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Selective CO_2 adsorption and theoretical simulation of a stable Co(II)-based metal-organic framework with tunable crystal size

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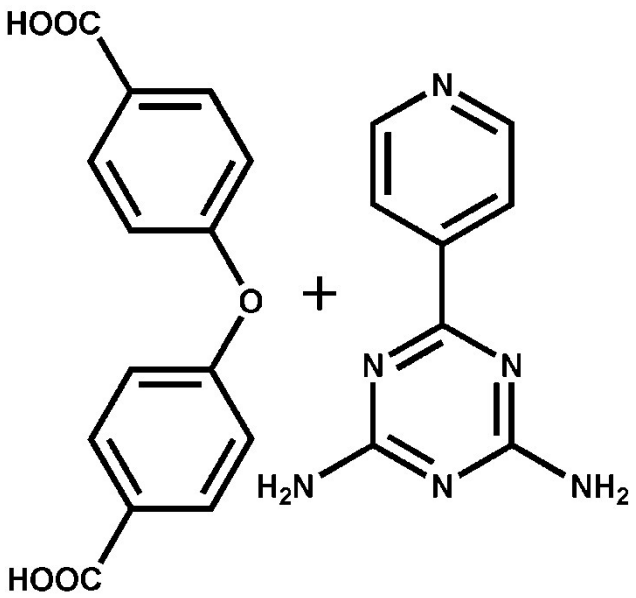

Scheme S1. The H_2OBA ligand (left) and PTD ligand (right).

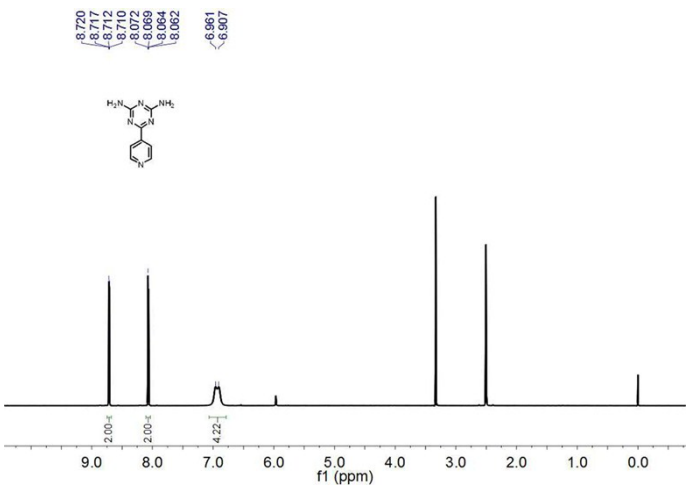

Fig. S1 The ^{1}H NMR spectrum of PTD ligand.

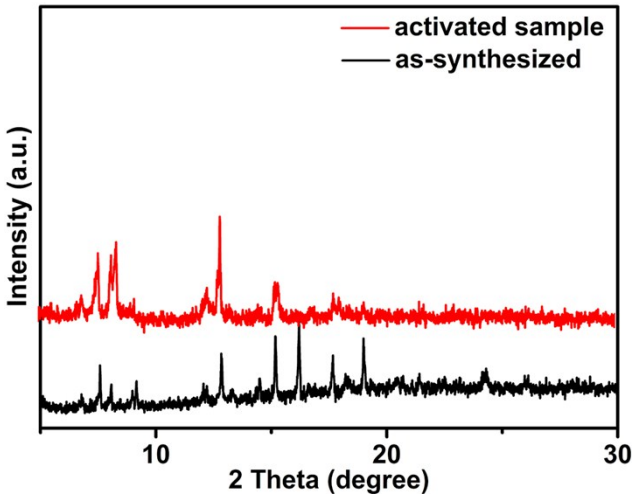

Fig. S2 PXRD patterns of complex **1** activated by acetone at 175^{o}C in vacuum.

Table S1. Crystallographic data for compound **1**.

