Electronic Supplementary Material (ESI) for CrystEngComm

Electronic Supplementary Information

A Novel Metal-Organic Framework Displaying Reversibly Shrinking and Expanding Pore Modulation

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Table 1 Crystal and Structure Refinement Data for **1** and **2**

	1	**2**
Empirical formula	$C_{30}H_{36}Co_2N_4O_{13}$	$C_{30}H_{30}Co_2N_4O_{10}$
Formula weight	778.44	724.44
Temperature *(K)*	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)*/c*	*P*2(1)*/c*
a (Å)	15.771(2)	14.36(2)
b (Å)	14.711(2)	14.75(2)
c (Å)	8.3852(12)	8.276(13)
a (°)	90°	90°
β (°)	102.485(2)°	99.746(19)°
γ (°)	90°	90°
Volume ($Å^3$)	1899.4(5)	1728(5)
Crystal size (mm)	0.25 x 0.21 x 0.19	0.24 x 0.18 x 0.11
Z	2	2
D_{calc} ($g \cdot cm^{-3}$)	1.267	1.392
μ (mm^{-1})	0.925	1.017
F(000)	744	744
θ range (°)	2.65 to 25.50	2.76 to 25.49
Reflections collected	14211	3151
Independent reflections	3533 [R(int) = 0.0321]	3151 [R(int) = 0.1270]
Data/restraints/parameters	3533 / 6 / 209	3151 / 0 / 209
Goodness-of-fit	1.091	1.040
Final *R* indices [$I>2\sigma(I)$]	R_1= 0.0339, ωR_2= 0.0931	R_1= 0.0804, ωR_2= 0.1734
R indices (all data)	R_1= 0.0418, ωR_2= 0.0968	R_1= 0.1424, ωR_2= 0.1915

Table S1 Selected bond lengths (Å) and angles (º) for **1** and **2**

1			
Co(1)-O(4)#1	2.0539(17)	Co(1)-O(3)#2	2.0548(18)
Co(1)-O(1)	2.0855(18)	Co(1)-N(1)	2.130(2)
Co(1)-N(2)	2.145(2)	Co(1)-O(5)	2.168(2)
O(4)#1-Co(1)-O(3)#2	94.95(7)	O(4)#1-Co(1)-O(1)	171.08(7)
O(3)#2-Co(1)-O(1)	93.85(7)	O(4)#1-Co(1)-N(1)	99.64(7)
O(3)#2-Co(1)-N(1)	95.02(7)	O(1)-Co(1)-N(1)	78.12(7)
O(1)#1-Zn(1)-N(4)	87.93(7)	O(1)-Zn(1)-N(4)	92.07(7)
O(4)#1-Co(1)-N(2)	89.90(8)	O(3)#2-Co(1)-N(2)	86.85(8)
O(1)-Co(1)-N(2)	92.03(8)	N(1)-Co(1)-N(2)	170.06(8)
O(4)#1-Co(1)-O(5)	83.82(7)	O(3)#2-Co(1)-O(5)	174.35(7)
O(1)-Co(1)-O(5)	87.56(7)	N(1)-Co(1)-O(5)	90.63(8)
N(2)-Co(1)-O(5)	87.63(8)		
2			
Co(1)-O(4)#1	2.050(5)	Co(1)-O(3)#2	2.079(6)
Co(1)-O(1)	2.085(5)	Co(1)-N(1)	2.129(5)
Co(1)-N(2)	2.148(6)	Co(1)-O(5)	2.160(5)
O(4)#1-Co(1)-O(3)#2	94.66(19)	O(4)#1-Co(1)-O(1)	171.9(2)
O(3)#2-Co(1)-O(1)	93.41(19)	O(4)#1-Co(1)-N(1)	100.4(2)
O(3)#2-Co(1)-N(1)	93.5(2)	O(1)-Co(1)-N(1)	78.12(19)
O(4)#1-Co(1)-N(2)	90.8(2)	O(3)#2-Co(1)-N(2)	86.4(2)
O(1)-Co(1)-N(2)	90.7(2)	N(1)-Co(1)-N(2)	168.8(2)
O(4)#1-Co(1)-O(5)	84.4(2)	O(3)#2-Co(1)-O(5)	174.16(17)
O(1)-Co(1)-O(5)	87.69(19)	N(1)-Co(1)-O(5)	92.3(2)
N(2)-Co(1)-O(5)	87.9(2)		

Symmetry codes for **1**: #1 -x+1, y-1/2, -z+3/2; #2 x, -y+1/2, z+1/2; #3 x, -y+1/2, z-1/2; #4 -x+1, y+1/2, -z+3/2; #5 -x, -y, -z+2; Symmetry codes for **2**: #1 -x+2, y+1/2, -z+1/2; #2 x, -y+3/2, z-1/2; #3 x, -y+3/2, z+1/2; #4 -x+2, y-1/2, -z+1/2; #5 -x+1,-y+2, -z-1.

