Supporting information

Synthesis of Zeolitic Tetrazolate-Imidazolate Frameworks (ZTIFs) in Ethylene Glycol

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Materials and general methods

All chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H and N were measured on a Vario MICRO E III elemental analyzer. The IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. ^{1}HNMR experiments were carried out on a Bruker spectrometer operating at resonance frequencies of 400 MHz. Powder X-ray diffraction data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of 5° min^{-1}. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N_2 (30-600 °C range) at a heating rate of 10 °C min^{-1}. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer. The gases adsorption isotherms were measured by using ASAP-2020 volumetric adsorption equipment.

Synthesis of $Zn_5(tz)_2(nim)_8$ (ZTIF-11): the mixture of $Zn(NO_3)_2{\cdot}6(H_2O)$ (0.25 mmol, 0.075 g), tetrazole (tz, 0.10 mmol, 0.007 g), 2-nitroimidazole (nim, 0.40 mmol, 0.045 g) in Ethylene Glycol (2 ml) was sealed in a 20 ml vial and heated to 120 ^{o}C for 1 days, and then cooled to room-temperature. The pale yellow polyhedral crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 51%). The micro-synthesis condition of ZTIF-11 can be scalable to 0.43 gram scale by using the same reaction conditions in a larger volume (23 mL Teflon-lined stainless steel reactor). The co-existence of tz and nim in ZTIF-11 are proved by ^{1}HNMR. To prove the phase purity of the bulk sample, the powder-XRD (PXRD) and elemental analysis (EA) of the

activated samples are presented here. A comparison calculated/found EA of the activated samples proved the phase purity of the sample. The ratio of these two ligands has been obtained from the single crystal data as well as EA results. Anal. Calcd for $C_{26}H_{18}N_{32}O_{16}Zn_5$: Calcd. C, 22.93; H, 1.33; N, 32.92; Found C, 22.99; H, 1.38; N, 32.85. IR (KBr cm^{-1}): 2936 (m), 1652 (s), 1500(s), 1365 (vs), 1281 (m), 951 (s), 794 (m), 695 (m).

Synthesis of Zn_2(ptz)(nim)$_3$ (ZTIF-12): $Zn(NO_3)_2 \cdot 6(H_2O)$ (0.25 mmol, 0.075 g), 5-phenyl-1H-tetrazole (ptz, 0.125 mmol, 0.018 g), 2-nitroimidazole (nim, 0.375 mmol, 0.042 g) in Ethylene Glycol (2 ml) was sealed in a 20 ml vial and heated to 120 ^oC for 2 days, and then cooled to room-temperature. The yellow crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 55%). Anal. Calcd for $C_{16}H_{11}N_{13}O_6Zn_2$: Calcd. C, 31.39; H, 1.81; N, 29.75; Found C, 31.30; H, 1.85; N, 29.86. IR (KBr cm^{-1}): 2922 (w), 1669 (s), 1457 (s), 1386 (vs), 1284 (m), 1075 (s), 758 (m), 687 (m).

Synthesis of Zn(ett) (nim) (ZTIF-13): the mixture of $Zn(NO_3)_2 \cdot 6(H_2O)$ (0.25 mmol, 0.075 g), 5-(Ethylthio)-1H-tetrazole (ett, 0.25 mmol, 0.033 g), 2-nitroimidazole (nim, 0.25 mmol, 0.028 g) in Ethylene Glycol (2 ml) was sealed in a 20 ml vial and heated to 120 ^oC for 2 days, and then cooled to room-temperature. The yellow crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 60%). Anal. Calcd for $C_6H_7N_7O_2SZn$: Calcd. C, 23.50; H, 2.30; N, 31.97; Found C, 23.61; H, 2.39; N, 31.86. IR (KBr cm^{-1}): 2933 (m), 1671 (s), 1499 (s), 1390 (vs), 1281 (m), 1095 (s), 760 (m), 697 (m).

Table S1. The BET surface areas and CO_2 uptake capacities of some ZTIFs.

