Zeolitic Imidazolate Frameworks Capable of Kinetic Separation of Propane and Propene

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Supporting Information

1. Synthesis of 2-chloroimidazole (2-cim)

To a 300-mL, three-neck, round-bottom flask equipped with a magnetic stirrer and argon inlet, were added *N*-tritylimidazole (3.14 g, 0.01 mol) and anhydrous THF (140 mL). The stirrer was started, and the solution was cooled to -78 °C (acetone/dry ice). *n*-BuLi (2.5 M in hexanes, 8.0 mL, 0.02 mol) was added via syringe resulting in reddish solution. This solution was stirred for 60 min whereupon hexachloroethane (5.0 g, 0.021mol) in THF (25 mL) was added in portions. The reaction mixture was stirred for 1 additional hour and then quenched with saturated aqueous ammonium chloride (100 mL). The cooling bath was removed, and when the reaction flask reached room temperature the contents were transferred to a 500 mL separatory funnel, extraced with ethyl acetate (50 mL × 2). The organic layer was separated, washed with water and brine, and dried over anhydrous sodium sulfate. After filtration, the solvents were evaporated under reduced pressure resulting in a slightly yellow solid. The solid was refluxed with 5% acetic acid in methanol (75 mL) for 24 hours. Upon evaporation of the solvent, water was added to the residue. Extraction with hexanes effectively removed the triphenylmethane impurity. Evaporation of water *in vacuo* afforded off-white solid as pure 2-chloroimidazole (2-cim, 0.70 g, 69% overall yield from *N*-triylimidazole).

2. Crystal growth of 1-3

Zinc nitrate hexahydrate (120 mg, 0.4 mmol) and 2-cim (108 mg, 1 mmol) were added to methanol (4 mL) in a glass vial. The mixture was homogenized by sonication for 2 minutes. Then the vial was capped and placed into 100 °C oven for 2 days. Colorless polyhedral crystals of **1** were obtained (42 mg). Similarly, crystals of **2** (55 mg) were

obtained by reacting zinc nitrate hexahydrate (121 mg, 0.4 mmol) and 2-bim (120 mg, 0.8 mmol) in ethanol (95%, 4 mL) for 2 days.

To a mixture of 2-methylimidazole (0.20g, 2.5 mmol) and zinc nitrate hexhydrate (0.35g, 1.2 mmol) in a glass vial was added *N*,*N*-dimethylformamide (DMF, 15 mL). Three drops of concentrated nitric acid was added to the suspension to obtain a clear solution. The vial was capped and placed in an isothermal oven at 120 °C for 2 days. Big polyhedral crystals were obtained (40 mg, see **Figure S1**).

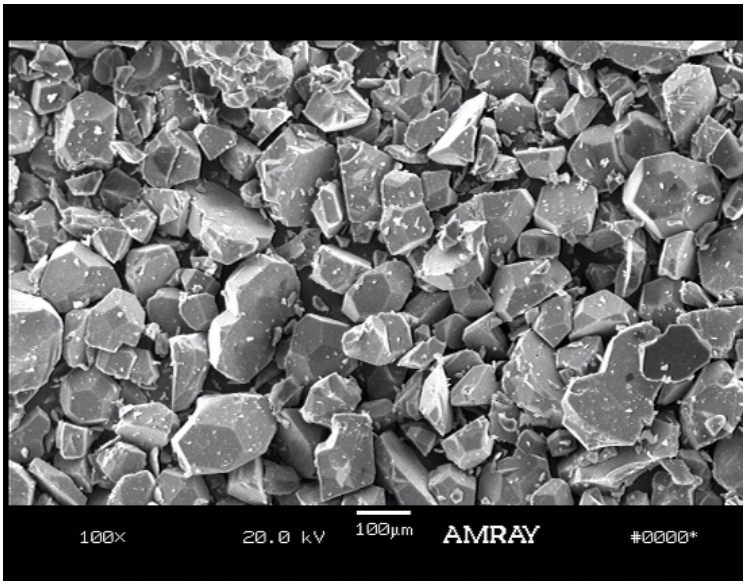

Figure S1. Scanning electronic micrograph of the as-synthesized crystals of **3**.

