

***Electronic Supporting Information (ESI)***

**Edge-directed assembly of a 3D 2p-3d heterometallic metal–organic framework based on cubic Co<sub>8</sub>L<sub>12</sub> cage**

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## Experimental Section

**Materials and General Methods.** All the solvents and reagents for synthesis were obtained commercially and used as received. IR spectra were measured on a TENSOR 27 OPUS (Bruker) FT-IR spectrometer using KBr pellets in 4000~400  $\text{cm}^{-1}$  range. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240C analyzer. Thermogravimetric analyses (TGA) were carried out on a Rigaku standard TG-DTA analyzer under  $\text{N}_2$  with a heating rate of  $10^\circ\text{C min}^{-1}$ , with an empty  $\text{Al}_2\text{O}_3$  crucible used as reference. The room-temperature X-ray powder diffraction spectra (XRPD) were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator. XPS spectrum was recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Ka X-ray source ( $h\nu = 1486.6 \text{ eV}$ ), hybrid (magnetic/electrostatic) optics and a multi-channel plate and delay line detector (DLD). The XPS spectrum was recorded using an aperture slot of  $300 * 700$  microns, and survey spectra were recorded with a pass energy of 160 eV, and high resolution spectra with a pass energy of 40 eV. The calibration of binding energy scale was performed with the C 1s line (284.6 eV) from the carbon contamination layer. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed with ICP-9000(N+M) (USA Thermo Jarrell-Ash Corp). Magnetic data were collected using crystals of the sample on a Quantum Design MPMS-XL-7 SQUID magnetometer. The data were corrected using Pascal's constants to calculate the diamagnetic susceptibility and experimental correction for the sample holder was applied. Simulation of the XRPD pattern was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at <http://www.iucr.org>.

**Synthesis of  $\{[\text{Co}_3\text{Na}_6(\text{TzDC})_4(\text{H}_2\text{O})_6] \cdot 7\text{H}_2\text{O}\}_n$  (1).** A mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.4 mmol),  $\text{H}_3\text{TzDC}$  (0.2 mmol),  $\text{NaOH}$  (1 mmol) and  $\text{H}_2\text{O}$  (5 mL) was sealed in a teflon-lined mautoclave and heated to  $150^\circ\text{C}$ . After maintained for 48 h, the reaction vessel was cooled to room temperature and red crystals were collected with ca 40% yield based on  $\text{H}_3\text{TzDC}$ . FT-IR (KBr pellets,  $\text{cm}^{-1}$ ): 3324s, 1678s, 1620s, 1556w, 1396s, 1367s, 1310s, 1284m, 1231s, 1183w,

1137s, 1066w, 1007w, 853s, 816s, 789s, 702s, 667w, 545s. Anal. Calcd for  $C_{16}H_{26}N_{12}O_{29}Co_3Na_6$ : C, 16.49; H, 2.25; N, 14.43%. Found: C, 16.73; H, 2.66; N, 14.13%.

**X-ray Crystallography.** Single crystal X-ray diffraction measurements were carried out on Rigaku Saturn70 diffractometer at 133(2) K for **1**. The determinations of unit cell parameters and data collections were performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and unit cell dimensions were obtained with least-squares refinements. Semi-empirical absorption corrections were applied using CrystalClear program.<sup>S1</sup> The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.<sup>S2</sup> The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on  $F^2$ . In **1**, from the difference Fourier map, a number of diffused scattered peaks with electron density were observed, which can be attributed to the disordered water molecules and  $Na^+$  ions. Attempts to model these peaks were unsuccessful because the residual electron density peaks obtained were diffused. PLATON/SQUEEZE<sup>S3</sup> was used to refine the structure further. The dissociative water molecules were calculated based upon TG analyses, elemental analysis. The presence of additional disordered  $Na^+$  ion in the framework was confirmed by inductively coupled plasma atomic emission spectroscopy (The calculated stoichiometric ratio of Co and Na of **1** are about 1 : 2 by ICP analysis.) and charge balance considerations. Table S1 shows crystallographic crystal data and structure processing parameters. Selected bond lengths and bond angles are listed in Table S2. CCDC-917264 (**1**) contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

S1 CrystalClear, *Rigaku Corporation*, Tokyo, Japan, 2008.