Compounds	BET ($m^2\ g^{-1}$)	Crystal density ($m^2\ g^{-1}$)	273K ($cm^3\ g^{-1}$)	273K ($cm^3\ cm^{-3}$)	RT ($cm^3\ g^{-1}$)	RT ($cm^3\ cm^{-3}$)	Ref.
ZTIF-1	1430	0.954	86	82.0	49.0 (295K)	46.7 (295K)	1
FIR-30	1420	0.640					2
HZIrF-1R	1026	1.281	73	93.5	40.0 (293K)	51.2 (293K)	3
ZTIF-6	790	1.059	53	56.1	24.0 (300K)	25.4 (300K)	4
ZTIF-11	460.56	1.467	76.2	111.8	60.2 (296K)	88.3 (296K)	this work

RT: room temperature.

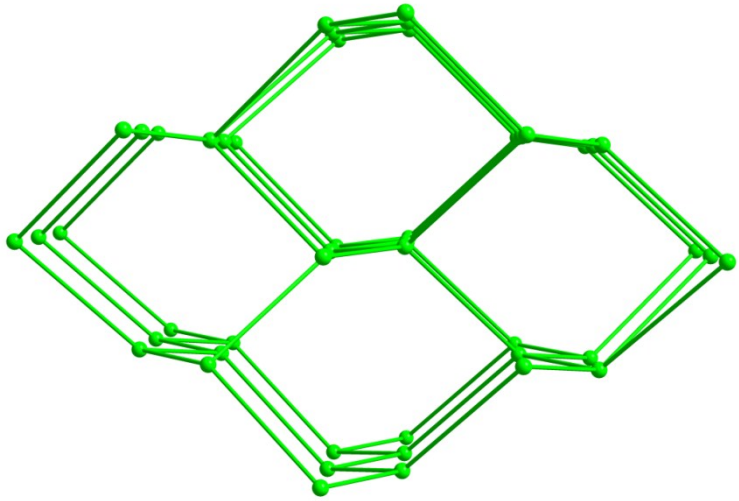

Fig. S1. The 4-connected **dmp** topology in ZTIF-13.

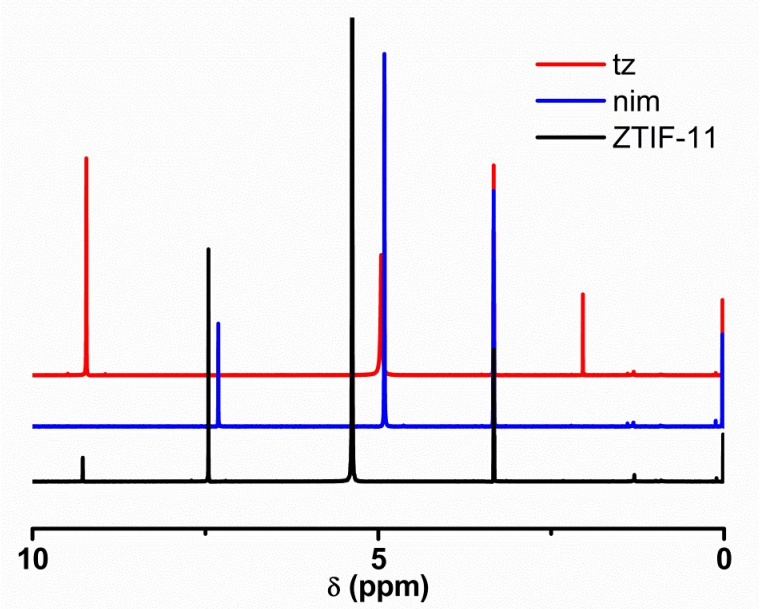

Fig. S2. The ^{1}HNMR spectra of tz (red line), nim (blue line) and ZTIF-11 (black line) dissolved by HCl in MeOD solvent.

The co-existence of tz and nim in ZTIF-11 are proved by ^{1}HNMR. The ^{1}HNMR spectrum of ZTIF-11 dissolved in HCl (Fig. S2) shows both peaks around 7.46 ppm of 2-nitroimidazole and 9.27 ppm of tetrazole.