3. Selected crystallographic and thermal data of 1, 2 and 3

Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	C8.1 H12.4 Cl2 N4 O2.1 Zn	
Formula weight	335.42	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	I-43m	
Unit cell dimensions	a = 16.9824(4) Å	α= 90°.
	b = 16.9824(4) Å	β= 90°.
	c = 16.9824(4) Å	γ = 90°.
Volume	4897.8(2) $Å^3$	
Z	12	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	1.829 mm^{-1}	
F(000)	2036	
Crystal size	0.19 x 0.08 x 0.05 mm^3	
Theta range for data collection	1.70 to 30.49°.	
Index ranges	-24<=h<=24, -23<=k<=24, -24<=l<=24	
Reflections collected	21497	
Independent reflections	1415 [R(int) = 0.0265]	
Completeness to theta = 30.49°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9141 and 0.7226	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1415 / 0 / 70	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0654	
R indices (all data)	R1 = 0.0264, wR2 = 0.0660	
Absolute structure parameter	0.005(14)	
Largest diff. peak and hole	0.651 and -0.243 e.$Å^{-3}$	

Table 2. Crystal data and structure refinement parameters for **2**.

Empirical formula	C6.33 H5.33 Br2 N4 O0.33 Zn	
Formula weight	368.00	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	I-43m	
Unit cell dimensions	a = 17.065(2) Å	α= 90°.
	b = 17.065(2) Å	β= 90°.
	c = 17.065(2) Å	γ = 90°.
Volume	4969.6(10) $Å^3$	
Z	12	
Density (calculated)	1.476 Mg/m^3	
Absorption coefficient	6.284 mm^{-1}	
F(000)	2088	
Crystal size	0.19 x 0.08 x 0.05 mm^3	
Theta range for data collection	2.39 to 30.50°.	
Index ranges	-20<=h<=9, -7<=k<=24, -19<=l<=24	
Reflections collected	8026	
Independent reflections	1434 [R(int) = 0.0558]	
Completeness to theta = 30.50°	99.2 %	
Max. and min. transmission	0.7441 and 0.3814	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1434 / 6 / 56	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0320, wR2 = 0.0672	
R indices (all data)	R1 = 0.0398, wR2 = 0.0695	
Absolute structure parameter	-0.015(19)	
Largest diff. peak and hole	0.620 and -0.416 $e.Å^{-3}$	

Table 3. Crystal data and structure refinement parameters for **3**.

Empirical formula	C8 H14.32 N4 O2.16 Zn	
Formula weight	266.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	I-43m	
Unit cell dimensions	a = 17.0629(3) Å	α= 90°.
	b = 17.0629(3) Å	β= 90°.
	c = 17.0629(3) Å	γ = 90°.
Volume	4967.74(15) $Å^3$	
Z	12	
Density (calculated)	1.069 Mg/m^3	
Absorption coefficient	1.476 mm^{-1}	
F(000)	1652	
Crystal size	.23 x .21 x .2 mm^3	
Theta range for data collection	2.92 to 30.45°.	
Index ranges	-24<=h<=23, -24<=k<=15, -14<=l<=15	
Reflections collected	8628	
Independent reflections	1410 [R(int) = 0.0330]	
Completeness to theta = 30.45°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	.889 and .812	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1410 / 0 / 45	
Goodness-of-fit on F^2	0.880	
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.1051	
R indices (all data)	R1 = 0.0366, wR2 = 0.1064	
Absolute structure parameter	-0.03(3)	
Largest diff. peak and hole	0.766 and -0.377 $e.Å^{-3}$	