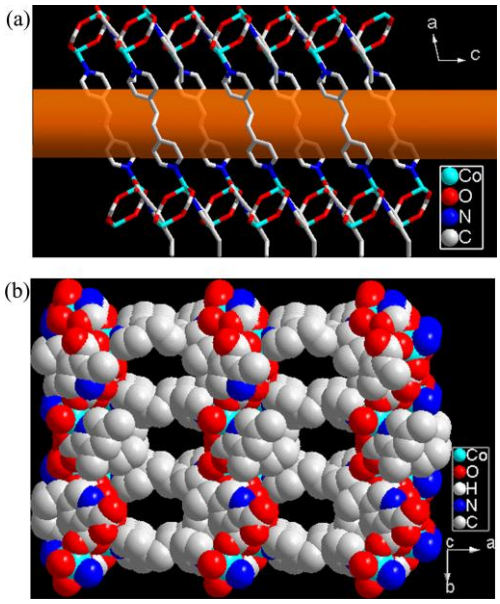

Fig. S1 (a) Side view of the 1D channel for **1.** (b) A space-filling view of the 3D microporous framework with approximately 25.2 % of solvent-accessible volume for **1**.

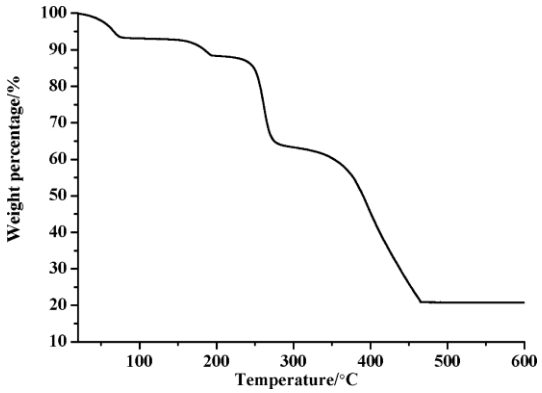

Fig. S2 TG curves for **1.**

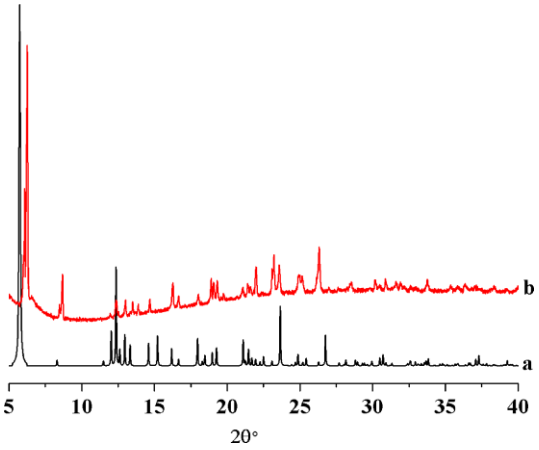

Fig. S3 XRPD patterns. (a) Simulated **1**. (b) Drying of **1** at 200 °C for 0.5 h.

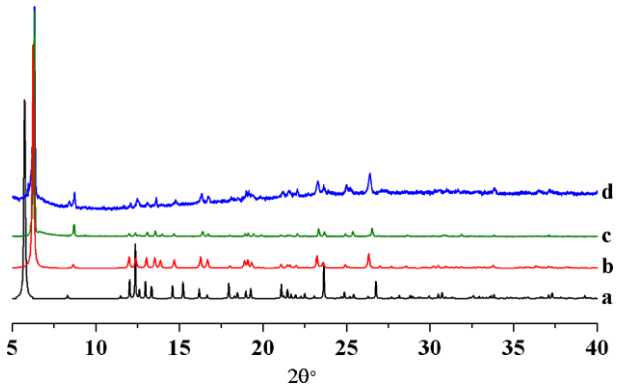

Fig. S4 XRPD patterns. (a) Simulated **1**. (b) Simulated **2**. (c) Drying of **1** in vacuo at 110 °C for 0.5 h (2). (d) **2** exposed to CH_3CH_2OH vapor.