Compound	Compound **1**
empirical formula	$C_{75}H_{77}N_9O_{29}Co_2$
formula weight	1686.22
T [K]	293(2)
crystal system	orthorhombic
space group	*Fdd*2
a [Å]	39.377
b [Å]	43.654
c [Å]	38.551
α [°]	90.00
β [°]	90.00
γ [°]	90.00
V	66267.80
Z	16
ρ_{calcd} [g cm^{-3}]	0.984
μ [mm^{-1}]	0.644
F(000)	19968
reflections collected	110280
independent reflections	27283
GOF	1.001
R_1,[a] $I > 2\sigma(I)$	0.0489
wR_2,[b] $I > 2\sigma(I)$	0.1484

[a] $R_1 = \sum(||F_0| - |F_c||)/\sum|F_0|$. [b] $wR_2 = [\sum w(|F_0|^2 - |F_c|^2)^2/\sum w(F_0^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and bond angles (°) for complex **1**.

Co(1)-O(16)	1.990(5)	Co(2)-O(2)	2.049(5)	Co(3)-O(19)	2.116(6)
Co(1)-O(7)	2.001(5)	Co(2)-O(17)	2.079(5)	Co(4)-O(4)#2	2.012(5)
Co(1)-O(1)	2.019(5)	Co(2)-N(1)	2.117(5)	Co(4)-O(20)	2.014(6)
Co(1)-O(12)	2.073(5)	Co(3)-O(10)	2.020(5)	Co(4)-O(14)#3	2.029(5)
Co(1)-N(6)#1	2.101(5)	Co(3)-O(5)#2	2.031(5)	Co(4)-O(9)	2.072(5)
Co(2)-O(11)	2.015(5)	Co(3)-O(15)#3	2.034(5)	Co(4)-N(12)#4	2.074(5)
Co(2)-O(6)	2.021(5)	Co(3)-N(7)	2.115(5)		
O(16)-Co(1)-O(7)		163.9(2)	O(10)-Co(3)-O(5)#2		91.2(2)
O(16)-Co(1)-O(11)		91.6(3)	O(10)-Co(3)-O(15)#3		94.0(2)
O(7)-Co(1)-O(1)		89.9(3)	O(5)#2-Co(3)-O(15)#3		159.06(19)
O(16)-Co(1)-O(12)		87.2(2)	O(10)-Co(3)-N(7)		100.3(2)
O(7)-Co(1)-O(12)		86.6(3)	O(5)#2-Co(3)-N(7)		99.0(2)
O(1)-Co(1)-O(12)		162.2(2)	O(15)#3-Co(3)-N(7)		100.0(2)
O(16)-Co(1)-N(6)#1		100.9(2)	O(10)-Co(3)-O(19)		163.4(2)
O(7)-Co(1)-N(6)#1		94.5(2)	O(5)#2-Co(3)-O(19)		85.6(2)
O(1)-Co(1)-N(6)#1		102.1(2)	O(15)#3-Co(3)-O(19)		83.7(2)
O(12)-Co(1)-N(6)#1		95.6(2)	N(7)-Co(3)-O(19)		96.3(3)
O(11)-Co(2)-O(6)		89.9(2)	O(4)#2-Co(4)-O(20)		92.7(2)
O(11)-Co(2)-O(2)		162.8(2)	O(4)#2-Co(4)-O(14)#3		166.3(2)
O(6)-Co(2)-O(2)		88.7(2)	O(20)-Co(4)-O(14)#3		88.3(2)
O(11)-Co(2)-O(17)		90.2(2)	O(4)#2-Co(4)-O(9)		86.6(2)
O(6)-Co(2)-O(17)		161.9(2)	O(20)-Co(4)-O(9)		161.0(2)
O(2)-Co(2)-O(17)		85.9(2)	O(14)#3-Co(4)-O(9)		88.1(2)
O(11)-Co(2)-N(1)		101.7(2)	O(4)#2-Co(4)-N(12)#4		96.5(2)
O(6)-Co(2)-N(1)		101.3(2)	O(20)-Co(4)-N(12)#4		105.1(2)
O(2)-Co(2)-N(1)		95.5(2)	O(14)#3-Co(4)-N(12)#4		96.5(2)
O(17)-Co(2)-N(1)		96.4(2)	O(9)-Co(4)-N(12)#4		93.8(2)

Symmetry codes: #1: x+1/4, -y+7/4, z-1/4; #2: x+1/4, -y+5/4, z+1/4; #3: x-1/4, -y+7/4, z+1/4; #4: x-1/4, -y+5/4, z-1/4

Table S3. The elemental analyses (C, H, N) of as-synthesized and desolvated compound **1**, respectively.