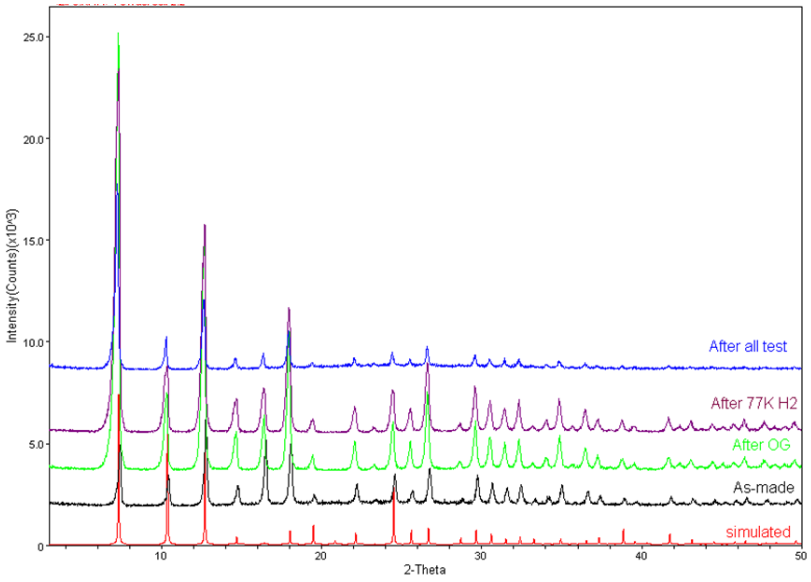

Figure S2. Calculated (red) and observed powder X-ray diffraction patterns of **3**.

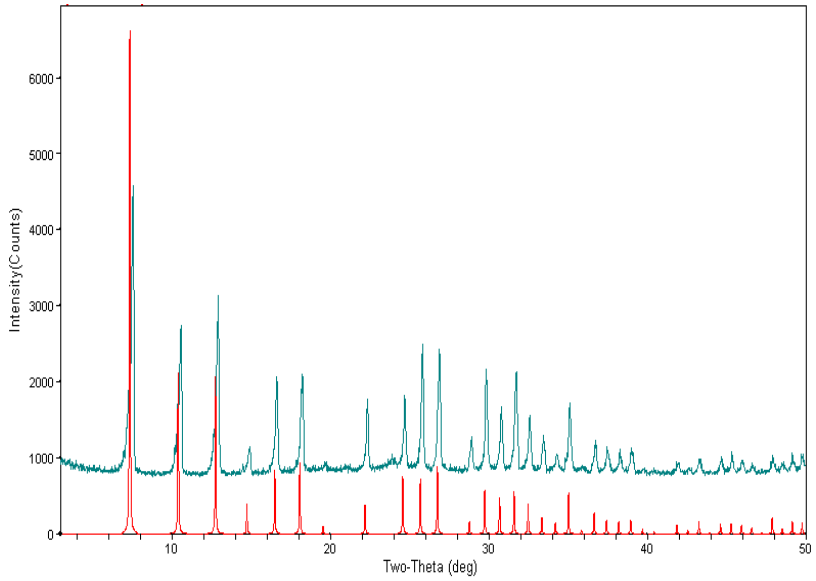

Figure S3. Calculated (red) and observed (blue) powder X-ray diffraction patterns of **1**.

