Supplementary Material (ESI) for Chemical Communications

Supporting Information

Selective gas adsorption in microporous metal-organic framework constructed of Co^{II}_4 clusters

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Experimental Details

General Method. All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. Infrared spectra were recorded on a PerkinElmer spectrum One FT-IR spectrophotometer. UV/vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda 35 UV/vis spectrophotometer. Elemental analyses were recorded on a PerkinElmer EA 2400 Analyzer. Powder X-ray diffraction (PXRD) data were recorded with a Mac Science M18XHF-22 diffractometer at 50 kV and 100 mA for Cu Kα (λ = 1.54050 Å) with a scan speed of 5 ^{o}/min and a step size of 0.02^{o} in 2θ. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under N_2 (g) at a scan rate of 5 °C/min on a TA Q50 and a TA Q10, respectively. X-ray photoelectron spectra were measured on SIGMA PROBE at 15 kV and 70 W for Al K_α. Magnetic susceptibility data were recorded on SQUID magnetometer (MPMS – 5, Quantum Design).

Synthesis of $[Co^{II}_4(\mu\text{-}OH_2)_4(MTB)_2(H_2O)_4]_n \cdot 13n$DMF•$11n H_2O$ (SNU-15). The aqueous solution (1.0 mL) of $Co(NO_3)_2$•$6H_2O$ (30.0 mg, 0.103 mmol) and the DMF/EtOH solution (3:1 v/v, 4.0 mL) of methanetetrabenzoic acid (H_4MTB)[S1] (25.0 mg, 0.050 mmol) were mixed in a Teflon vessel settled in an autoclave. The mixture was heated at 90 °C for 24 h, and then cooled to room temperature. Pink crystals formed, which were filtered, washed with EtOH, and dried briefly in air. Yield: 73 mg (55%). Anal. Calcd for $Co_4C_{97}H_{161}N_{13}O_{48}$: C, 46.36; H, 6.46; N, 7.25. Found: C, 46.27; H, 6.49; N, 7.20. FT-IR (KBr pellet, cm^{-1}): ν_{OH}, 3411 (br); $\nu_{CH3(DMF)}$, 2931; $\nu_{C=O(DMF)}$, 1664; $\nu_{C=C(aromatic)}$, 1603; $\nu_{C=O(bridging\ carboxylate)}$, 1545; $\nu_{C=C}$, 1498.[S2] UV/vis (diffuse reflectance, λ_{max}): 254, 529 nm.

Synthesis of $[Co^{II}_4(\mu\text{-}OH_2)_4(MTB)_2]_n$ (SNU-15'). The crystals of **SNU-15** were heated in a Schlenk tube at 220 °C under vacuum (0.65 mmHg) for 24 h. The crystals lost the transparency together with the color change from pink to violet. Anal. Calcd for $Co_4C_{58}H_{40}O_{20}$: C, 53.89; H, 3.12; N, 0.0. Found: C,

53.83; H, 3.46; N, 0.0. FT-IR (Nujol, cm^{-1}): ν_{OH}, 3412 (br); $\nu_{C=C(aromatic)}$, 1602; $\nu_{C=O(bridging\ carboxylate)}$, 1532. UV/vis (diffuse reflectance, λ_{max}): 287, 572 nm.

X-ray Crystallography. Diffraction data of **SNU-15** were collected with an Enraf-Nonius Kappa CCD diffractometer ($Mo_{K\alpha}$, λ = 0.71073 Å, graphite monochromator). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects by using DENZO.[S2] The scaling and the global refinement of crystal parameters were performed by SCALEPACK.[S2] No absorption correction was made. The crystal structure was solved by the direct methods[S3] and refined by full-matrix least-squares refinement using the SHELXL97 computer program.[S3] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined using a riding model. The density of the disordered guest molecule was flattened by using the SQUEEZE option of PLATON.[S4] The crystallographic data of **SNU-15** are summarized in Table S1 and selected bond distances and angles are listed in Table S2.

Gas Sorption Study A measured amount of **SNU-15** was introduced into a Quantachrome Autosorb-3B gas sorption apparatus. All guest molecules and coordinating water molecules in **SNU-15** are removed by putting the sample in the preheated mantle at 220 °C and evacuating under 10^{-5} Torr for 24 h. If **SNU-15** was heated by increasing the temperature from room temperature to 220 °C, guest molecules were not completely removed probably because DMF guest molecules moved to the vacant coordination sites of Co^{II}, which were generated by the release of coordinating water molecules.[S5] Gas sorption isotherms for N_2, H_2, and O_2 were monitored at 77 K and those for CO_2 and CH_4 were measured at 195 K and 273 K at each equilibrium pressure by the static volumetric method.

