Supporting Information

for

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A mixed-cluster approach for building a highly porous Co(II)-isonicotinic acid framework: gas sorption properties and computational analyses

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Experimental Section

Materials and Methods. All the chemicals purchased were of reagent grade and used without further purification. Analyses for C, H, and N were carried out on a Perkin-Elmer 240 CHN elemental analyzer. Powder X-ray diffraction measurements were recorded on a Rigaku D/Max-2500 X-ray diffractometer using Cu Kα radiation. TGA were performed on a Labsys NETZSCH TG 209 Setaram apparatus with a heating rate of 10 °C/min in nitrogen atmosphere. The gas sorption isotherms were collected on a Micromeritics 3Flex surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) N_2, CO_2 and H_2 gases were applied in all measurements. The experimental temperatures were maintained by liquid nitrogen (77 K) and temperature-programmed water bath (273 and 293 K).

Synthesis of $(H_2N(CH_3)_2)[Co_8(\mu_2\text{-}OH)_4(\mu_3\text{-}OH)_4(\mu_4\text{-}OH)(Ina)_8](H_2O)_{15}(DMA)_9\}_n$ (1). A mixture of Hina (9.5 mg, 0.05 mmol), $CoCl_2 \cdot 6H_2O$ (36 mg, 0.15 mmol) was dissolved in a mixed solvent of DMA (2.5 mL) and H_2O (0.5 mL) solution in a screw-capped vial. After addition of HBF_4 (37%, aq, 0.5 mL), the vial was heated at 120 °C for 72 h under autogenous pressure. Red crystals were obtained after filtration, washed with DMA. Yield: 34% based on the Hina ligand. Elemental analysis (calcd)found for **1**: $C_{86}H_{160}Co_8N_{18}O_{49}$: C, (38.56)38.23; H, (6.11)5.97; N, (9.48)9.33. Elemental analysis (calcd)found for activated **1**: C, (36.45)36.19; H, (3.00)3.32; N, (7.65)7.88. IR (KBr disks, selected bands, cm^{-1}): 3388m, 3116w, 1615s, 1558s, 1401s, 1317m, 1185s, 1077s, 835m, 775s, 632s.

X-ray Single Crystal Analysis. Data was collected on an Agilent Technologies SuperNova Single Crystal Diffractometer at low temperature equipped with graphite-monochromatic Mo Kα

radiation (λ = 0.71073 Å). The structure of **1** was solved by SHELXS (direct methods) and refined by SHELXL (full matrix least-squares techniques) in the Olex2 package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. For the highly disordered nature of the solvents, they could not be finely made out in the refinement, so the SQUEEZE routine of PLATON was applied to remove the diffraction contributed from the highly disordered guest molecules.[2] The chemical formula of **1** was determined by the combination of the crystal data, TGA, and elemental analysis.

GCMC Simulation Methodlody Grand canonical Monte Carlo (GCMC) simulations were performed for the adsorption of H_2 in **1** by the Sorption module of Material Studio according to the reference.[3] The framework and gas molecules were considered to be rigid. Before the simulation, the $H_2N(CH_3)_2$ ion was manually built and geometry optimization using the VAMP module with MNDO/d function, then the $H_2N(CH_3)_2$ ion was put into the framework of **1** via the Locate task to make the framework neutral. The H_2 molecule was modeled as a two-site rigid molecule with H-H bond length of 0.74 Å. The partial charges for atoms of **1** were derived from QEq method and QEq_neutral1.0 parameter. One unit cells were used during the simulations. All parameters for gas molecules and atoms of **1** were modeled with the universal forcefield (UFF) embedded in the MS modeling package. Simulation of H_2 uptake for **1a** was performed with Fixed loading task in MS. The Maximum loading steps was set to 2000000, Equilibration steps were set to 2000000, and production steps were set to 2000000, tepmerature were set to 77 K. The favorable bonding sites between H_2 and the MOF was simulated by using the Locate task.

