Supporting Information

A Highly stable Metal- and Nitrogen-doped Nanocomposite derived from Zn/Ni-ZIF-8 with CO_2 capture and separation

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S-1. Synthetic materials and measurements.

Materials.

All chemicals were obtained commercially and used without additional purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), and methanol (MeOH) were obtained from Sinopharm Chemical Reagent Co., Ltd, 2-methylimidazole (HMeIM) was purchased from J&K Scientific Company.

Measurements.

Powder X-ray diffraction (PXRD) patterns of the samples were analyzed with monochromatized Cu-Kα (λ = 1.54178 Å) incident radiation by Bruker D8 Advance X-ray diffractometer operating at 40 kV voltage and 50 mA current. PXRD patterns were recorded from 5° to 80° (2θ) at 298 K. The morphology and size of as-obtained products were investigated using transmission electron microscope (TEM, JEM-2010). Raman spectra were recorded on an Invia Raman spectrometer, with an excitation laser wavelength of 514.5 nm. Elemental analyses (C, H, and N) were conducted on Perkin-Elmer 2400 CHN elemental analyzer, Zn and Ni were determined by a JY-ULTIMA2 ICP atomic emission spectrometer. The N_2， CO_2，and CH_4 adsorption isotherms were measured using a Quantachrome automatic volumetric gas adsorption analyzer. The samples were degassed at 60 °C for 4 h and 200 °C for 7 h prior to analysis (increasing rate: 10 °C•min^{-1}, outgas rate: 50 mbar•min^{-1}).

S-2. Synthetic methods.

Violet sample Zn/Ni-ZIF-8 was synthesized by stirring the mixtures of $Zn(NO_3)_2 \cdot 6H_2O$ (0.988 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.988 mmol), and HMeIM (15.808 mmol) in methanol (60 mL) for 24 hours. After washed with methanol (30 mL) for three times, violet powders were obtained. ZIF-8 was synthesized according the literature.[1]

The pyrolysis procedures of Zn/Ni-ZIF-8 were conducted in a horizontal quartz reactor under an N_2 flowing atmosphere at 1000 °C for 1 hour with the heating rate of 5 °C•min^{-1} to afford the composite, the yield is 32.5%. The calcination procedures of ZIF-8 were conducted under the same conditions, the yield is 40%.

S-3. The powder X-ray diffraction (PXRD) patterns of samples.

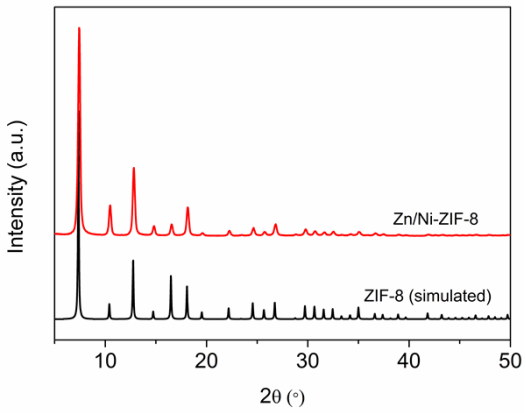

Figure S1. PXRD patterns of Zn/Ni-ZIF-8.

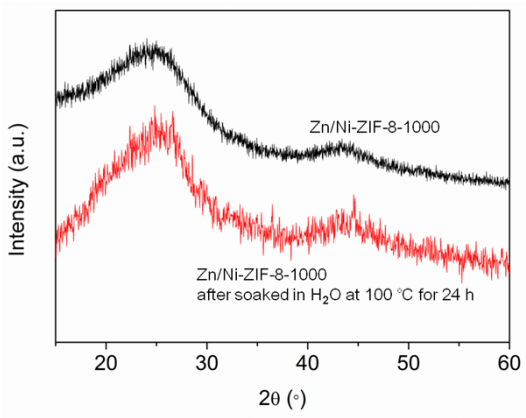

Figure S2. PXRD patterns of Zn/Ni-ZIF-8-1000 and after soaked in H_2O at 100 °C for 24 h.

S-4. Raman spectrum of sample.