S2 (a) G. M. Sheldrick, *SHELXL97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, *SHELXS97, Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S3 A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, 2003.

**Table S1.** Crystal data and structure refinement details for **1<sup>a</sup>**.

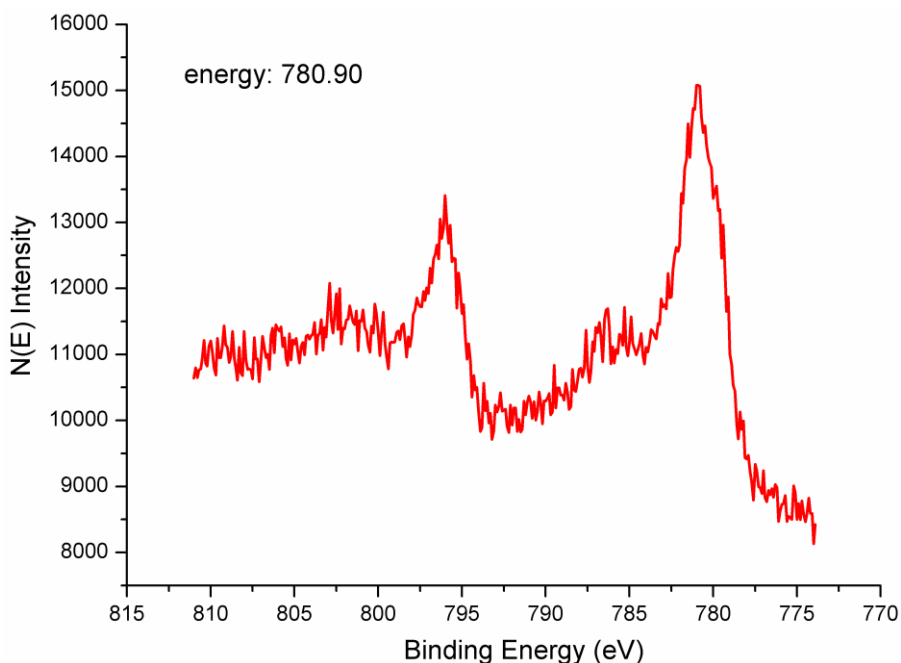
Formula	C <sub>48</sub> H <sub>78</sub> N <sub>36</sub> O <sub>87</sub> Co <sub>9</sub> Na <sub>18</sub>
Fw	3495.54
Crystal system	trigonal
Space group	<i>R</i> -3
<i>a</i> (Å)	24.377(3)
<i>b</i> (Å)	24.377(3)
<i>c</i> (Å)	24.856(5)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	120
<i>V</i> (Å <sup>3</sup> )	12792(5)
<i>Z</i>	3
$\mu$ (mm <sup>-1</sup> )	0.992
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.095
<i>R</i> (int)	0.0751
GOF on <i>F</i> <sup>2</sup>	1.079
<i>R<sub>I</sub></i> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0737
<i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.2255

<sup>a</sup> $R_I = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ ; <sup>b</sup>  $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$ .

