A flexible MMOF exhibiting high selectivity for CO_2 over N_2, CH_4 and other small gases

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Supporting Information

I. General Information

All chemicals were purchased from Aldrich, Acros or VWR and used as received without further purification unless stated otherwise. Thermogravimetric data were collected on a TA Q50 Analyzer with a temperature ramping rate of 10 °C/min from room temperature to 600 °C under nitrogen gas flow. Powder X-ray diffraction patterns were recorded on a Rigaku D/M-2200T automated diffractometer (Ultima+) using Cu Kα radiation (λ = 1.5406 Å). Graphite monochromator was used and the generator power settings were at 40 kV and 40 mA. Data were collected between a 2θ of 3-50° with a step size of 0.02° at a scanning speed of 2.0 deg/min.

II. Synthesis

A mixture of zinc (II) nitrate hexahydrate (0.2975g 1.0 mmol), 1,2-bis(4-pyridyl)-ethane-bpe (0.1842g, 1.0 mmol) and 4,4'-biphenyldicarbpxylic acid or H_2bpdc (0.2422g, 1 mmol) in DMF (15 mL) and toluene (0.8 mL) was heated in a programmable oven at 170 °C for 72 hours before it was cooled to room temperature at a rate of 0.1°C /min. The yellow block-shaped crystals of **1** were filtered, rinsed with DMF (10 mL) and dried under vacuum oven for 10 mins (85% yield based on zinc nitrate).

III. Small gas adsorption experiments

All gas sorption experiments were performed on a volumetric gas sorption analyzer (Autosorb-1 MP, Quantachrome Instruments). Liquid nitrogen and liquid argon were used as coolant to achieve cryogenic temperatures (77 and 87K). Ultra high purity N_2, CO, CO_2, O_2 and CH_4 (99.999%) were used. The initial outgassing process for each sample was carried out at 433K overnight (under vacuum). Outgassed samples in the amount of ~85-90mg were used for gas sorption measurements and the weight of each sample was recorded before and after outgassing to confirm the removal of guest molecules. The outgassing procedure was repeated on the same sample between experiments for 0.5~1 hour. Pore properties (e.g. pore volume, pore size, and surface area) were analyzed using Autosorb v1.50 software. The PXRD patterns of the simulated, as-synthesized (**1**), guest-free (**1′**) and DMF solvent regenerated samples, as well as those obtained in-situ as a function of CO_2 pressure, are shown in Figs. S1-S2. The in-situ PXRD measurements were carried out as a function of CO_2 pressure using a specially designed sample holder for the PXRD unit. A guest-free sample was loaded in the sample holder and vacuum was applied to remove any gas residue. Full data set was then collected after the sample holder was refilled with CO_2 gas to a certain pressure and equilibrium was reached. The surface areas estimated from CO_2 adsorption isotherms are 88.4m^2/g (BET) and 137.8 m^2/g (Langmuir), respectively (Table S1). The total pore volume was estimated to be 0.08 cc/g (Table S1). TG analysis (Fig. S3) indicated a weight loss of 15.13 wt% in the temperature range of 80-140 °C, in excellent agreement with the calculated percentage weight of gust DMF molecules, 15.5%. Comparisons of adsorption isotherms of CO_2 with CO and O_2 at 298K up to 1 atm are shown in Figs. S4 and S5, respectively. Single-component separation ratios of CO_2/N_2 at 25 °C are tabulated in Table S2 for **1’**, and compared with those of MOF74-Mg and SNU-M10. Single-component gas uptakes in **1’** and separation ratios of CO_2 with other small gases at 25 °C are listed in Table S3. Selected single crystal data are listed in Table S4-S5.

IV. Stability under water vapor

The stability of the title compound in water vapor was examined at both room temperature and 60 °C. About 25 mg of sample (**1**) was loaded in an open vial suspended on the top of a closed glass jar containing water. The vial had no contact with water surface. The PXRD patterns were collected after 2 hrs and 6 hrs, respectively. The water was then heated to 60 °C and the same procedure was repeated again. Based on the PXRD data shown in Figure S6, it is clear that the sample remained highly crystalline in both cases.