Elements	C (%)	H (%)	N (%)
as-synthesized compound **1**	52.94	4.23	7.65
desolvated compound **1**	57.18	3.12	5.98

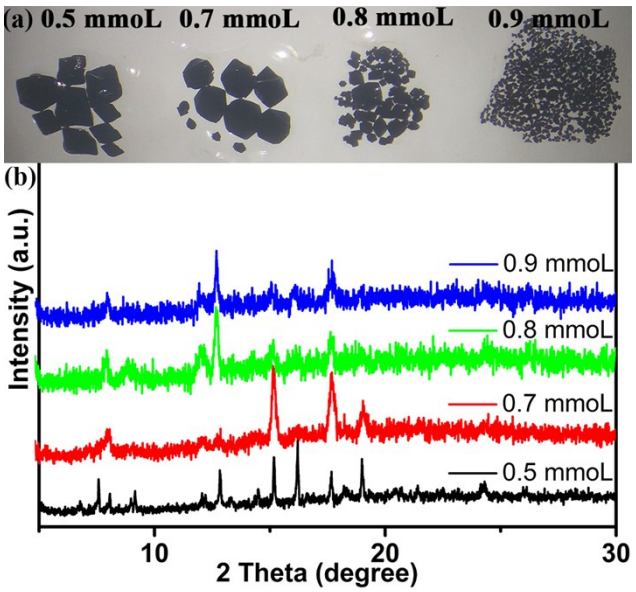

Fig. S3 (a) In the same lens, the photographic plates of compound **1** synthesized by using different molar PTD ligands; (b) PXRD patterns of complex **1** with different crystal size, which is constructed by changing the amounts of PTD added.

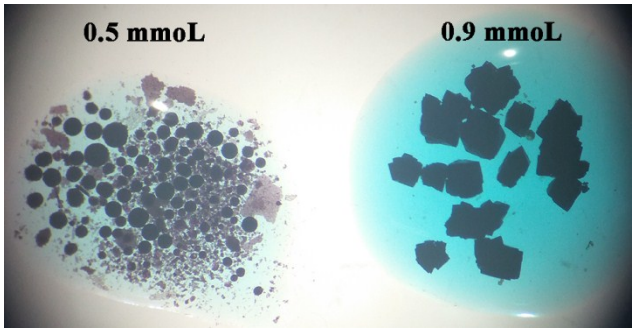

Fig. S4 In the same lens, the photographic plates of reaction product through using different molar PTD ligands at 120°C for only 6 h.

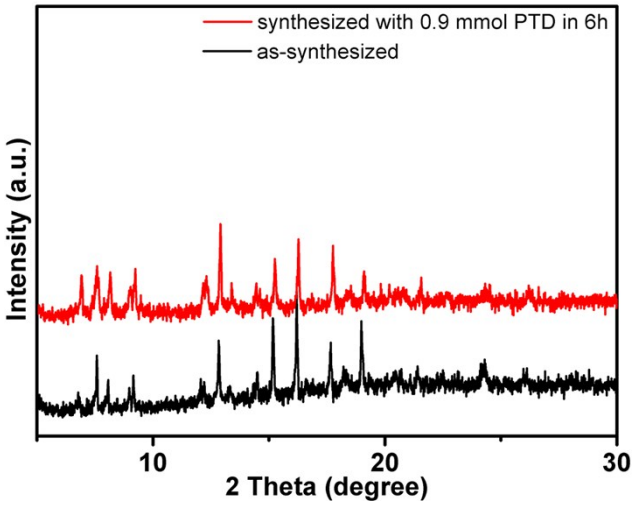

Fig. S5 PXRD patterns of as-synthesized compound **1** and compound synthesized with 0.9 mmol PTD in 6h. The excellent matching suggests that two compounds are

isostructural.

