Supporting Information

Adjustment of Performance and Stability in Isostructural Zeolitic Tetrazolate-Imidazolate Frameworks

Hai-Zhen Li[1#], Dong-Ying Du[2#], Yayong Sun[1], Fei Wang[1]* and Jian Zhang[1]

[1]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, the Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China. E-mail: wangfei04@fjirsm.ac.cn.

[2]National & Local United Engineering Lab for Power Battery, Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China.

Experimental section

Materials and instrumentation: All reagents were purchased commercially and used without further purification. All syntheses were carried out in a 20 ml vial under autogenous pressure. All Powder X-ray diffraction analyses were recorded on a Rigaku Dmax2500 diffractometer with Cu Kα radiation (λ = 1.54056 Å) with a step size of 5°. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. Elemental analyses (C, H, N) were performed on a Flash EA 2000 elemental analyzer. ^{1}H NMR experiments were carried out on a Bruker spectrometer operating at resonance frequencies of 400 MHz. The gases adsorption isotherms were measured by using ASAP 2020 volumetric adsorption equipment.

Synthesis of $Zn(5\text{-etz})_{0.84}(2\text{-mim})_{1.14}$ (ZTIF-9): The mixture of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (0.5 mmol, 0.110 g), 5-ethyltetrazole (Hetz, 0.5 mmol, 0.049 g), 2-methylimidazole (Hmim, 0.5 mmol, 0.041 g) in *N*,*N*-dimethylformamide (DMF, 2 mL) and ethanol (2 mL) was sealed in a 20 mL vial and heated to 120 °C for 3 days, and then cooled to room-temperature. The colorless polyhedral crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 55%). Anal. Calcd for ZTIF-9 (activated): Calcd. C, 35.55; H, 4.18; N, 33.16; Found C, 35.33; H, 4.18; N, 33.09

Synthesis of $Zn(5\text{-vtz})_{0.63}(2\text{-mim})_{1.37}$ (ZTIF-10): The mixture of $Zn(CH_3CO_2)_2{\cdot}2H_2O$ (0.5 mmol, 0.110 g), 5-vinyltetrazole (Hvtz, 0.5 mmol, 0.050 g), Hmim (0.5 mmol, 0.041 g) in DMF (2 mL) and ethanol (2 mL) was sealed in a 20 mL vial and heated to 120 °C for 3 days, and then cooled to room-temperature. The pale yellow polyhedral crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 52%). Anal. Calcd for ZTIF-10 (activated): Calcd. C, 37.48; H, 3.73; N, 31.11; Found C, 37.59; H, 3.81; N, 30.71.

The co-existence of 5-etz and 2-mim in ZTIF-9 and 5-vtz and 2-mim in ZTIF-10 are proved by ^{1}H NMR. In combination with elemental analysis (EA) results, the ratio of Hetz to Hmim is 3:4 in ZTIF-9, And 5:11 in ZTIF-10.

Table *S1*. Crystallographic Data and Structure Refinement Details for **ZTIF-9** and **ZTIF-10**.

Compounds	**ZTIF-9**	**ZTIF-10**
Formula	$C_{50}H_{70}N_{40}Zn_7$	$C_{59}H_{70}N_{42}Zn_8$
Formula weight	1689.22	1890.74
Crystal system	Cubic	Cubic
Space group	*I*-43*m*	*I*-43*m*
a (Å)	17.0156(7)	17.0183(5)
b (Å)	17.0156(7)	17.0183(5)
c (Å)	17.0156(7)	17.0183(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	4926.6(6)	4928.9(3)
Z	12	12
μ (Mo K*a*) (mm^{-1})	1.939	1.938
F (000)	1416.0	1416.0
Temperature (K)	100	100
Observed data [($I > 2\sigma(I)$]	2188	2269
R_{int}	0.0269	0.0110
Data/restraints/parameters	810/0/39	780/7/42
R_1, wR_2 [$I > 2\sigma(I)$]	0.0544, 0.1653	0.0256, 0.0772
R_1, wR_2 (all data)	0.0563, 0.1661	0.0258, 0.0777
Goodness-of-fit on F^2	1.135	1.107
CCDC No.	1961700	1961701