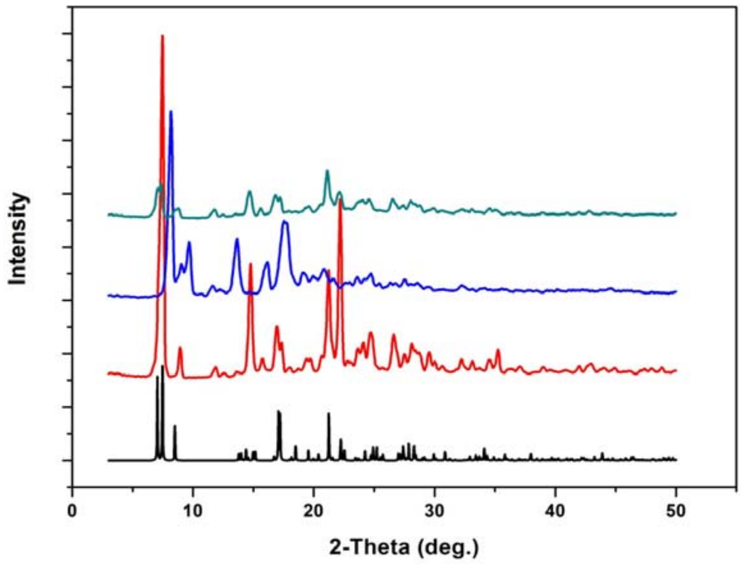

Figure S1. PXRD patterns of as-synthesized sample of **1** (red), guest-free **1’** (blue), and **1’** after being heated in DMF at 80 °C for 6 hours (dark-green). The pattern in black (bottom) is calculated from the single crystal structure of **1**.

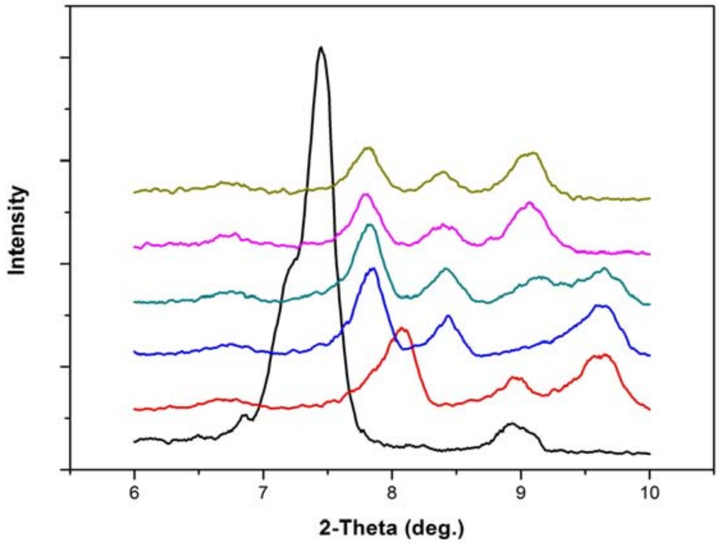

Figure S2. Room temperature PXRD patterns at low angles (2θ = 6-10°) for as-synthesized sample **1** (black), guest-free sample **1’** (red), **1’** after refilling CO_2 at 0.05 atm (blue, first step), **1’** after refilling CO_2 at 0.2 atm (green, second step), **1’** after refilling CO_2 at 0.6 atm (pink) and **1’** after refilling CO_2 at 1 atm (yellow, third step).