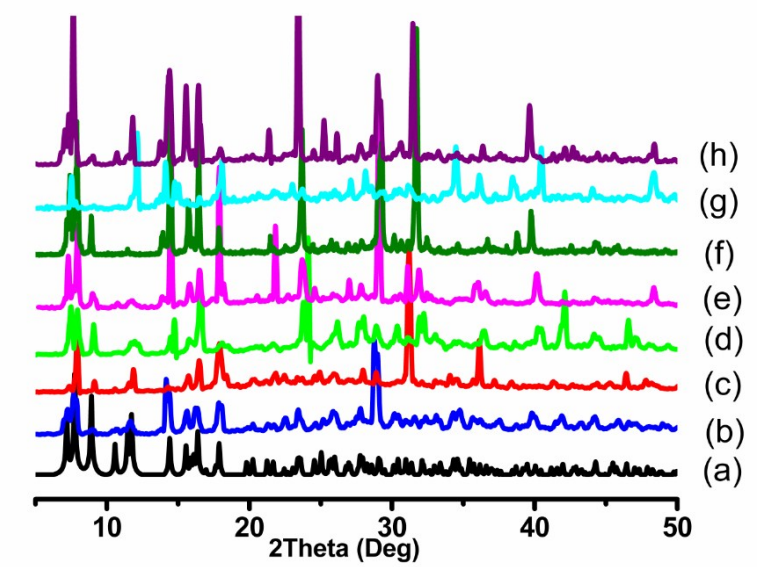

Fig. S3. The powder XRD patterns of ZTIF-11 under different conditions: (a) simulated; (b) as-synthesized; (c) soaked in alcohol for 7 days; (d) soaked in CH_2Cl_2 for 7 days; (e) soaked in DMF for 7 days; (f) soaked in CH_3OH at 65 ^oC for 7 days; (g) soaked in water for 7 days and (h) after degas.

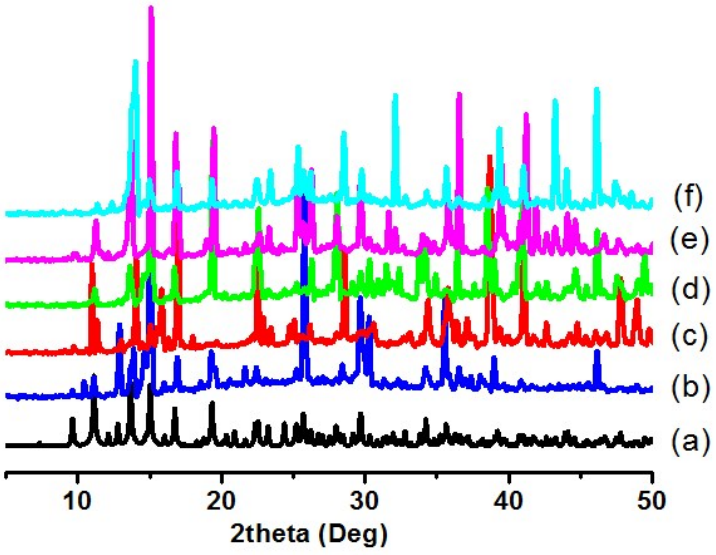

Fig. S4. The powder XRD patterns of ZTIF-12 under different conditions: (a) simulated; (b) as-synthesized; (c) soaked in alcohol for 7 days; (d) soaked in CH_2Cl_2 for 7 days; (e) soaked in DMF for 7 days; (f) soaked in CH_3OH at 65 ^oC for 7 days and (g) soaked in water for 7 days.