Estimation of Isosteric Heat of H_2 Adsorption. The isosteric heat of H_2 adsorption was estimated for **SNU-15'** from the H_2 sorption data measured at 77 K and 87 K, by using a virial-type expression (eq 1).[S6] In eq 1, P is pressure (atm), N is the amount adsorbed H_2 gas (mg/g), T is temperature (K), and m

and n represent the number of coefficients required to adequately describe the isotherms. The parameters a_i and b_i are independent of temperature. The equation was fit with the **R** statistical software package,[S7] and m and n were gradually increased until the contribution of extra added a and b coefficients became statistically insignificant in the overall fit.

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

To estimate the values of the isosteric heat of H_2 adsorption, eq 2 was applied, where R is the universal gas constant. The isotherms and fitted virial parameters are presented in Figure S7.

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad (2)$$

(S1) (*a*) M. Grimm, B. Kirste, H. Kurreck, *Angew. Chem. Int. Ed.* 1986, **12**, 1097-1098; (*b*) S. Dapperheld, E. Steckhan, K. G. Brinkhaus, T. Esch, *Eur. J. Inorg. Chem.* 1991, **124**, 2557-2567.

(S2) Z. Otwinowsky, W. Minor, *Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods in Enzymology*; D. W. Carter, R. M. Sweet, Eds.:Academic Press: New York, 1996 Vol. 276, pp 307-326.

(S3) G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467.

(S4) P. v. d. Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* 1990, ***46***, 194.

(S5) Y.-G. Lee, H. R. Moon, Y. E. Cheon, M. P. Suh, *Angew. Chem. Int. Ed.* 2008, **47**, 7741-7745.

(S6) (*a*) M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann, J. R. Long, *J. Am. Chem. Soc.* 2006, **128**, 16876-16883; (*b*) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* 2006, **189**, 1304-1315; (*c*) L. Czepirski, J. Jagiello, *Chem. Eng. Sci.* 1989, **44**, 797–801.

(S7) **R** statistical software package is available online at http://www.r-project.org.

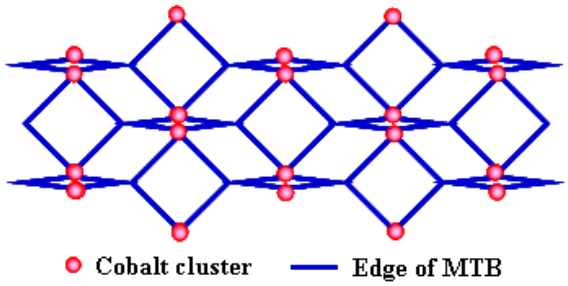

Fig. S1 The schematic view for the channels of rhombic aperture in **SNU-15**.

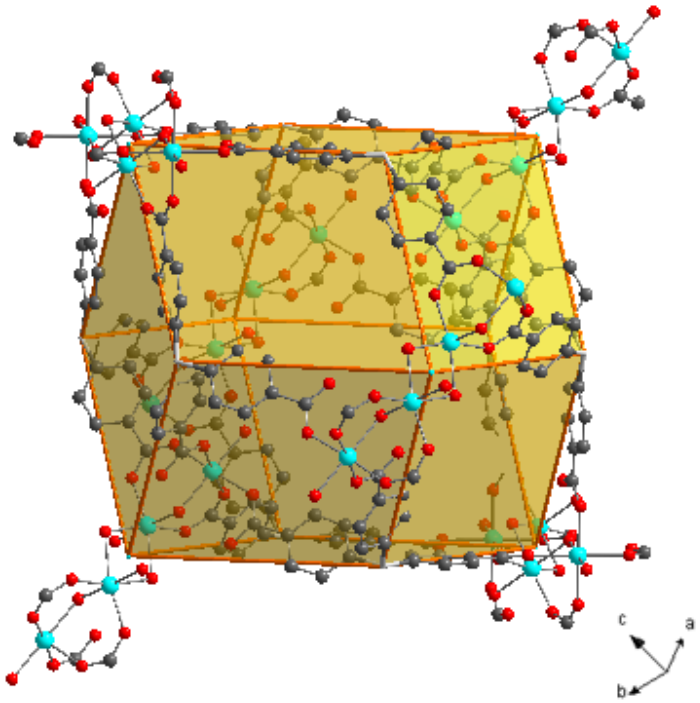

Fig. S2 X-ray structure of **SNU-15**. Color Scheme: cobalt^{II}, blue; oxygen, red; carbon, gray.