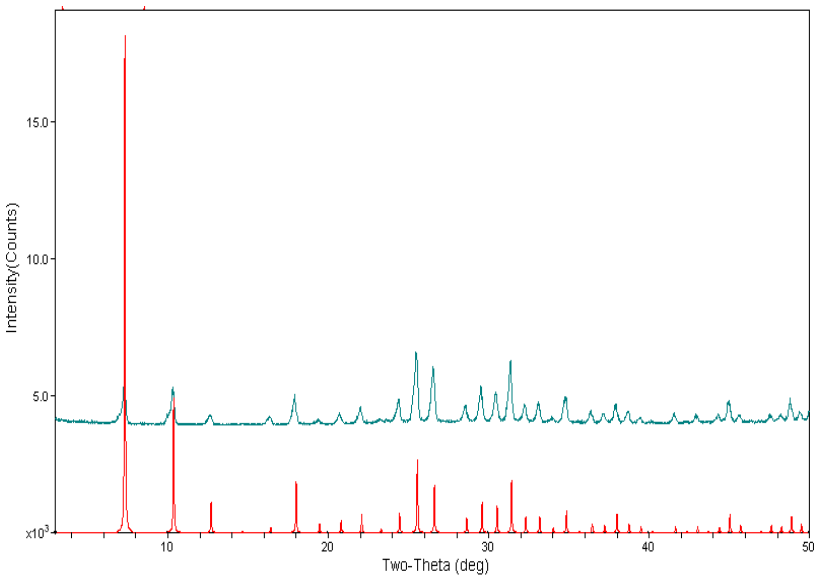

Figure S4. Calculated (red) and observed (blue) powder X-ray diffraction patterns of **2**.

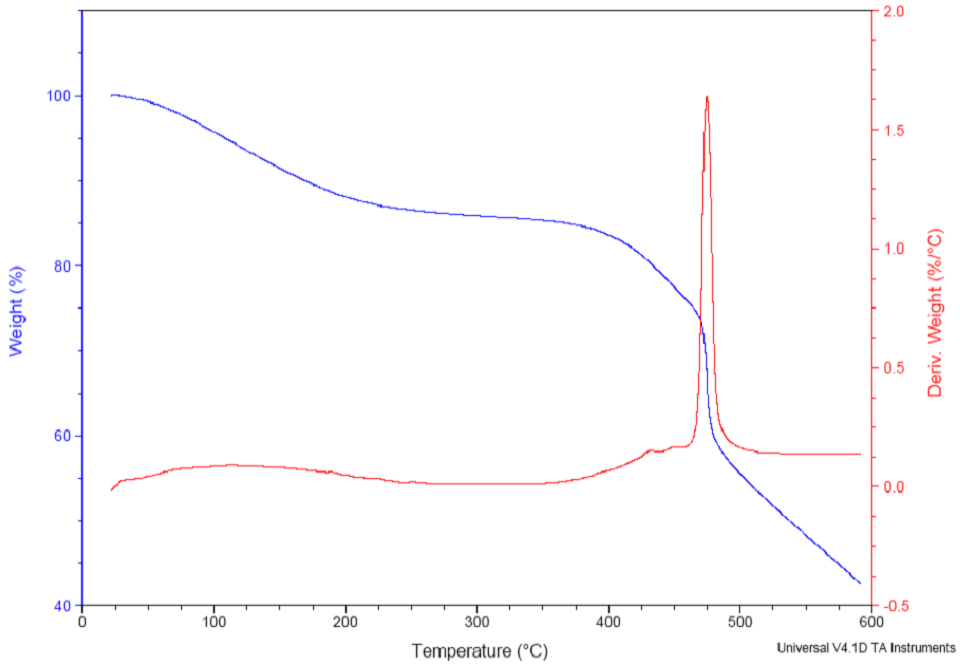

Figure S5. Thermogavimetric analysis of **1**.