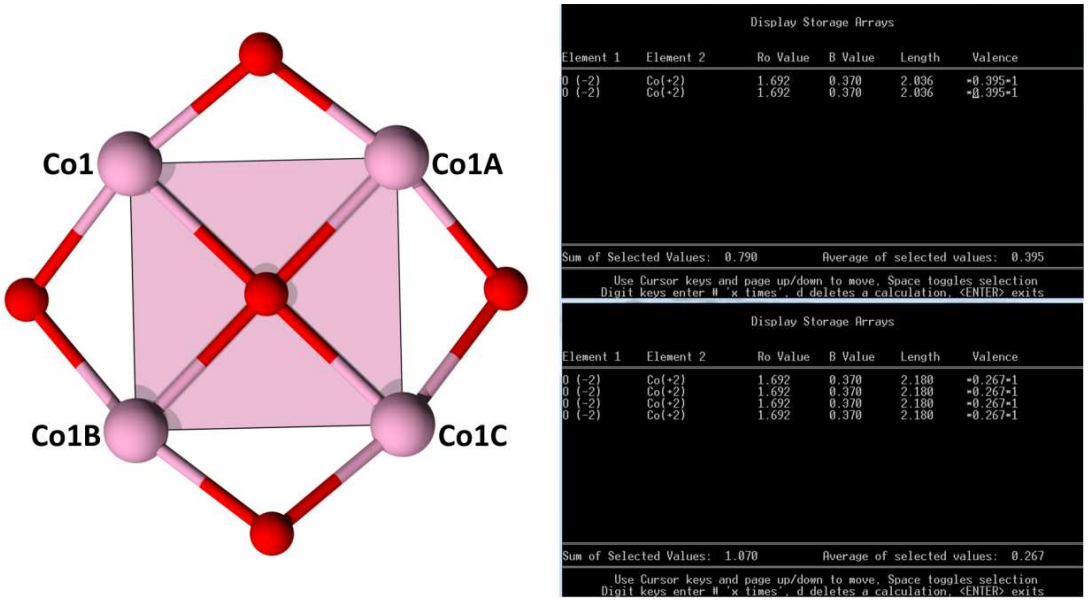


Figure S1. The planar $Co_4(\mu_4\text{-OH})(\mu_2\text{-OH})_4$ cluster in **1** and the BVS calculation results.

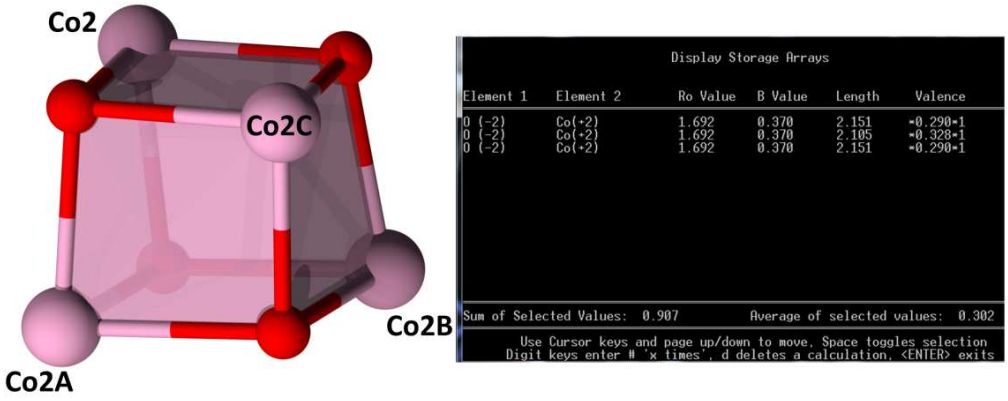


Figure S2. The cuboidal $Co_4(\mu_3\text{-OH})_4$ cluster in **1** and the BVS calculation results.