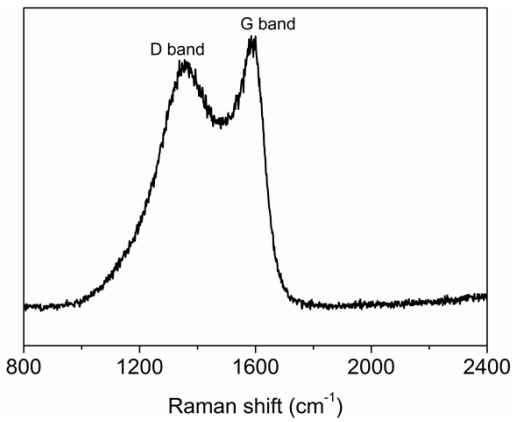

Figure S3. Raman spectrum of Zn/Ni-ZIF-8-1000 shows two broad peaks located at

1351 and 1600 cm^{-1}. The ratio of peak intensity (I_D/I_G) is 0.976.

S-5. EDX spectra of sample.

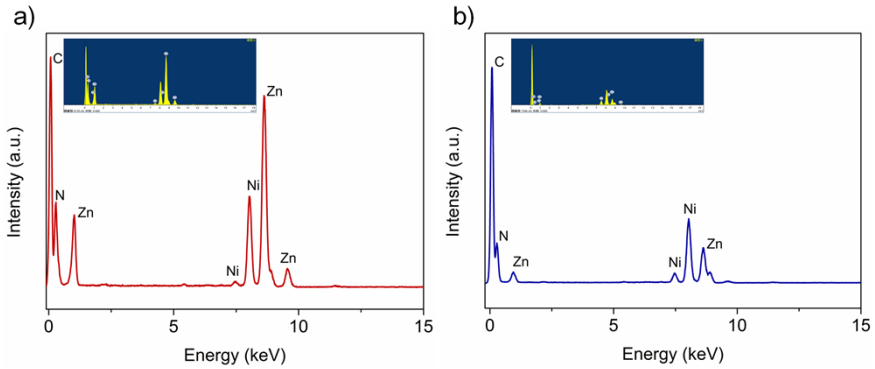

Figure S4. EDX plots of a) Zn/Ni-ZIF-8 and b) Zn/Ni-ZIF-8-1000. The inserts are the measure photos.

S-6. X-ray photoelectron spectroscopy (XPS) of sample.

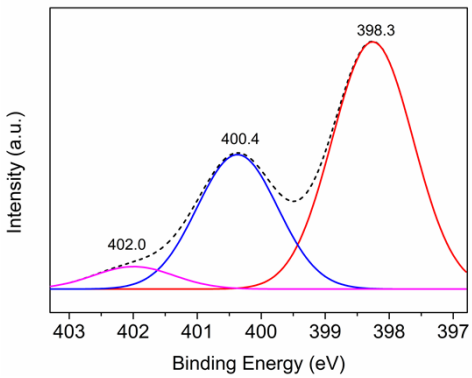

Figure. S5 X-ray photoelectron spectra (XPS) of the N 1s for Zn/Ni-ZIF-8-1000.

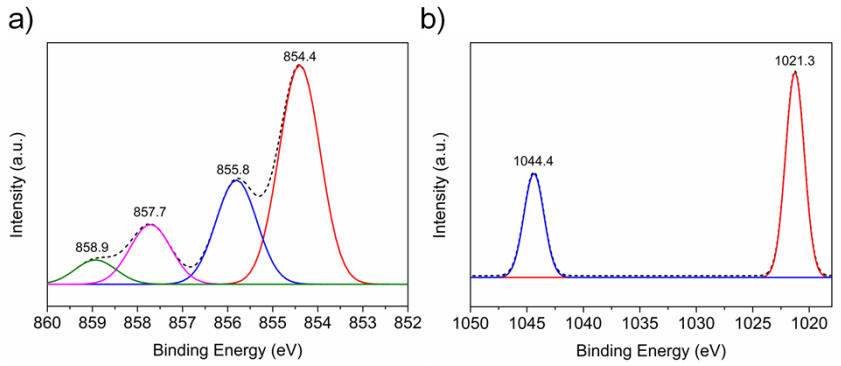

Figure. S6 X-ray photoelectron spectra (XPS) of the Zn/Ni-ZIF-8-1000: a) Ni 2p 2/3

and b) Zn 2p 2/3 and 2p 1/2.

