Supporting Information

A Doubly Interpenetrated Metal-Organic Framework of pcu Topology for Selective Separation of Propylene from Propane

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SYNTHESIS OF LIGANDS

Synthesis of 2,5-bis(4-pyridyl) thiazolo-[5,4-*d*] thiazole (Py_2TTz). A mixture of dithiooxamide (1 g, 8.3 mmol) and 4-pyridinecarboxaldehyde (2 mL, 22 mmol) were added into 50mL anhydrous DMF. The obtained reaction mixture was refluxed for 8h at 155 ^{o}C. After cooling overnight, a yellow crystalline product was obtained, which was filtered, washed with water, and dried in air (1.48 g, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (d, J = 6.0 Hz, 2H), 7.88 (d, J = 6.4 Hz, 4H).

Synthesis of 2-chloro-1,4-benzenedicarboxylic acid (2-Cl-H_2BDC). A mixture of 3-chloro-4-methylbenzoic acid (1 g, 6.5 mmol) and potassium permanganate (3.16g, 19.8mmol) was dissolved in 30 mL aqueous potassium hydroxide solution (KOH, 5%). The resultant solution was refluxed overnight at 110 ^{o}C. After cooling to room temperature,

the black precipitate was removed through filtration. The obtained colorless filtrate was acidified with concentrated hydrochloric acid to pH 1 to get the white precipitate of 2-Cl-H_2BDC, which was then collected by filtration, washed with water, and dried in air at 80 ^oC (0.71g, 54% yield).

SUPPLEMENTAL TABLE AND FIGURES

Table S1. Crystallographic and Refinement Parameters for **1**

Crystal data	1
Molecular formula[a]	$C_{30}H_{13}Cl_2N_4O_8S_2Zn_2$

Formula weight[a]	823.20
Temperature/K	273.15
Crystal system	Triclinic
Space group	*P*-1
a/Å	10.8529(7)
b/Å	10.9058(6)
c/Å	19.7841(11)
α/°	91.038(2)
β/°	97.961(2)
γ/°	104.293(3)
Volume/Å^3	2243.9(2)
Z	2
ρ_{calc} g/cm^3	1.218
Solvent-accesible void space[b]/ %	34.9
Theoretical pore volume[b]/ cm^3/g	0.287
μ/mm^{-1}	1.322
F(000)	822
Crystal size/mm^3	0.04 × 0.02 × 0.02
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	3.958 to 65.896
Index ranges	-16 ⩽ h ⩽ 16, -16 ⩽ k ⩽ 16, -29 ⩽ l ⩽ 29
Reflections collected	9976
Goodness-of-fit on F^2	0.738
Final R indexes [I>=2σ (I)]	R_1 = 0.0632, wR_2 = 0.1855[c]
CCDC no.	2016038

[a]Molecular formula and formula weight were calculated based on the crystal structure without guest molecules. [b]Calculation based on the crystal structure using PLATON software. [c]$R_1 = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$ $wR_2 = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0^2)]^{1/2}$.

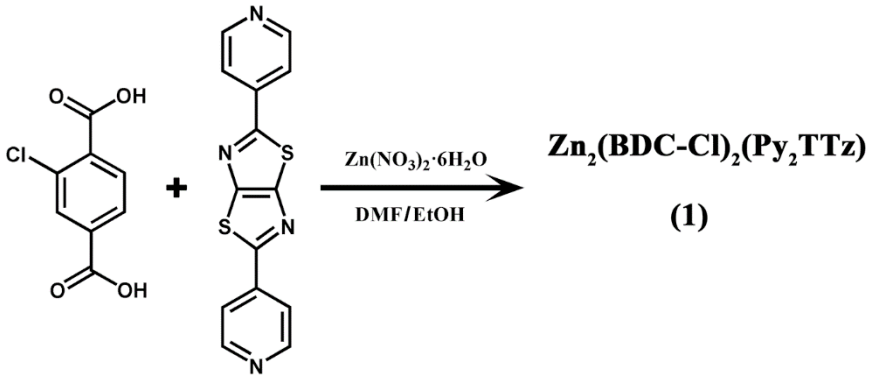

Figure S1. Schematic synthesis of 1.

