Supporting Information

A Microporous, Moisture-Stable, and Amine-Functionalized Metal-Organic Framework for Highly Selective Separation of CO_2 from CH_4

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Experimental

1. Synthesis of 1

All starting materials for synthesis were purchased commercially and were used without further purification. The compound **1** was prepared by the reaction of indium chloride, $InCl_3$ (0.1106 g, 0.5 mmol), 2-aminoterephthalic acid (0.0924 g, 0.51 mmol), and 10 mL DMF in a 100 mL autoclave. The reaction mixture was heated in a circulated air oven at 403 K for 24 h to yield yellow octahedron-shaped crystal of **1** (Yield: 50%). Elemental analysis (%) calcd for $(Me_2NH_2)In(NH_2BDC)_2{\cdot}DMF{\cdot}H_2O$: C, 41.32; H, 4.43; N, 9.18. Found: C, 41.34; H, 4.43; N, 9.19.

2. Preparation of fully desolvated 1a ($(Me_2NH_2)In(NH_2BDC)_2$)

The resultant crystalline material was immersed in anhydrous DMF for three 12 h periods. Then, the solid was soaked in chloroform for 3 days to exchange the remaining solvates (DMF and water), and the supernatant was decanted every 12 hours and replenished with fresh chloroform. Finally, the compound was dried under vacuum at room temperature for 24 h to remove chloroform (**1**-$CHCl_3$), and then heated at 80 °C overnight to give the completely activated sample (**1a**). Elemental analysis caldc (%) for $(Me_2NH_2)In(NH_2BDC)_2$ (519.16): C, 41.61%; H, 3.47%; N, 8.09%. Found: C, 41.55%; H, 3.48%; N, 8.07%.

3. Single-crystal X-ray crystallography

Single crystal X-ray diffraction analysis of **1** was performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA with Mo Kα radiation ($\lambda = 0.71073$ Å) at 110(2) K. The empirical absorption corrections were performed using the APEX II program.[1] The structures were solved by direct methods and refined on F^2 by full-matrix least squares technique using the SHELX-97 program package.[2] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. The routine SQUEEZE

(PLATON)[3] was applied to the structures in order to remove diffuse electron density associated with badly disordered water, $[(Me)_2NH_2]^+$, and DMF molecules. The crystallographic data for In-N-MOF is given in Table S1. Selected bond lengths and bond angles are given in Table S2.

Crystallographic data for **1**: orthorhombic *Fddd*, with a = 15.300(2) Å, b = 26.902(4) Å, c = 31.342(5) Å, V = 12900(3) Å^3, Z = 16, μ(Mo Ka) = 0.759 mm^{-1}, ρ = 0.974 g cm^{-3}, T = 110 K, reflection numbers collected = 13601, unique reflections (Rint) = 2896 (0.0333), R_1 $[I > 2\sigma(I)]$ = 0.0278 and wR_2 (all data) = 0.0758, GOF = 1.073.

4. Characterization

Elemental analyses for C, H, and N were carried out by using a Vario EL III Elemental Analyzer. Infrared (IR) spectra were recorded (4000-400 cm^{-1}) as KBr disks on a Bruker TENSOR 27 Fourier Transform Infrared spectrometer. Thermogravimetry analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch) under a flow of N_2 at a heating rate of 10 °C/min between ambient temperature and 800 °C. Powder XRD investigations were carried out on a Bruker D8-Advanced diffractometer at 40 kV and 40 mA with Cu Kα (λ = 1.5406 Å) radiation.

5. Sorption measurements

The low-pressure gas adsorption measurements were performed on an automatic volumetric adsorption apparatus (Micrometrics ASAP 2020). High-pressure adsorption isotherms of CO_2 and CH_4 were measured with an automatic high-pressure gas adsorption apparatus (BELSORP-HP, BEL Japan, Inc.) at 298 K. Prior to measurements, the activated sample was further treated under high vacuum at 353 K overnight.