**Table S2.** Bond lengths [Å] and angles [°] for complex **1**<sup>a</sup>.

complex 1			
Co1–N5A	1.996(4)	Co1–N1	1.989(4)
Co1–N4	1.997(4)	Co1–O8	2.002(3)
Co1–O1	2.010(3)	Co1–O5A	2.020(3)
Co2–N3	1.994(4)	Co2–O3	2.006(3)
Co3–O1W	2.087(4)	Na1–O2	2.331(4)
Na1–O4	2.318(4)	Na1–O7B	2.320(4)
Na1–O6B	2.327(4)	Na1–O3W	2.365(4)
Na1–O2W	2.393(5)		
N5A–Co1–N1	99.11(14)	N5A–Co1–N4	97.48(14)
N1–Co1–N4	98.28(14)	N5A–Co1–O8	89.59(13)
N1–Co1–O8	171.29(13)	N4–Co1–O8	80.17(14)
N5A–Co1–O1	171.05(13)	N1–Co1–O1	79.99(13)
N4–Co1–O1	91.45(14)	O8–Co1–O1	91.45(13)
N5A–Co1–O5A	79.63(14)	N1–Co1–O5A	89.78(13)
N4–Co1–O5A	171.80(14)	O8–Co1–O5A	92.09(13)
O1–Co1–O5A	91.45(13)	N3C–Co2–N3D	97.69(13)
N3C–Co2–O3D	91.14(13)	N3D–Co2–O3D	80.00(13)
N3–Co2–O3D	171.11(13)	O3D–Co2–O3C	91.43(13)
O7B–Na1–O4	90.65(18)	O7B–Na1–O6B	87.93(19)
O4–Na1–O6B	177.05(15)	O7B–Na1–O2	177.07(17)
O4–Na1–O2	89.31(16)	O6B–Na1–O2	91.97(18)
O7B–Na1–O3W	90.02(18)	O4–Na1–O3W	92.76(17)
O6B–Na1–O3W	89.82(19)	O2–Na1–O3W	92.91(17)
O7B–Na1–O2W	91.24(18)	O4–Na1–O2W	86.72(17)
O6B–Na1–O2W	90.73(19)	O2–Na1–O2W	85.83(17)
O3W–Na1–O2W	178.64(17)	O1WC–Co3–O1W	90.04(16)
O1WA–Co3–O1W	89.96(16)	O1WA–Co3–O1WD	179.997(1)
O1W–Co3–O1WE	180.00(17)		

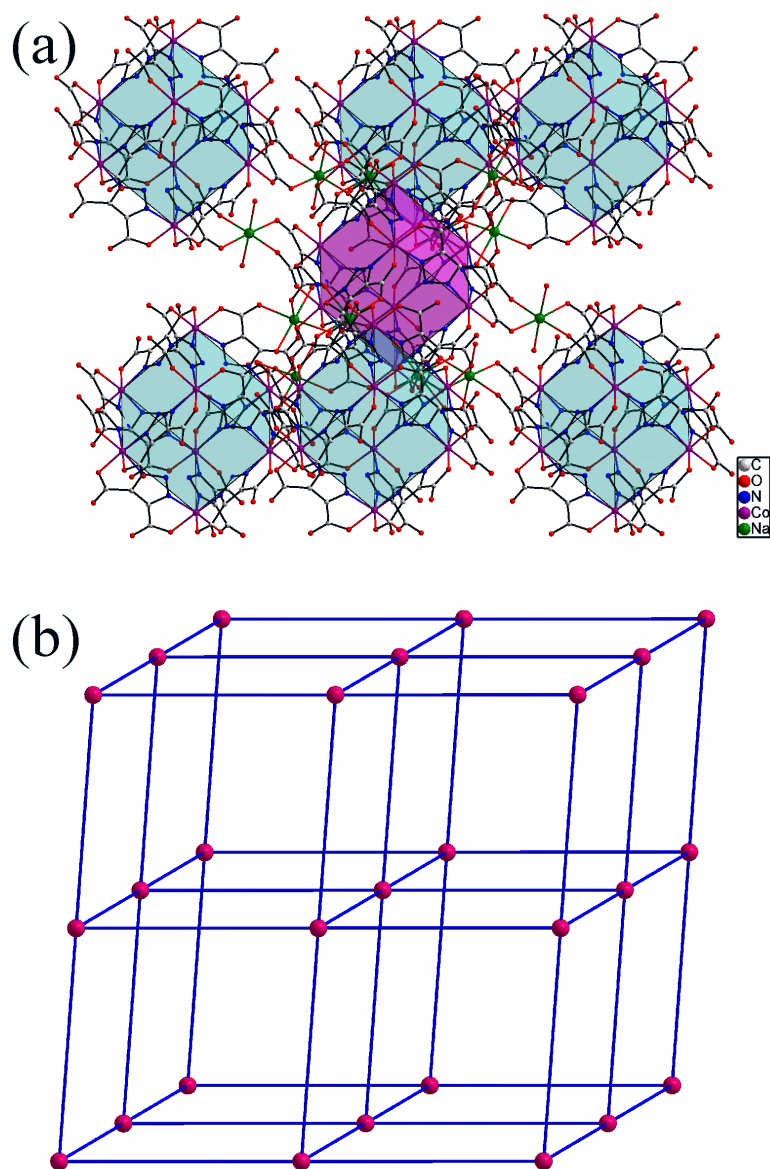
<sup>a</sup>symmetry codes: A,  $x-y+2/3, x+1/3, -z+1/3$ ; B,  $-y+4/3, x-y+2/3, z-1/3$ ; C,  $-y+1, x-y+1, z$ ; D,  $-x+y, -x+1, z$ ; E,  $-x+2/3, -y+4/3, -z+1/3$ .