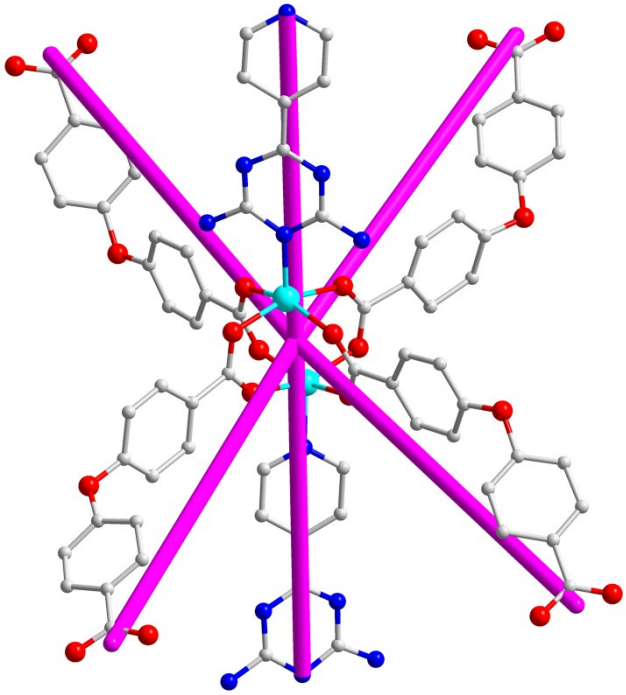

Fig. S6 The $Co_2O_8N_2$ paddle-wheel SBU and its topological structure.

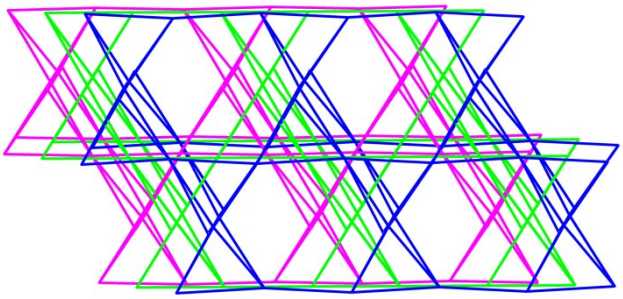

Fig. S7 Schematic illustration of the three-fold parallel interpenetrated topology.

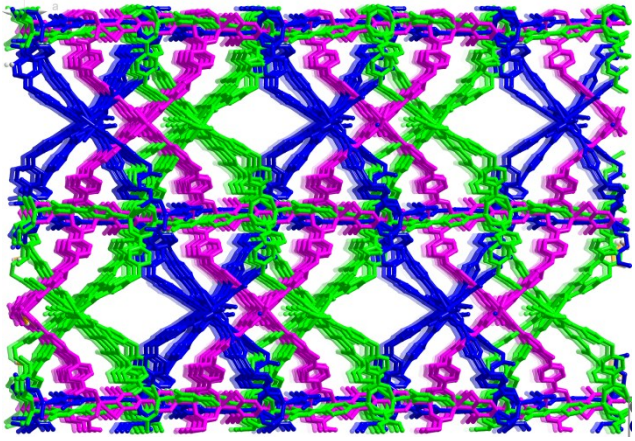

Fig. S8 The 3D interpenetrated framework of compound **1**, showing the 1D channels.

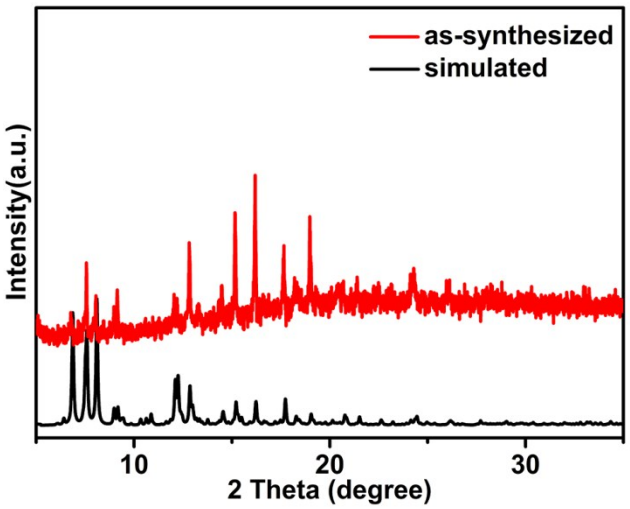

Fig. S9 PXRD spectra of complex **1**.