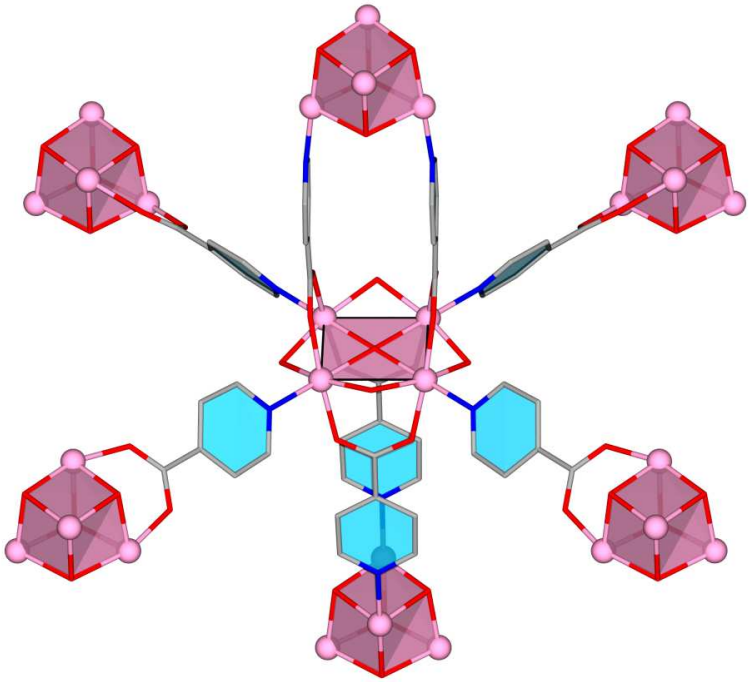


Figure S3. The representation for six-connected $Co_4(\mu_4\text{-OH})(\mu_2\text{-OH})_4$ cluster.

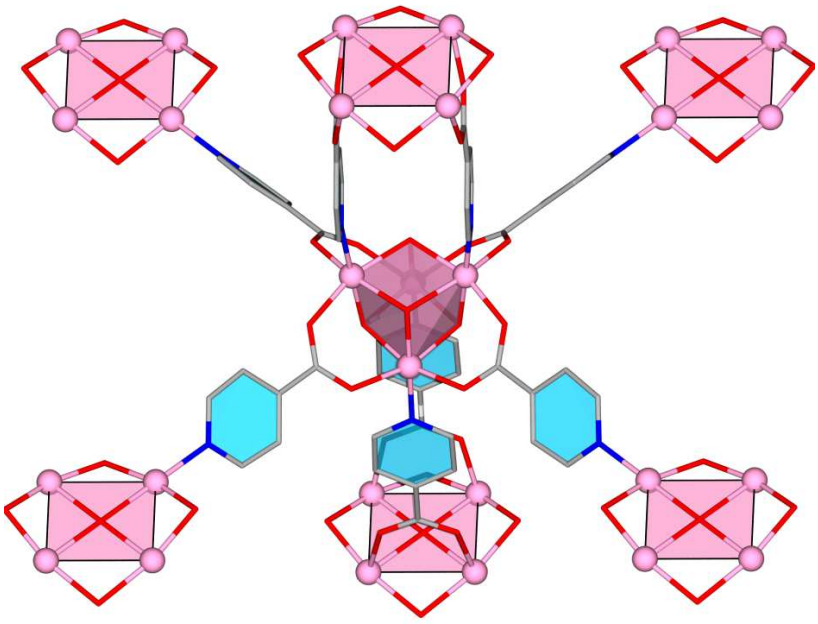


Figure S4. The representation for six-connected $Co_4(\mu_3\text{-OH})_4$ cluster.