S-7. N_2 adsorption analyses.

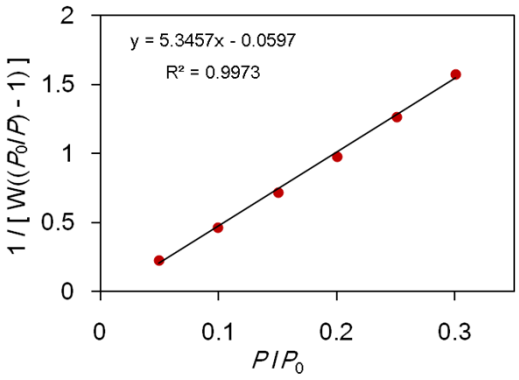

Figure S7. Langmuir equation fitting curve for Zn/Ni-ZIF-8-1000 N_2 isotherm (adsorption branch data points, P/P_0 = 0.05–0.30). Surface area 750 $m^2 \bullet g^{-1}$, linearity 0.9973.

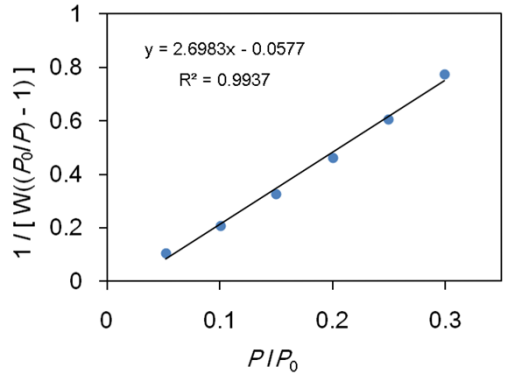

Figure S8. Langmuir equation fitting curve for Zn/Ni-ZIF-8 N_2 isotherm (adsorption branch data points, P/P_0 = 0.05–0.30). Surface area 1700 $m^2 \bullet g^{-1}$, linearity 0.9937.

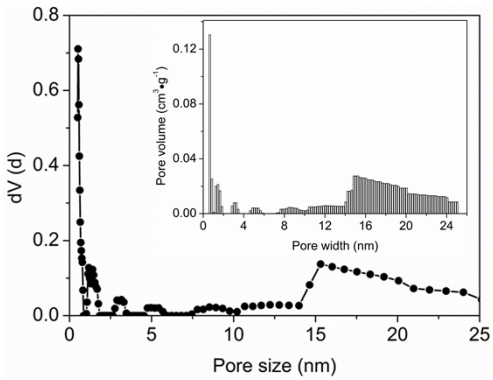

Figure S9. Pore size distributions (DFT) for Zn/Ni-ZIF-8-1000.

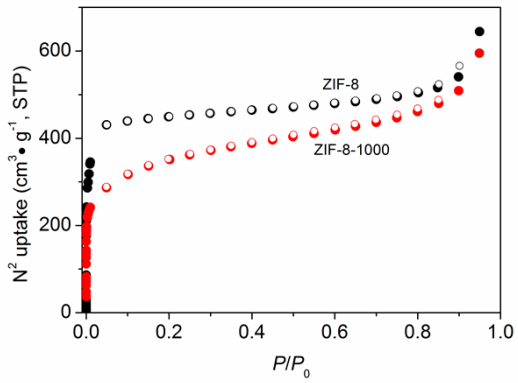

Figure S10. The nitrogen (N_2) adsorption/desorption isotherms of ZIF-8 (black) and ZIF-8-1000 (red) at 77 K.

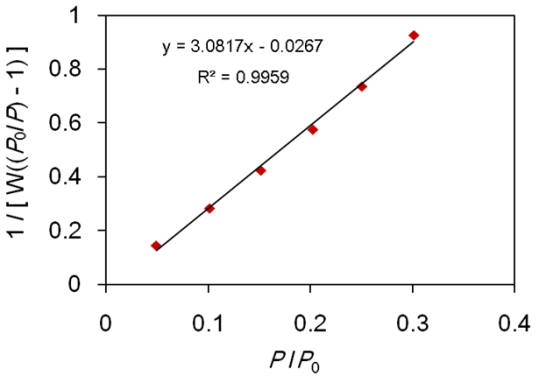

Figure S11. Langmuir equation fitting curve for Zn/Ni-ZIF-8-1000 N_2 isotherm (adsorption branch data points, P/P_0 = 0.05–0.30). Surface area 1260 $m^2 \bullet g^{-1}$, linearity 0.9959.