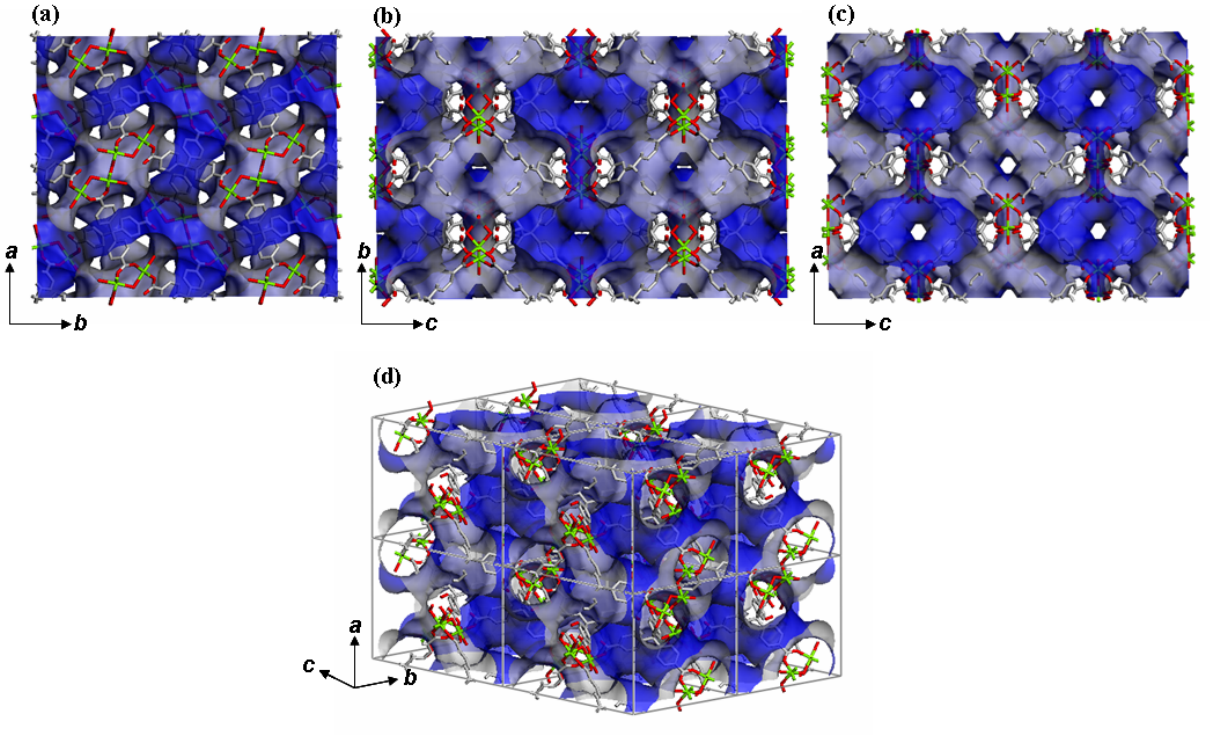

Fig. S3 X-ray crystal structure of **SNU-15**, showing the curved 3D channels in the surface view. Views seen on the (a) *ab* plane, (b) *bc* plane, and (c) *ac* plane. (d) A view showing the curved channels. Color scheme: cobalt, green; oxygen, red; carbon, gray.