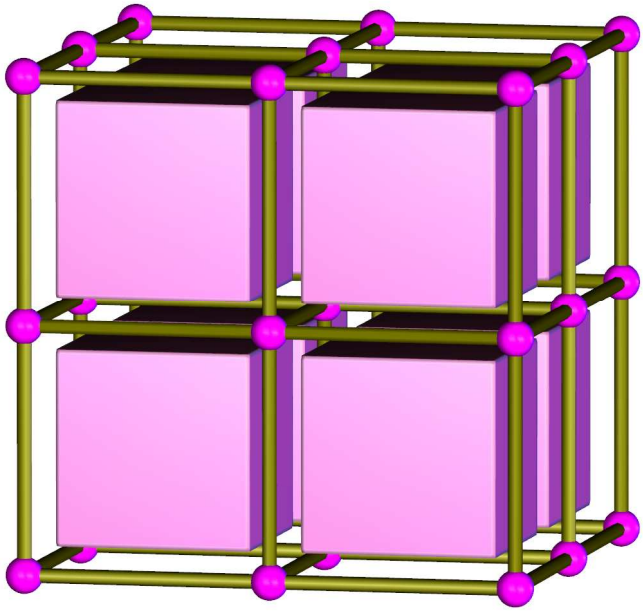


Figure S5. Natural tiling of **1**.

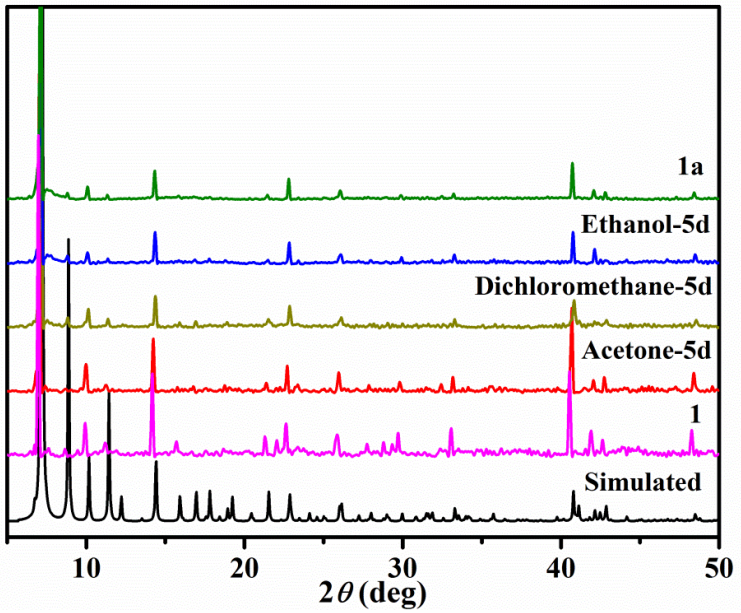


Figure S6. The PXRD patterns of **1** in different solvents.

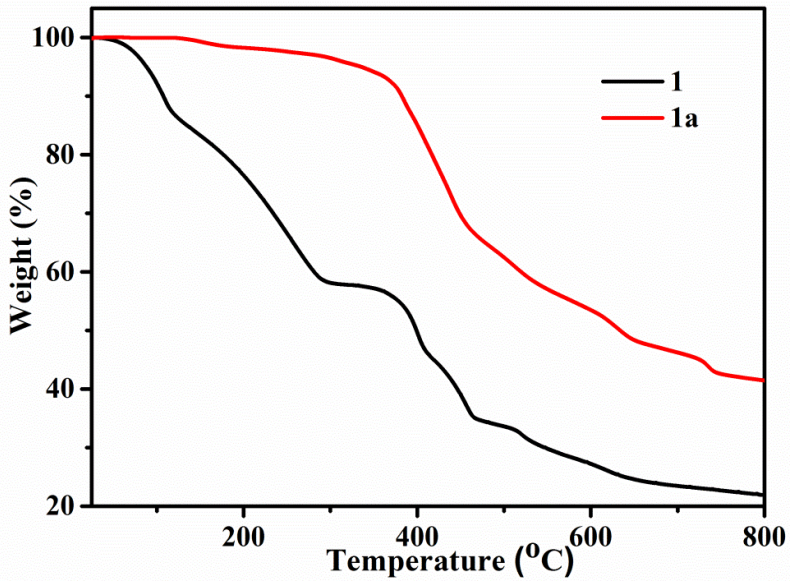


Figure S7. TGA curves for **1** and **1a**.

