Electronic Supporting Information (ESI)

for

Doping cobalt into a [Zn_7] cluster-based MOF for tuning magnetic behaviours and inducing fluorescence signal mutation

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Experimental Section

Materials and methods.

All chemicals were commercially purchased and used as received.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer (Perkin-Elmer, USA). Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra were 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. IR spectrum was measured in the range of 400-4000 cm^{-1} on a Tensor 27 OPUS FT-IR spectrometer using KBr pellets (Bruker, German). UV-vis spectrum was recorded at room temperature on a computer-controlled Jasco V-550 Spectrometer (JASCO Corp.) Fluorescence spectra were recorded at room temperature on a Varian Cary Eclipse fluorescence spectrometer (Varian, USA).

X-ray Crystallography.

The crystallographic data of **Co-Zn-MOF** were collected on a Rigaku SCX-mini diffractometer at 298(2) K with Mo-Kα radiation (λ = 0.71073 Å). The crystal data were solved by direct methods and refined by a full-matrix least-square method on F^2 using the *SHELXL-97* crystallographic software package.[S1] Zinc and cobalt atoms in **Co-Zn-MOF** were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. But zinc and cobalt atoms possess site-occupancy disorder in the same position which is confirmed by the inductively coupled plasma (ICP) analysis and magnetism measurements. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of organic ligands were added theoretically, riding on the concerned atoms and refined with fixed thermal factors, and those of OH groups were located in a difference map and were refined with an O–H distance restraint of 0.85(1) Å. Lattice water hydrogen atoms were not added in **Co-Zn-MOF F**. Further details of crystal data and structure refinement for **Co-Zn-MOF** were summarized as follows. Selected bond lengths of **Co-Zn-MOF** were given in Table S1. Full crystallographic data for **Co-Zn-MOF** have been deposited with the CCDC (955704). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.[S2]

Reference

S1 (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.

S2 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data for Co-Zn-MOF: $C_{48}H_{34}N_{24}O_9Zn_5Co_2$, *Mr* = 1535.85; Trigonal, *R*-3*c*; *a* = 13.988(2) Å, *b* = 13.988(2) Å, *c* = 47.981(10) Å, γ = 120°; *V* = 8130(2) Å^3; *Z* = 6; D_{calc} = 1.880 Mg/m^3; *T* = 298(2) K.; Reflections collected/unique = 21852/1597, R_{int} = 0.0545; R_1 = 0.0382, wR_2 = 0.0759 (I > 2θ(I)); R_1 = 0.0444, wR_2 = 0.0783 (all data) and *GOF* = 1.096.

Crystal data for Zn-MOF: $C_{48}H_{34}N_{24}O_9Zn_7$, *Mr* = 1548.58; Trigonal, *R*-3*c*; *a* = 13.934(2) Å, *b* = 13.934(2) Å, *c* = 48.052(10) Å, γ = 120°; *V* = 8080(2) Å^3; *Z* = 6; D_{calc} = 1.910 Mg/m^3; *T* = 293(2) K.; Reflections collected/unique = 24128/2065, R_{int} = 0.1216; R_1 = 0.0507, wR_2 = 0.1109 (I > 2θ(I)); R_1 = 0.0785, wR_2 = 0.1231 (all data) and *GOF* = 1.044.

