Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

Two-Dimensional Metal-Organic Frameworks for Selective Separation of CO_2/CH_4 and CO_2/N_2

Stephen Charles King,[a] Rui-Biao Lin,*[a] Hailong Wang,[a] Hadi D. Arman,[a] and Banglin Chen*[a]

[a] Department of Chemistry, University of Texas at San Antonio One UTSA Circle, San Antonio, Texas 78249-0698, USA Fax: (+1)210-458-7428, E-mail: banglin.chen@utsa.edu

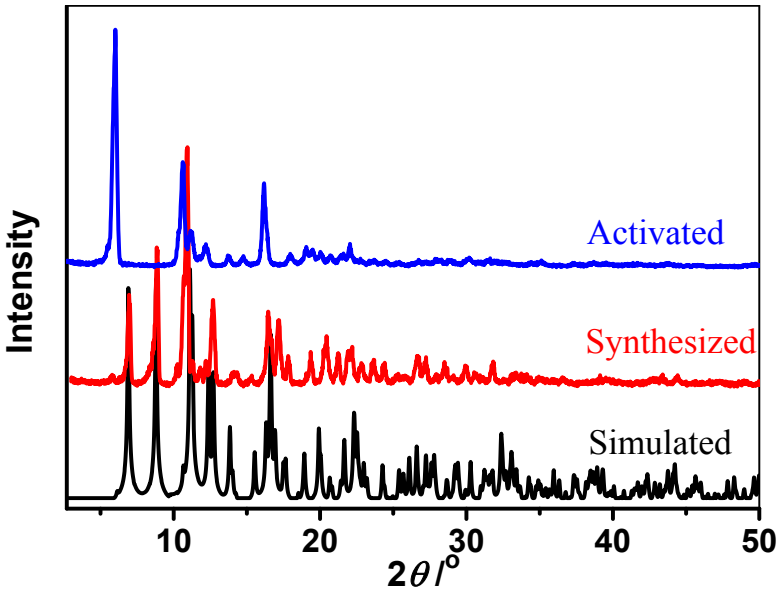

Figure S1. Powder X-ray diffraction patterns of **1** (red) and activated **1a** (blue), in comparison with a simulated powder pattern based on the reported $[Zn_2(TMTA)(H_2O)_2]\cdot NO_3\cdot 6H_2O\cdot DEF$ structure (black line).

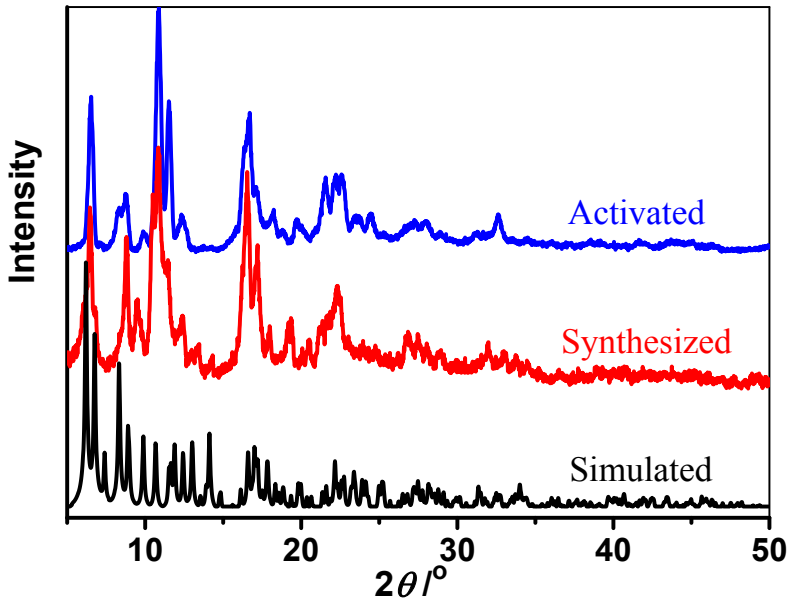

Figure S2. Powder X-ray diffraction patterns of **2** (red) and activated **2a** (blue), in comparison with a simulated powder pattern based on the single-crystal $[Zn_3(TETA)_2(DMF)_4]\cdot 3DMF$ structure (black line).