Analysis of H_2 and CO_2 Adsorption Isotherms using Virial fitting:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1a** at 273, 283 and 298 K, where P is the pressure, N is the adsorbed amount, T is the temperature, ai and bi are virial coefficients, and m and N are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

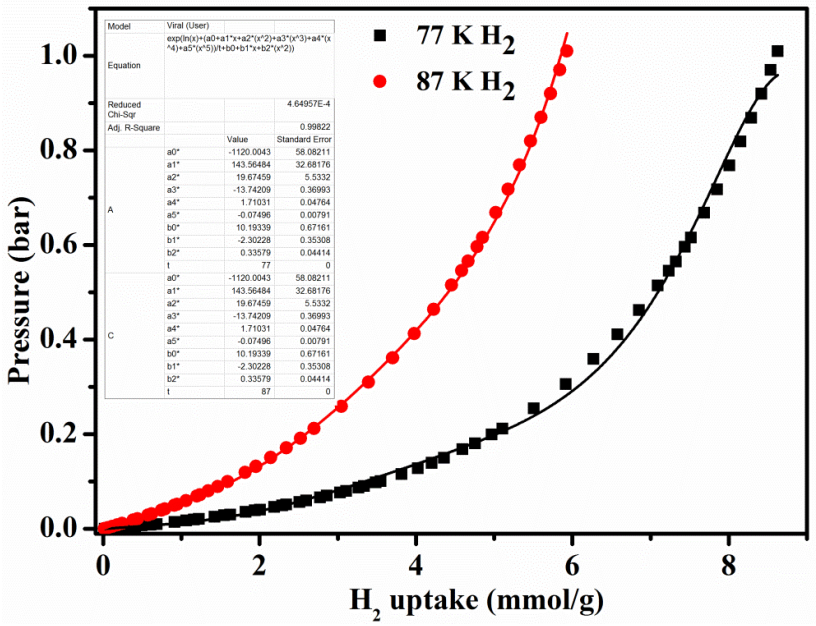


Figure S8. The virial fits for the H_2 sorption isotherms at 77 K and 87 K.