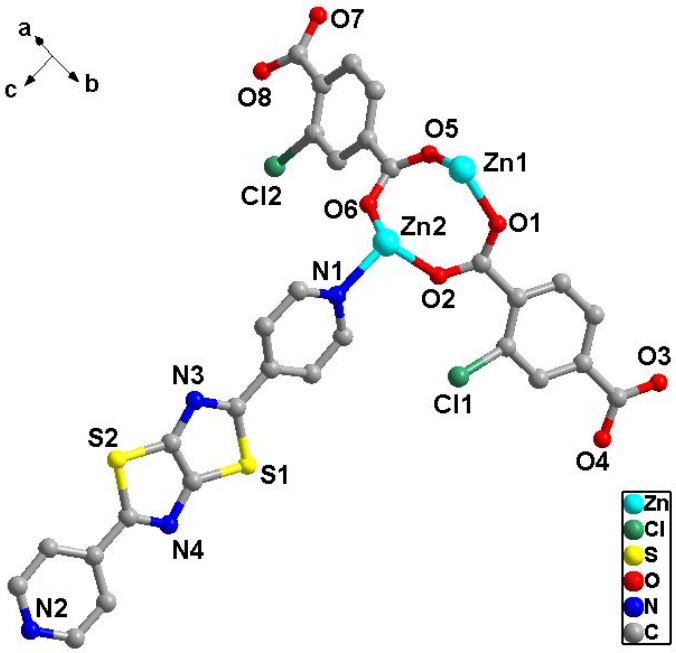

Figure S2. The asymmetric unit of 1.

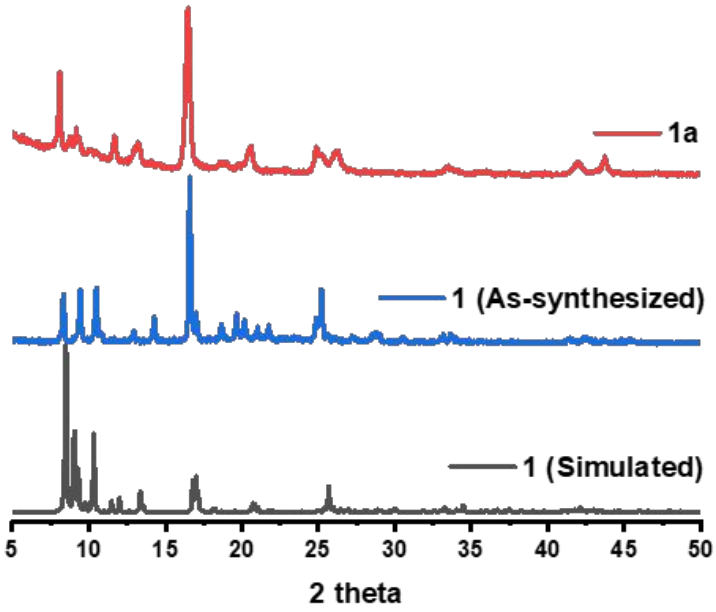

Figure S3. Powder x-ray diffraction of **1** and **1a**.