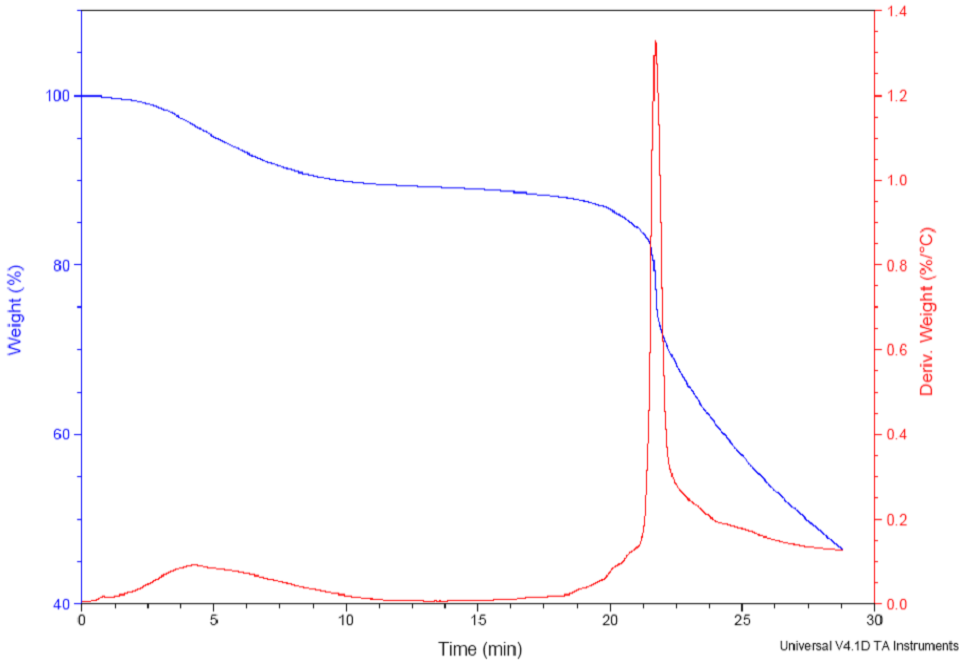

Figure S6. Thermogavimetric analysis of **2**.

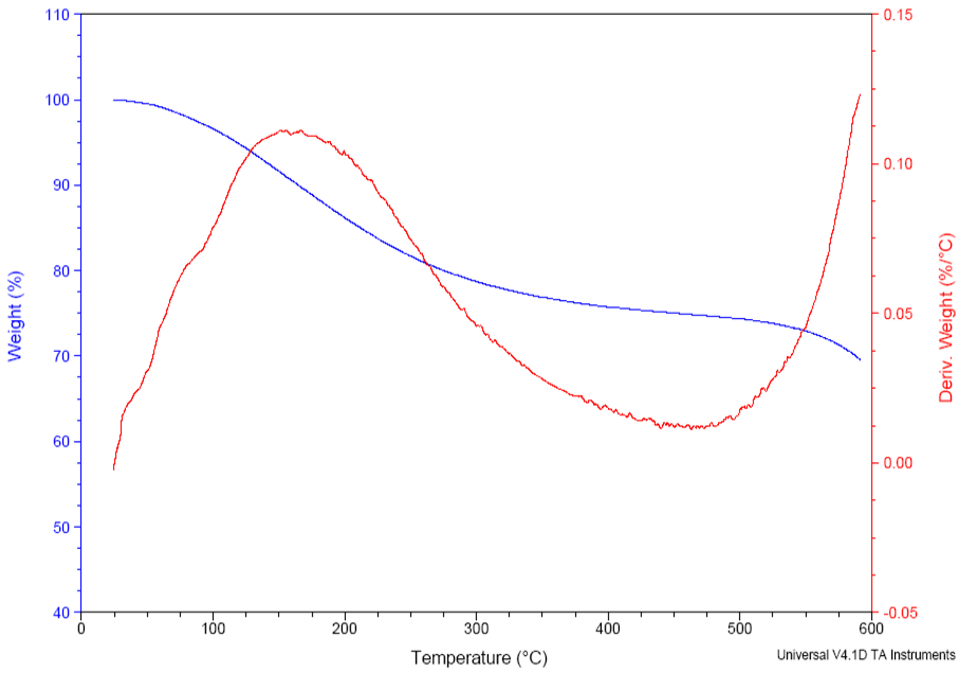

Figure S7. Thermogavimetric analysis of **3**.

4. Adsorption measurement

Adsorption measurements were made using a computer controlled thermogravimetric balance consisting of a TA51 electrobablance and associated TA-2000/PC control system. This one atmosphere, gas flow through electrobalance system was controlled via Macintosh-based LabView control software, Kinetic Systems interface, mass flow controllers and Eurotherm temperature controller. The samples were activated at 300 °C (400 °C for **3**) for 2 hours in dry nitrogen prior to the sorption measurement. All isotherm data are fitted with the Langmuir equation. D/r^2 values are obtained by applying Crank's solution for diffusion in a plane sheet adsorbent (Crank, 1957).