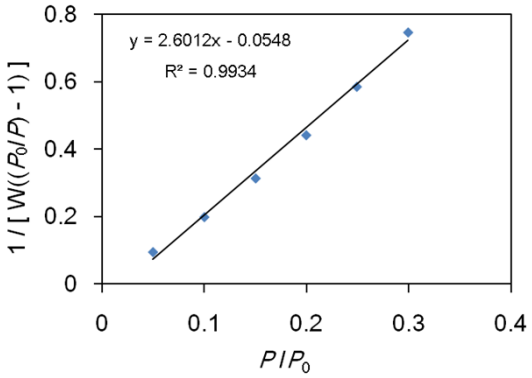

Figure S12. Langmuir equation fitting curve for Zn/Ni-ZIF-8 N_2 isotherm (adsorption

branch data points, P/P_0 = 0.05–0.30). Surface area 1690 $m^2 \cdot g^{-1}$, linearity 0.9934.

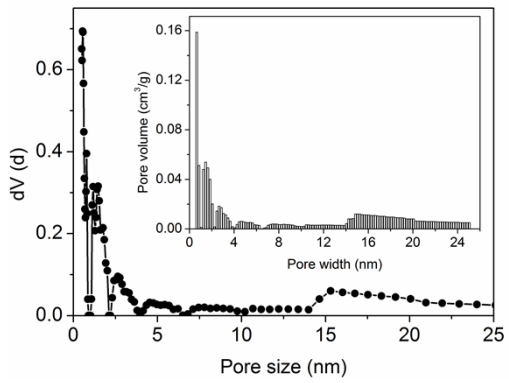

Figure S13. Pore size distributions (DFT) for ZIF-8-1000.

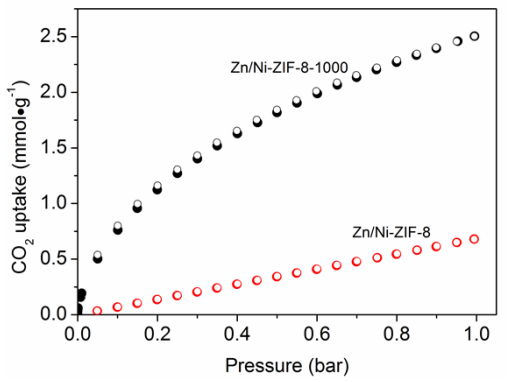

Figure S 14. The comparison of CO_2 adsorption isotherms collected at 298 K for Zn/Ni-ZIF-8-1000 (Black) and Zn/Ni-ZIF-8 (red).

Table S1. The comparison of CO_2 uptake for for Zn/Ni-ZIF-8-1000 and ZIF-8-1000.

	CO_2 uptake ($cm^3 \cdot g^{-1}$) 273 K	CO_2 uptake ($cm^3 \cdot g^{-1}$) 298 K	CO_2 uptake ($cm^3 \cdot g^{-1}$) 313 K
Zn/Ni-ZIF-8-1000	95.3	56.1	49.3
ZIF-8-1000	88.0	54.8	42.6

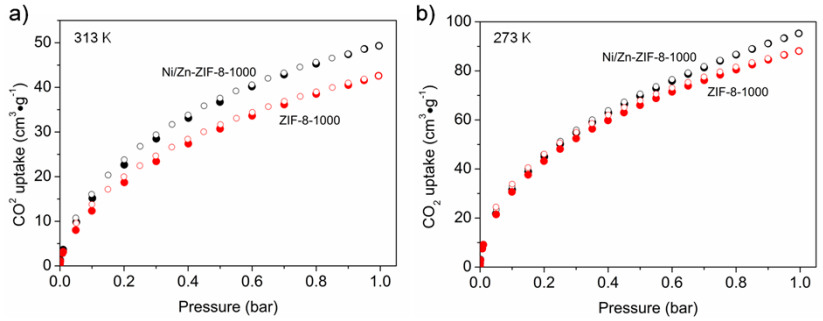

Figure S 15. The comparison of CO_2 adsorption isotherms collected at a) 313 K and b) 273 K for Zn/Ni-ZIF-8-1000 (Black) and ZIF-8-1000 (red).