6. Breakthrough experiments

Breakthrough experiments were carried out in a column packed with 850 mg of pelletized sample. Prior to measurements, the sample was treated at 333 K overnight under pure Ar (>99.999%) with a flow rate of 30 ml/min. Breakthrough experiments were performed at 303 K by step changes from Ar to an equimolar CO_2–CH_4 gas mixtures (CO_2: purity >99.999%, moisture <5 ppm; CH_4: purity >99.99%, moisture <10 ppm) at a total flow rate of 12 ml/min. The gas stream at the outlet of the column was analyzed on-line with a mass spectrometer (MS).

References

[1] Bruker. *APEXII software, Version 6.3.1, Bruker AXS Inc*, Madison, Wisconsin, USA (2004).

[2] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.

[3] A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, **2005**.

Table S1. Crystal data and structure refinement details of **1**.

Empirical Formula	$C_{16}H_{10}InN_2O_8$ [a]
Formula weight	473.08
Crystal System	orthorhombic
Space group	Fddd
a (Å)	15.300(2)
b (Å)	26.902(4)
c (Å)	31.342(5)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V(Å^3)	12900(3)
Z	16
F (000)	3728
D_{calc} (mg/cm^3)	0.974
Absorption coefficient (mm^{-1})	0.759
GOF	1.073
Crystal size (mm)	0.3 × 0.28× 0.22
θ range for data collection (°)	2.48-25.20
Limiting indices	$-17 \leq h \leq 18$
	$-29 \leq k \leq 32$
	$-19 \leq l \leq 37$
Reflections collected / unique	13601/2896
Completeness to $\theta = 26.99$	99.2%
Data/restraints/parameters	2896/124
Final R indices [I > $2\sigma(I)$]	$R_1 = 0.0278$, $wR_2 = 0.0758$
R indices (all data)	$R_1 = 0.0342$, $wR_2 = 0.0778$

$R = \sum(\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert)/\sum\lvert F_o\rvert$

$wR = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o)^2]^{1/2}$.

[a] Guest molecules have been removed with PLATON SQUEEZE.

Table S2. Selected bond distances (Å) and angles (°).

In(1)-O(1)^{i}	2.2438(17)	In(1)-O(2)^{i}	2.2840(15)
In(1)-O(1)	2.2438(17)	In(1)-O(2)	2.2840(15)
In(1)-O(4)^{ii}	2.2656(17)	In(1)-O(3)^{ii}	2.2995(15)
In(1)-O(4)^{iii}	2.2656(17)	In(1)-O(3)^{iii}	2.2995(15)
In(1)-O(1)^{i}	2.2438(17)	In(1)-O(2)^{i}	2.2840(15)
In(1)-O(1)	2.2438(17)	In(1)-O(2)	2.2840(15)
O(1)^{i}-In(1)-O(1)	96.21(10)	O(1)-In(1)-O(2)	57.74(6)
O(1)-In(1)-O(2)^{i}	82.83(7)	O(1)^{i}-In(1)-O(2)	82.83(7)
O(1)-In(1)-O(3)^{ii}	139.09(6)	O(1)^{i}-In(1)-O(3)^{iii}	139.09(6)
O(1)-In(1)-O(3)^{iii}	84.02(6)	O(1)^{i}-In(1)-O(3)^{ii}	84.02(6)
O(1)-In(1)-O(4)^{ii}	162.94(6)	O(1)^{i}-In(1)-O(4)^{iii}	162.94(6)
O(1)-In(1)-O(4)^{ii}	90.25(8)	O(1)-In(1)-O(4)^{iii}	90.25(8)
O(1)^{i}-In(1)-O(2)^{i}	57.74(6)	O(2)^{i}-In(1)-O(2)	120.92(9)
O(2)-In(1)-O(3)^{ii}	81.89(6)	O(2)^{i}-In(1)-O(3)^{iii}	81.89(6)
O(2)-In(1)-O(3)^{iii}	128.47(6)	O(2)^{i}-In(1)-O(3)^{iii}	128.47(6)
O(3)^{iii}-In(1)-O(3)^{ii}	121.60(6)	O(4)^{iii}-In(1)-O(4)^{ii}	88.06(9)

Symmetry codes: (i) 0.75-x, 0.75-y, z; (ii) 0.5-x, -0.25+y, 0.25+z; (iii) 0.25+x, 1-y, 0.25+z)