Figures in Supporting Information

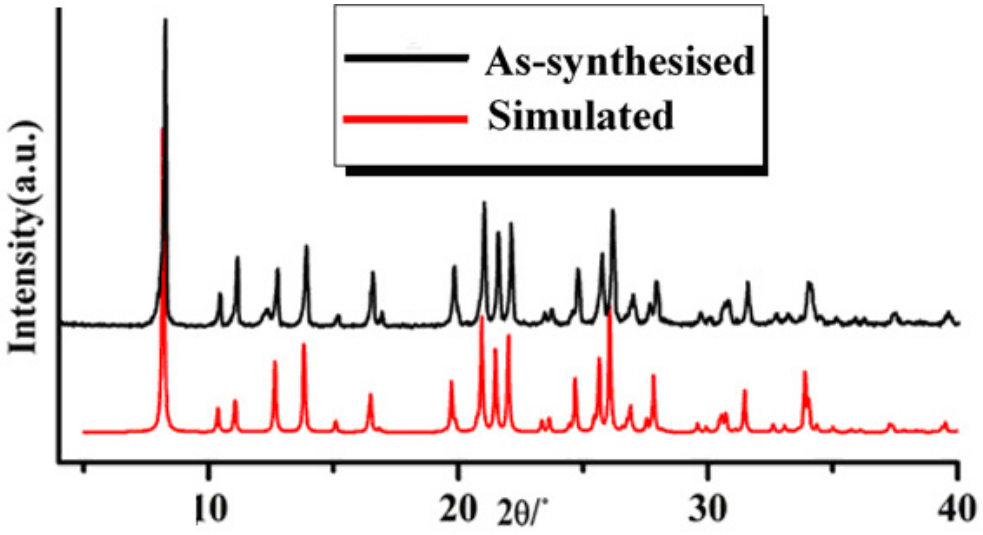

Fig. S1 XRPD patterns for **Co-Zn-MOF**.

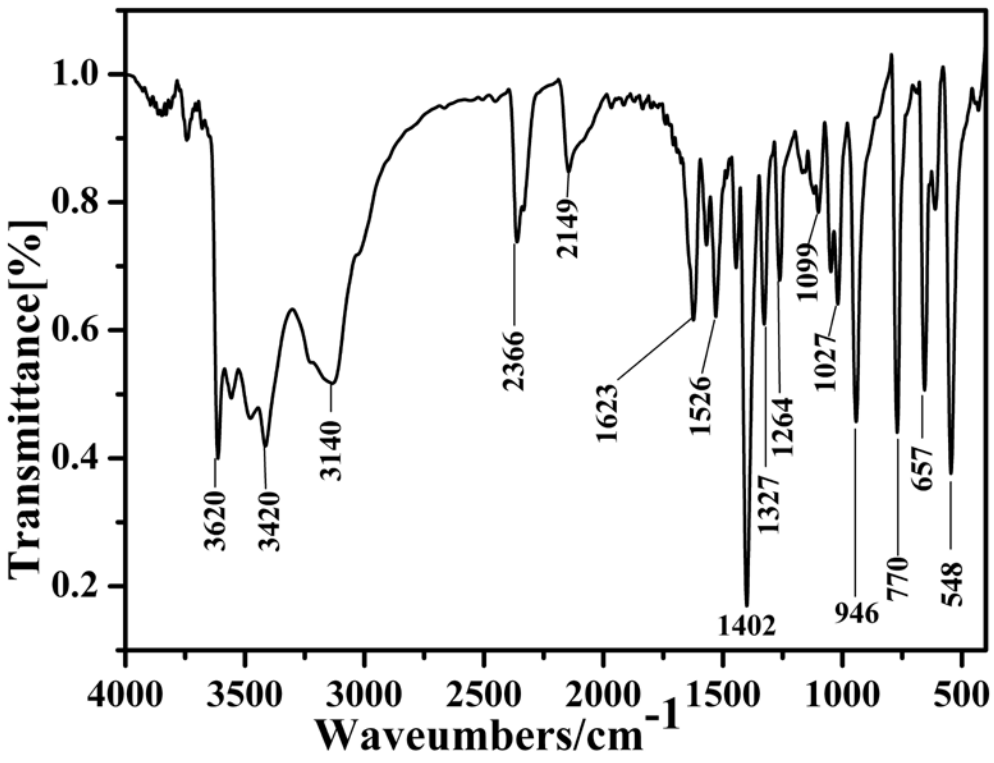

Fig. S2 IR spectrum of compound **Co-Zn-MOF**.