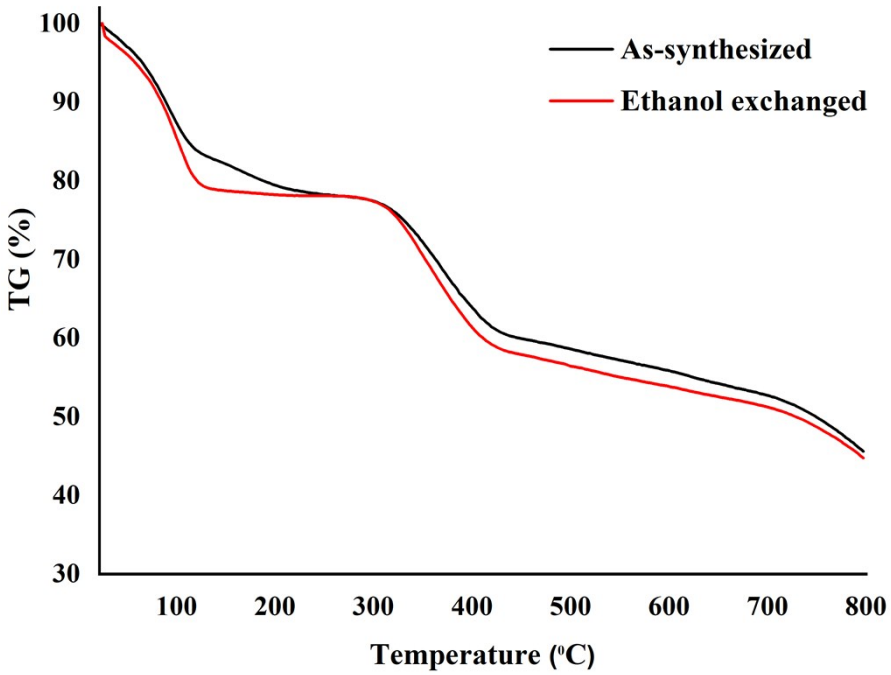

Figure S1. The TG plots of **ZTIF-9** under different conditions.

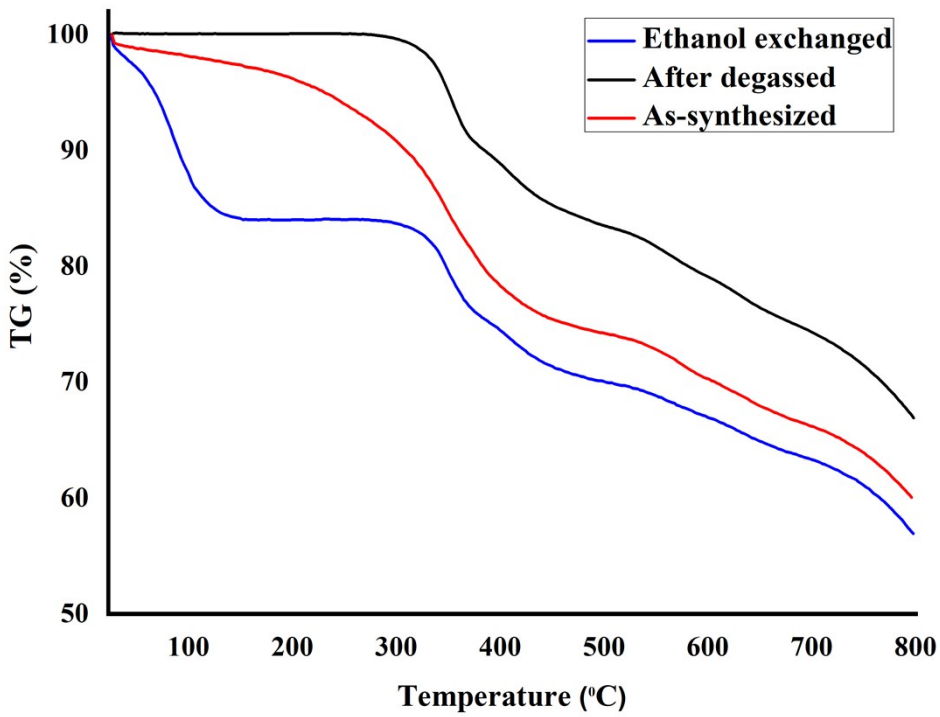

Figure S2. The TG plots of **ZTIF-10** under different conditions.

The TGA traces of the ZTIF-9 and ZTIF-10 samples and the samples after being immersed in dry ethanol solvents at 60 °C for three days are shown in Figure S1 and Figure S2, showing effective solvent-exchange. In particular, in the TGA trace of ethanol-exchanged samples of ZTIF-10, the initial

gradual weight-loss step of 10.6% till 325 °C were replaced by a small initial step (16.6% of weight loss) at 125 °C temperature, a plateau to ca. 325 °C and a sharp weight loss from that point onwards indicates the decomposition of the material. The TGA trace of ethanol-exchanged samples after degassed shows that the samples were fully activated. Similarly, for ZTIF-9 after ethanol exchanged, a small initial step (13.0% of weight loss) at 134 °C temperature, a plateau to ca. 290 °C and a sharp weight loss from that point onwards indicates the decomposition of the material.