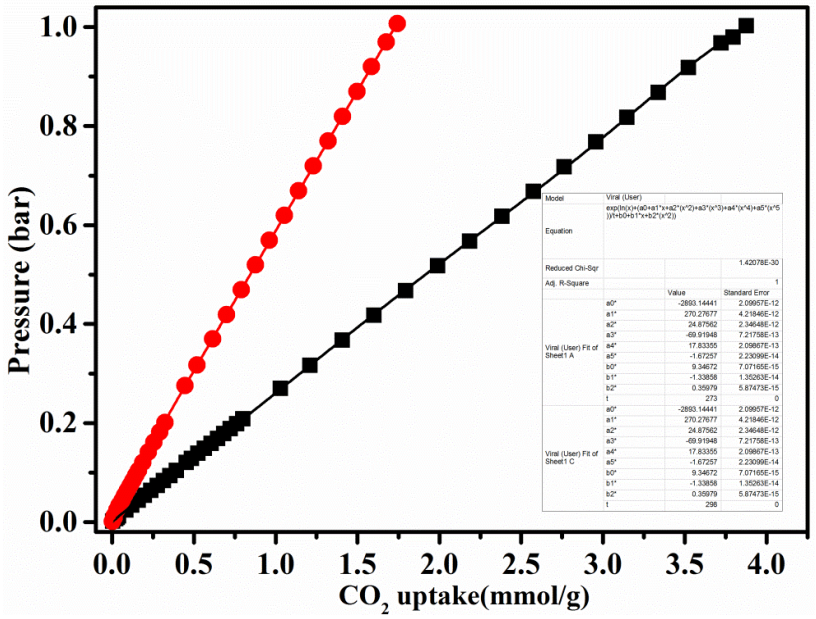
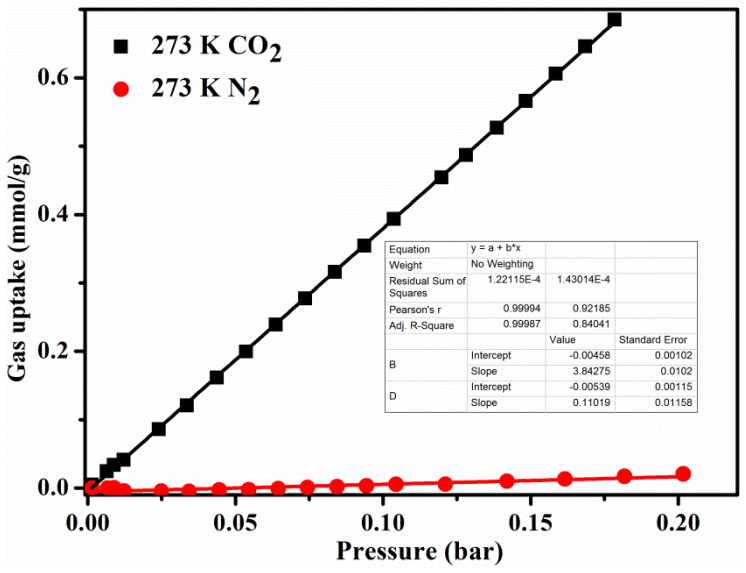
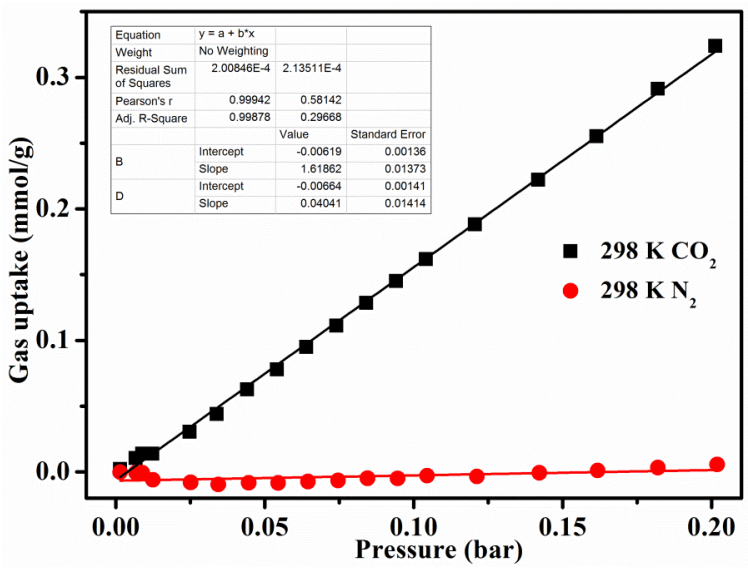


Figure S9. The virial fits for the CO_2 sorption isotherms at 273 K and 283 K.



(a)



(b)

Figure S10. Linear fitting of the low-pressure region of CO_2 and N_2 adsorption isotherms measured at 298 K.

Table S1. Comparison of surface area and H_2 adsorption capacities in selected isonicotinic acid-based MOFs.

Material	Surface Area (m^2/g) BET	Langmuir	Pore Volume cm^3/g	H_2 Uptake wt%	H_2 Q_{st} kJ/mol	Ref.
1a	1500	1667	0.621	1.71	9.2	**This work**
MCF-38		544	0.2	1.9	7.4	1
MCF-39	-	-	-	-	-	2
MCF-40	452	547	0.23	1.33	7.4	3
MCF-41	834	917	0.38	1.54	6.8	3
$Co_9(Ina)_{18}(\mu_2\text{-}OH_2)_4(H_2O)_2$(guest)	600	835	0.314	1.40	6.45	4
$Co_9(INA)_{18}(H_2O)_6]\cdot 11DMF\cdot 15H_2O$	910	1016	0.39	1.5	6.3	5
$[Co_8(OH)(ina)_8(N_3)_8X]$	482	738		0.71		6
$Co_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_4(\mu\text{-}H_2O)_4(ina)_8](NO_3)_2$		459		1.1	7.4	7
$[CuIn(ina)_4]_2$(DMF)	175	244				8
Co-FINA-1(FINA = F-substituent INA)	547.3	841.6		1.97		9
Co-FINA-2	152.8	238.3		0.82		9
$\{[Co_6(\mu_3\text{-}OH)_4(Ina)_8](H_2O)_{10}(DMA)_2\}_n$	631	739	0.267	1.25		10

