Supporting Information

An octacobalt cluster based, (3,12)-connected, magnetic, porous coordination polymer

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Materials and Measurements. All solvents and starting materials for synthesis were purchased commercially and were used as received. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analysis (C, H, N) was performed on a Perkin-Elmer 240 elemental analyzer. Thermogravimetric analysis (TGA) was performed at a rate of 10 °C/min under air using a NETZSCH TG 209 system. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (CuKα, 1.5418 Å).

Synthesis of 1, MCF-32. A mixture of 2,6-di-*p*-carboxyphenyl-4,4'-bipyridine[1] (H_2dcpbpy, 0.030 g, 0.075 mmol) and $CoSO_4 \cdot 7H_2O$ (0.042 g, 0.15 mmol) in *N,N'*-dimethylformamide (DMF) (8 mL) and ethanol (1 mL) was placed in a Teflon-lined stainless steel vessel (12 mL) and heated at 155 °C for 60 h, and then cooled to room temperature at a rate of 5 °C/h. The resulting red

octahedral-like crystals of **1** were isolated by washing with DMF/ethanol, and dried in vacuo. The yield was ~35 mg (48.2%, based on H_2dcpbpy). Anal. Calc. for $C_{140}H_{224}Co_8N_{20}O_{72}S_2$: C, 43.39; H, 5.83; N, 7.23. Found: C, 43.32; H, 5.78; N, 7.17%. IR (KBr, cm^{-1}): 3393m, 2928w, 1657vs, 1595s, 1540m, 1393vs, 1254w, 1103m, 1017m,791w.

Sorption Measurements. The sorption isotherms for N_2 and H_2 were measured by using a BELmax adsorption equipment at 77 K. The as-synthesized samples (weight 105 mg) were treated by heating at 85 ºC for 6 h and subsequent 120 ºC for 3 h in a quartz tube under high vacuum to remove the solvent molecules prior to measurements.

Magnetic Measurements. Magnetic susceptibility measurements were performed on polycrystalline samples fixed with GE7031 varnish on a Quantum Design MPMS-XL7 SQUID. Data were corrected for the diamagnetic contribution calculated from Pascal constants.

Crystallography. The diffraction data were collected at 150(2) K with a CrysAlis CCD, Oxford Diffraction Ltd. with an imaging-plate detector diffractometer using graphite-monochromated CuKα (λ = 1.5418 Å) radiation with the ω scan mode. Absorption corrections were carried out utilizing SADABS routine.[2] The structure was solved by the direct methods and refined by full-matrix least-squares refinements based on F^2.[3] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms added to their geometrically ideal positions and refined isotropically except that the hydrogen atoms on the coordinated water molecules were located from the electron density and then refined using a riding model. Disorder of the terminal pyridyl ring of dcpbpy ligand was modeled by allowing two alternative positions for C12/C12' and C13/C13' with the occupancies of 0.50, respectively. Due to the presence of large cavities in the structure and heavily disordered solvent molecules in the cavities, the crystal of **1** scattered weakly and only low-angle data could be detected. An attempt to locate and refine the solvent molecules failed. Thus the SQUEEZE routine of PLATON[4] was applied to remove the contributions to the scattering from the solvent molecules. The reported refinement is of the guest-free structure using the *.hkp file produced using the SQUEEZE routine. Crystal data for **1**: $C_{96}H_{68}Co_8N_8O_{32}S_2$, M = 2381.14, tetragonal, space group $P4_2/nmc$ (No. 137), a = 17.7875(2), c = 32.8115(8) Å, V = 10381.4(3) $Å^3$, Z = 2, T = 150(2) K, ρ = 0.762 g cm^{-3}, μ = 5.412 mm^{-1}, 32895 reflections measured, 4270 unique (R_{int} = 0.1205) which were used in all calculations, final R_1 = 0.0585 and wR_2 = 0.1434 for $I > 2\sigma[I]$, and S = 0.947 (after SQUEEZE), (R_1 = 0.1015

and wR_2 = 0.2766 ($I > 2\sigma[I]$), and S = 1.163 without employing PLATON/SQUEEZE).

The final formula for **1** was determined by combining single-crystal structure, elemental microanalysis and TGA.