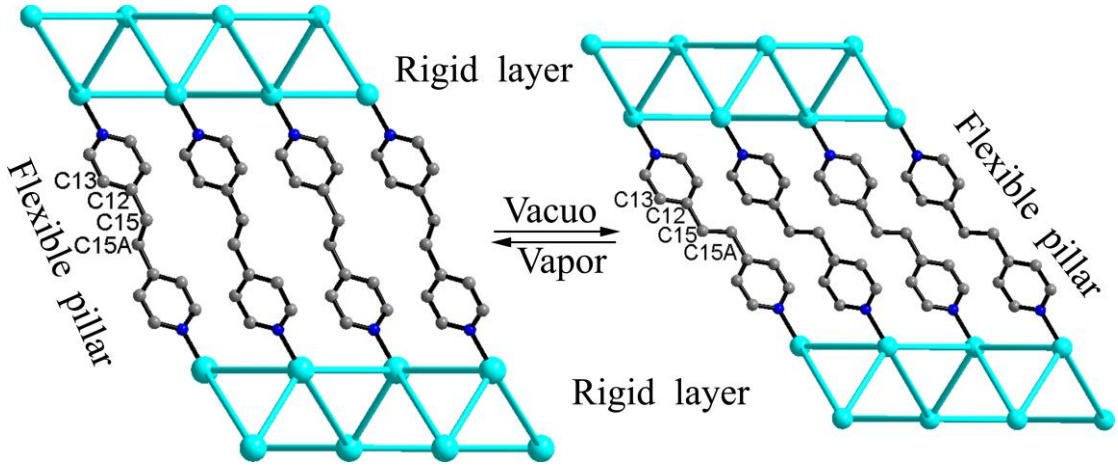

Fig. S5 Schematic representation of reversible transformations of **1** and **2** showing the torsion angle of bonds C13=C12-C15-C15A for bpa molecule to quantify the rotation of the C-C single bonds.

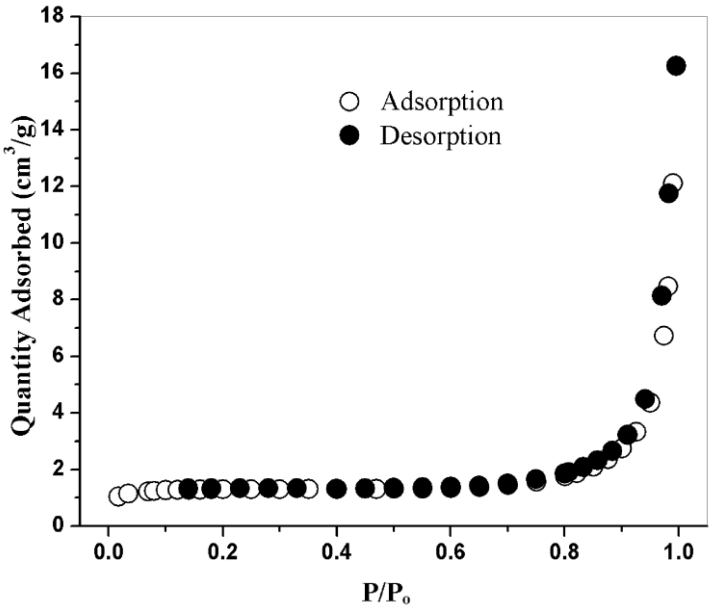

Fig. S6 N_2 adsorption isotherm for **1**.

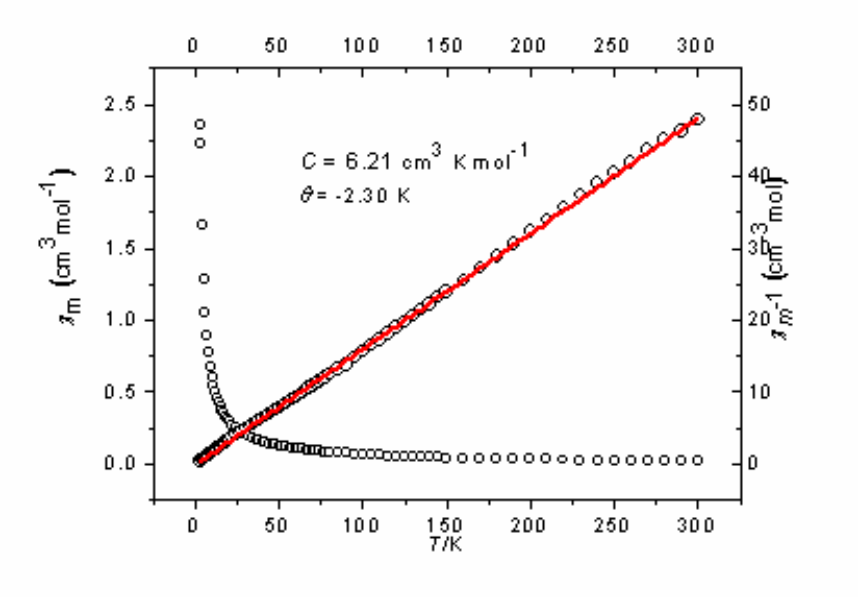

Fig. S7 Experiment temperature dependence of χ_M and χ_M^{-1} for **1**.