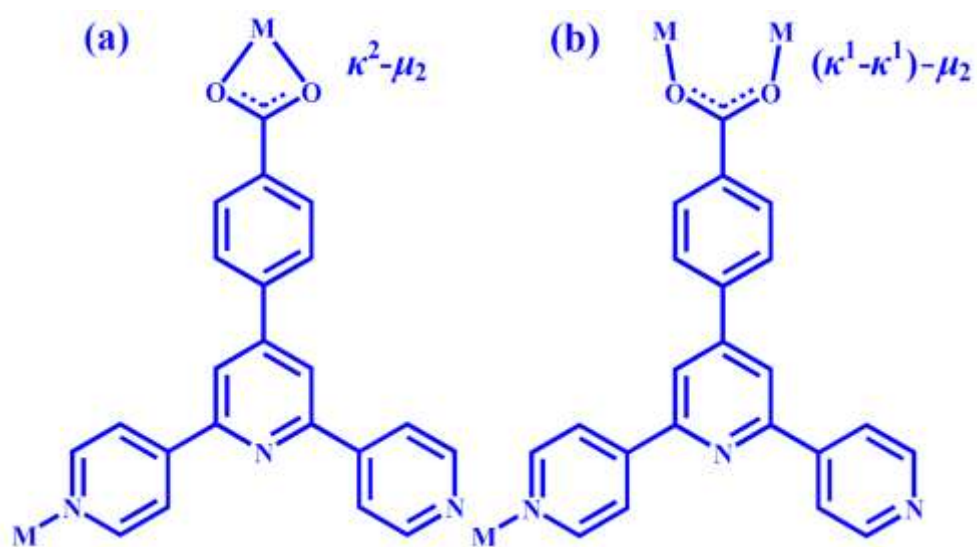
- 1 (a) G. M. Sheldrick, *SHELXS 97, Program for Crystal Structure Solution*, University of Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXTL 97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, 1997.

Table S1. Selected bond lengths [Å] and angles [°] for compound **1**.

Co(1)-O(2)#1	1.984(2)	Co(1)-O(1)	2.045(2)
Co(1)-O(3)#2	2.132(2)	Co(1)-N(1)	2.144(3)
Co(1)-N(4)#3	2.156(3)	Co(1)-O(4)#2	2.278(2)
N(4)-Co(1)#4	2.156(3)	O(2)-Co(1)#1	1.984(2)
O(3)-Co(1)#5	2.132(2)	O(4)-Co(1)#5	2.278(2)
O(2)#1-Co(1)-O(1)	113.31(9)	O(2)#1-Co(1)-O(3)#2	149.52(10)
O(1)-Co(1)-O(3)#2	97.17(9)	O(2)#1-Co(1)-N(1)	89.68(10)
O(1)-Co(1)-N(1)	87.88(10)	O(3)#2-Co(1)-N(1)	91.61(10)
O(2)#1-Co(1)-N(4)#3	90.54(10)	O(1)-Co(1)-N(4)#3	91.44(10)
O(3)#2-Co(1)-N(4)#3	88.53(10)	N(1)-Co(1)-N(4)#3	179.32(12)
O(2)#1-Co(1)-O(4)#2	90.32(9)	O(1)-Co(1)-O(4)#2	156.34(9)
O(3)#2-Co(1)-O(4)#2	59.21(9)	N(1)-Co(1)-O(4)#2	91.15(10)
N(4)#3-Co(1)-O(4)#2	89.50(10)		

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z+1; #2 -x-1, y+1/2, -z+3/2; #3 x+1, -y+1/2, z+1/2; #4 x-1, -y+1/2, z-1/2; #5 -x-1, y-1/2, -z+3/2.

Supporting Figures



Scheme S1. The different coordination modes of tpba ligands in **1**.