Complex **1** exhibits a novel (3,12)-connected topological net with a point symbol of $(4^3)_4(4^{12}6^{34}8^{20})$ and a vertex symbol of 4.4.4.4.4.4.4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).6(4).8(12).8(12).8(12).8(12).8(12).8(12).8(12).8(12).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20) by OLEX and TOPOS[5], which is obviously different with the theoretically predicted **ttt** net with a point symbol of $(4^3)_4(4^{12}6^{42}8^{12})$ and a vertex symbol of 4.4.4.4.4.4.4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(4).6(4).6(4).6(4).6(4).6(4).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).

The computed results of (3,12)-connected net of **1** by TOPOS 4.0 are as follows:

```
Structure consists of 3D framework with ZEZD4
Coordination sequences
----------------------
ZD1:   1   2   3    4    5    6    7     8     9    10
Num    3  30  22  142   61  336  120   606   199   960
Cum    4  34  56  198  259  595  715  1321  1520  2480
----------------------
ZE1:   1   2   3    4    5    6    7     8     9    10
Num   12  12  88   42  244   92  480   162   796   252
Cum   13  25 113  155  399  491  971  1133  1929  2181
----------------------
TD10=2420

Vertex symbols for selected sublattice
--------------------------------------
ZD1 Point (Schlafli) symbol:{4^3}
Extended point symbol:[4.4.4]
--------------------------------------
ZE1 Point (Schlafli) symbol:{4^12.6^34.8^20}
Extended point symbol:
[4.4.4.4.4.4.4.4.4.4.4.4.6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(2).6(4).6(4).6(4).6(
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12).8(12).8(12).8(12).8(12).8(12).8(12).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(20).8(
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20).8(20).8(20)]

Point (Schlafli) symbol for net: {4^12.6^34.8^20}{4^3}4
3,12-c net with stoichiometry (3-c)4(12-c); 2-nodal net

The computed results of (3,12)-connected net of 1 by SYSTRE are as follows:

Structure #1 - "1 in P4(2)/nmc; PPT 1; [2243]; 6[4^2.6^2]+[6^4] = 2[4a^2.6a^2]+4[4b^2.6a.6c]+[6c^4]".
Structure of dimension 3.
Given space group is P1.