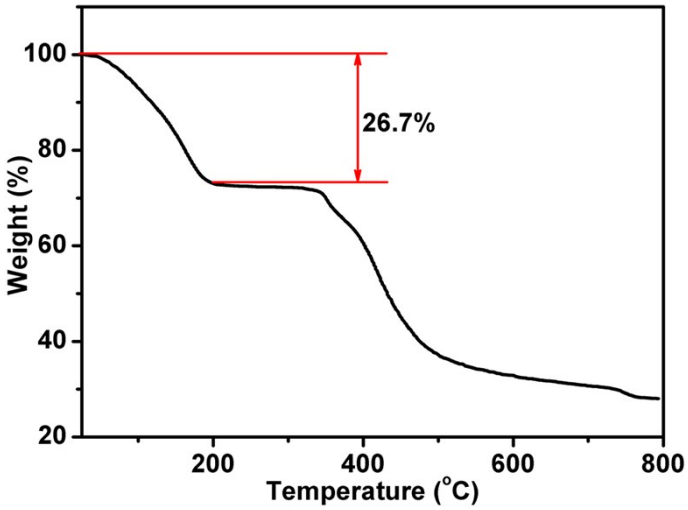

Fig. S10 TGA curve of complex **1**.

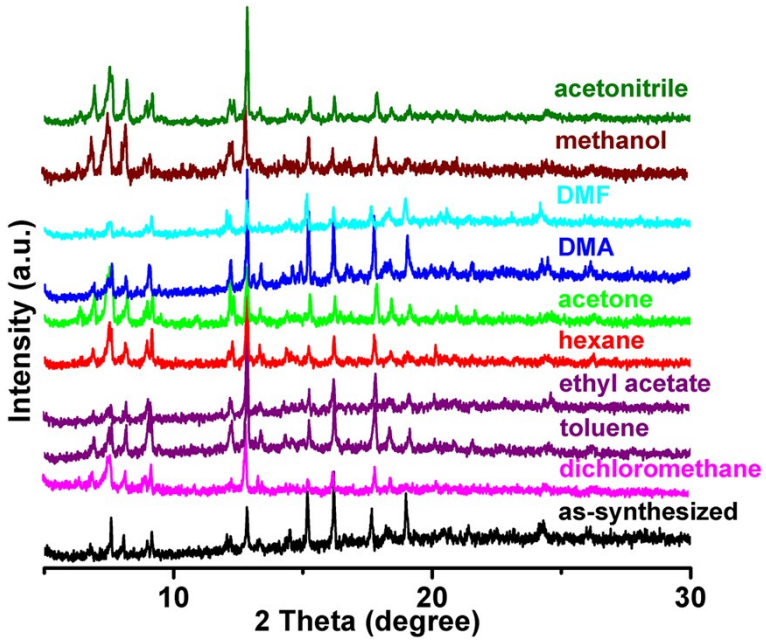

Fig. S11 PXRD patterns of complex 1 dispersed in different boiling organic solvents.

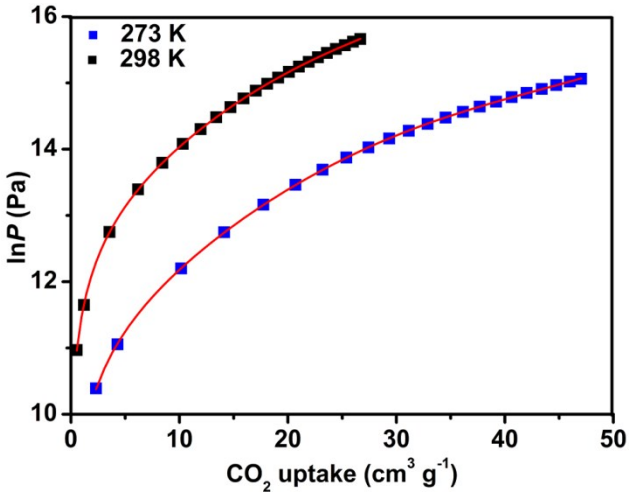

Fig. S12 Virial analyses of the CO_2 adsorption data at 273 and 298 K for compound **1**. Fitting results: a_0 = -5410.822, a_1 = 55.02785, a_2 = -8.65607, a_3 = 0.58575, a_4 = -0.01225, Chi^2 = 0.00004, R^2 = 0.99998.