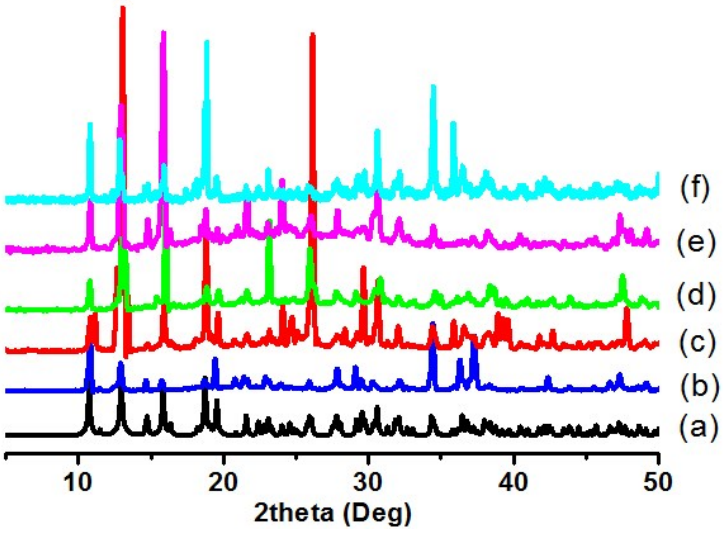

Fig. S5. The powder XRD patterns of ZTIF-13 under different conditions: (a) simulated; (b) as-synthesized; (c) soaked in alcohol for 7 days; (d) soaked in CH_2Cl_2 for 7 days; (e) soaked in DMF for 7 days; (f) soaked in CH_3OH at 65 ^oC for 7 days and (g) soaked in water for 7 days.

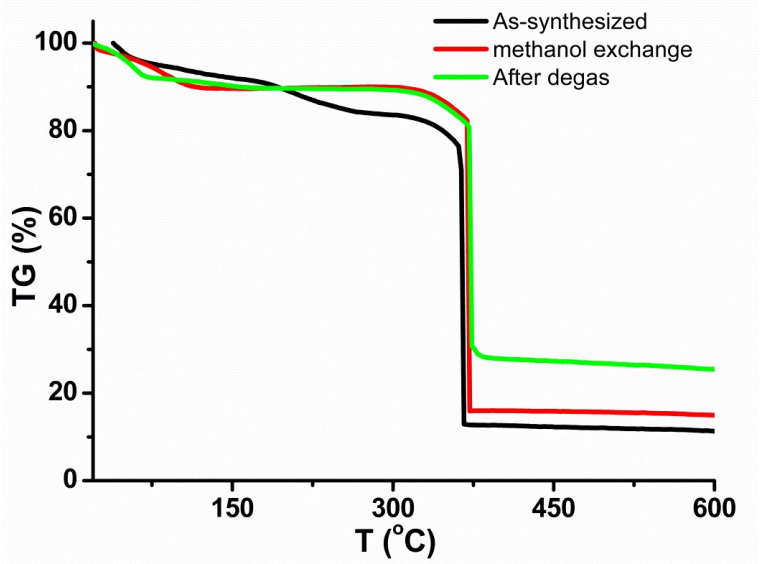

Fig. S6. The TG plots of (a) ZTIF-11 under different conditions.

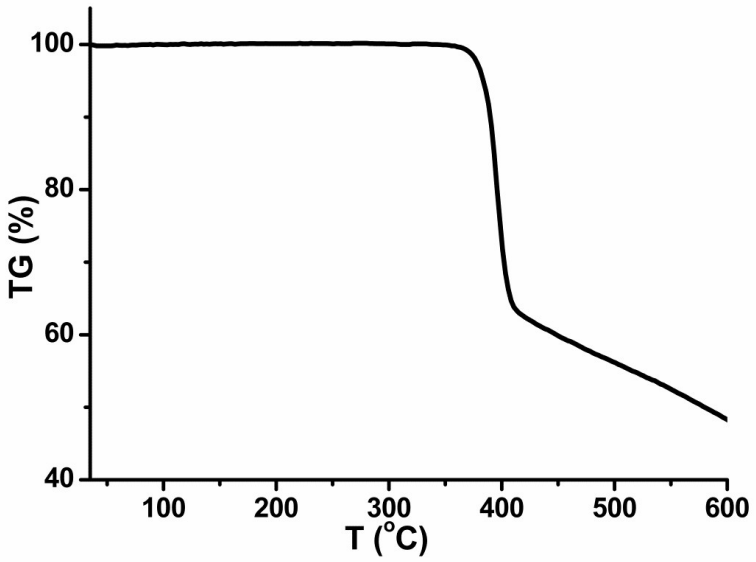

Fig. S7. The TG plots of ZTIF-12.