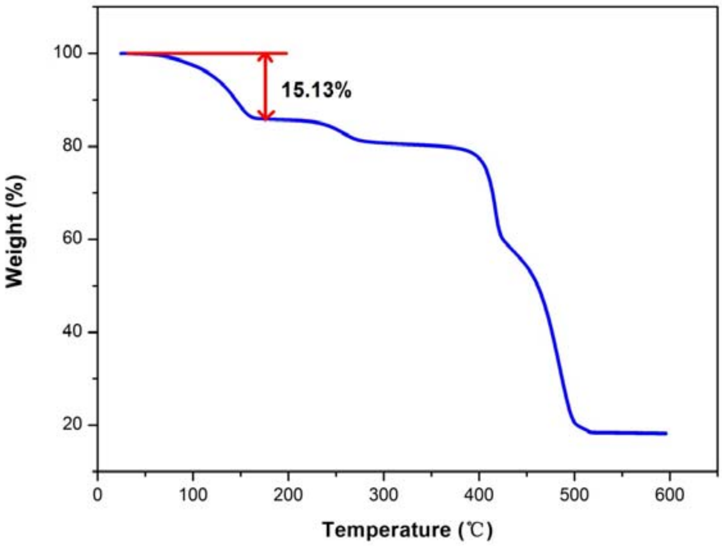

Figure S3. Thermogravimetric analysis of a freshly prepared sample of **1**, showing a good agreement between the observed weight loss of DMF (15.13 wt%) and the calculated value (15.5 wt%).

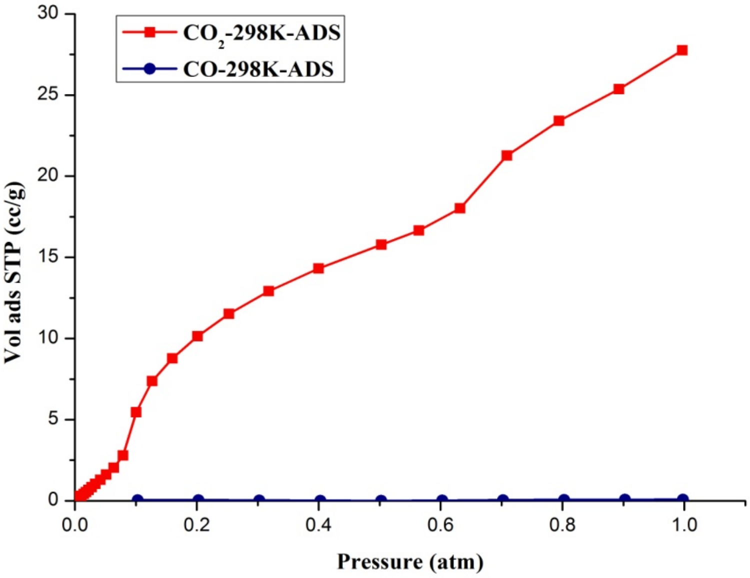

Figure S4. Comparison of room temperature adsorption isotherms of CO_2 and CO on **1’**.

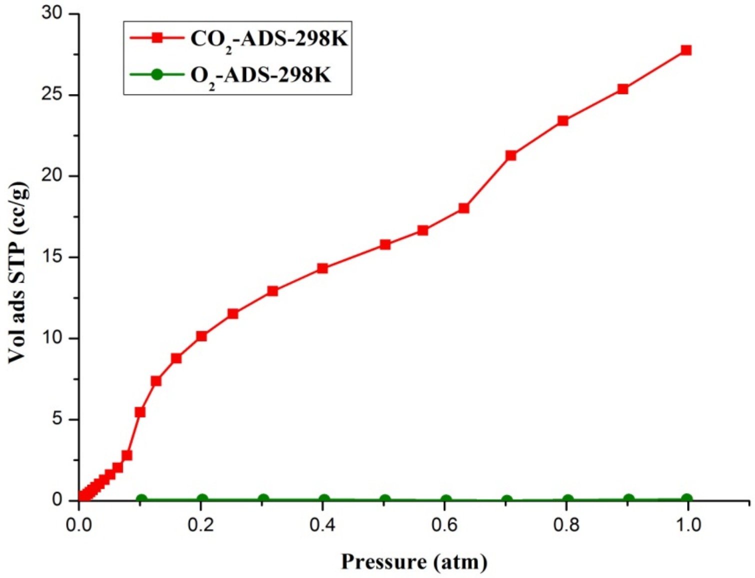

Figure S5. CO$_2$ and O$_2$ adsorption isotherms on **1'** at room temperature.