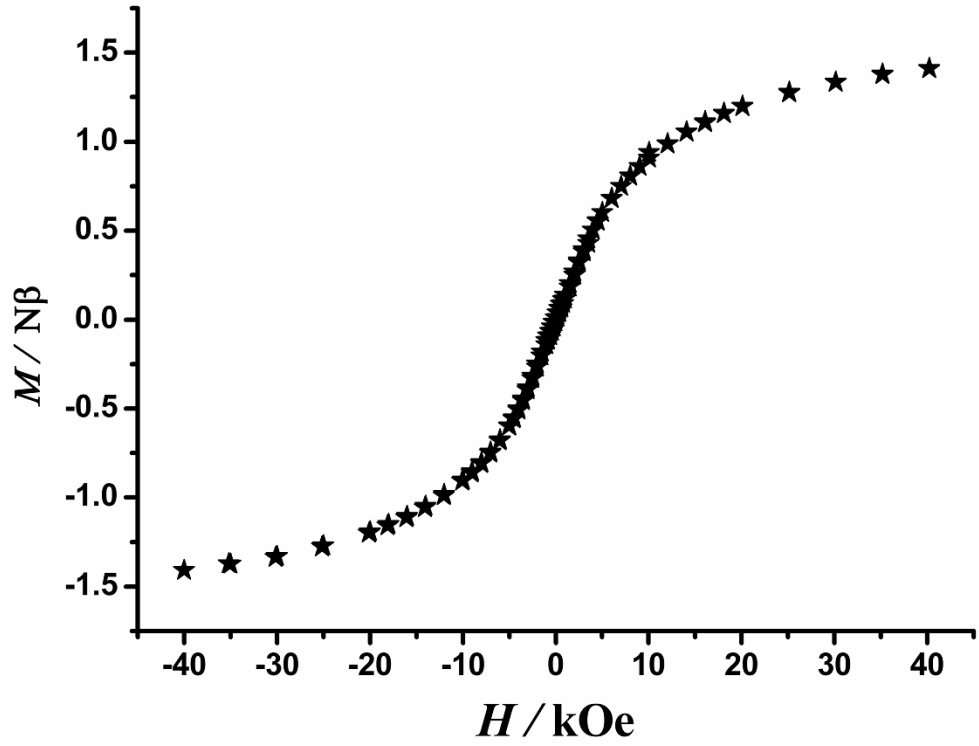

Fig. S3 The magnetic hysteresis loop at 2 K for **Co-Zn-MOF**.

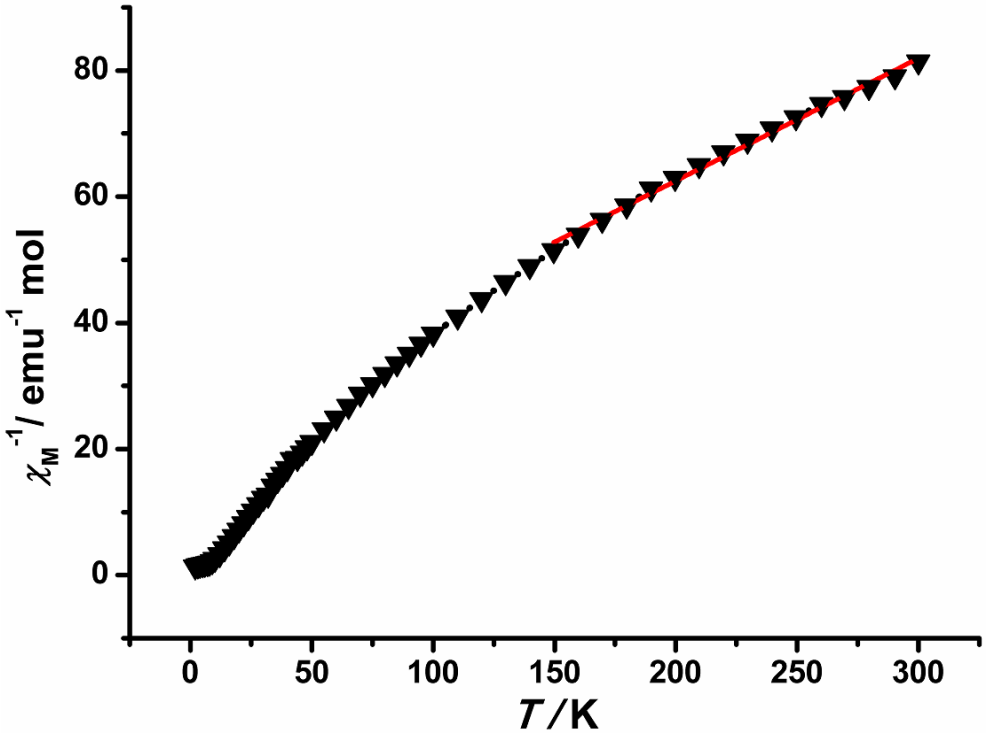

Fig. S4 The χ_M^{-1} *vs.* *T* curve (▼) for **Co-Zn-MOF** (red solid line for the Curie–Weiss fitting).