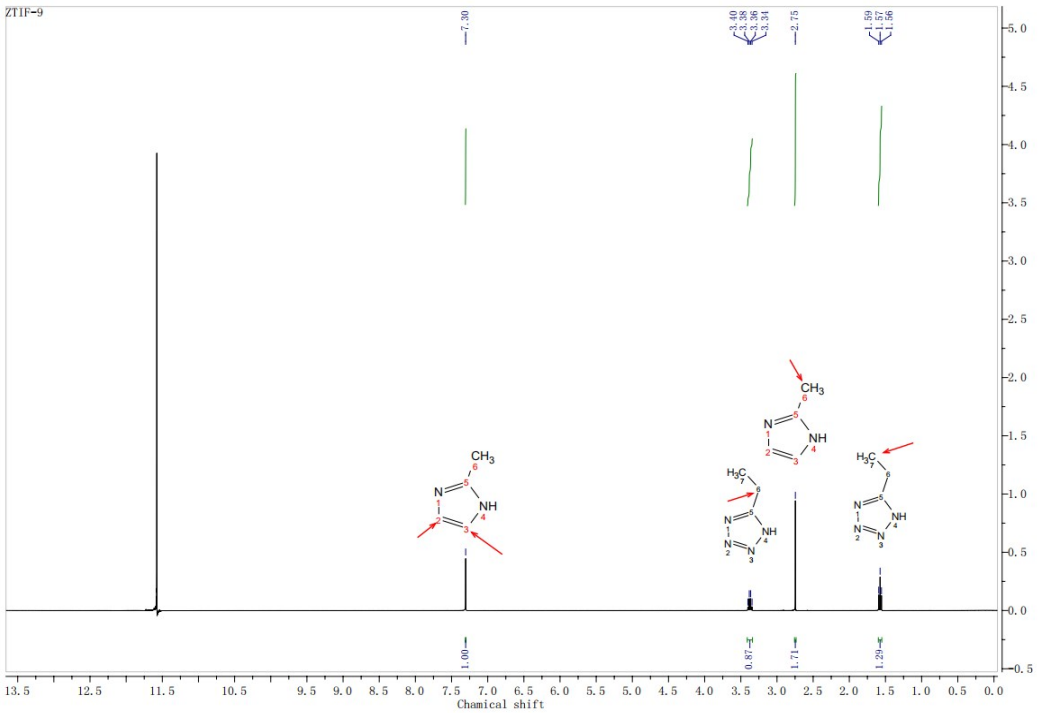

Figure S3. The ^{1}HNMR spectra of **ZTIF-9** in CF_3COOD solvent.

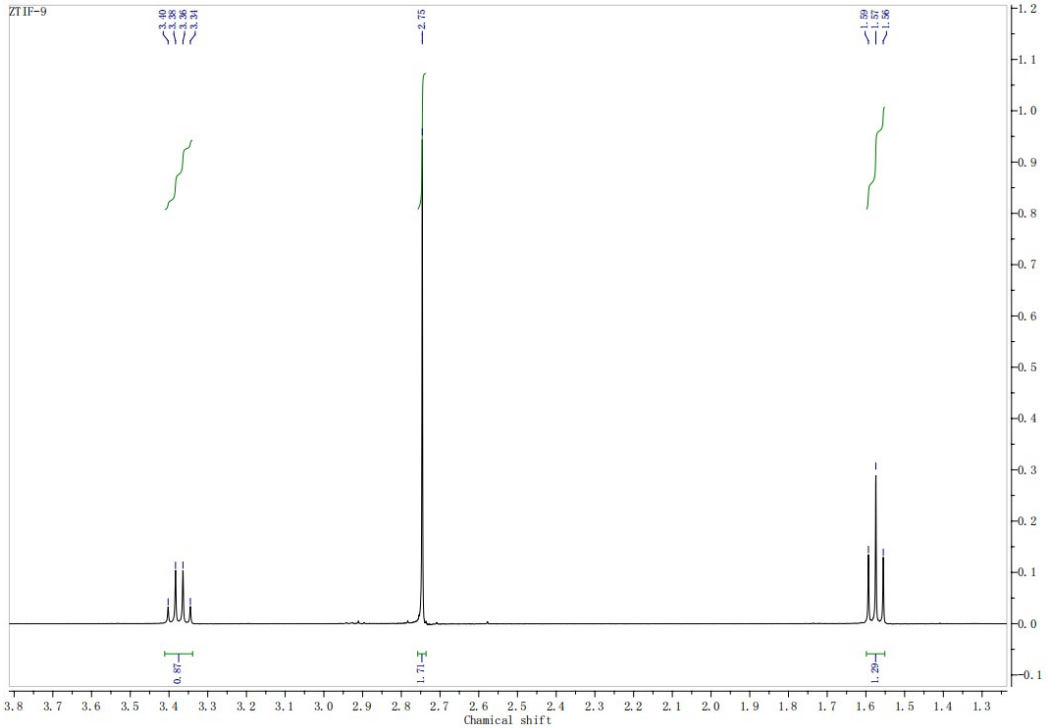

Figure S4. The high field zone ^{1}HNMR spectra of **ZTIF-9** in CF_3COOD solvent.