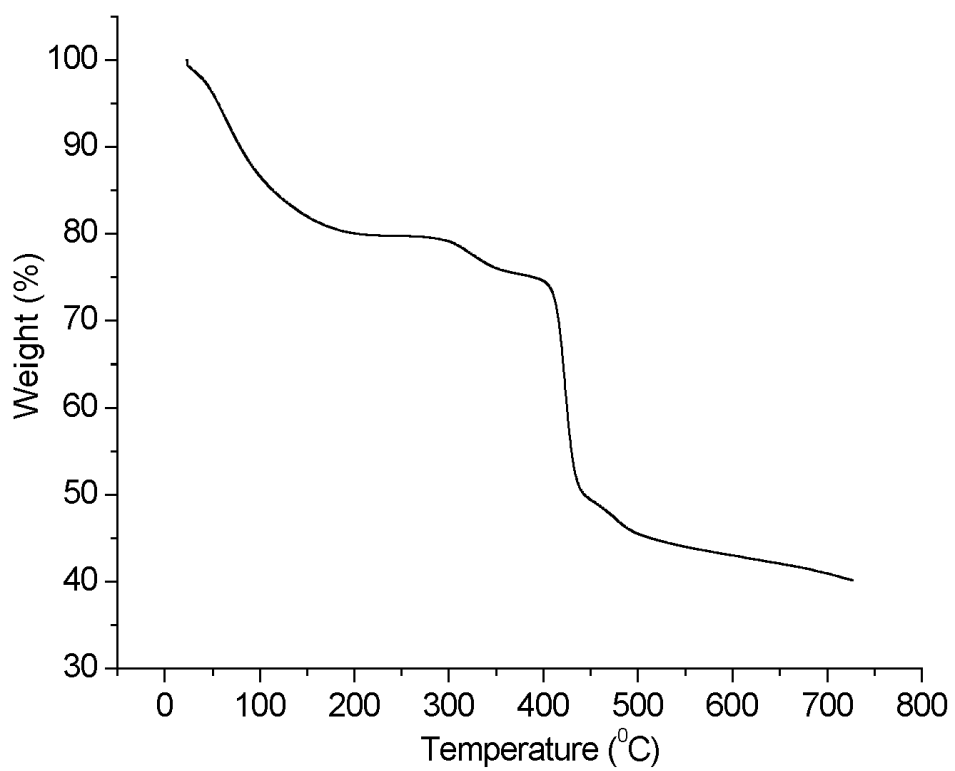
**Fig. S1** XPS spectrum of complex **1**. The characteristic peak of  $\text{Co}^{3+}$   $2\text{P}_{3/2}$  level of 779.2–779.6 eV with 15.1 eV splitting is not observed.<sup>S4</sup> Simultaneously, the Co 2p spectrum above agrees well with that for spinel  $\text{Co}^{2+}[\text{Mn}^{3+}]_2\text{O}_4$ ,<sup>S5</sup> accompanying with a strong shake-up satellite, which also provide the evidence that all cobalt ions are divalent. This is in agreement with the results from magnetic data of **1** at room temperature.

References:

- S4. (a) S. H. Xiang, X. T. Wu, J. J. Zhang, R. B. Fu, S. M. Hu and X. D. Zhang, *J. Am. Chem. Soc.*, 2005, **127**, 16352, (b) J. L. Gautier, E. Rios, M. Gracia, J. F. Macro and J. R. Gancebo, *Thin solid Films.*, 1997, **311**, 51, (c) T. J. Chuang, C. R. Brundle and D. W. Rice, *Surf. Sci.*, 1976, **59**, 413.
- S5. V. A. M. Brabers and F. Van Setten, *J. Phys. D: Appl. Phys.*, 1983, **16**, L169.

