

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} ($\lambda = 1.5418 \text{ \AA}$, 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- K_{α} , $\lambda = 1.54178 \text{ \AA}$). Thermogravimetric analysis (TGA) was carried out in a static N_2 with a heating rate of 10 °C/min.

Preparation of **1**

H₄BPTC (8 mg, 0.025 mmol), Co(NO₃)₂•6H₂O (58.2 mg, 0.2 mmol), pyrazine (16 mg, 0.2 mmol), KOH (1.5 ml, 0.1 M) and DMF-C₂H₅OH-H₂O (15 ml, 1:1:1) were added to a small vial, which was sealed and put into a programmed oven, slowly heated to 80°C from room temperature in 300 minutes, kept at 80°C for 4320 min. After slowly cooled to 30°C in 500 minutes, light red block crystals of **1** were separated in 81% yield based on ligand H₄BPTC. 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(NO₃)₂•6H₂O (2.9 mg, 0.01 mmol), H₄BPTC (1 mg, 0.003 mmol), 4,4'-bipy (1.6 mg, 0.01 mmol), HCl (0.2 ml, 0.5 M) in DMF-C₂H₅OH-H₂O (1 ml, 4:1:1) were sealed in a pressure-resistant glass tube and put into a programmed oven, slowly heated to 120°C from room temperature in 500 minutes, kept at 120°C for 4320 min, After slowly cooled to 30°C in 800 minutes, light red block crystals of **2** were separated in 73% yield based on ligand H₄BPTC. 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-K α , $\lambda = 1.54178$ 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 $1.5 \times U_{\text{eq}}$ 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 ₇ CoN ₂ O ₄	C ₁₈ H ₁₁ CoN ₂ O 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 [$I > 2\sigma(I)$]	4871	18500
Parameters	106	226
GOF	1.078	1.085
Final R indices [$I > 2\sigma(I)$] ^{a,b}	$R_1 = 0.0768,$ $wR_2 = 0.2564$	$R_1 = 0.0725,$ $wR_2 = 0.2031$
R indices (all data)	$R_1 = 0.0885,$ $wR_2 = 0.2708$	$R_1 = 0.0786,$ $wR_2 = 0.2087$
$\Delta\rho$ (e Å ⁻³)	0.558 and -0.852	1.659 and -1.202

Fig. S1: TGA curve of 1

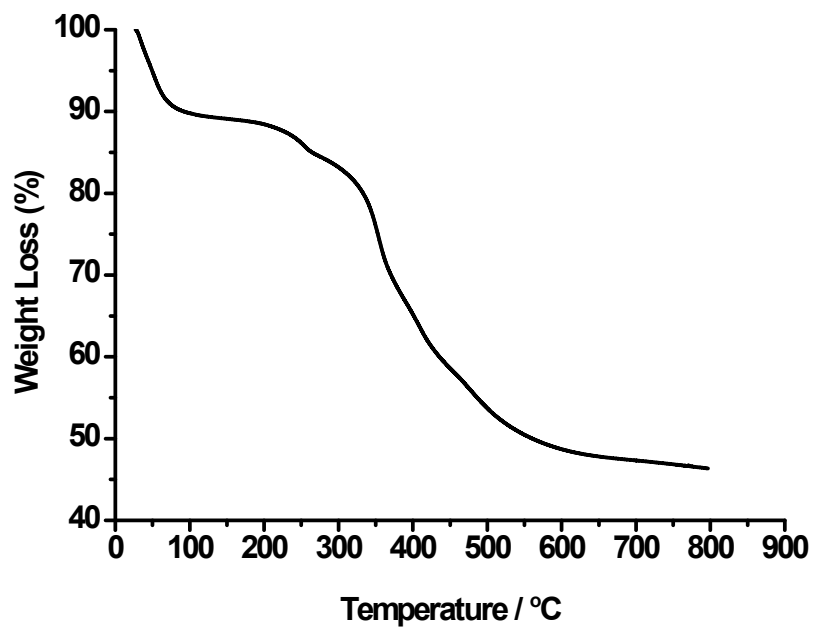


Fig. S2: TGA curve of 2

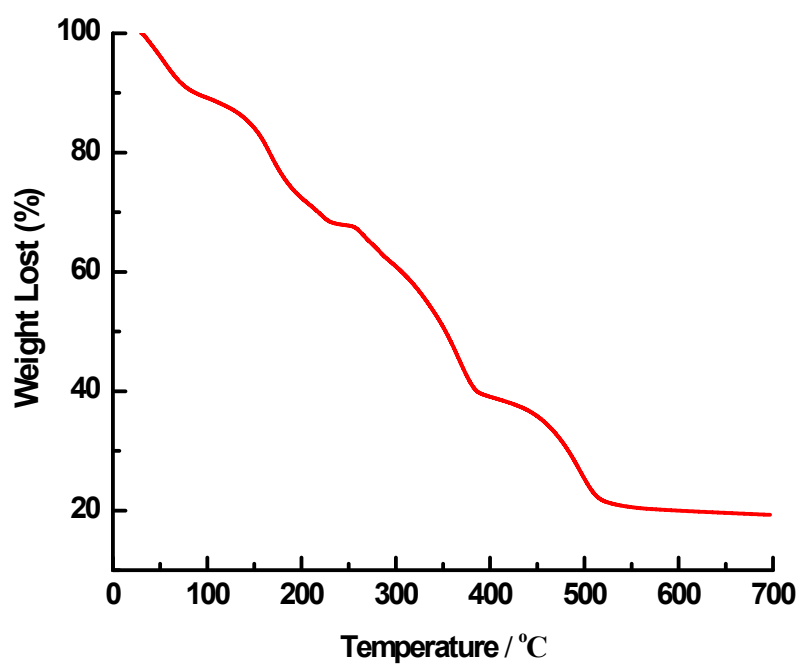


Fig. S3: XRD of 1

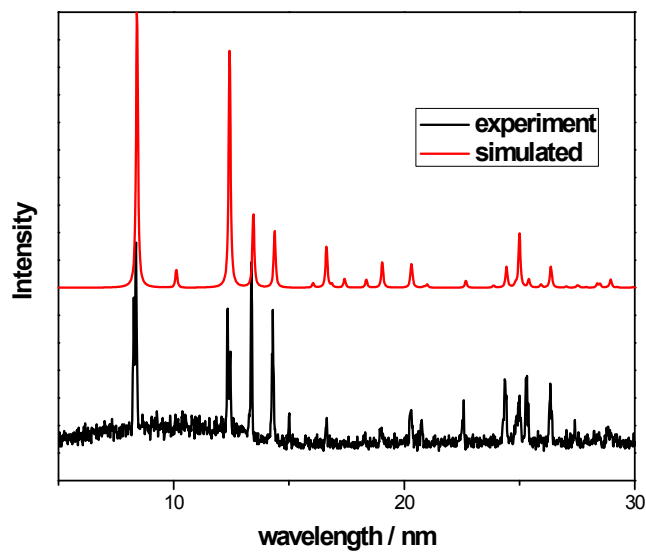


Fig. S4: XRD of 2