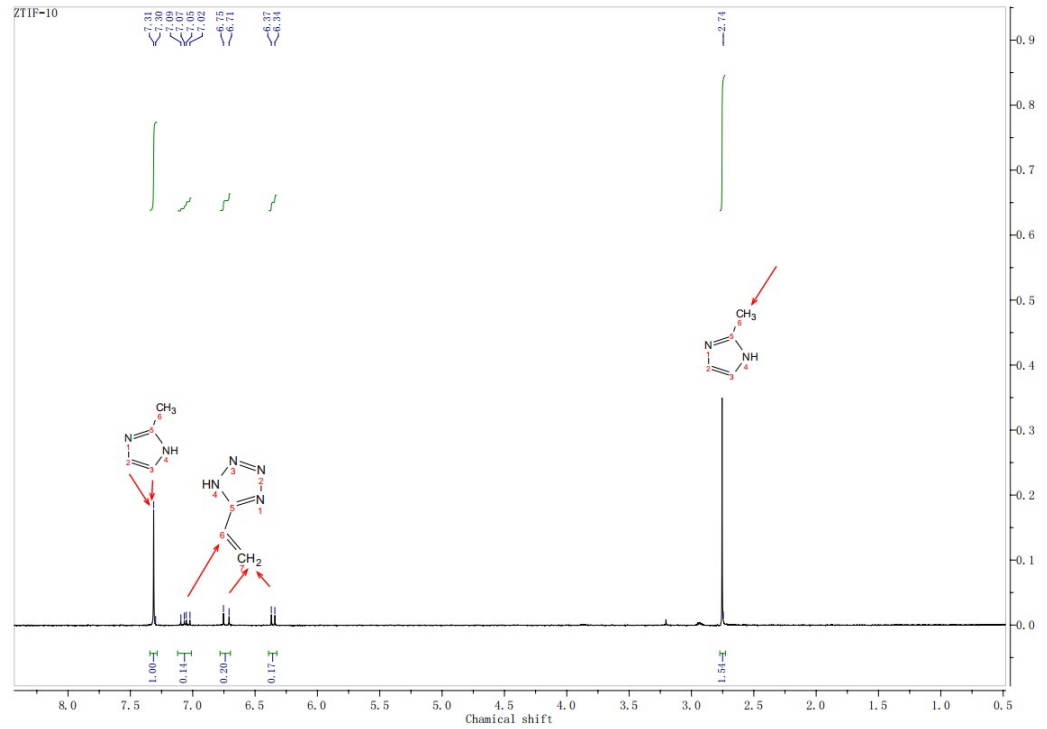

Figure S5. The ^{1}HNMR spectra of **ZTIF-10** in CF_3COOD solvent.