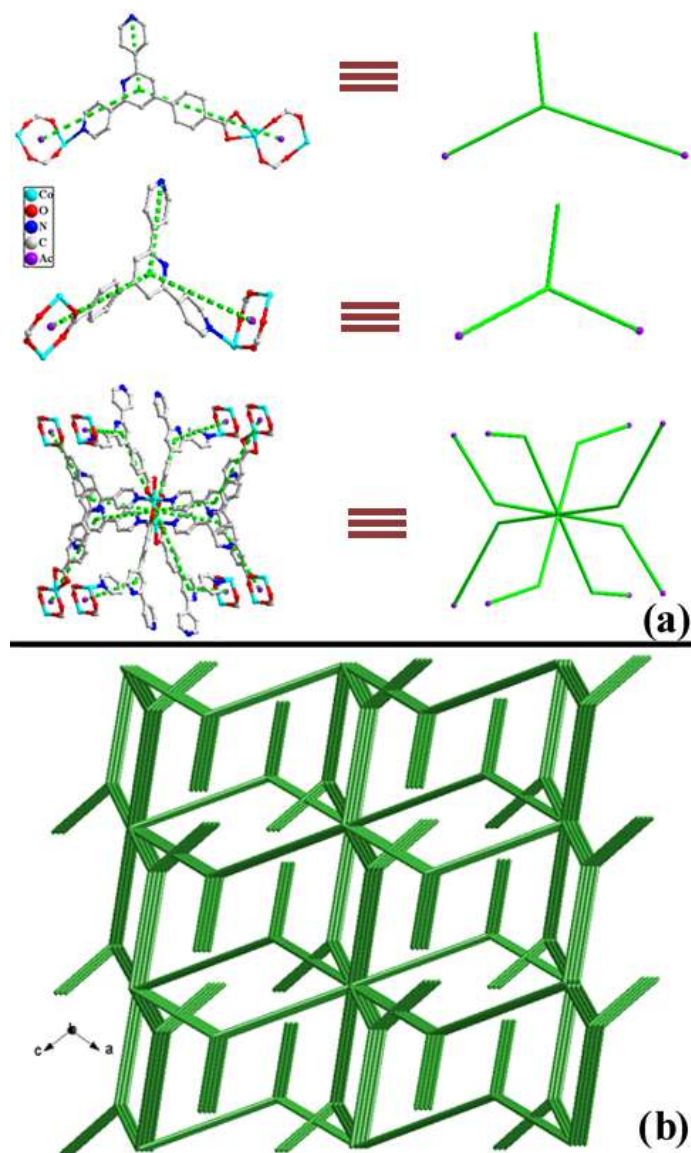


Fig. S1. (a) Perspective and simplified views of the eight-connected SBU center and two types of linkers (tpba ligands) involving dangling arms in **1** (the arms in eight-connected SBU center are omitted for clarity). (b) Schematic representation of the single 8-connected self-threading framework of **1**.

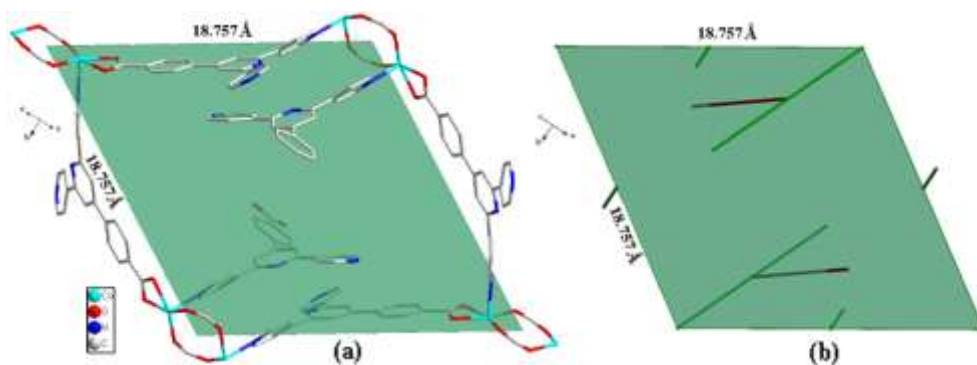


Fig. S2. The detail of self-threading character in **1**. The tetragonal window $[\text{Co}_8(\text{tpba})_4(\text{CO}_2)_8]$ with approximately dimensions of $18.757 \times 18.757 \text{ \AA}$ is highlighted by green and the self-threading arms are highlighted by purple lines.