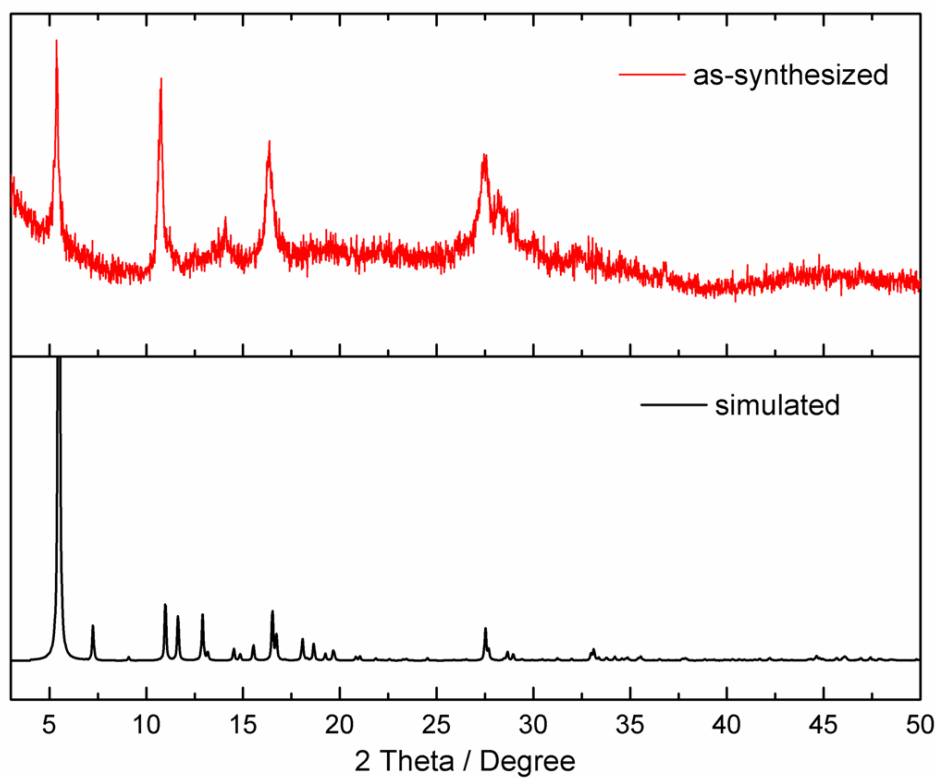


**Fig. S2** (a) Schematic representation of the 6-connected cages in **1**. (b) Schematic illustrations of the pcu topology of the 3D network.