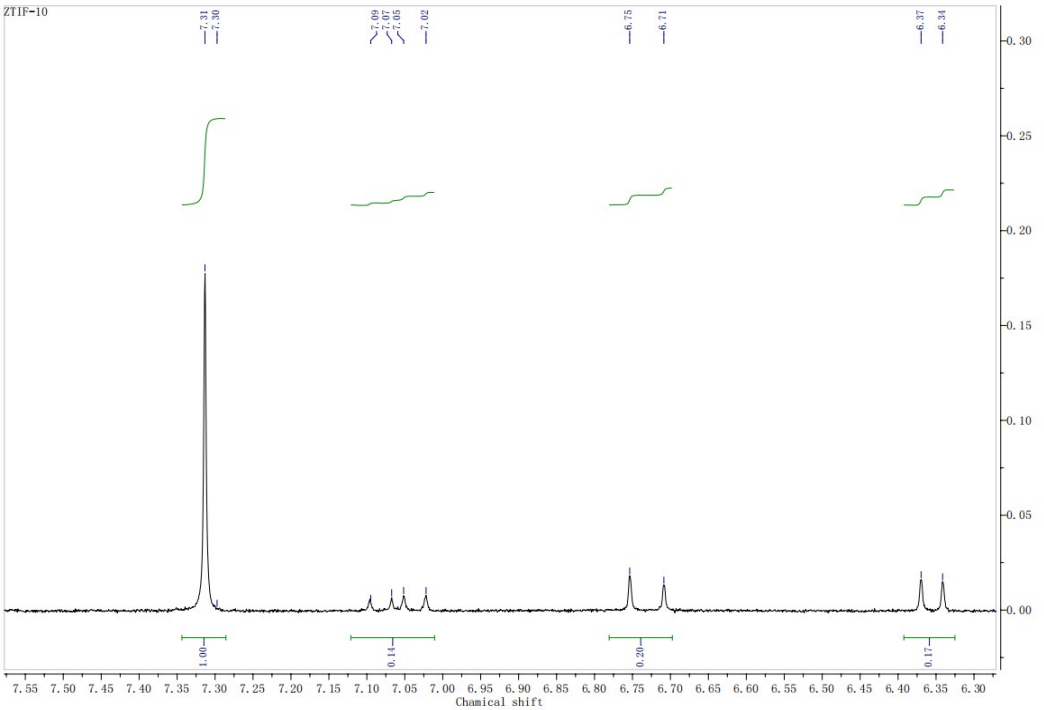

Figure S6. The low field zone ^{1}HNMR spectra of **ZTIF-10** in CF_3COOD solvent.

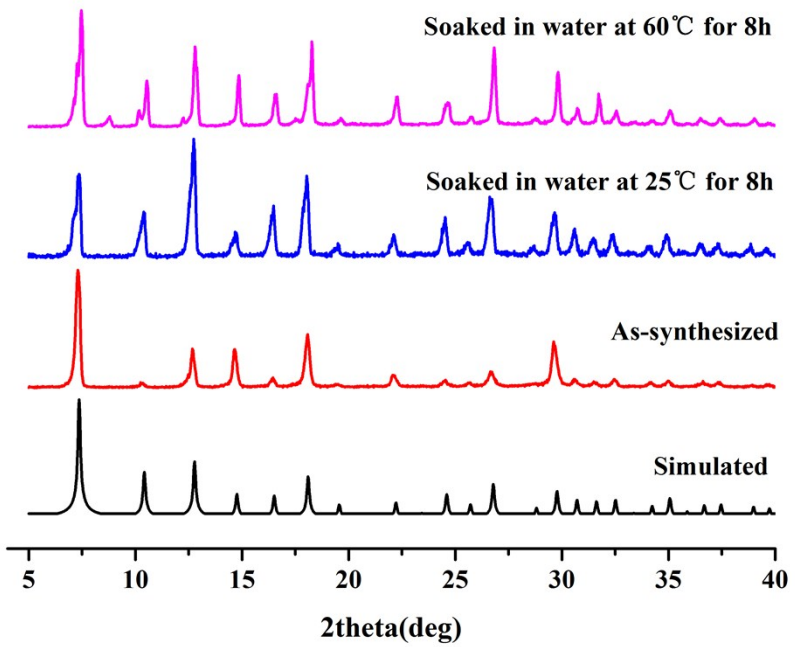

Figure S7. The powder XRD patterns of **ZTIF-1** soaked in water.

Table *S2.* The gas uptake summary of ZTIF-9 and ZTIF-10

Gas(ml/g) / T(K)	C_2H_2	CO_2
273(ZTIF-9)	88.6	55.3
298(ZTIF-9)	46.5	27.3
273(ZTIF-10)	65.2	37.3
298(ZTIF-10)	36.9	26.7

Isosteric heat of gas adsorption

The gas sorption data for ZTIFs measured up to 1 bar at different temperatures were fitted by the virial equation (1) to estimate the enthalpy of adsorption.

$$\ln(P) = \ln(N) + 1/T(a_0 + a_1N + a_2N^2 + ...) + (b_0 + b_1N + b_2N^2 + b_3N^3 + \ldots) \quad (1)$$

Where P is the pressure, N is the amount adsorbed, T is the temperature, a_0, a_1 a_2 ... and b_0 b_1 b_2 … are the temperature independent empirical parameters.

The isosteric heat of adsorption was estimated from the following equation (2) as a function of gas uptake.

$$Q_{st} = -R(A_0 + A_1n + A_2n^2 + \ldots) \quad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant of 8.314 J $K^{-1}mol^{-1}$.