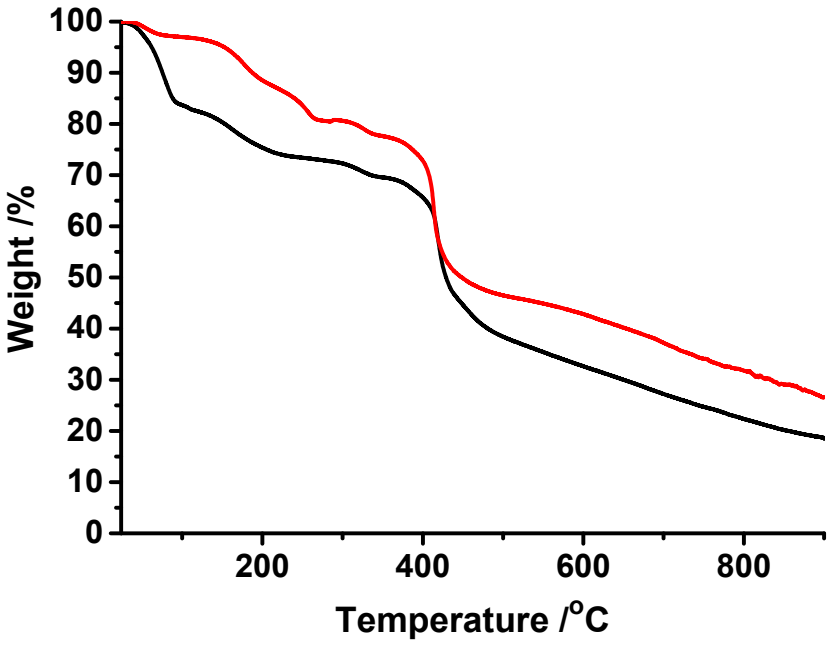

Figure S3. TGA curves of **1** (black) and activated **1a** (red)

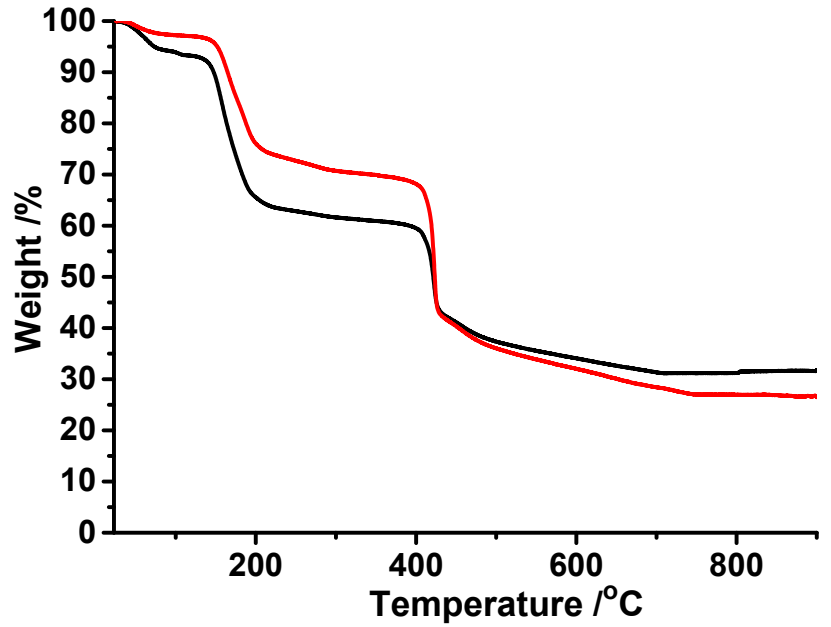

Figure S4. TGA curves of **2** (black) and activated **2a** (red)