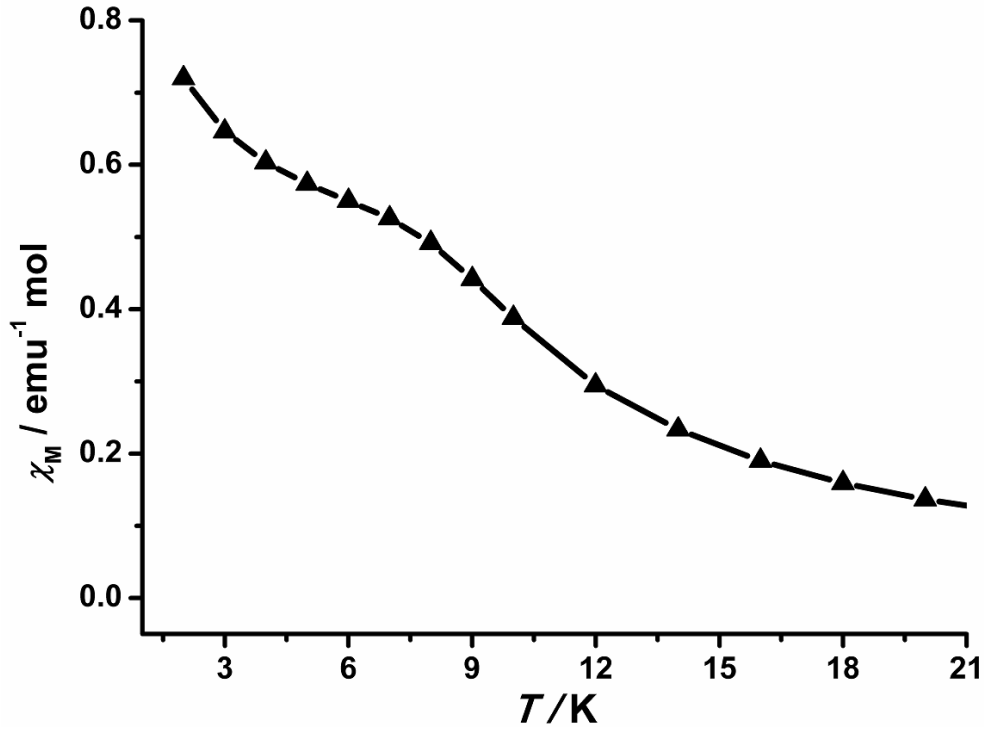

Fig. S5 The χ_M *vs.* *T* curve (▲) at 2-20 K for **Co-Zn-MOF**.

Table S1 The selected bond lengths [Å] and angles [º] of compound **Co-Zn-MOF**.