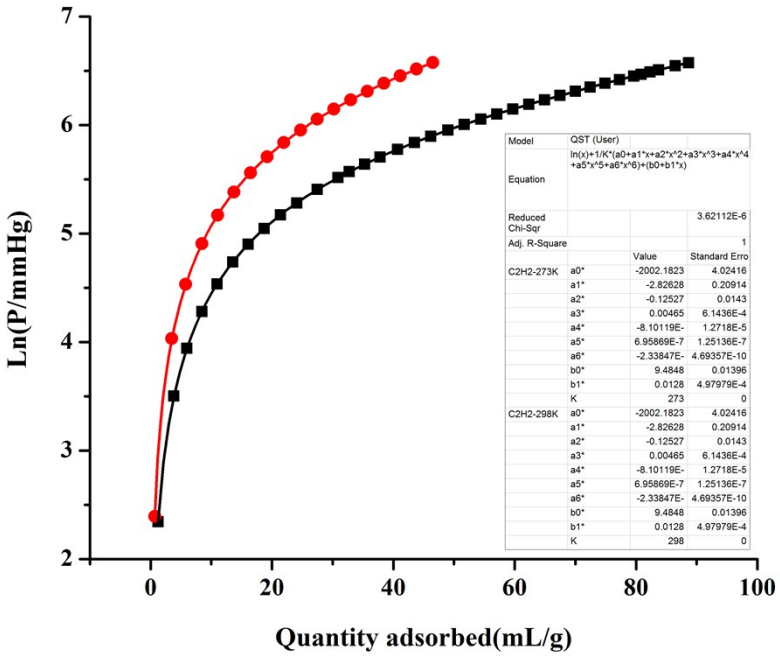

Figure S8. The C_2H_2 sorption isotherms for **ZTIF-9** fitting by virial method.

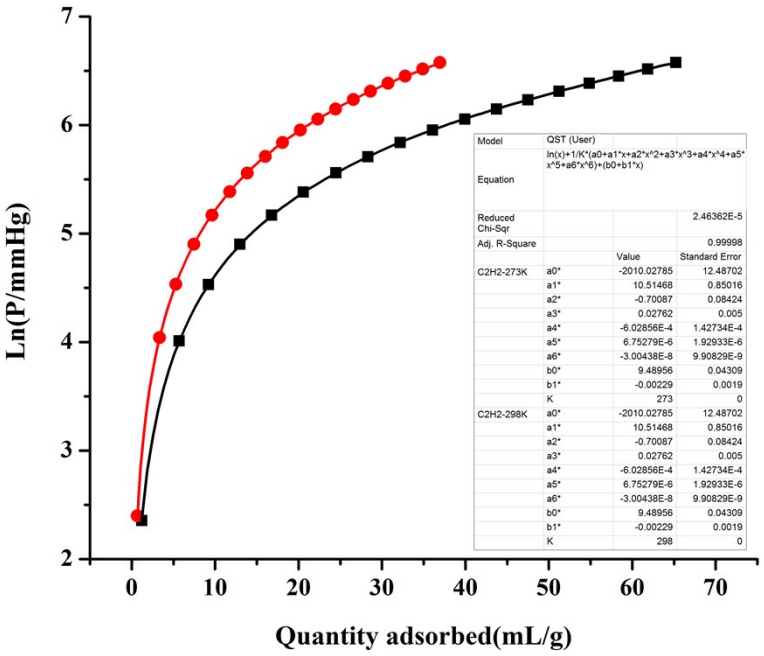

Figure S9. The C_2H_2 sorption isotherms for **ZTIF-10** fitting by virial method.

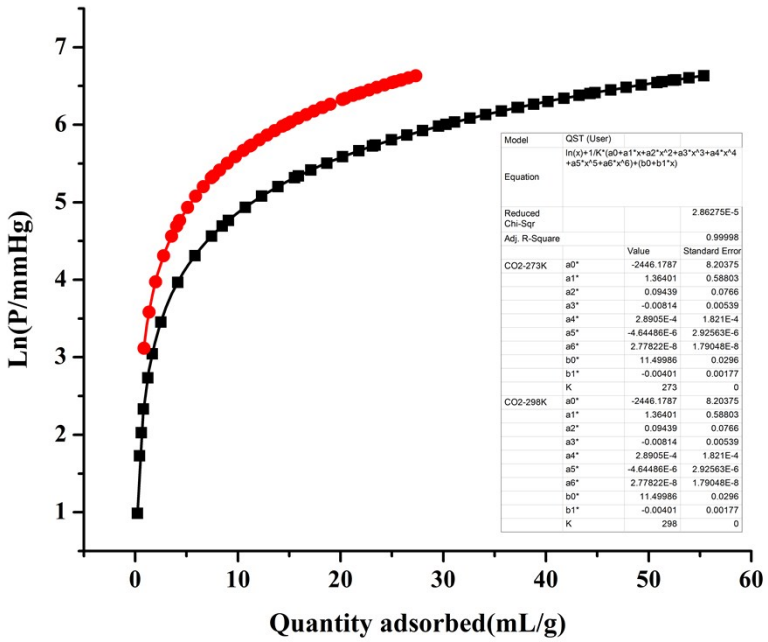

Figure S10. The CO_2 sorption isotherms for **ZTIF-9** fitting by virial method.