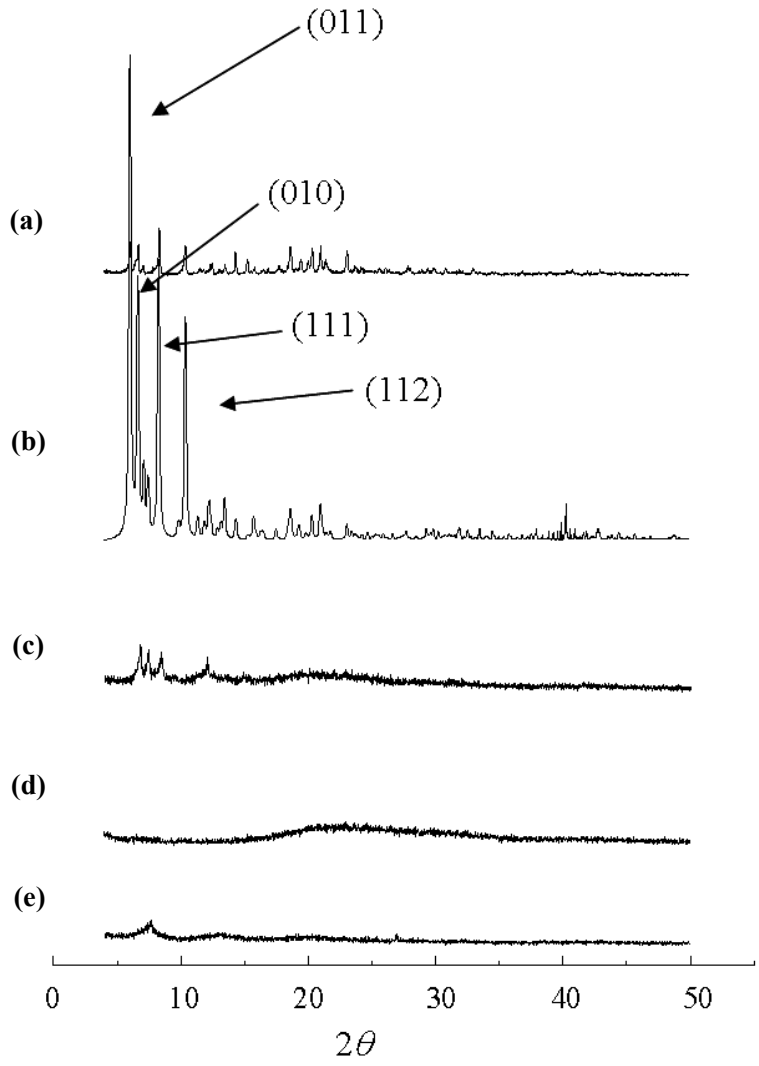

Fig. S4 The PXRD patterns for (a) **SNU-15** as prepared, (b) simulated pattern derived from X-ray single crystal data of **SNU-15**, (c) desolvated solid **SNU-15'** obtained by heating **SNU-15** at 120 °C under vacuum (0.65 mmHg) for 24 h, and (d) solid isolated after **SNU-15'** was immersed in DMF/EtOH/H_2O (3:1:1, v/v) for 24 h. (e) solid isolated after **SNU-15'** was exposed to the vapor of DMF/H_2O (10/0.2, v/v) at 38 °C for 120 h.

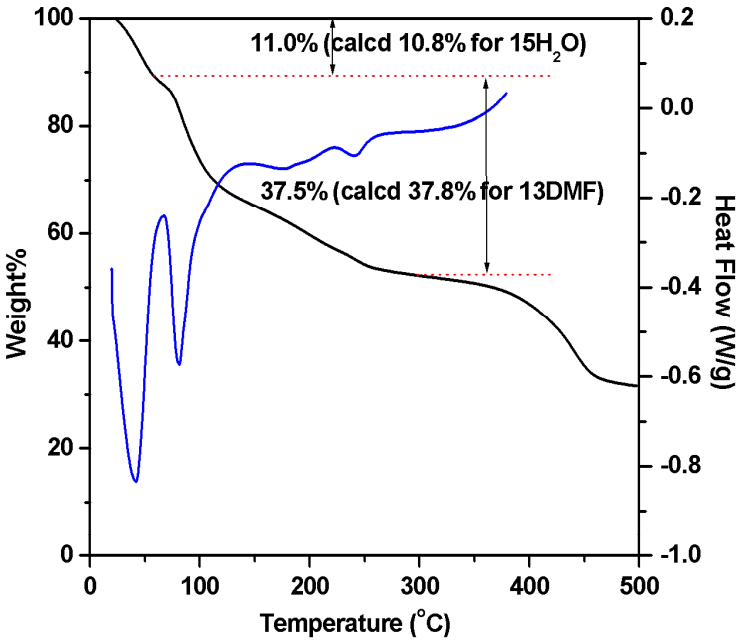

Fig. S5 TGA and DSC data of **SNU-15**.

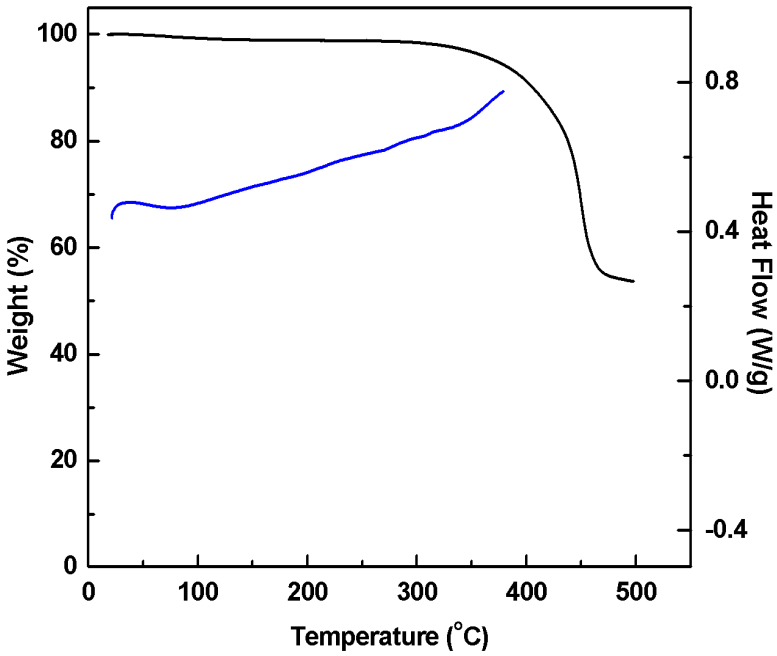

Fig. S6 TGA and DSC data of **SNU-15'**.