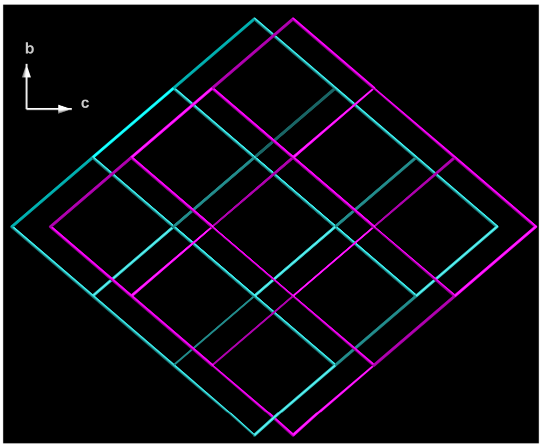

Figure S1. Showing the 2-fold interpenetration and remaining channels along the *a* axis.

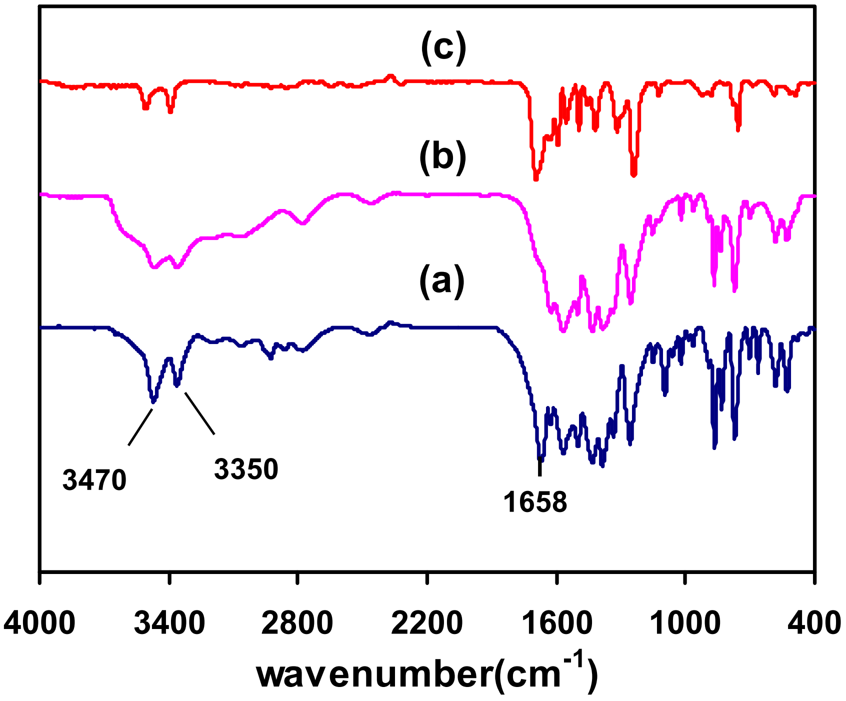

Figure S2. IR spectra of the as-synthesized **1** (a), **1**-$CHCl_3$ (b), and 2-aminoterephthalic acid (c): 3350 and 3470 cm^{-1} (N–$H_{2\text{-aminoterephthalic acid}}$), 1658 cm^{-1} (C=$O_{DMF}$). The absence of the peak at 1658 cm^{-1} for **1**-$CHCl_3$ indicates that the DMF molecules in **1** were efficiently removed after soaking **1** in $CHCl_3$.