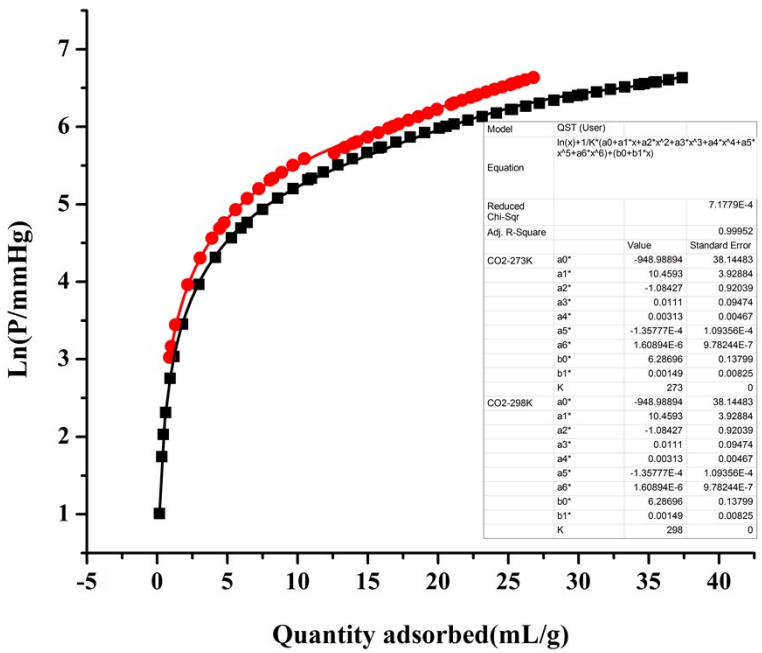

Figure S11. The CO_2 sorption isotherms for **ZTIF-10** fitting by virial method.

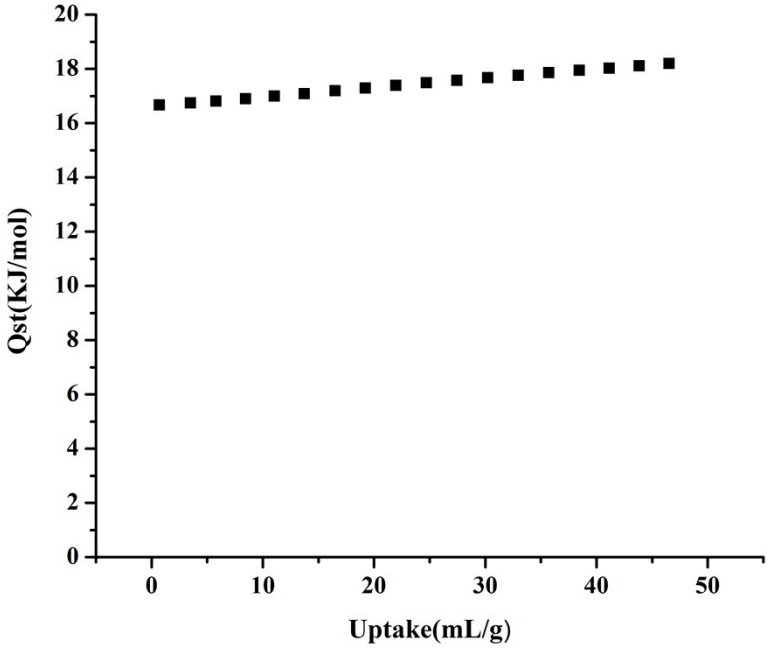

Figure S12. Isosteric heat of C_2H_2 adsorption of **ZTIF-9**.