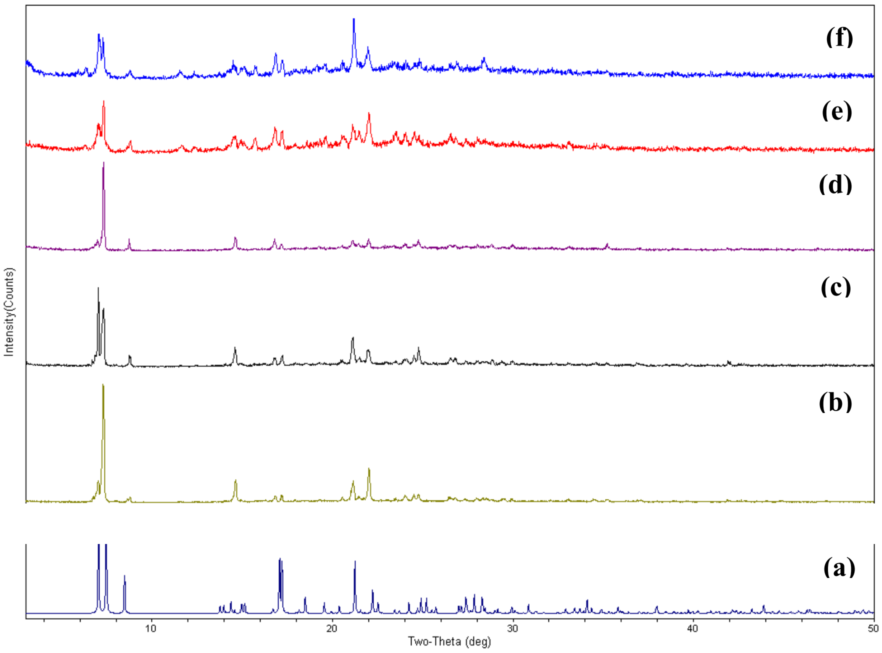

Figure S6. PXRD patterns of **1** taken after exposure to water vapor at room temperature and 60°C. (a) simulated; (b) before exposure; (c) after 2 hrs at RT; (d) after 6 hrs at RT; (e) after 2 hours at 60°C; and (f) after 6 hours at 60°C.

Table S1. Pore characteristics of $[Zn_2(bpdc)_2(bpe)]\cdot 2DMF$(**1**).

BET Surface Area (P/P_0=0.05-0.25) (m^2/g)	Langmuir Surface Area (P/P_0=0.05-0.25) (m^2/g)
88.4	137.8
Total Pore Volume (cc/g)	
Experimental	Calculated
0.08 (P/P_0 = 0.99)	0.2*

*Calculated by Platon from single crystal data of **1**.

Table S2. Single-component separation ratios of CO_2/N_2 at 25 °C.

Pressure (atm)	Separation Ratio (v/v)		
	1’	MOF-74-Mg	SNU-M10[1]
0.09	98	81	6
0.16	99	49	7
0.5	169	20	27
1	360	12	98

Table S3. Single-component gas uptake in **1’** and separation ratios at 25 °C.

Pressure (atm)	Gas	Gas Uptake (STP, cc/g)	wt%	CO_2/Gas Ratio (v/v)
0.09	CO_2	6.02	1.18	
	N_2	0.061	0.0076	98
	CH_4	0.082	0.0059	73
	CO	0.041	0.0051	147
	O_2	0.054	0.0077	111
0.16	CO_2	8.77	1.72	
	N_2	0.088	0.011	99
	CH_4	0.160	0.012	53
	CO	0.041	0.005	213
	O_2	0.071	0.010	124
0.5	CO_2	15.78	3.10	
	N_2	0.093	0.012	169
	CH_4	0.63	0.045	25
	CO	0.027	0.0034	584
	O_2	0.042	0.0060	376
1	CO_2	27.76	5.46	
	N_2	0.077	0.0096	360
	CH_4	1.15	0.082	24
	CO	0.079	0.0098	351
	O_2	0.085	0.012	327

Table S4. Crystal data and structure refinement for **1**.