Co-Zn-MOF (M=$Co_{2/7}$/$Zn_{5/7}$)			
M(1)-O(2)#7	1.961(6)	M(2)-O(1)#1	1.937(3)
M(1)-O(2)#8	1.961(6)	M(2)-O(1)	1.937(3)
M(1)-O(2)	1.961(6)	M(2)-N(1)#1	2.041(3)
M(1)-O(1)#7	1.961(3)	M(2)-N(1)	2.041(3)
M(1)-O(1)#8	1.961(3)	M(3)-O(2)#2	1.931(6)
M(1)-O(1)	1.961(3)	M(3)-O(2)#3	1.931(6)
M(3)-O(2)#4	1.931(6)	M(3)-N(4)	2.012(3)
M(3)-N(4)#5	2.012(3)	O(2)-M(3)#3	1.931(6)
M(3)-N(4)#6	2.012(3)	O(2)-M(3)#3	1.931(6)
O(2)#7-Zn(1)-O(2)#8	20.3(4)	O(1)#1-Zn(2)-O(1)	109.90(19)
O(2)#7-Zn(1)-O(2)	20.3(4)	O(1)#1-Zn(2)-N(1)#1	116.82(13)
O(2)#8-Zn(1)-O(2)	20.3(4)	O(1)-Zn(2)-N(1)#1	111.37(12)
O(2)#7-Zn(1)-O(1)#7	96.1(3)	O(1)#1-Zn(2)-N(1)	111.37(12)
O(2)#8-Zn(1)-O(1)#7	113(3)	O(1)-Zn(2)-N(1)	116.82(13)
O(2)-Zn(1)-O(1)#7	113(3)	N(1)#1-Zn(2)-N(1)	89.52(18)
O(2)#7-Zn(1)-O(1)#8	113(3)	O(2)#2-Zn(3)-O(2)#3	20.6(4)
O(2)#8-Zn(1)-O(1)#8	96.1(3)	O(2)#2-Zn(3)-O(2)#4	20.6(4)
O(2)-Zn(1)-O(1)#8	113(3)	O(2)#3-Zn(3)-O(2)#4	20.6(4)
O(1)#7-Zn(1)-O(1)#8	111.07(9)	O(2)#2-Zn(3)-N(4)#5	108(2)
O(2)#7-Zn(1)-O(1)	113(3)	O(2)#3-Zn(3)-N(4)#5	128.0(10)
O(2)#8-Zn(1)-O(1)	113(3)	O(2)#4-Zn(3)-N(4)#5	113(3)
O(2)-Zn(1)-O(1)	96.1(3)	O(2)#2-Zn(3)-N(4)#6	113(3)
O(1)#7-Zn(1)-O(1)	111.07(9)	O(2)#3-Zn(3)-N(4)#6	108(2)
O(1)#8-Zn(1)-O(1)	111.07(9)	O(2)#3-Zn(3)-N(4)	113(3)
O(2)#4-Zn(3)-N(4)#6	128.0(10)	O(2)#4-Zn(3)-N(4)	108(2)
N(4)#5-Zn(3)-N(4)#6	101.61(10)	N(4)#5-Zn(3)-N(4)	101.61(10)
O(2)#2-Zn(3)-N(4)	128.0(10)	N(4)#6-Zn(3)-N(4)	101.61(10)
Symmetry transformations used to generate equivalent atoms: #1: -x+4/3, -x+y+2/3, -z+1/6; #2: x-y, x, -z; #3: -x+1, -y+1, -z; #4: y, -x+y+1, -z; #5: -y+1, x-y+1, z; #6: -x+y, -x+1, z; #7: -x+y+1, -x+1, z; #8: -y+1, x-y, z.			

Table S2 The selected bond lengths [Å] and angles [º] of compound **Zn-MOF**.

Zn-MOF parent			
Zn(1)-O(2)#1	1.927(7)	Zn(2)-N(1)	2.035(4)
Zn(1)-O(1)#2	1.959(4)	Zn(3)-O(2)	1.886(7)
Zn(1)-O(1)#3	1.959(4)	Zn(3)-N(4)	2.005(4)
Zn(1)-O(1)	1.959(4)	Zn(3)-N(4)#5	2.005(4)
Zn(2)-O(1)	1.925(4)	Zn(3)-N(4)#6	2.005(4)
Zn(2)-O(1)#4	1.925(4)	Zn(3)-H(2)	2.050(10)
Zn(2)-N(1)#4	2.035(4)	O(2)-Zn(1)#1	1.927(7)
O(2)#1-Zn(1)-O(1)#2	107.93(13)	O(1)-Zn(2)-N(1)	116.37(17)
O(2)#1-Zn(1)-O(1)#3	107.93(13)	O(1)#4-Zn(2)-N(1)	111.37(16)

O(1)#2-Zn(1)-O(1)#3	110.97(12)	N(1)#4-Zn(2)-N(1)	89.4(2)
O(2)#1-Zn(1)-O(1)	107.93(13)	O(2)-Zn(3)-N(4)	116.69(11)
O(1)#2-Zn(1)-O(1)	110.97(12)	O(2)-Zn(3)-N(4)#5	116.69(11)
O(1)#3-Zn(1)-O(1)	110.97(12)	N(4)-Zn(3)-N(4)#5	101.39(13)
O(1)-Zn(2)-O(1)#4	110.6(2)	O(2)-Zn(3)-N(4)#6	116.69(11)
O(1)-Zn(2)-N(1)#4	111.38(16)	N(4)-Zn(3)-N(4)#6	101.39(13)
O(1)#4-Zn(2)-N(1)#4	116.37(17)	N(4)#5-Zn(3)-N(4)#6	101.39(13)

Symmetry transformations used to generate equivalent atoms: #1: -x+4/3, -y+5/3, -z-1/3; #2: -y+1, x-y+1, z; #3: -x+y, -x+1, z; #4: x-y+2/3, -y+4/3, -z-1/6; #5: -x+y+1, -x+2, z; #6: -y+2, x-y+1, z.