Supporting Information

Investigation of the Effect of Pore Size on Gas Uptake in Two *fsc* Metal-Organic Frameworks

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Materials and Methods

All of the reagents and solvents employed were commercially available and used as received without further purification. Elemental analysis was carried out on a CE instruments EA 1110 elemental analyzer. X-ray powder diffractions were measured on a Bruker AXS D8 Advance with Cu K_α (λ = 1.5418 Å, 40.0 kV, 30.0 mA) radiation. Gas sorption experiments were carried out on the surface area analyzer ASAP-2020. The intensity data of **1** and **2** were collected at 150 K on an Agilent Xcalibur Eos Gemini diffractometer with Enhance (Cu) X-ray Source (Cu-Kα, λ = 1.54178 Å). Thermogravimetric analysis (TGA) was carried out in a static N_2 with a heating rate of 10 °C/min.

Preparation of 1

H_4BPTC (8 mg, 0.025 mmol), $Co(NO_3)_2•6H_2O$ (58.2 mg, 0.2 mmol), pyrazine (16 mg, 0.2 mmol), KOH (1.5 ml, 0.1 M) and DMF-C_2H_5OH-H_2O (15 ml, 1:1:1) were added to a small vial, which was sealed and put into a programmed oven, slowly heated to 80℃ from room temperature in 300 minutes, kept at 80℃ for 4320 min. After slowly cooled to 30℃ in 500 minutes, light red block crystals of **1** were separated in 81% yield based on ligand H_4BPTC. Elemental analysis: Anal. Calc.: C 44.26, H 6.12, N 9.11 %. Found: C 43.41, H 5.88, N 9.12 %.

Preparation of 2

A mixture of $Co(NO_3)_2•6H_2O$ (2.9 mg, 0.01 mmol), H_4BPTC (1 mg, 0.003 mmol), 4,4'-bipy (1.6 mg, 0.01 mmol), HCl (0.2 ml, 0.5 M) in DMF-C_2H_5OH-H_2O (1 ml, 4:1:1) were sealed in a pressure-resistant glass tube and put into a programmed oven, slowly heated to 120℃ from room temperature in 500 minutes, kept at 120℃ for 4320 min, After slowly cooled to 30℃ in 800 minutes, light red block crystals of **2** were separated in 73% yield based on ligand H_4BPTC. Elemental analysis: Anal. Calc.: C 47.82, H 5.73, N 9.11 %. Found: C 47.37, H 4.88, N 8.99 %.

X-ray Crystallography

The intensity data of **1** and **2** were collected at 150 K on an Agilent Xcalibur Eos Gemini diffractometer with Enhance (Cu) X-ray Source (Cu-Kα, λ = 1.54178 Å). Absorption corrections were applied by using the multi-scan method. Data were integrated and corrected for Lorentz, polarization, and absorption effects. Space group determinations were made based on systematic absences, E statistics, and successful refinement of the structure. Structures were solved by direct method and refined by full-matrix least-squares on F^2 using *SHELXTL* [S1-3]. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 or 1.5 × U_{eq} of the attached atom. For **1**, the solvent accessible void volumes in the crystals are occupied by disordered DMF, EtOH and water molecules. No satisfactory disorder model could be achieved, and therefore *PLATON/SQUEEZE* routine [S4] was used to remove these electron densities. Crystal and refinement parameters are listed in Table S1. CCDC No. 981845, 981846 for **1** and **2**.

References

[S1] R.H. Blessing, Acta. Crystallogr. 1995, A51, 33.

[S2] G.M. Sheldrick, *SHELXS 97: Program for Crystal Structure Solution,* University of Göttingen: Göttingen, Germany, 1997.

[S3] G.M. Sheldrick, *SHELXL 97: Program for Crystal Structure refinement,* University of Göttingen: Göttingen, Germany, 1997.

[S4] Spek, A. *J. Appl. Crystallogr.* 2003, 36, 7-13.

Table S1. Crystallographic Data for 1 and 2

Complexes	**1**	**2**
Formula	$C_{12}H_7CoN_2O_4$	$C_{18}H_{11}CoN_2O_4$
M_r	302.13	378.22
Crystal system	orthorhombic	monoclinic
Space group	Pbam	$P2_1/c$
a (Å)	13.2606(15)	11.3988(2)
b (Å)	17.5002(17)	17.3695(2)
c (Å)	7.1051(11)	13.24337(19)
α (deg)	90	90
β (deg)	90	92.4376(15)
γ (deg)	90	90
Z	4	4
V (Å^3)	1648.8(4)	2619.71(7)
D_c(g cm^{-3})	1.217	0.959
μ(mm^{-1})	8.259	5.281
F(000)	608	768
no. of unique reflns	1601	4680
no. of obsd reflns[I > 2σ(I)]	4871	18500
Parameters	106	226
GOF	1.078	1.085
Final R indices [I > 2σ(I)][a,b]	R_1 = 0.0768, wR_2 = 0.2564	R_1 = 0.0725, wR_2 = 0.2031
R indices (all data)	R_1 = 0.0885, wR_2 = 0.2708	R_1 = 0.0786, wR_2 = 0.2087
Δρ (e Å^{-3})	0.558 and -0.852	1.659 and -1.202