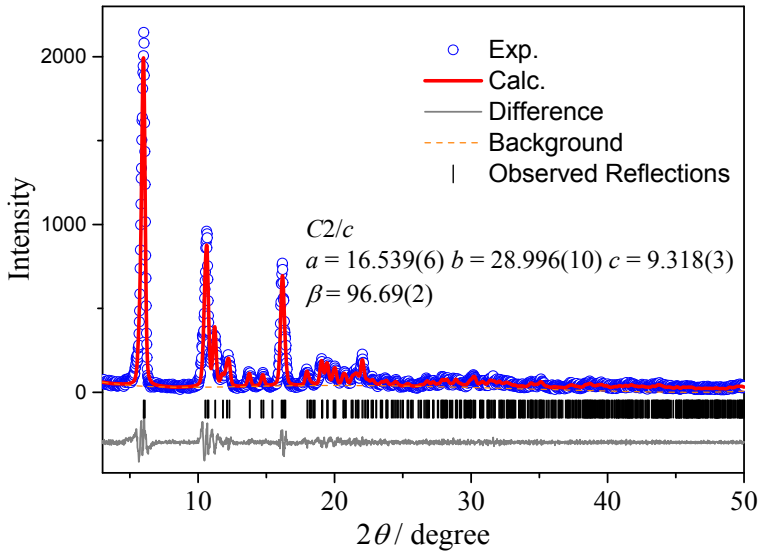

Figure S5. Pawley refinements of the PXRD patterns for **1a** (R_{wp} = 14.71%, R_p = 10.96%).

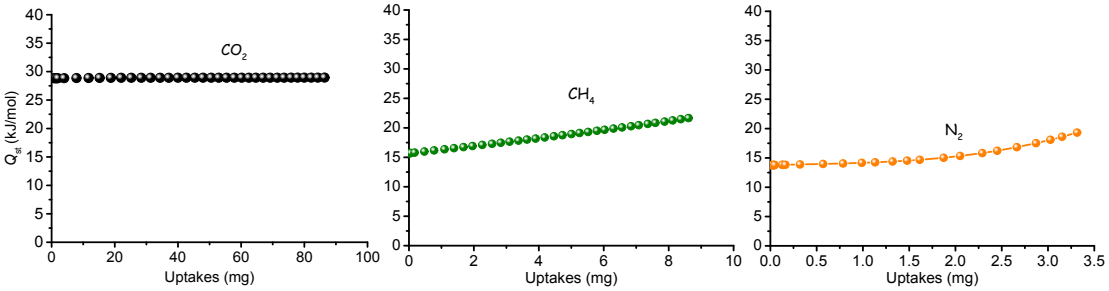

Figure S6. The coverage-dependent adsorption enthalpies of **1a** towards CO_2, CH_4, and N_2.

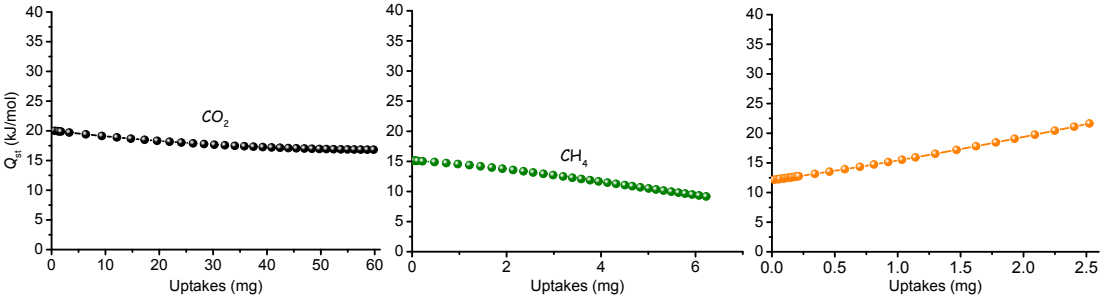

Figure S7. The coverage-dependent adsorption enthalpies of **2a** towards CO_2, CH_4, and N_2.