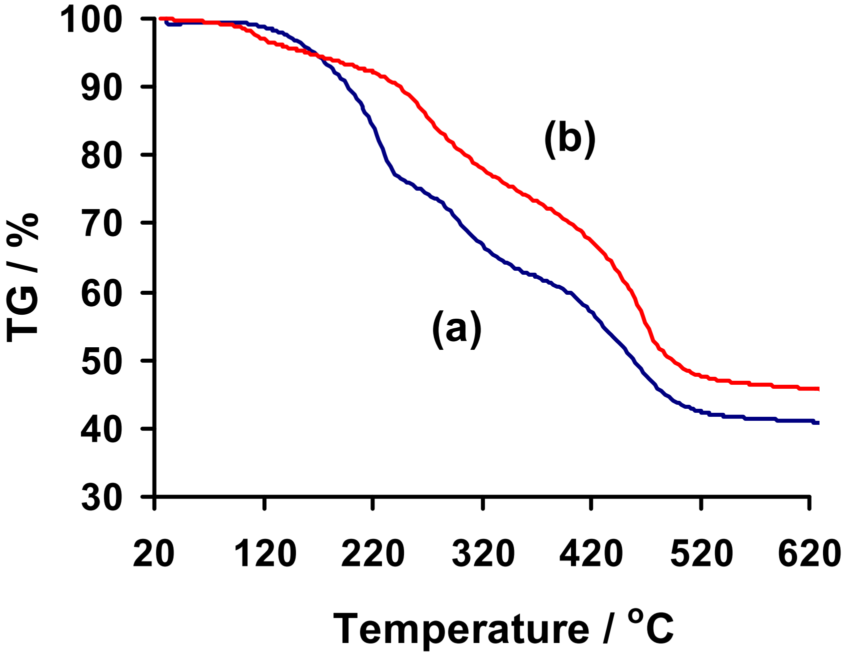

Figure S3. TGA curves for the as-synthesized **1** (a), and **1**-$CHCl_3$ (b). The weight loss of 10.1 wt% between 30 and 240 °C in **1**-$CHCl_3$ corresponds to the loss of the water and Me_2NH neutral molecules per formula unit (calcd. 11.5 wt%).

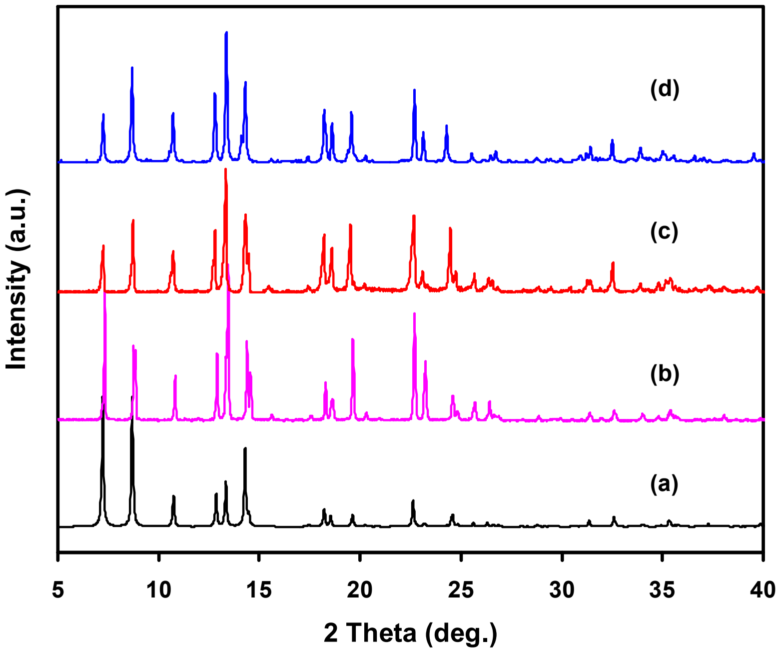

Figure S4. PXRD patterns of **1**: (a) simulated; (b) as-synthesized; (c) desolvated **1a**; (d) **1a** in humid air for 30 days.

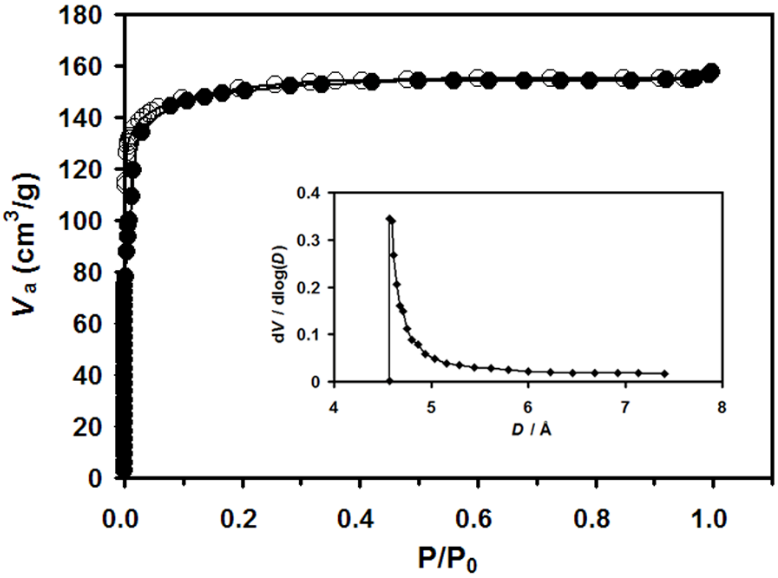

Figure S5. N_2 isotherms and micropore size distribution (inset) for the desolvated **1a**.