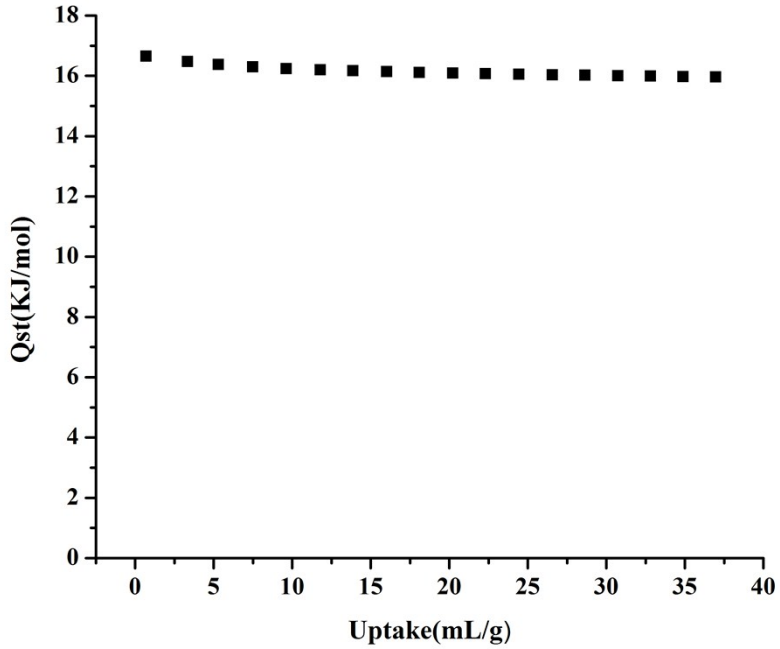

Figure S13. Isosteric heat of C_2H_2 adsorption of **ZTIF-10**.

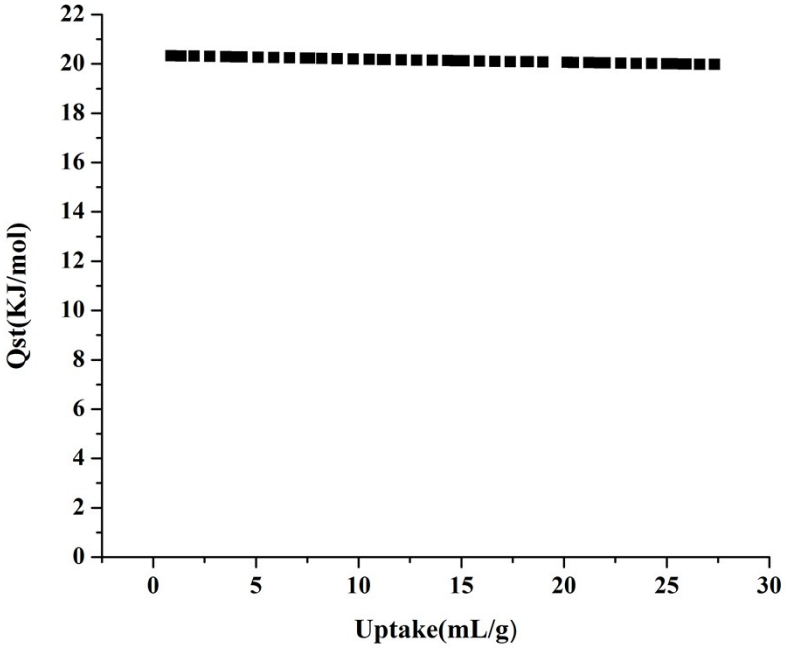

Figure S14. Isosteric heat of CO_2 adsorption of **ZTIF-9**.

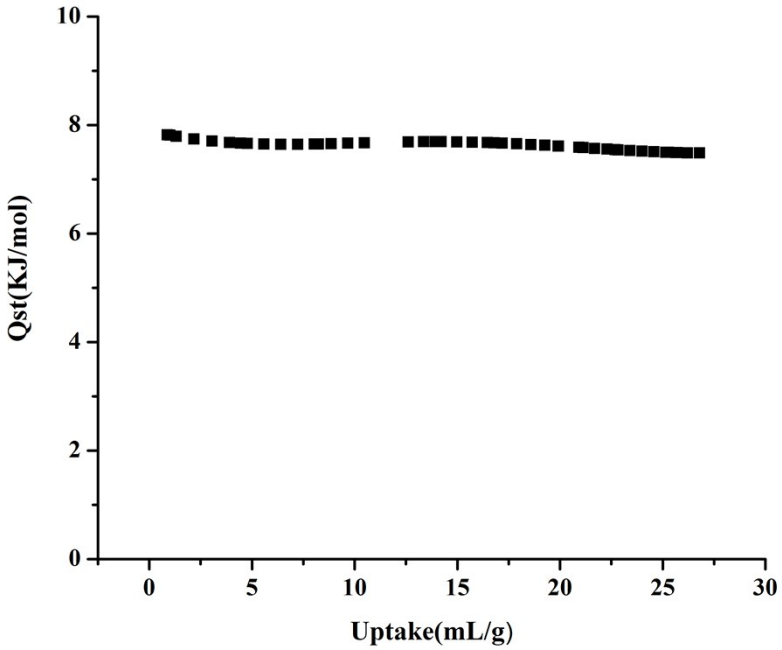

Figure S15. Isosteric heat of CO_2 adsorption of **ZTIF-10**.