Identification code	jz1-53b	
Empirical formula	C23 H21 N2 O5 Zn	
Formula weight	470.79	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.4310(18) Å	α= 90°.
	b = 6.6400(5) Å	β= 108.464(1)°.
	c = 24.9341(17) Å	γ = 90°.
Volume	4150.7(5) $Å^3$	
Z	8	
Density (calculated)	1.507 Mg/m^3	
Absorption coefficient	1.222 mm^{-1}	
F(000)	1944	
Crystal size	0.35 x 0.09 x 0.03 mm^3	
Theta range for data collection	1.72 to 30.53°.	
Index ranges	-37<=h<=37, -9<=k<=9, -35<=l<=34	
Reflections collected	23638	
Independent reflections	6358 [R(int) = 0.0607]	
Completeness to theta = 30.53°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.963 and 0.674	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6358 / 674 / 304	
Goodness-of-fit on F^2	1.003	
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1166	
R indices (all data)	R1 = 0.0775, wR2 = 0.1271	
Largest diff. peak and hole	1.213 and -1.095 e.$Å^{-3}$	

Table S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	642(1)	-1257(1)	309(1)	16(1)
O(1)	837(1)	486(3)	967(1)	22(1)
O(2)	885(1)	-2429(3)	1425(1)	24(1)
O(3)	29(1)	7374(3)	4760(1)	17(1)
O(4)	639(1)	9549(3)	4662(1)	21(1)
C(1)	868(1)	-578(4)	1411(1)	18(1)
C(2)	878(1)	601(4)	1927(1)	15(1)
C(3)	1006(1)	2642(4)	1976(1)	20(1)
C(4)	978(1)	3738(4)	2436(1)	21(1)
C(5)	809(1)	2844(4)	2859(1)	17(1)
C(6)	686(1)	797(4)	2809(1)	18(1)
C(7)	723(1)	-310(4)	2352(1)	18(1)
C(8)	734(1)	4067(4)	3326(1)	16(1)
C(9)	1029(1)	5819(4)	3514(1)	24(1)
C(10)	921(1)	7033(4)	3915(1)	24(1)
C(11)	518(1)	6534(4)	4143(1)	16(1)
C(12)	239(1)	4753(4)	3974(1)	18(1)
C(13)	346(1)	3539(4)	3571(1)	20(1)
C(14)	385(1)	7904(4)	4549(1)	16(1)
N(1A)	1165(3)	-3403(13)	237(5)	11(1)
C(15A)	1281(3)	-5180(14)	547(4)	16(1)
C(16A)	1723(2)	-6316(10)	549(2)	20(1)
C(17A)	2050(2)	-5676(9)	242(2)	20(1)
C(18A)	1934(2)	-3899(8)	-68(2)	19(1)
C(19A)	1492(3)	-2763(8)	-70(3)	18(1)
C(20A)	2532(3)	-6921(11)	256(2)	32(2)
N(1B)	1199(4)	-3160(13)	235(5)	11(1)
C(15B)	1246(3)	-4963(15)	530(4)	16(1)
C(16B)	1582(2)	-6468(10)	452(3)	18(2)
C(17B)	1870(2)	-6169(7)	79(3)	22(1)
C(18B)	1822(3)	-4365(8)	-215(3)	19(1)
C(19B)	1487(3)	-2861(8)	-137(4)	18(1)
C(20B)	2234(3)	-7776(10)	-20(4)	37(2)

N(51)	2431(1)	6725(5)	1690(1)	43(1)
O(51)	2468(1)	9385(5)	1131(1)	66(1)
C(51)	2261(1)	8451(6)	1424(2)	46(1)
C(52)	2894(2)	5719(8)	1634(2)	61(1)
C(53)	2154(2)	5772(8)	2037(2)	68(1)

References:

1. H. S. Choi and M. P. Suh, *Angew. Chem., Int. Ed*, 2009, **48**, 6865.