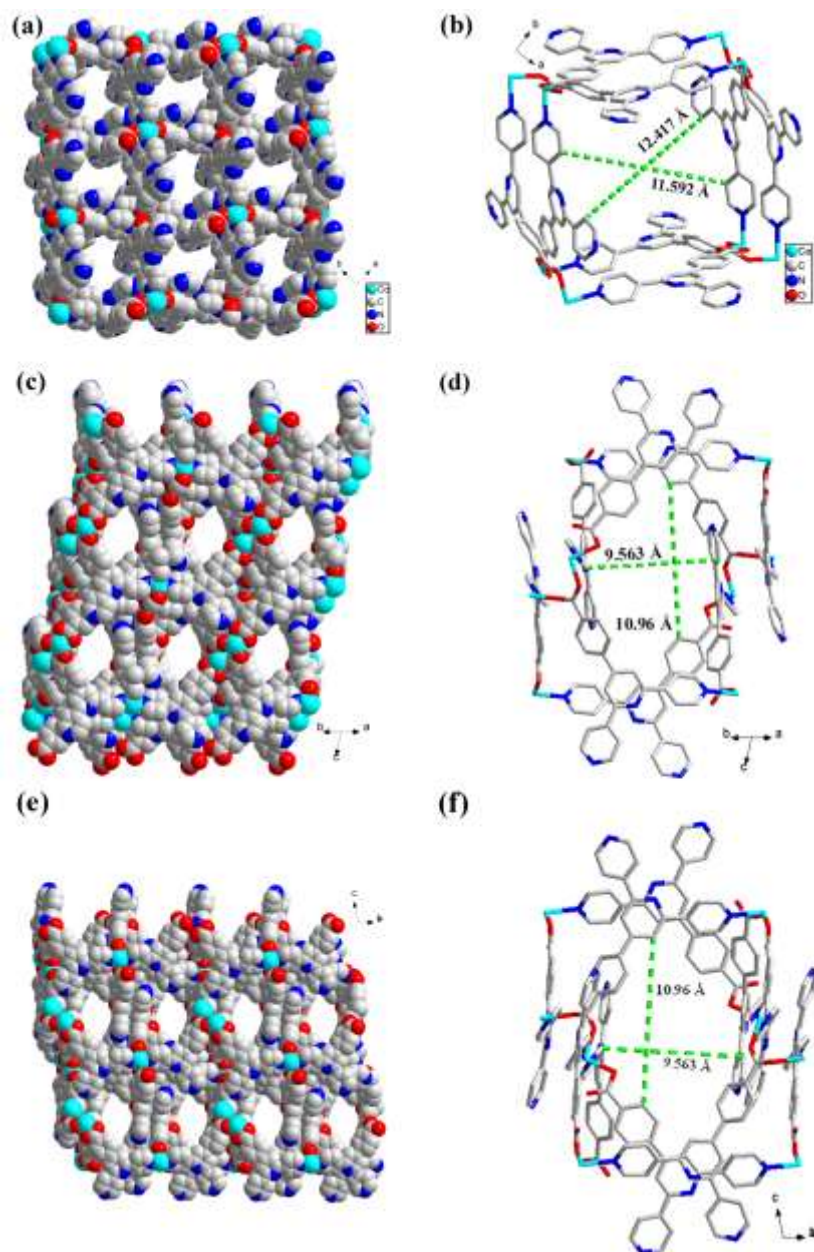


Fig. S3. Space-filling and perspective views of an individual 3D self-threading framework of **1** in three-directional open channels of approximately 12.417×11.592 Å along the [0 0 1] direction (a and b), of 10.96×9.563 Å along the [2 1 0] direction (c and d) and of 10.96×9.563 Å along the $[2\bar{1}0]$ direction (e and f).

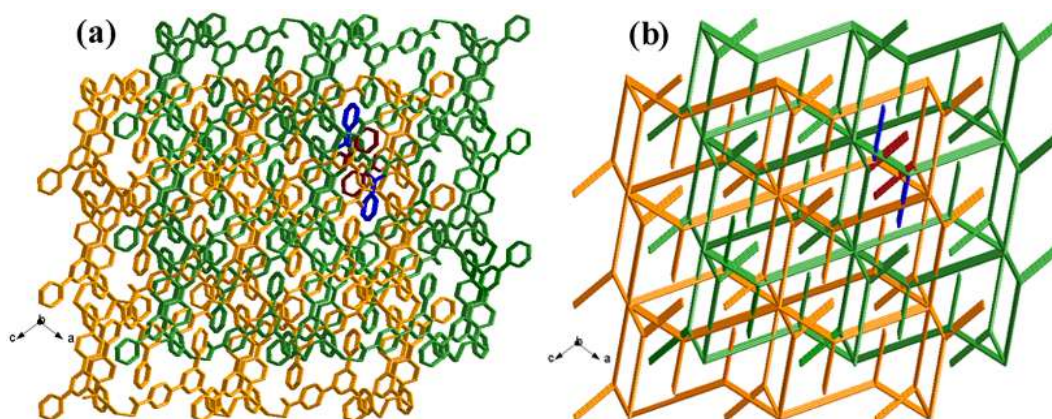


Fig. S4. Perspective (a) and schematic (b) views of the self-threading and polythreading features in the 2-fold interpenetrating framework of **1**. The polythreading and self-threading arms are highlighted by blue and purple lines.