Fig. S1: TGA curve of 1

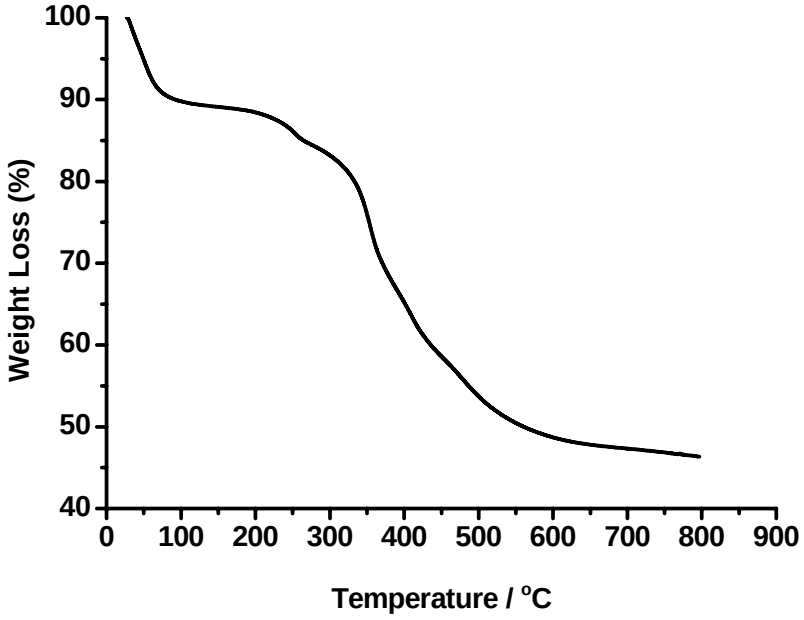

Fig. S2: TGA curve of 2

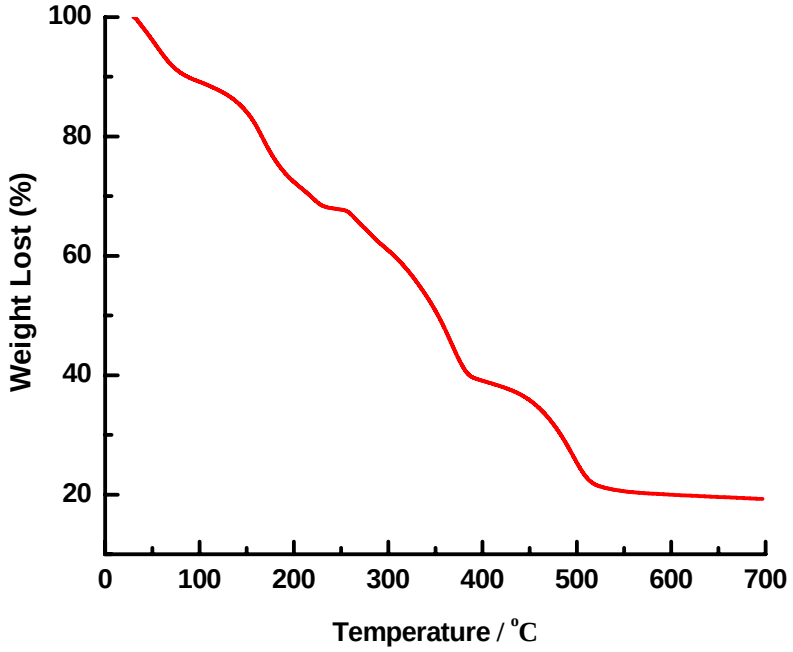

Fig. S3: XRD of 1

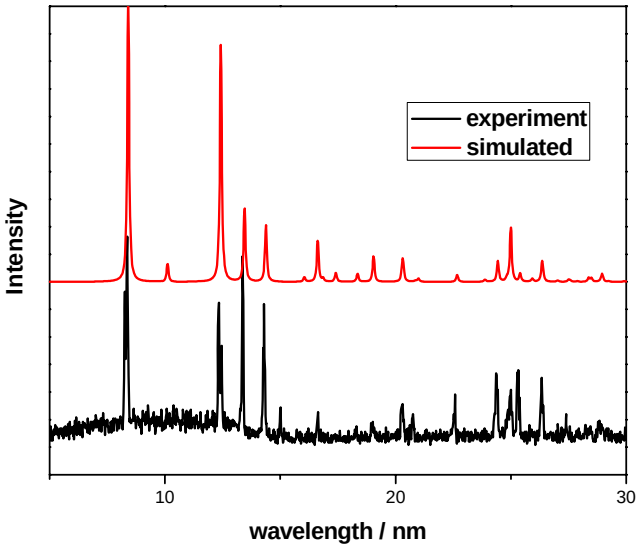

Fig. S4: XRD of 2