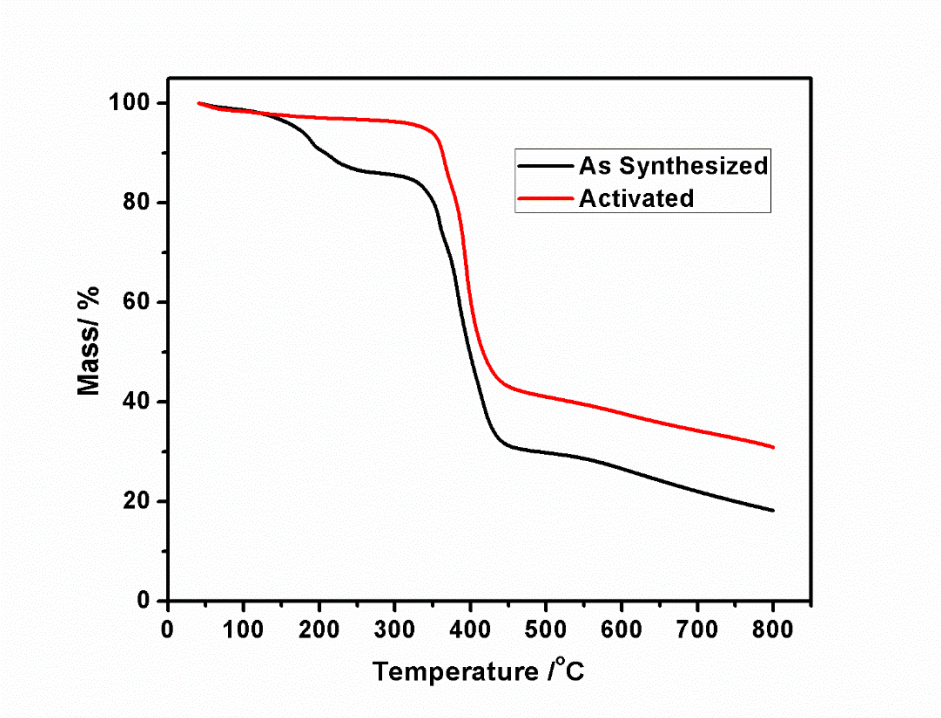

Figure S4. TGA of **1** and **1a**.

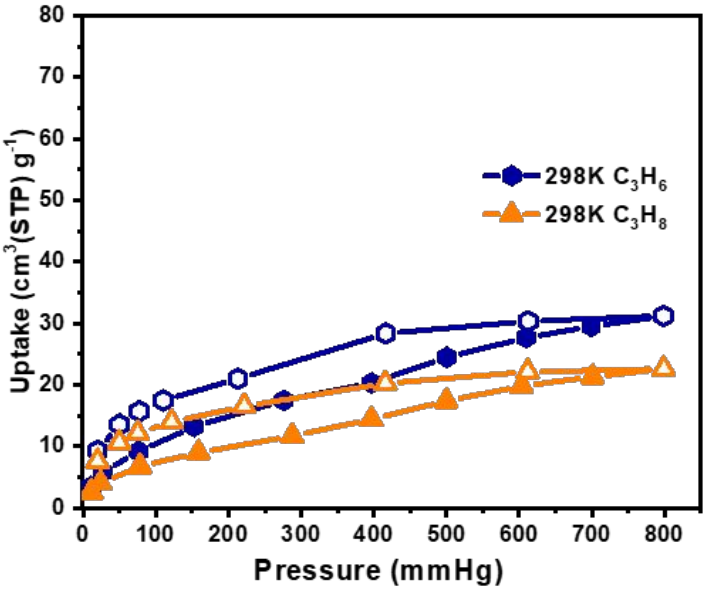

Figure S5. C_3H_6 and C_3H_8 adsorption isotherms of **1a** at 298 K.

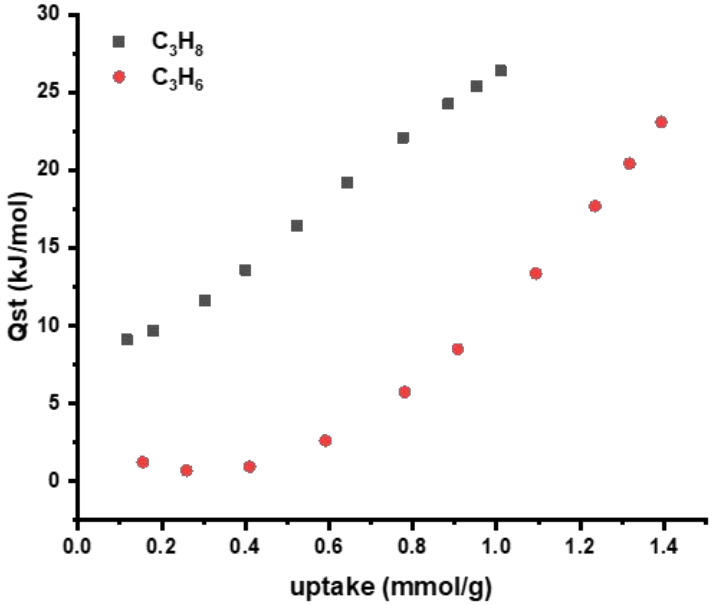

Figure S6. Heat of adsorption for C_3H_6 and C_3H_8.