10 nodes and 24 edges in repeat unit as given.
Given repeat unit is accurate.
Point group has 16 elements.
2 kinds of node.
Equivalences for non-unique nodes:
4 --> 2; 3 --> 1; 5 --> 1; 6 --> 1; 7 --> 1; 8 --> 1; 9 --> 1; 10 --> 1
Coordination sequences:
Node 2: 12 12 88 42 244 92 480 162 796 252
Node 1: 3 30 22 142 61 336 120 606 199 960
TD10 = 2420.2000
Ideal space group is P42/nmc.
Ideal group differs from given (P42/nmc vs P1). (using second origin choice)
Structure is new for this run.
Relaxed cell parameters:
a = 1.73205, b = 1.73205, c = 2.44949
alpha = 90.0000, beta = 90.0000, gamma = 90.0000
Cell volume: 7.34847
Relaxed positions:
Node 2: 0.75000 0.25000 0.25000
Node 1: 0.25000 0.08333 0.41667
Edges:
0.25000 0.08333 0.41667 <-> 0.25000 -0.25000 0.75000
0.25000 0.08333 0.41667 <-> 0.75000 0.25000 0.25000
Edge centers:
0.25000 -0.08333 0.58333
0.50000 0.16667 0.33333
Edge statistics: minimum = 1.00000, maximum = 1.00000, average = 1.00000
Angle statistics: minimum = 33.55731, maximum = 146.44269, average = 99.92198
Shortest non-bonded distance = 0.57735