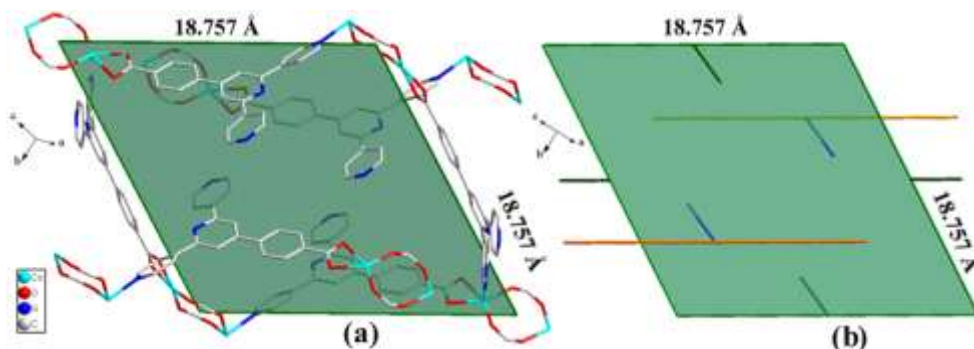


Fig. S5. The detail of polythreading character in **1**. The tetragonal window $[\text{Co}_8(\text{tpba})_4(\text{CO}_2)_8]$ with approximately dimensions of $18.757 \times 18.757 \text{ \AA}$ is highlighted by green and the polythreading arms are highlighted by blue lines.

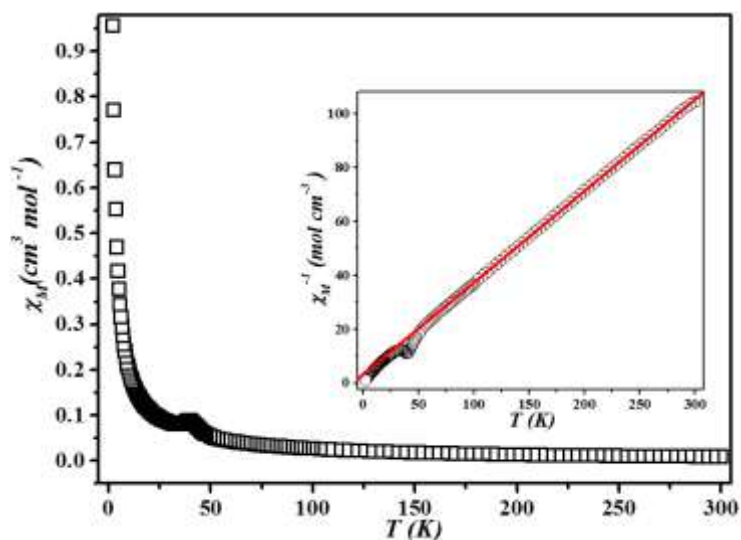


Fig. S6. Temperature dependence of the magnetic susceptibility χ_M for compound **1**.
Insert: Temperature dependence of χ_M^{-1} for compound **1**.

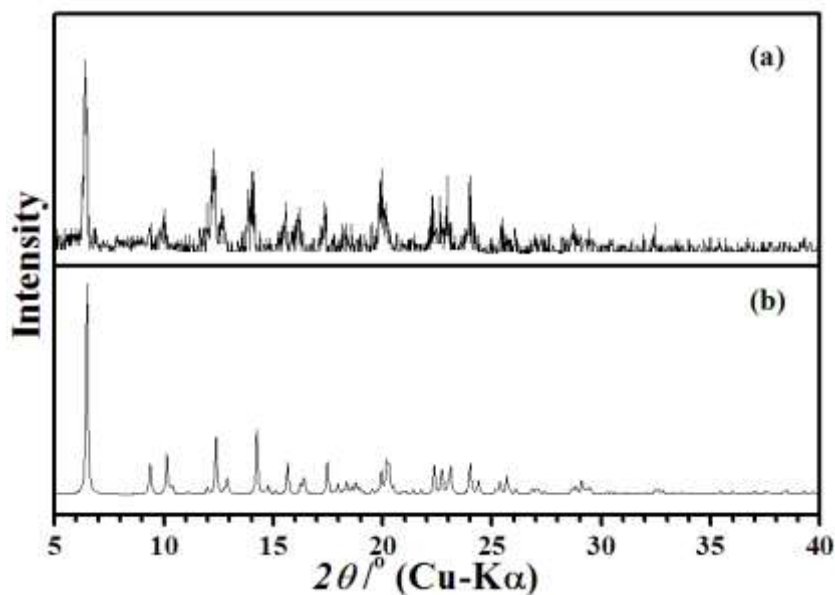


Fig. S7. The XRPD patterns for: (a) as-synthesized samples of **1**, and (b) simulated one based on the single-crystal structure of **1**.