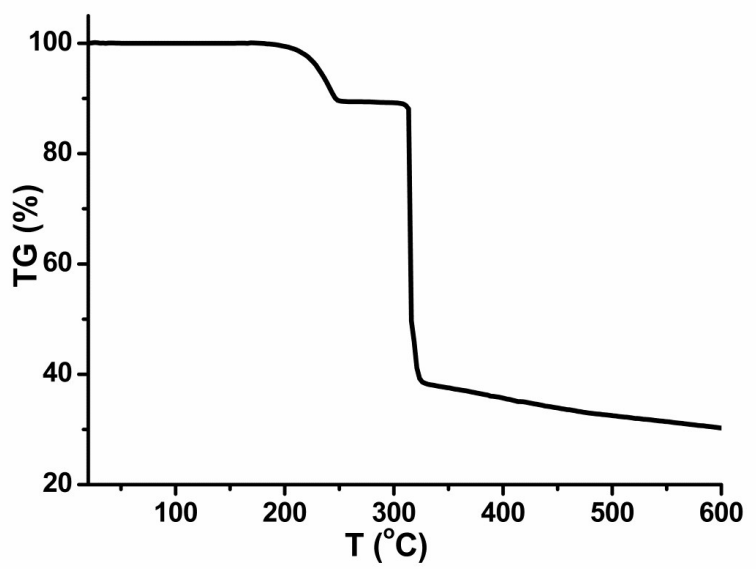

Fig. S8. The TG plots of ZTIF-13.

Isosteric heat of gas adsorption

The isosteric heats of adsorption were calculated according to Clausius-Clapeyron equation:

$$\frac{\partial(\ln P)}{\partial(1/T)} = -\frac{Qst}{R} \qquad (1)$$

where $\mathbf{Q_{st}}$ is the isosteric heats of adsorption, **R** is gas constant (8.314 J/(K mol^{-1})). As is shown in

Fig. S9, the isosteric heats of CO_2 adsorption for ZTIF-11 are between 22.2 to 24.7 kJ/mol. The isosteric heats of CH_4 adsorption (Fig. S10) for ZTIF-11 are between 16.3 to 17.9 kJ/mol.

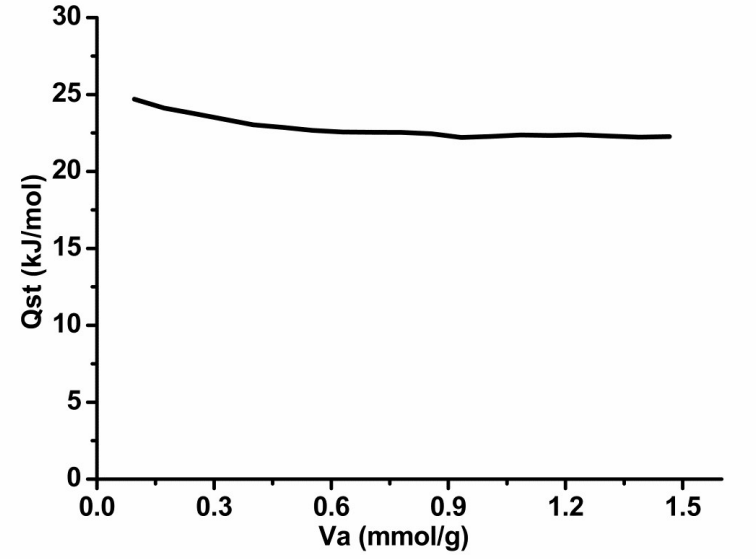

Fig. S9. The isosteric heat of CO_2 adsorption for **ZTIF-11** estimated by Clausius-Clapeyron equation.