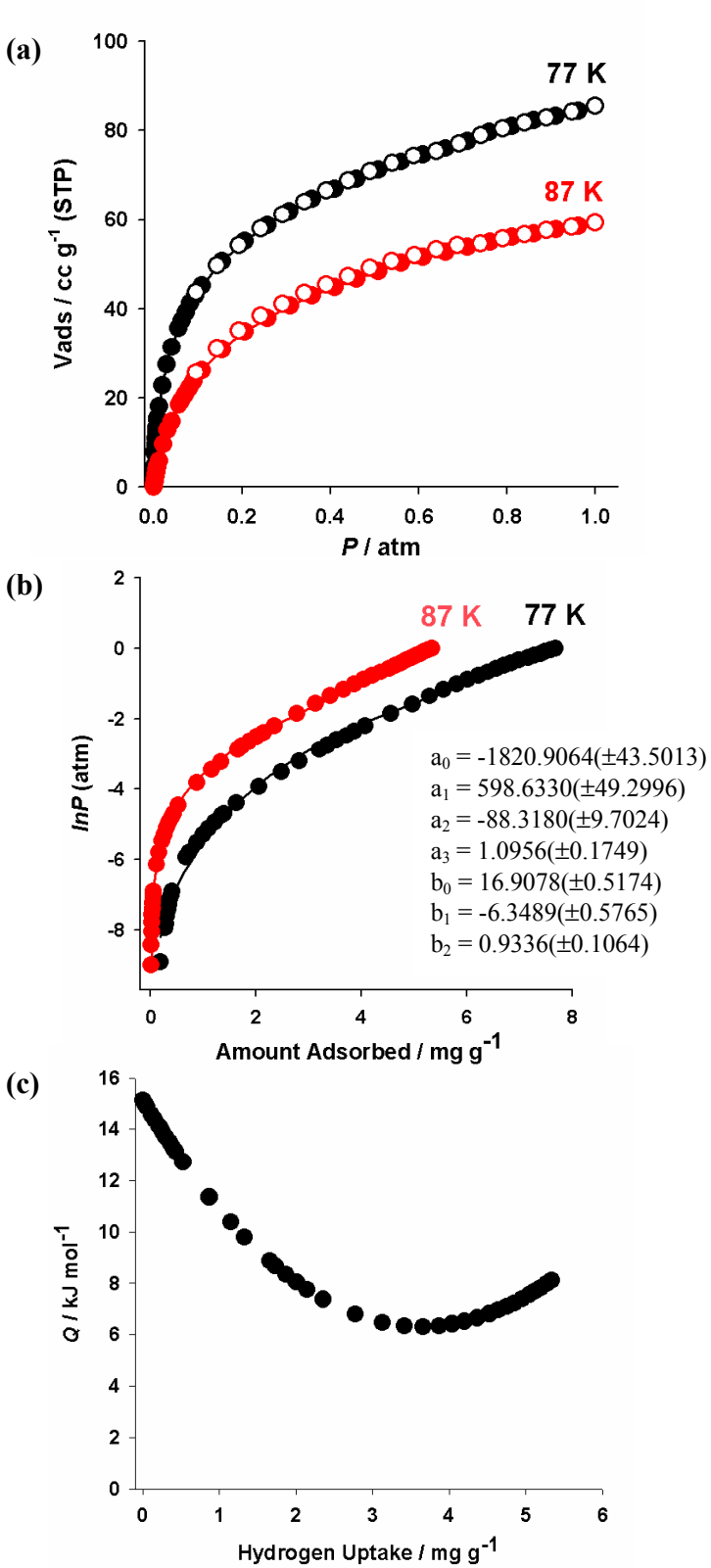

Fig. S7 (a) The H_2 adsorption isotherms at 77 K (black) and 87 K (red) for **SNU-15'**, (b) Virial equation fit of the H_2 adsorption isotherms, and (c) Isosteric heat of H_2 adsorption. Filled shape, adsorption; open shape, desorption.

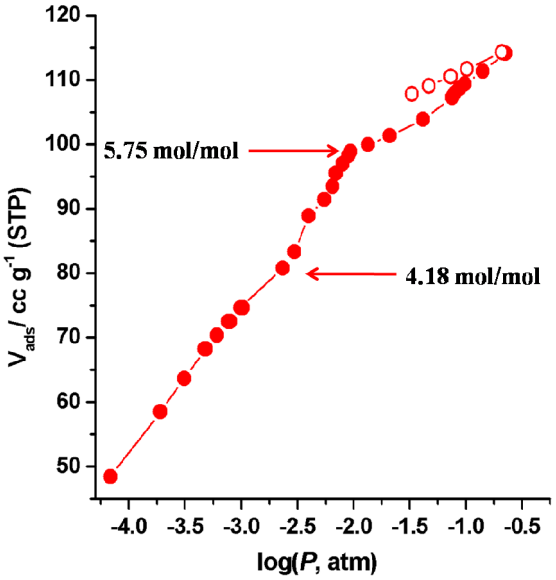

Fig. S8 The O_2 gas sorption isotherm at 77 K for **SNU-15'**. Filled and open symbols represent adsorption and desorption data, respectively.