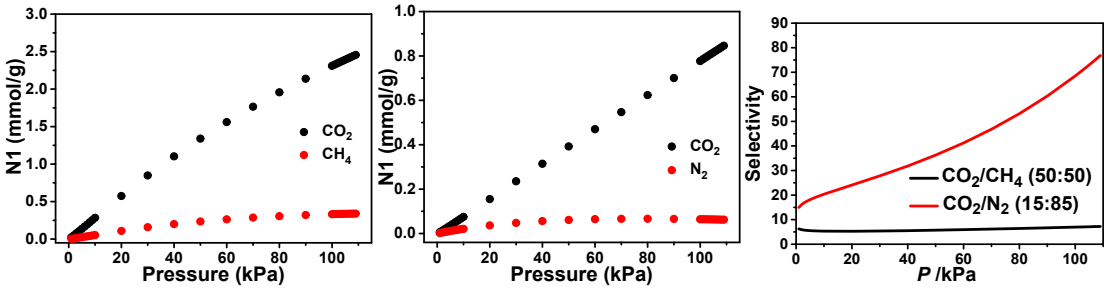

Figure S8. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of **1a** for mixed CO_2/CH_4 (CO_2/CH_4 = 50:50) and CO_2/N_2 (CO_2/N_2 = 15:85) at 273 K, respectively.

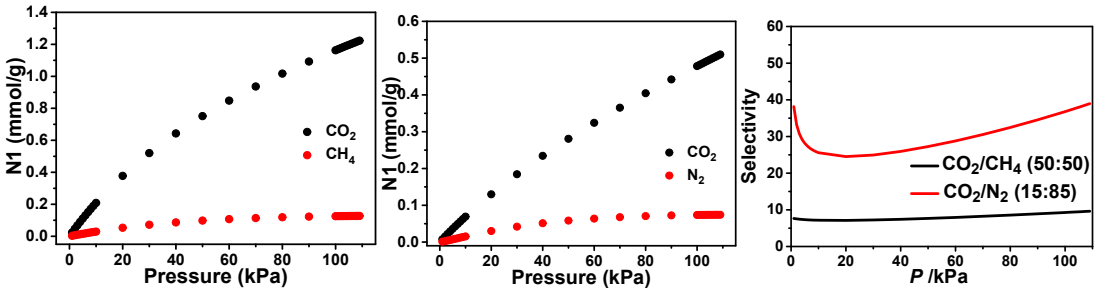

Figure S9. Mixture adsorption isotherms and adsorption selectivity predicted by IAST of **2a** for mixed CO_2/CH_4 (CO_2/CH_4 = 50:50) and CO_2/N_2 (CO_2/N_2 = 15:85) at 273 K, respectively.

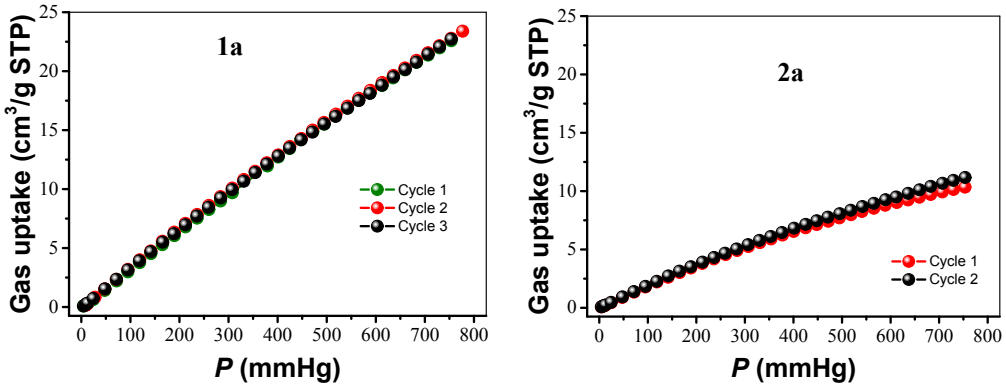

Figure S10. Repeatability of CH_4 adsorption at 273 K for **1a** (black) and **2a** (red).