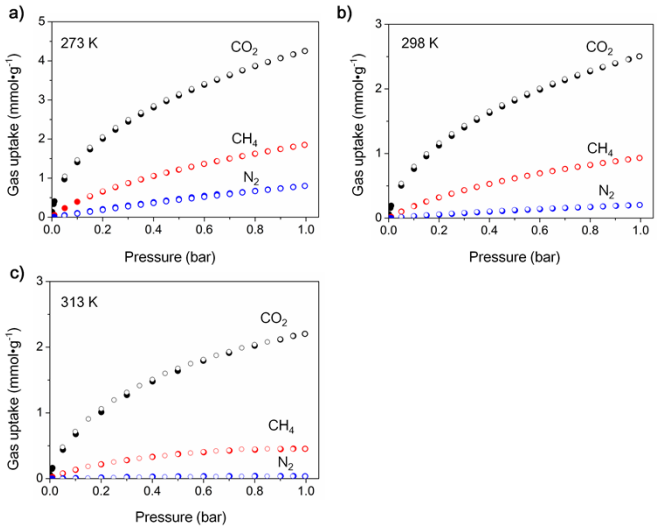

Figure S16. CO_2, CH_4, and N_2 adsorption isotherms of Zn/Ni-ZIF-8-1000 collected at a) 273 K, b) 298 K and c) 313K.

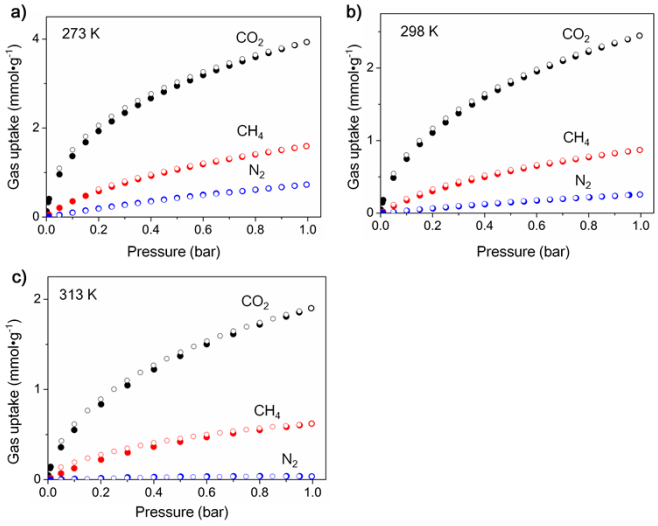

Figure S17. CO_2, CH_4 and N_2 adsorption isotherms of ZIF-8-1000 collected at a) 273 K, b) 298 K and c) 313K.

S-8. Gas selectivity analyses.

The isosteric heats of adsorption.

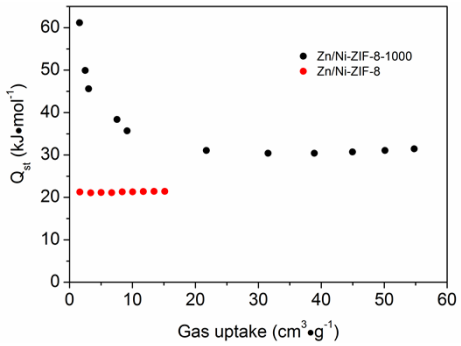

Figure S18. The isosteric heats of adsorption of CO_2 for Zn/Ni-ZIF-8 and Zn/Ni-ZIF-8-1000. The calculations were collected at 273K, 283K, and 298K. The results are 61.2 and 21.3 kJ•mol^{-1}, respectively.