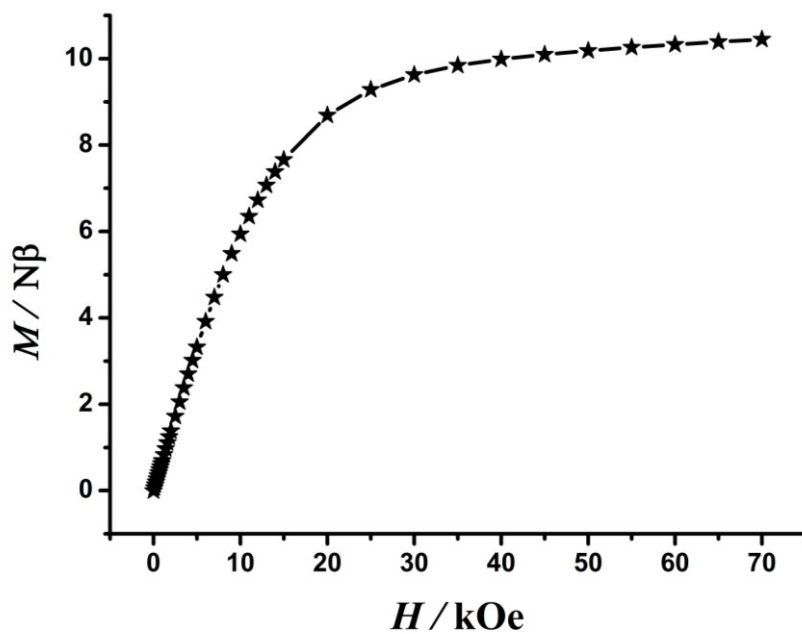


**Fig. S3** Thermogravimetric curve of complex 1.

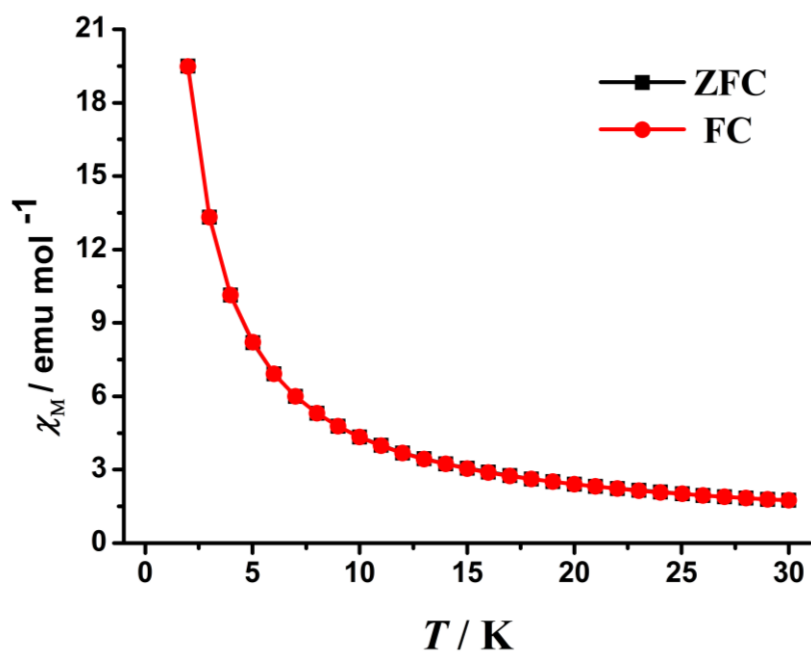




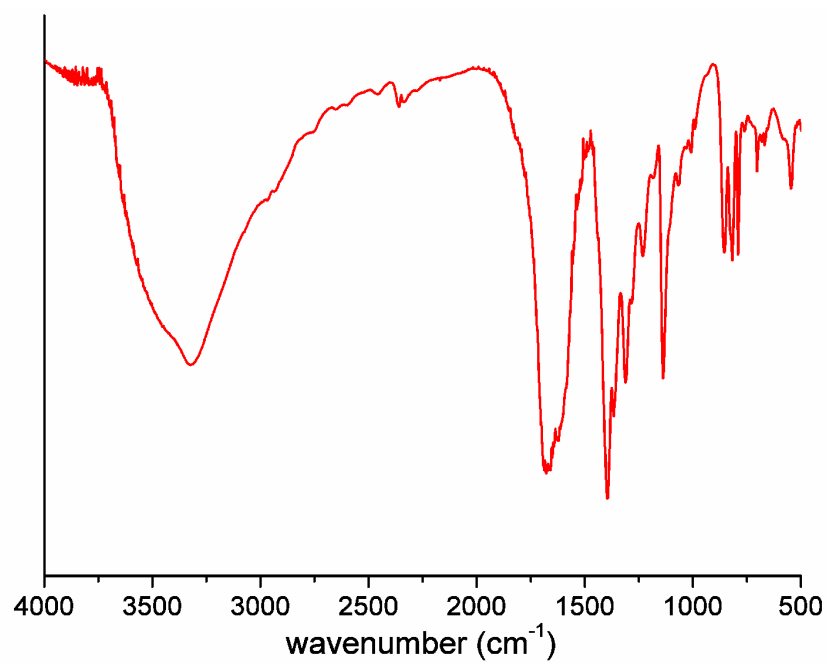
**Fig. S4** The XRPD patterns of complex **1**: the as-synthesized patterns (red) and the simulated patterns based on X-ray single-crystal data (black).



**Fig. S5** The  $M$  vs.  $H$  plot for **1** measured at 2 K.



**Fig. S6** The FC/ZFC curves at low temperature for 1.



**Fig. S7** IR spectrum of complex **1**.