The peak positions of simulated and experimental XRPD patterns are in agreement with each other, indicating the good phase purity of compound **1**. The differences in intensity may be due to the preferred orientation of the crystalline powder sample

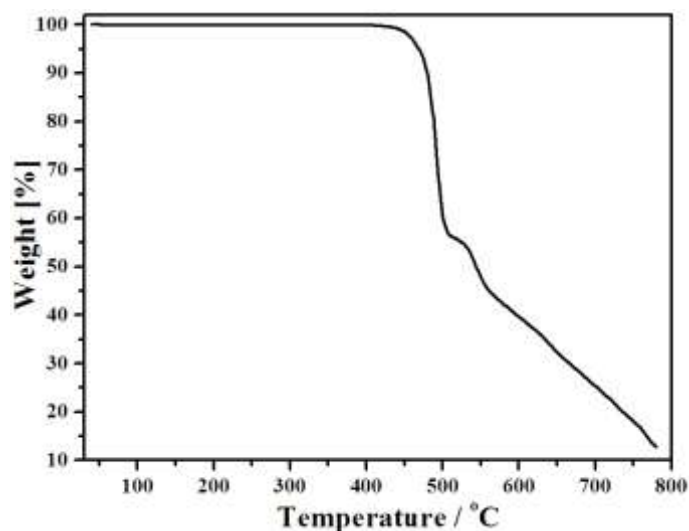


Fig. S8. The TG curves of compound **1**.

The TG curves of **1** display two steps of weight losses (Fig. S8). The first weight loss is 44.04% from 400 to 516 °C and the second weight loss is 43.21% from 516 to 780 °C, both corresponding to the loss of tpba ligand. The total weight loss of 87.25% is slightly less than the calculated value of 90.20%, if the final product is assumed to be CoO, which indicates that the decomposing process is not complete due to the use of nitrogen protection.

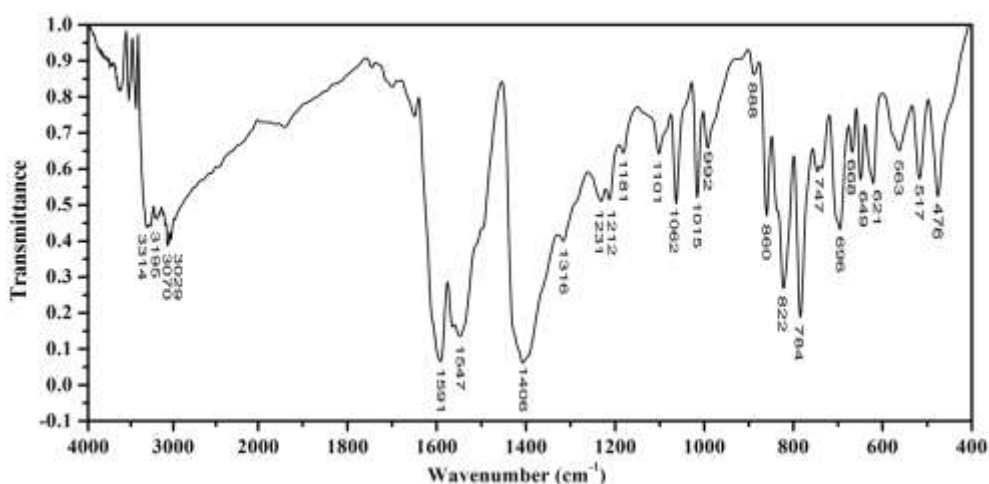


Fig. S9. The IR spectrum for compound **1**. IR (KBr pellet): 3314(m), 3195(m), 3070(m), 3029(m), 1591(s), 1547(s), 1406(s), 1316(w), 1231(w), 1212(w), 1181(w), 1101(w), 1062(m), 1015(m), 992(m), 888(w), 860(w), 822(s), 784(s), 747(w), 696(s), 668(w), 649(w), 621(m), 563(w), 517(m), 476(m).

The characteristic bands of the carboxylate groups in compound **1** are clearly shown in the IR spectrum (Fig. S9), which are at 1591 and 1547 cm^{-1} for the antisymmetric stretching and 1406 cm^{-1} for symmetric stretching.