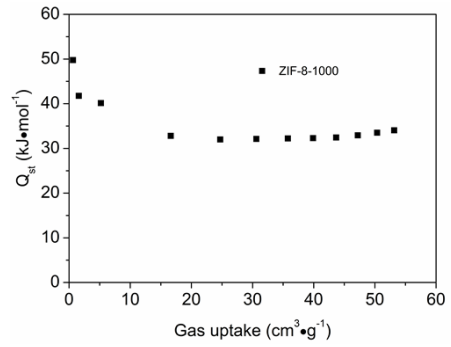

Figure S19. The isosteric heats of adsorption of CO_2 for ZIF-8-1000. The calculations were collected at 273K, 283K, and 298K. The result is 49.7 kJ•mol^{-1}.

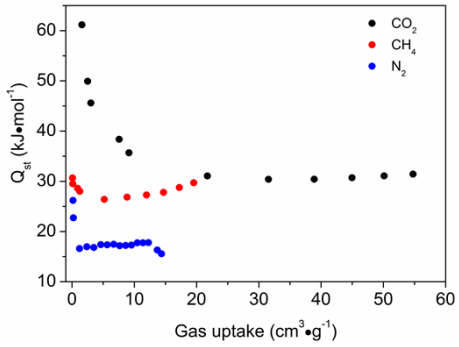

Figure S20. The isosteric heats of adsorption of CO_2, CH_4, and N_2 for Zn/Ni-ZIF-8-1000. The calculations were collected at 273K, 283K, and 298K. The results are 61.2, 30.7, and 26.2 kJ•mol^{-1} for CO_2, CH_4, and N_2, respectively.

Initial slope calculation.

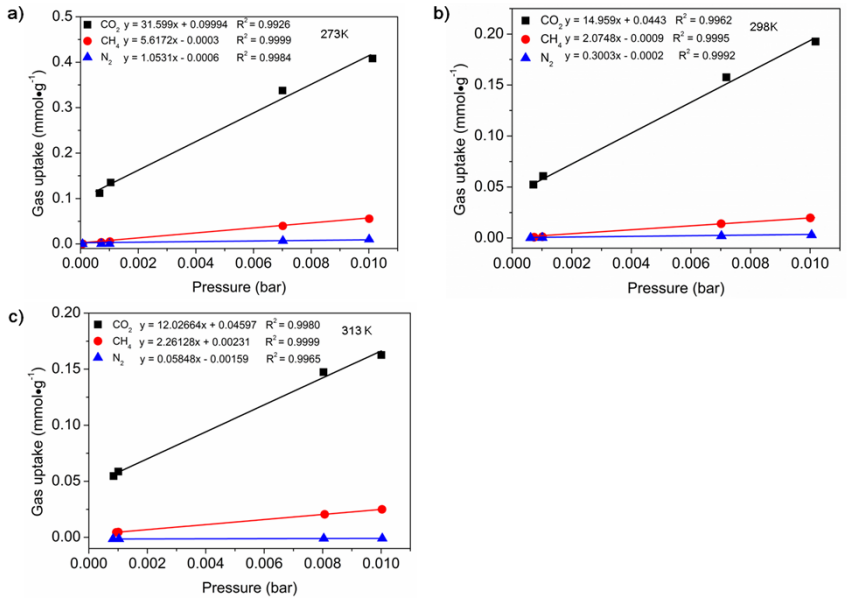

Figure S21. Initial slope calculation of Zn/Ni-ZIF-8-1000 for CO_2, CH_4 and N_2 isotherms collected at a) 273 K, 298K and 313 K.