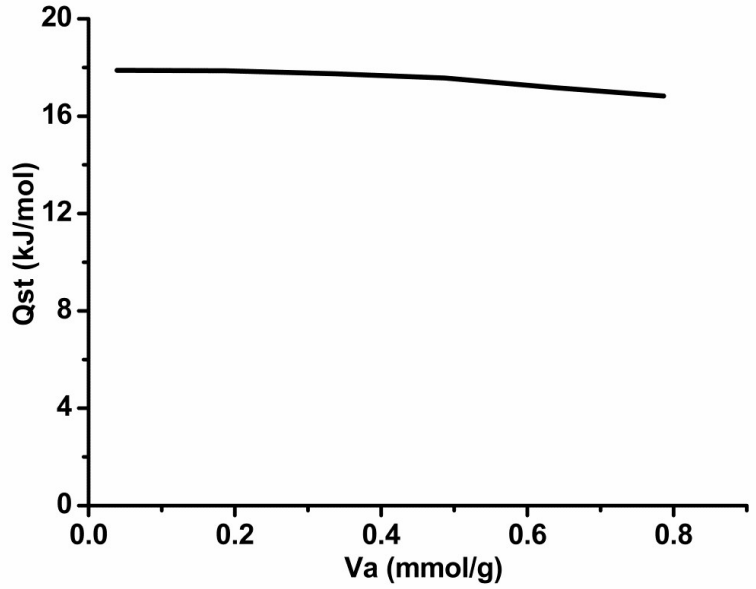

Fig. S10. The isosteric heat of CH_4 adsorption for **ZTIF-11** estimated by Clausius-Clapeyron equation.

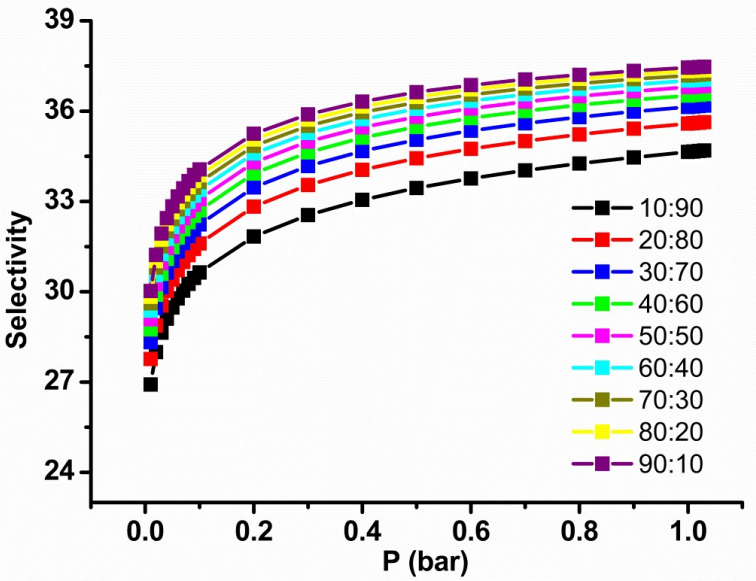

Fig. S11. Mixture adsorption selectivity predicted by IAST of ZTIF-11 for CO_2 over N_2 dependent on pressure at 296K.

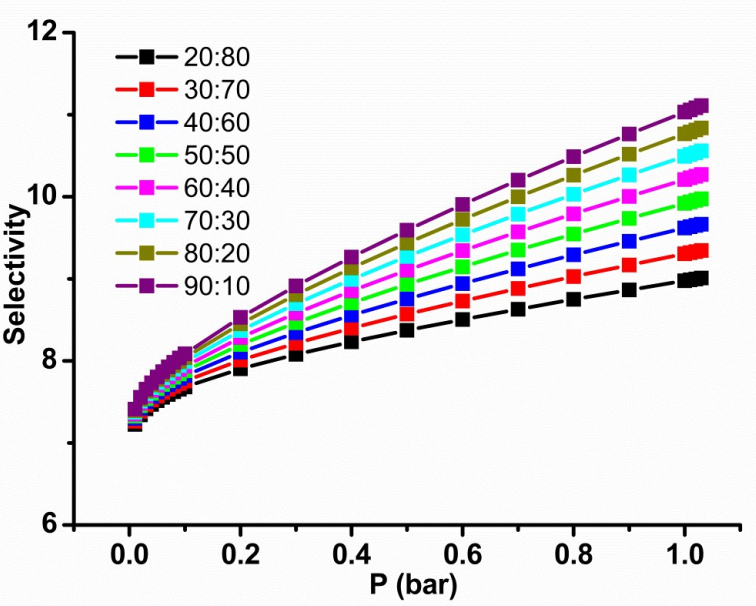

Fig. S12. Mixture adsorption selectivity predicted by IAST of ZTIF-11 for CO_2 over CH_4 dependent on pressure at 296K.

References

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