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Inside Back Cover: Windmill $Co_4\{Co_4(\mu_4\text{-}O)\}$ with 16 Divergent Branches Forming a Family of Metal-Organic Frameworks: Organic Metrics Control Topology, Gas Sorption, and Magnetism. *Chem. - A Eur. J.* **2016**, *22*, 12199–12199.

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Table S2. Crystal data and structure refinement for **1**.

Empirical formula	$C_{48}H_{32}Co_8N_8O_{25}$
Formula weight	1592.25
Temperature/K	293(2)
Crystal system	tetragonal
Space group	I-4m2
a/Å	17.3699(10)
b/Å	17.3699(10)
c/Å	19.8944(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6002.4(8)
Z	2
ρ_{calc}g/cm^3	0.881
μ/mm^{-1}	1.120
F(000)	1584.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.33 to 49.978
Reflections collected	9679
Independent reflections	2825 [R_{int} = 0.0714, R_{sigma} = 0.0815]
Data/restraints/parameters	2825/84/132
Goodness-of-fit on F^2	0.997
Final R indexes [I>=2σ (I)]	R_1 = 0.0675, wR_2 = 0.1700
Final R indexes [all data]	R_1 = 0.0860, wR_2 = 0.1823
Largest diff. peak/hole / e Å^{-3}	1.94/-0.62
Flack parameter	0.46(3)

Table S3. Bond Lengths for **1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Co1	O1	2.1803(15)	N2	Co1^{9}	2.093(11)
Co1	O2^{1}	2.035(5)	N2	C8	1.330(19)
Co1	O2	2.035(5)	N2	C8^{10}	1.330(19)
Co1	O3	2.064(6)	N2	C10^{10}	1.37(3)
Co1	O3^{2}	2.064(6)	N2	C10	1.37(3)
Co1	N2^{3}	2.093(11)	N1	C4^{6}	1.317(11)
Co2	O4	2.104(6)	N1	C4	1.317(11)
Co2	O4^{4}	2.150(4)	C2	C1	1.486(15)
Co2	O4^{5}	2.150(4)	C2	C3	1.341(12)
Co2	O5^{6}	2.041(6)	C2	C3^{6}	1.341(12)
Co2	O5	2.041(6)	C6	C5	1.480(16)
Co2	N1	2.075(9)	C6	C7	1.40(2)
O4	Co2^{5}	2.151(4)	C6	C7^{10}	1.40(2)
O4	Co2^{4}	2.151(4)	C6	C9	1.39(3)
O1	Co1^{7}	2.1803(15)	C6	C9^{10}	1.39(3)
O1	Co1^{1}	2.1803(15)	C1	O3^{6}	1.253(8)
O1	Co1^{8}	2.1803(15)	C5	O5^{10}	1.255(8)
O2	Co1^{7}	2.035(5)	C4	C3	1.396(15)
O3	C1	1.253(8)	C7	C8	1.41(2)
O5	C5	1.254(8)	C10	C9	1.35(4)

Symmetry codes: [1]1-Y,+X,-Z; [2]1-Y,1-X,-Z; [3]-1/2+Y,3/2-X,1/2-Z; [4]+Y,1-X,1-Z; [5]1-Y,+X,1-Z; [6]1-X,+Y,+Z; [7]+Y,1-X,-Z; [8]1-X,1-Y,+Z; [9]3/2-Y,1/2+X,1/2-Z; [10]+Y,+X,1-Z.