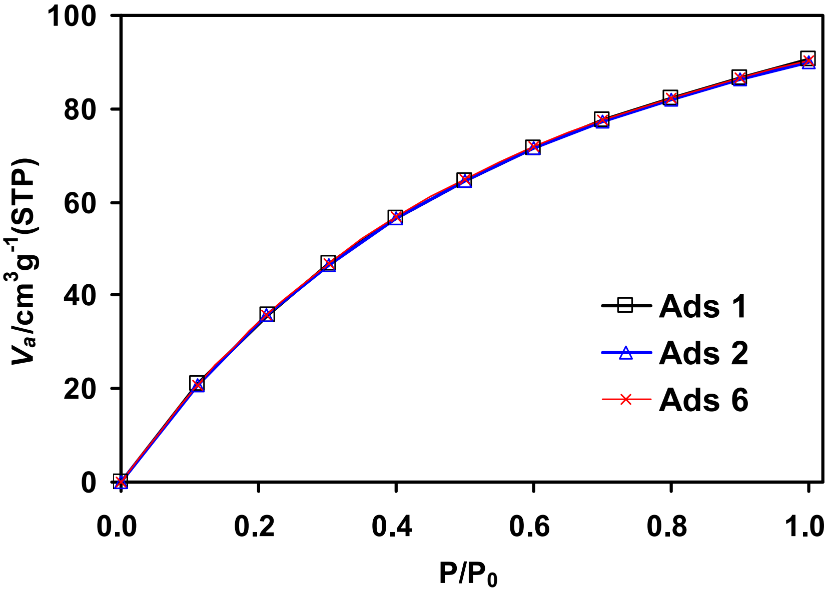

Figure S6. Reusability of **1a** for CO_2 adsorption at 273 K.

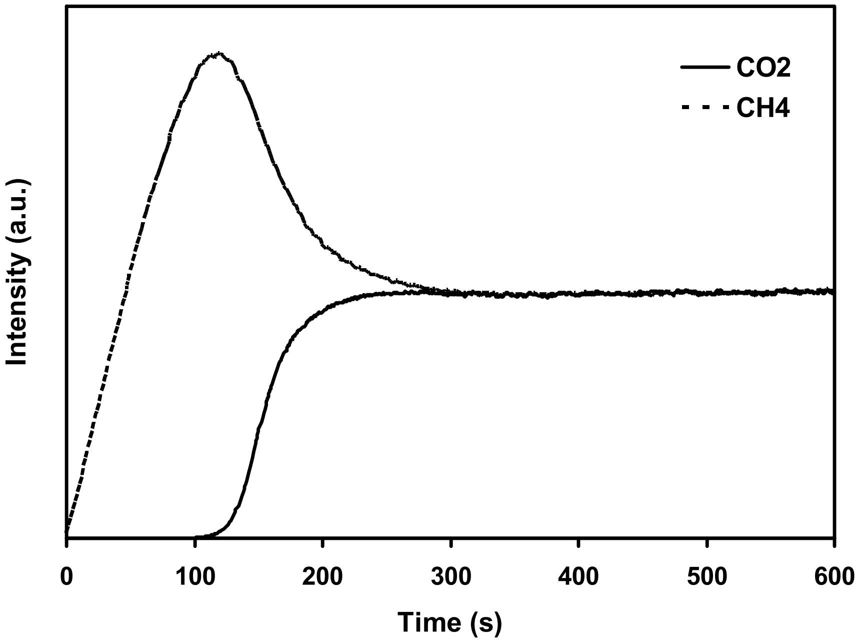

Figure S7. Breakthrough profile of an equimolar mixture of CO_2/CH_4 for a packed column of **1a** after exposing to humid air for 30 days at 303 K and 1 bar.