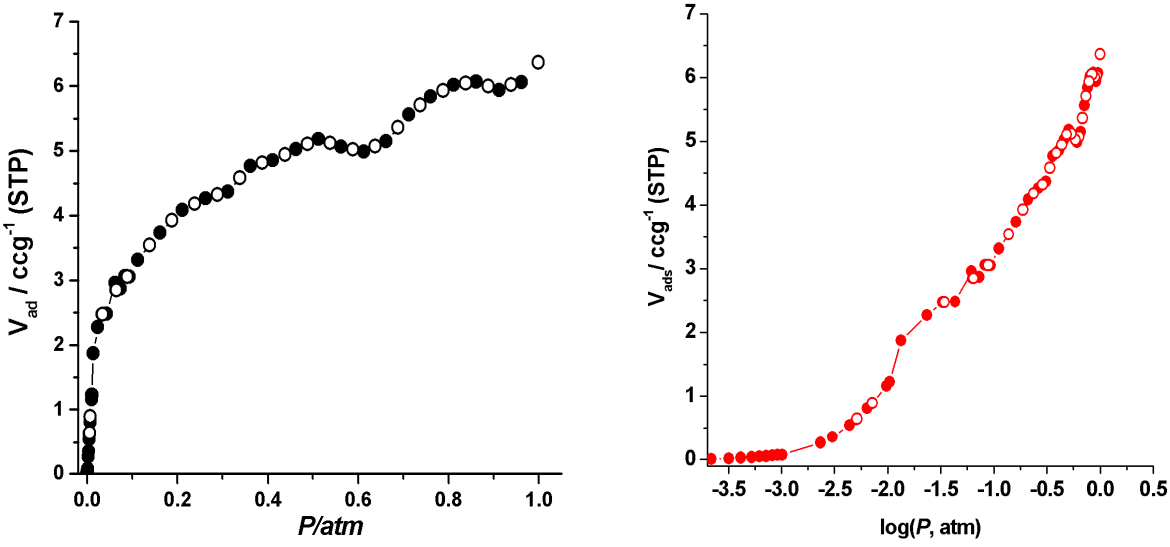

Fig. S9 The O_2 gas sorption isotherm at 290 K for **SNU-15'**. Filled and open symbols represent adsorption and desorption data, respectively.

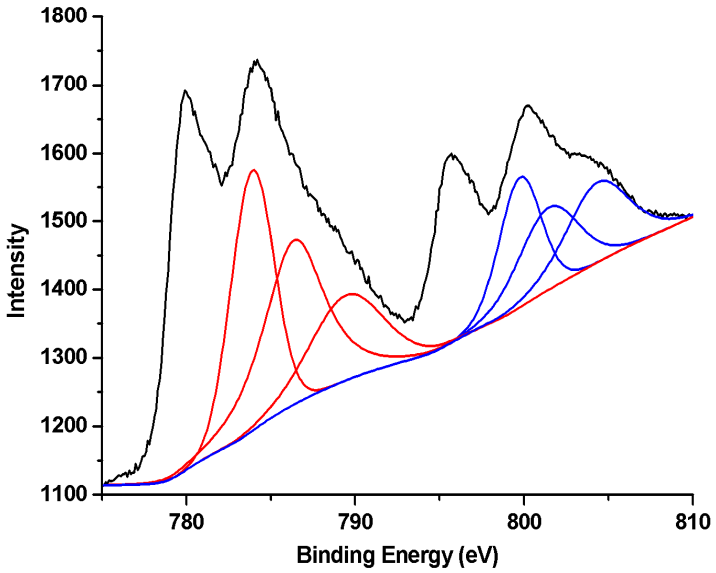

Fig. S10 XPS spectra of **SNU-15**. This has been measured to check if **SNU-15** contains both Co^{II} and Co^{III} metal species.

XPS signals of **SNU-15** and the related references

	$Co2p_{3/2}$		$Co2p_{1/2}$		ref
	Main peak (eV)	Satellite (eV)	Main peak(eV)	Satellite (eV)	
Co(II)	779.9	783.9 786.4 789.46	795.6	799.8 801.5 804.4	this work
Co(II)	780.6	786.2	796.6	802.3	S6
Co(II)	780.7	782.8 785.7 788.9	796.6	799.0 802.1 805.2	S7
Co(II)	781.0	783.0 785.8 788.9	796.7	799.1 802.1 805.2	S7
Co(II)	781.2	783.2 785.8 788.8	797.0	799.4 802.4 805.5	S7
Co(II)			796.6 794.8	802.3 804.3	S8
$Co(OH)_2$	781.0		-		S9

(S6) A. Foelske, H.-H. Strehblow, *Surf. Interface Anal.* 2000, **29**, 548-555.
(S7) T. Ivanova, A. Naumkin, A. Sidorov, I. Eremenko, M. Kiskin, *J. Electron Spectros. Relat. Phenom.* 2007, **156-158**, 200-203.
(S8) A. Kocijan, I. Milosev, B. Pihlar, *J. Mater. Sci.-Mater. Med.* 2004, **15**, 643-650.