Degrees of freedom: 4

Finished structure #1 - "1 in P4(2)/nmc; PPT 1; [2243]; 6[4^2.6^2]+[6^4] = 2[4a^2.6a^2]+4[4b^2.6a.6c]+[6c^4]".

References

1 A. R. Katritzky, Y.-K. Yang, B. Gabrielsen, J. Marquet, *J. Chem. Soc. Perkin Trans. II*, 1984, 857.

2 Bruker. *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconson, USA, 2002.

3 G. M. Sheldrick, SHELXL-97, program for the refinement of the crystal structures. University of Göttingen, Germany, 1997.

4 A. L. Spek, *J. Appl. Crystallogr*., 2003, **36**, 7.

5 (a) O. V. Dolomanov, A. J. Blake, N. R. Charmpness, M. Schröder, *J. Appl. Crystallogr*., 2003, **36**, 1283; (b) V. A. Blatov, 2007, http://www.topos.ssu.samara.ru/.

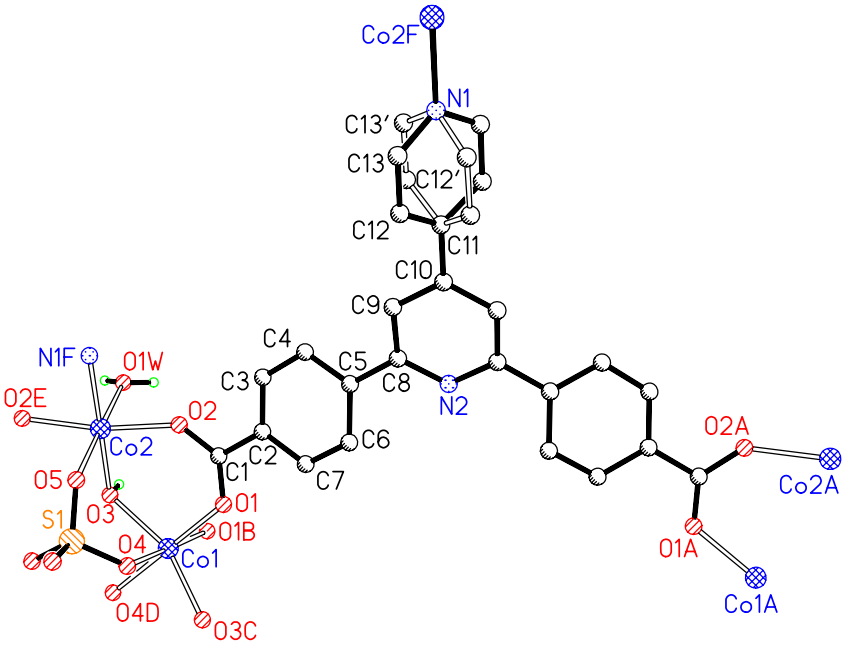

Fig. S1 The coordination environment of the Co^{2+} ions in **1** with the atom labels, the hydrogen atoms and solvent molecules are omitted.

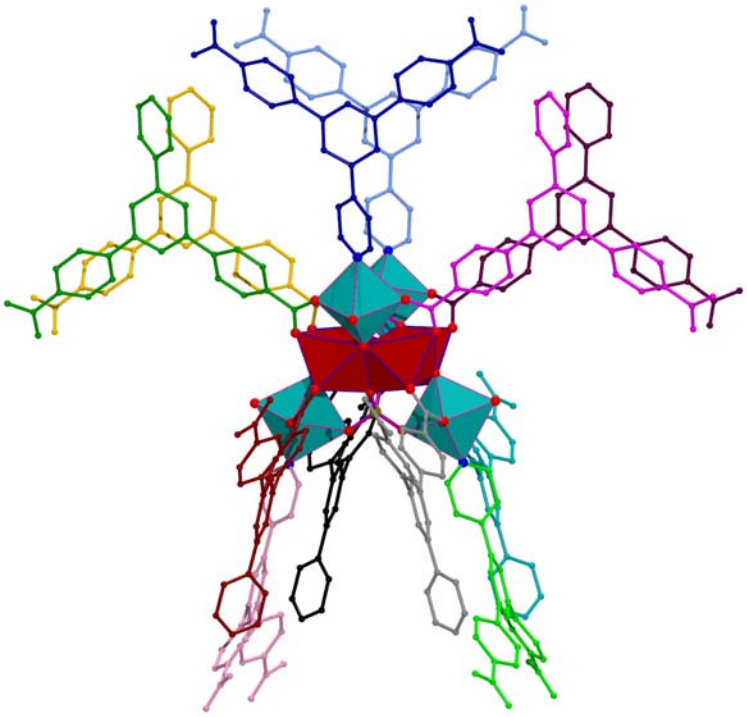

Fig. S2 Ball-and-stick diagram showing one novel Co_8 cluster in **1** ligated by twelve dcpbpy ligands. Co1, red polyhedron; Co2, cyan polyhedron.