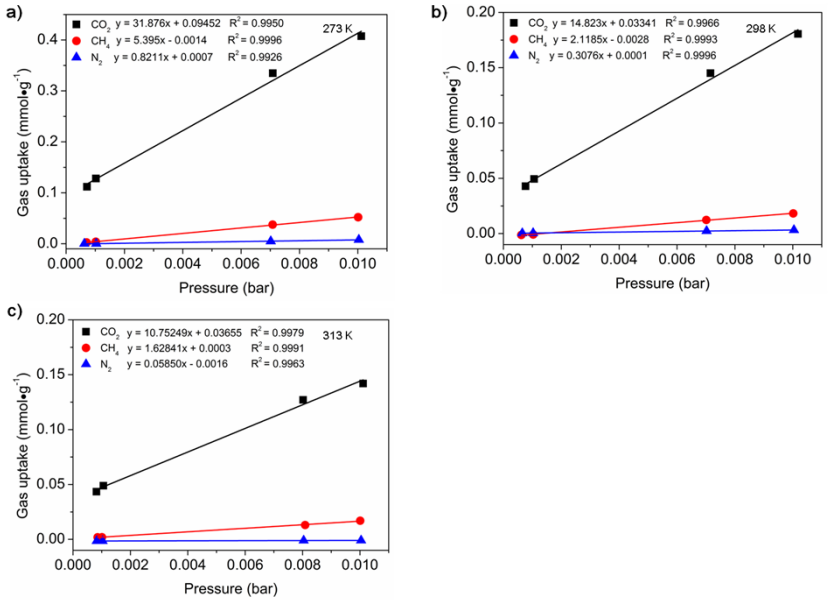

Figure S22. Initial slope calculation of ZIF-8-1000 for CO_2, CH_4 and N_2 isotherms collected at a) 273 K, b) 298 K, and 313 K.

Table S2. The comparison of gas selectivity (initial slope) results of Zn/Ni-ZIF-8-1000 and ZIF-8-1000.

	Zn/Ni-ZIF-8-1000			ZIF-8-1000		
	273 K	298 K	313 K	273 K	298 K	313 K
CO_2/N_2	30.0	50.0	205.7	38.8	48.2	183.8
CO_2/CH_4	5.6	7.2	5.31	5.9	7.0	6.6

IAST calculation..

In order to compare the efficacy of Zn/Ni-ZIF-8-1000 and ZIF-8-1000 for CO_2 over N_2 and CO_2 over CH_4 separation, we used the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz along with the pure component isotherm fits to determine the molar loadings in the mixture for specified partial pressures in the bulk gas phase. The dual-site Langmuir-Freundlich equation for CO_2, and the single-site Langmuir-Freundlich equation for N_2 and CH_4 adsorption were used for fitting of the 273 K and 298 K.

The adsorption selectivity for binary mixtures is defined by $S = (q_1/p_1)/(q_2/p_2)$.

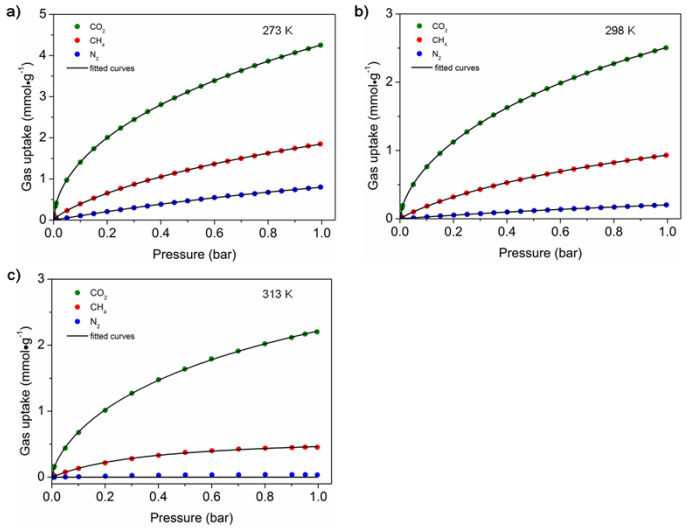

Figure S23. The corresponding isotherm fits (solid black lines) dual-site Langmuir model fits for CO_2 and single-site Langmuir model for CH_4 and N_2 of Zn/Ni-ZIF-8-1000 based on experimental pure component isotherms for CO_2 (olive circle), CH_4 (red circle) and N_2 (blue circle) at a) 273 K, b)298 K and c) 313 K.

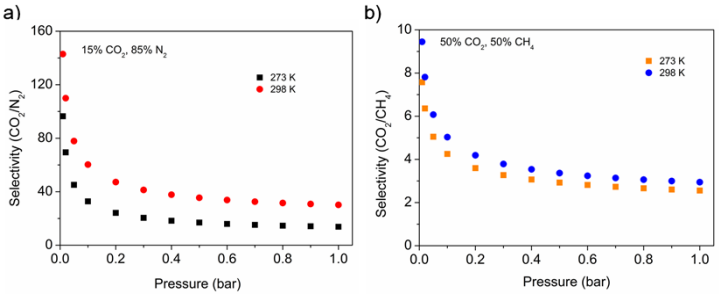

Figure S24. a) IAST adsorption selectivity of a) CO_2 over N_2 calculated under conditions of 15% CO_2 balanced with N_2 and b) CO_2 over CH_4 for 50/50 binary mixture for Zn/Ni-ZIF-8-1000 at 273 K and 298 K.