(S9) J. Chastain, C. R. King, J. F. Moulder, *Handbook of x-ray photoelectron spectroscopy : a reference book of standard spectra for identification and interpretation of XPS data*; Physical Electronics, 1995.

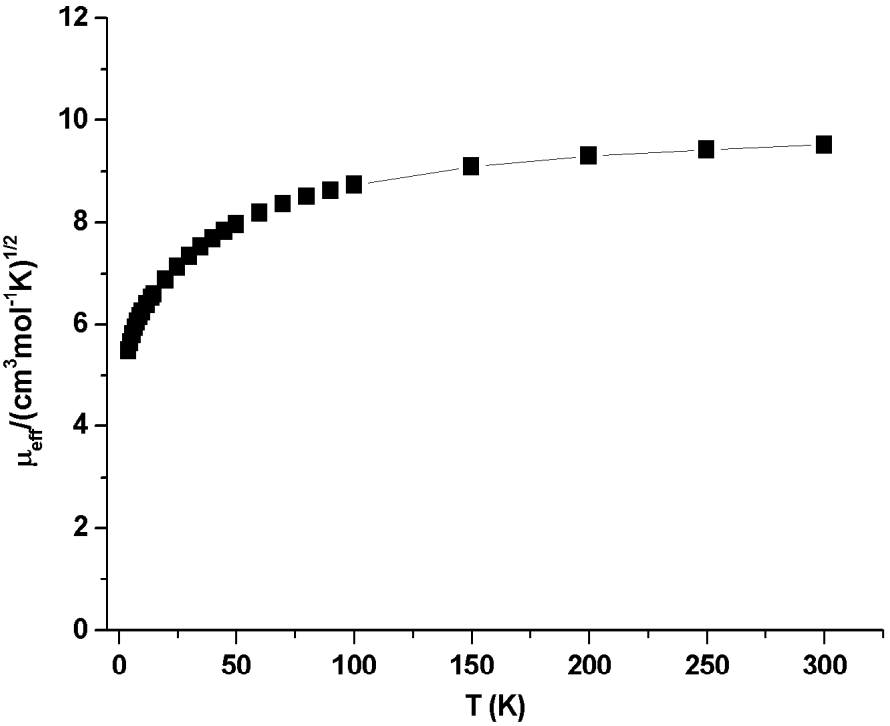

Fig. S11 Plot of μ_{eff} vs T for $[Co^{II}_4(\mu\text{-}OH_2)_4(MTB)_2]$ (**SNU-15'**). The measured values of μ_{eff} are in the range of 9.52 BM (300 K) – 5.64 BM (5 K), which are greater than the values for the magnetically dilute system of 4 Co^{II} with S = 3/2 (calcd. 7.75 BM) but smaller than the system with S = 6 (calcd. 13.0 BM).

Table S1. Crystallographic data for **SNU-15** [squeezed data for the guest solvent molecules]

empirical formula	$C_{58}H_{48}O_{24}Co_4$
crystal system	orthorhombic
pace group	*Pnnm*
fw	1364.00
a, Å	15.5094(4)
b, Å	17.8251(5)
c, Å	24.2210(7)
V Å^3	6696.1(3)
Z	2
ρ_{calc}, g/cm^3	0.677
temp, K	298(2)
λ, Å	0.71073
μ, mm^{-1}	0.523
goodness-of-fit (F^2)	0.846
F(000)	1392
reflection collected	14830
Independent reflections	7872 [R(int) = 0.0728]
data/parameters/restraints	7872 /203 /0
completeness to θ_{max} %	99.9
θ range for data collection (^{o})	1.42 – 27.50
diffraction limits (*h*, *k*, *l*)	$-20 \le h \le 20$, $-23 \le k \le 23$, $-31 \le l \le 31$
Refinement method	Full-matrix least-squares on F^2
R_1, wR_2 [$I>2\sigma(I)$]	0.0601[a], 0.1716[b]
R_1, wR_2 (all data)	0.1071[a], 0.1862[b]
largest peak and hole (e·Å^{-3})	0.458, -0.775

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1035P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Selected Bond Distances (Å) and Angles (°) for **SNU-15**