Table S1. Crystal data and structure refinements of **2**.

Complex	**2**
Formula.	$C_{78}H_{82}N_4O_{16}Zn_3$
F.W.	1527.65
Crystal system	Triclinic
Space group	*P*-1
a /Å	11.4427(17)
b /Å	14.514(2)
c /Å	16.196(3)
α/°	65.694(5)
β/°	69.783(5)
γ/°	73.998(5)
volume/Å^3	2272.2(6)
Z	1
D_{cald}/g cm^{-3}	1.116
μ / mm^{-1}	0.842
*F*000	796
$R_1{}^a$ $I>2\theta$	0.1319
$R_{w2}{}^b I>2\theta$	0.3180
$R_1{}^a$	0.1720
$R_{w2}{}^b$	0.3495

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, ^{b} $R_{w2} = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table S2. IAST selectivities of CO_2/CH_4 (CO_2/CH_4 = 50:50) and C_2H_2/N_2 (C_2H_2/N_2 = 15:85).

mixture	Temperature (K)	component proportion	IAST selectivity
1a			
CO_2/CH_4	273	50:50	7.0
CO_2/N_2	273	15:85	69.4
CO_2/CH_4	296	50:50	5.8
CO_2/N_2	296	15:85	39.3
2a			
CO_2/CH_4	273	50:50	9.3
CO_2/N_2	273	15:85	37.0
CO_2/CH_4	296	50:50	6.4
CO_2/N_2	296	15:85	38.4

Table S3. Equation parameters for the DSLF isotherm model.

Adsorbates	N_1^{max} (mmol/g)	b_1 (kPa^{-1})	$1/n_1$	N_2^{max} (mmol/g)	b_2 (kPa^{-1})	$1/n_2$
1a						
CO_2 (273 K)	5.84212	0.00312	1.09163	3.90591	0.00808	1.09707
CH_4 (273 K)	1.8189	0.00247	1.21258	0.69688	0.00278	1.16592
N_2 (273 K)	0.33714	0.00717	0.97884	0.10463	0.00214	1.32019
CO_2 (296 K)	3.70703	0.00279	1.11011	1.81594	0.01085	0.90231
CH_4 (296 K)	0.81515	0.00114	1.37365	0.51875	0.00357	1.13232
N_2 (296 K)	0.20737	0.00376	1.23743	0.04827	9.73155E-4	1.2096
2a						
CO_2 (273 K)	3.29637	2.88732E-4	1.36359	2.20458	0.02105	0.97376
CH_4 (273 K)	0.75567	0.00176	1.30619	0.36853	0.01383	0.90577
N_2 (273 K)	0.2728	0.00219	1.19577	0.13969	0.0033	1.28087
CO_2 (296 K)	2.77073	0.00906	0.96235	1.13709	0.00103	1.06798
CH_4 (296 K)	0.5847	0.00452	1.08803	0.30156	0.0028	1.27058
N_2 (296 K)	0.19832	0.00207	1.15664	0.087	0.00645	0.9631

Note: Dual-site Langmuir-Freundlich (DSLF) model is listed as below:

$$N = N_1^{max} \times \frac{b_1 p^{1/n1}}{1 + b_1 p^{1/n1}} + N_2^{max} \times \frac{b_2 p^{1/n2}}{1 + b_2 p^{1/n2}}$$

Where p (unit: kPa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N (unit: mol/kg) is the adsorbed amount per mass of adsorbent, N_1^{max} and N_2^{max} (unit: mol/kg) are the saturation capacities of sites **1** and **2**, b_1 and b_2 (unit: 1/kPa) are the affinity coefficients of sites **1** and **2**, and n_1 and n_2 represent the deviations from an ideal homogeneous surface.