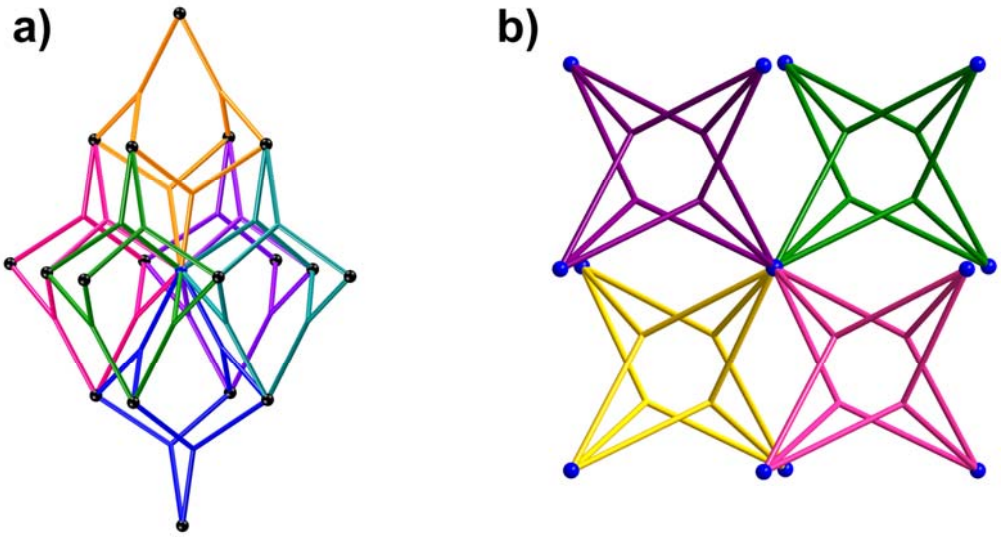

Fig. S3 (3,12)-Connected topological net of **1** (a) and **ttt** net (b) with one 12-connected vertex shared by six and four octahedral cages, respectively.

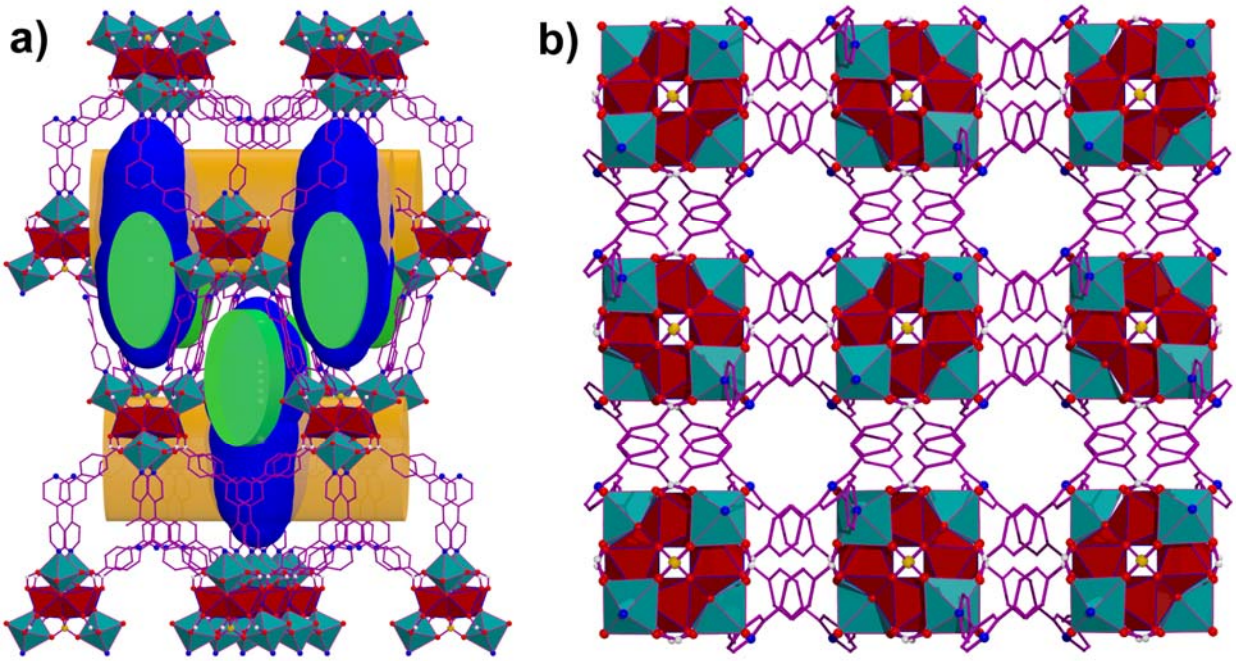

Fig. S4 3D network of **1** with two vertical channels formed along the *a*/*b* axis (orange and green cylinders, respectively) and converged at the centers of the cage (a), and packing representation of **1** along the *c* axis.

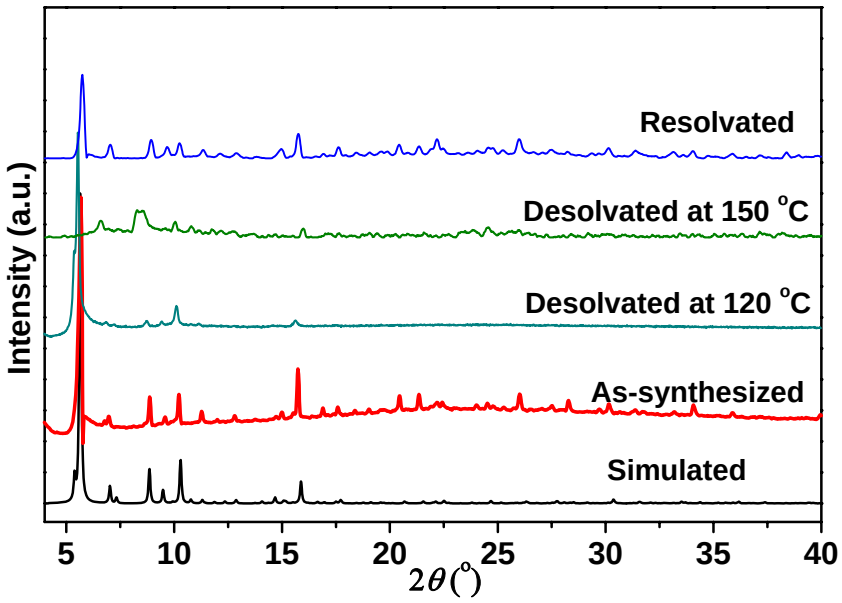

Fig. S5 PXRD patterns of **1** simulated from the X-ray single-crystal structure, as-synthesized, desolvated and resolvated samples.

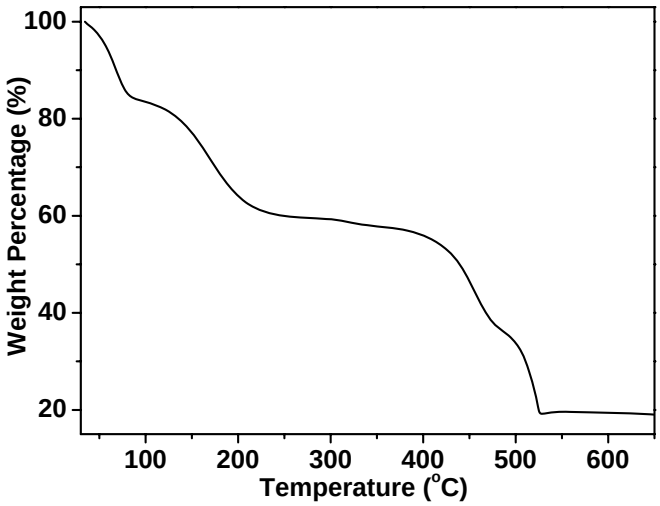

Fig. S6 TGA plot of the as-synthesized **1**.

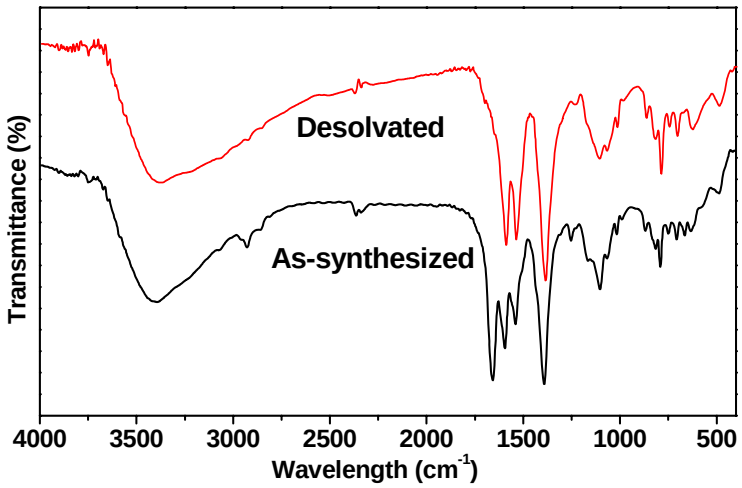

Fig. S7 IR spectra of the as-synthesized and desolvated **1**.

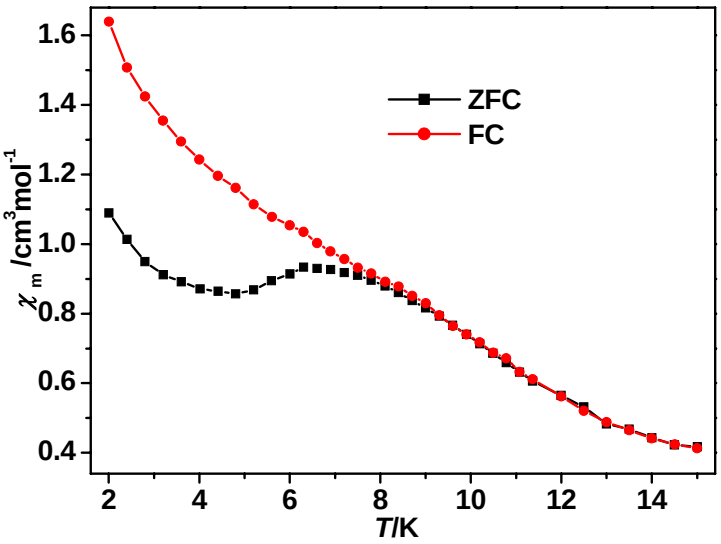

Fig. S8 FC and ZFC magnetizations measured for **1** at 50 Oe.

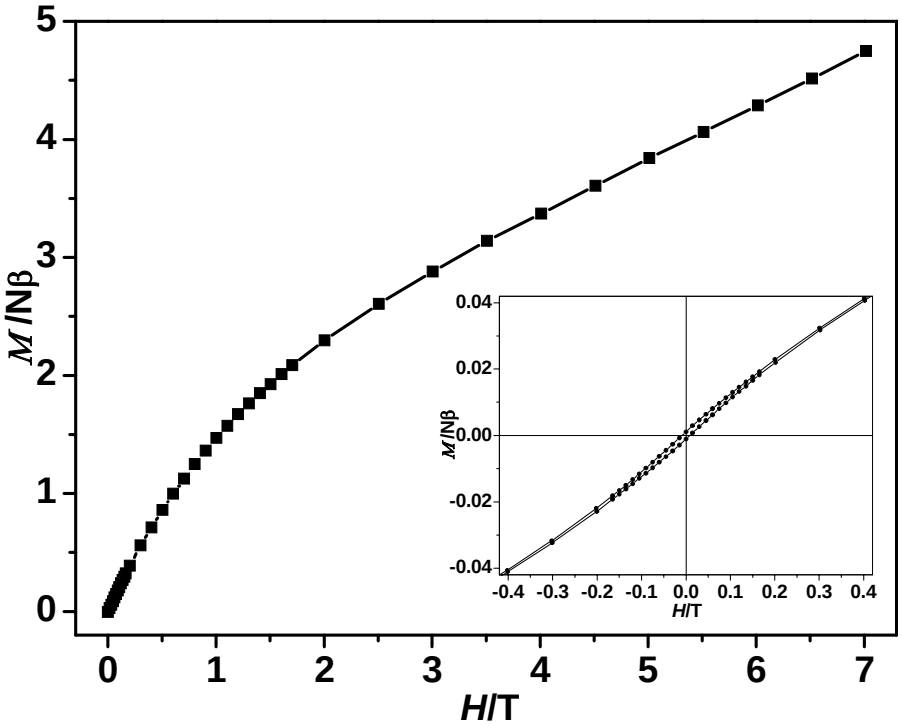

Fig. S9 The isothermal magnetization and the hysteresis curve of **1** at 1.8 K (lower right).