Co(1)-O(1)	2.079(2)	C(3)-C(4)	1.363(5)
Co(1)-O(3)	2.046(2)	C(4)-C(5)	1.396(4)
Co(1)-O(5)	2.219(3)	C(5)-C(6)	1.369(4)
Co(1)-O(6)	2.137(4)	C(5)-C(8)	1.546(4)
Co(2)-O(4)	2.046(3)	C(6)-C(7)	1.387(5)
Co(2)-O(5)	2.076(3)	C(8)-C(5)^{a}	1.546(4)
Co(2)-O(7)	2.101(4)	C(8)-C(13)	1.543(4)
Co(2)-O(8)	2.216(2)	C(9)-C(10)	1.509(5)
O(1)-C(1)	1.254(4)	C(10)-C(11)	1.345(4)
O(2)-C(1)	1.244(4)	C(10)-C(15)	1.382(5)
O(3)-C(9)	1.242(4)	C(11)-C(12)	1.364(4)
O(4)-C(9)	1.258(4)	C(12)-C(13)^{b}	1.384(4)
C(1)-C(2)	1.506(5)	C(13)-C(14)	1.402(4)
C(2)-C(3)	1.370(5)	C(14)-C(15)^{c}	1.393(5)
C(2)-C(7)	1.389(5)		
O(1)-Co(1)-O(1)^{d}	89.5(2)	C(1)-C(2)-C(3)	122.3(3)
O(1)-Co(1)-O(3)	88.9(1)	C(1)-C(2)-C(7)	120.2(3)
O(1)-Co(1)-O(3)^{d}	175.9(1)	C(2)-C(3)-C(4)	121.4(3)
O(1)-Co(1)-O(5)	91.13(9)	C(3)-C(4)-C(5)	122.0(3)
O(1)-Co(1)-O(6)	88.7(1)	C(4)-C(5)-C(6)	116.5(3)
O(3)-Co(1)-O(3)^{d}	92.5(2)	C(6)-C(5)-C(8)	122.9(3)
O(3)-Co(1)-O(5)	92.7(1)	C(4)-C(5)-C(8)	120.1(3)
O(3)-Co(1)-O(6)	87.6(1)	C(5)-C(6)-C(7)	121.7(3)
O(5)-Co(1)-O(6)	179.7(1)	C(2)-C(7)-C(6)	120.7(3)
O(4)-Co(2)-O(4)^{d}	102.7(2)	C(5)-C(8)-C(5)^{a}	102.8(3)
O(4)-Co(2)-O(5)	93.7(1)	C(5)-C(8)-C(13)	111.5(2)
O(4)-Co(2)-O(7)	88.1(1)	C(5)-C(8)-C(13)^{a}	114.5(2)
O(4)-Co(2)-O(8)	89.0(1)	C(13)-C(8)-C(13)^{a}	102.6(3)
O(4)^{d}-Co(2)-O(8)	166.7(1)	O(3)-C(9)-O(4)	126.7(3)
O(5)-Co(2)-O(7)	177.2(1)	O(3)-C(9)-C(10)	115.9(3)
O(5)-Co(2)-O(8)	91.9(1)	O(4)-C(9)-C(10)	117.3(3)
O(7)-Co(2)-O(8)	86.0(1)	C(11)-C(10)-C(15)	119.2(3)
O(8)-Co(2)-O(8)^{e}	78.7(1)	C(9)-C(10)-C(11)	119.8(3)
Co(1)-O(5)-Co(2)	111.4(1)	C(9)-C(10)-C(15)	120.9(3)
Co(1)-O(1)-C(1)	128.2(2)	C(10)-C(11)-C(12)	122.0(3)
Co(1)-O(3)-C(9)	136.7(2)	C(11)-C(12)-C(13)^{b}	121.6(3)
Co(2)-O(8)-Co(2)^{e}	101.3(1)	C(12)^{c}-C(13)-C(14)	116.4(3)
Co(2)-O(4)-C(9)	133.1(2)	C(8)-C(13)-C(12)^{c}	119.3(3)
O(1)-C(1)-O(2)	125.4(3)	C(8)-C(13)-C(14)	123.8(3)

O(2)-C(1)-C(2)	118.4(4)	C(13)-C(14)-C(15)[c]	121.2(3)
O(1)-C(1)-C(2)	116.2(4)	C(10)-C(15)-C(14)[b]	119.4(3)
C(3)-C(2)-C(7)	117.5(3)		

Symmetry relations: [a] -x+2,-y,z; [b] x-1/2,-y+1/2,-z+1/2; [c] x+1/2,-y+1/2,-z+1/2; [d] x,y,-z; [e] -x+2,-y+1,-z.

Table S3. Magnetic susceptibility data for **SNU-15'**

T/K	χ_M^{corr} T/cm^{3}mol^{-1}K
4.22551	3.729792
4.99833	3.938511
5.99869	4.173142
6.99914	4.36796
7.9988	4.537884
8.99947	4.689294
9.9994	4.82605
11.99486	5.057807
14.00121	5.295965
14.99716	5.401716
19.99723	5.883189
24.99542	6.305414
29.99974	6.682265
35.0024	7.020677
40.00504	7.325498
45.0064	7.600783
50.0201	7.853243
60.05363	8.30426
70.07859	8.667917
80.10724	8.976068
90.13922	9.240412
100.1615	9.474853
149.9949	10.27212
199.9969	10.73414
250.0208	11.03172
300.0421	11.24176