Table S4. Bond Angles for **1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2[1]	Co1	O1	83.71(16)	Co1[1]	O1	Co1[8]	180.00(4)
O2	Co1	O1	83.71(16)	Co1	O1	Co1[8]	90.0
O2	Co1	O2[1]	167.4(3)	Co1	O1	Co1[7]	180.0
O2	Co1	O3	90.1(3)	Co1	O2	Co1[8]	98.5(3)
O2[1]	Co1	O3	89.2(3)	C1	O3	Co1	129.1(6)
O2	Co1	O3[2]	89.2(3)	C5	O5	Co2	129.3(6)
O2[1]	Co1	O3[2]	90.1(3)	C8	N2	Co1[9]	120.8(9)
O2[1]	Co1	N2[3]	96.29(16)	C8[10]	N2	Co1[9]	120.8(9)
O2	Co1	N2[3]	96.29(16)	C8[10]	N2	C8	118.5(18)
O3[2]	Co1	O1	87.2(2)	C10	N2	Co1[9]	123.3(14)
O3	Co1	O1	87.2(2)	C10[10]	N2	Co1[9]	123.3(14)
O3	Co1	O3[2]	174.4(4)	C10	N2	C10[10]	113(3)
O3[2]	Co1	N2[3]	92.8(2)	C4[6]	N1	Co2	121.9(5)
O3	Co1	N2[3]	92.8(2)	C4	N1	Co2	121.9(5)
N2[3]	Co1	O1	180.0	C4	N1	C4[6]	115.8(11)
O4	Co2	O4[4]	84.8(3)	C3	C2	C1	121.2(5)
O4	Co2	O4[5]	84.8(3)	C3[6]	C2	C1	121.2(5)
O4[5]	Co2	O4[4]	80.0(2)	C3	C2	C3[6]	117.6(11)
O5[6]	Co2	O4	85.5(2)	C7[10]	C6	C5	120.8(8)
O5[6]	Co2	O4[5]	86.2(2)	C7	C6	C5	120.8(8)
O5	Co2	O4[4]	86.2(2)	C7[10]	C6	C7	118.5(17)
O5	Co2	O4	85.5(2)	C9[10]	C6	C5	120.4(14)
O5[6]	Co2	O4[4]	163.8(3)	C9	C6	C5	120.4(14)
O5	Co2	O4[5]	163.8(3)	C9	C6	C9[10]	119(3)
O5[6]	Co2	O5	106.1(4)	O3	C1	O3[6]	125.4(10)
O5	Co2	N1	95.0(3)	O3	C1	C2	117.3(5)
O5[6]	Co2	N1	95.0(3)	O3[6]	C1	C2	117.3(5)
N1	Co2	O4	179.1(4)	O5	C5	O5[10]	126.4(10)
N1	Co2	O4[5]	94.5(3)	O5	C5	C6	116.8(5)
N1	Co2	O4[4]	94.5(3)	O5[10]	C5	C6	116.8(5)
Co2	O4	Co2[5]	94.3(2)	N1	C4	C3	123.4(10)
Co2	O4	Co2[4]	94.3(2)	C2	C3	C4	119.9(10)
Co2[5]	O4	Co2[4]	100.0(2)	C6	C7	C8	118.2(16)
Co1[1]	O1	Co1[7]	90.0	N2	C8	C7	123.3(17)
Co1[8]	O1	Co1[7]	90.0	C9	C10	N2	125(3)
Co1	O1	Co1[1]	90.0	C10	C9	C6	118(3)

Symmetry codes: [1]2-X,-Y,1-Z; [2]1+X,+Y,+Z; [3]+X,1+Y,+Z; [4]2-X,1/2+Y,1/2-Z; [5]+X,-1+Y,+Z; [6]-1+X,+Y,+Z; [7]2-X,-1/2+Y,1/2-Z.