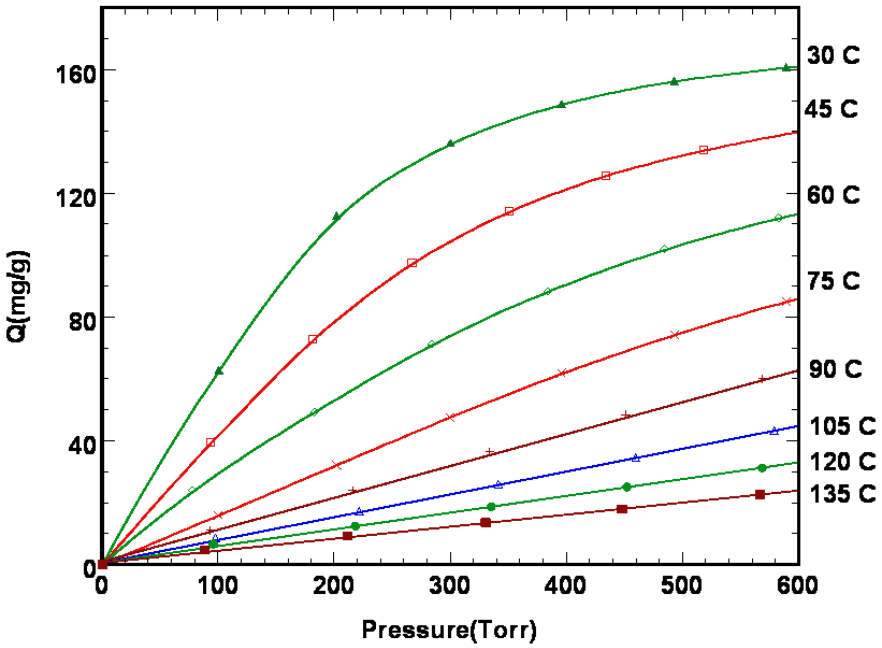

Figure S8. Propane adsorption isotherms for **3** at various temperatures.

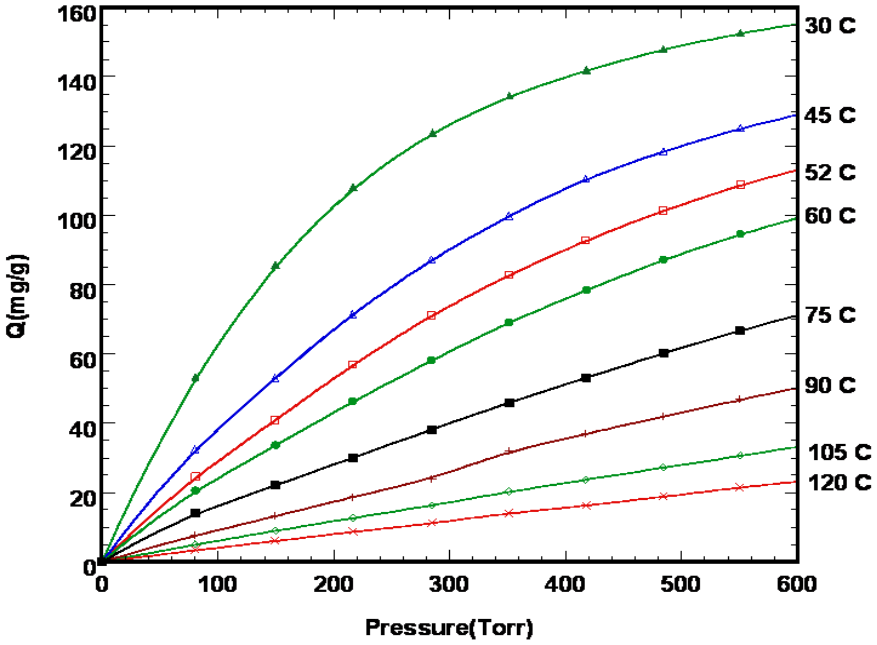

Figure S9. Propene adsorption isotherms for **3** at various temperatures.

Reference:

Crank, J. *The Mathematics of Diffusion*. Oxford University Press, London, **1957**.