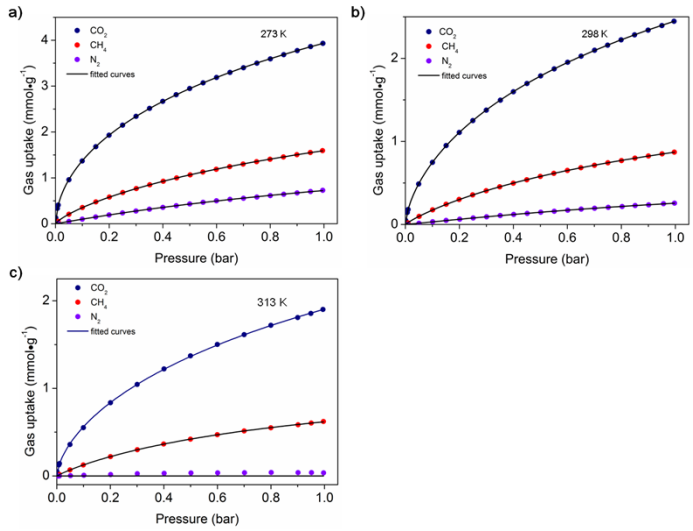

Figure S25. The corresponding isotherm fits (solid black lines) dual-site Langmuir model fits for CO_2 and single-site Langmuir model for CH_4 and N_2 based on experimental pure component isotherms of ZIF-8-1000 for CO_2 (navy circle), CH_4 (red circle) and N_2 (violet circle) at a) 273 K, b)298 K and c) 313 K.

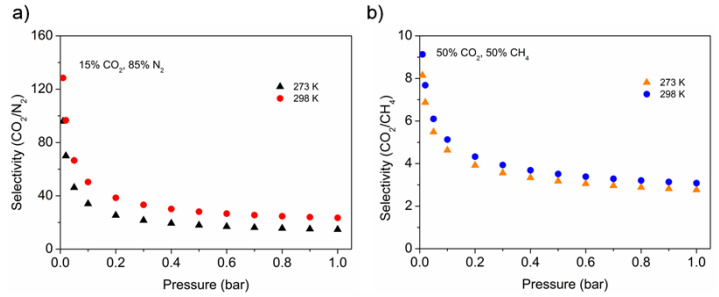

Figure S26. IAST adsorption selectivity of a) CO_2 over N_2 calculated under conditions of 15%CO_2 balanced with N_2 and b) CO_2 over CH_4 for 50/50 binary mixture for ZIF-8-1000 at 273 K and 298 K.

Table S3. The comparison of gas selectivity (IAST) results of Zn/Ni-ZIF-8-1000 and

ZIF-8-1000.

	Zn/Ni-ZIF-8-1000			ZIF-8-1000		
	273 K	298 K	313 K	273 K	298 K	313 K
CO_2/N_2[a]	13.8	30.2	124	14.7	23.5	102
CO_2/CH_4[b]	2.6	3	4.5	2.8	3	3.2

[a] Selectivity was calculated from IAST for 15/85 gas mixtures for CO_2/N_2

[b] Selectivity was calculated from IAST for 50/50 gas mixtures for CO_2/CH_4.

S-9. Elemental analyses.

Table S4. Elemental analyses data.

	C%	N%	H%	Zn%	Ni%
Zn/Ni-ZIF-8	41.75	24.53	4.42	26.4	0.65
Zn/Ni-ZIF-8-1000	72.80	9.46	0.85	2.93	1.66
Zn/Ni-ZIF-8-1000[a]	73.16	9.27	0.85	2.87	1.57

[a] after soaked in H_2O for 24 h at 100 °C.

References

[1] J. Cravillon, S. Münzer, S. Lohmeier, A. Feldhoff, K. Huber, and M. Wiebcke, *Chem. Mater.* 2009, **21**, 1410.