Supporting information

New Approach towards Zeolitic Tetrazolate-Imidazolate Frameworks (ZTIFs) with Uncoordinated N-heteroatom Sites For high CO_2 Uptake

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Materials and general procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C and H were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm-1 region) on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Rigaku MultiFlex diffractometer using Cu Kα radiation. ^{1}HNMR experiments were carried out on a Bruker spectrometer operating at resonance frequencies of 400 MHz. Inductively Coupled Plasma OES (ICP-OES) was performed on ULTIMA 2 ICP OES Spectrometer (Jobin Yvon, France). The N_2 adsorption isotherms were recorded by using a micromeritics ASAP 2020 surface area and porosity analyzer. The structure of **ZTIFs** were solved by direct methods and refined on F^2 by full-matrix, least-squares methods using the SHELXL-97 program package.

Synthesis of Zn(5-mtz)(2-eim)·x(guest) **(ZTIF-1)**: The mixture of $Zn(CH_3CO_2)_2{\cdot}2(H_2O)$ (0.5 mmol, 0.110 g), 5-methyltetrazole (5-mtz, 0.5 mmol, 0.043 g), 2-ethylimidazole (2-eim, 0.5 mmol, 0.48 g) in DMF (2 ml) and ethanol (2ml) was sealed in a 20 ml vial and heated to 120 ^{o}C for 3 days, and then cooled to room-temperature. The yellow polyhedral crystals were obtained, washed with ethanol, and dried at room temperature (Yield: 50%). The micro-synthesis condition of **ZTIF-1** can be scalable to 1 gram scale by using the same reaction conditions in a larger volume (50 mL Teflon-lined stainless steel reactor). The co-existence of 5-mtz and 2-eim in **ZTIF-1** are proved by ^{1}H NMR. 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 EA results.

Elemental analysis (activated) $C_7H_{10}N_6Zn$: Calcd. C, 34.71; H, 4.16; N, 34.71; Zn, 26.41. Found C, 27.78; H, 4.43; N, 28.02; Zn, 21.48.

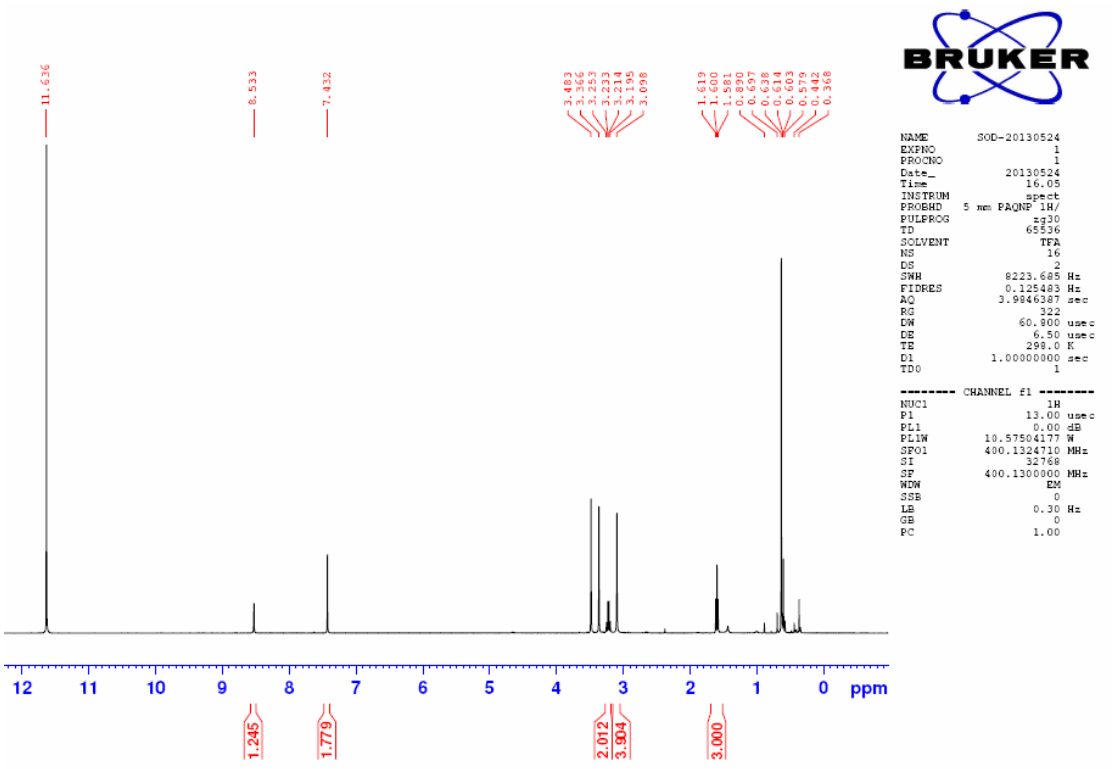

Figure s1. The ^{1}HNMR spectra of **ZTIF-1** in CF_3COOD solvent.

Synthesis of Zn(5-mtz)(2-pim)·x(guest) **(ZTIF-2)**: ZTIF-2 was obtained by the similar method as described for ZTIF-1 except for using 2-propylimidazole (2-pim) instead of 2-eim (Yield: 48%). The micro-synthesis condition of **ZTIF-2** can also be scalable to 1 gram scale by using the same reaction conditions in a larger volume (50 mL Teflon-lined stainless steel reactor). The co-existence of 5-mtz and 2-pim in **ZTIF-1** are proved by ^{1}H NMR. 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.

Elemental analysis (activated) $C_8H_{12}N_6Zn$: Calcd. C, 37.49; H, 4.72; N, 32.81; Zn, 24.97. Found C, 37.14; H, 4.9; N, 32.7; Zn, 24.25.

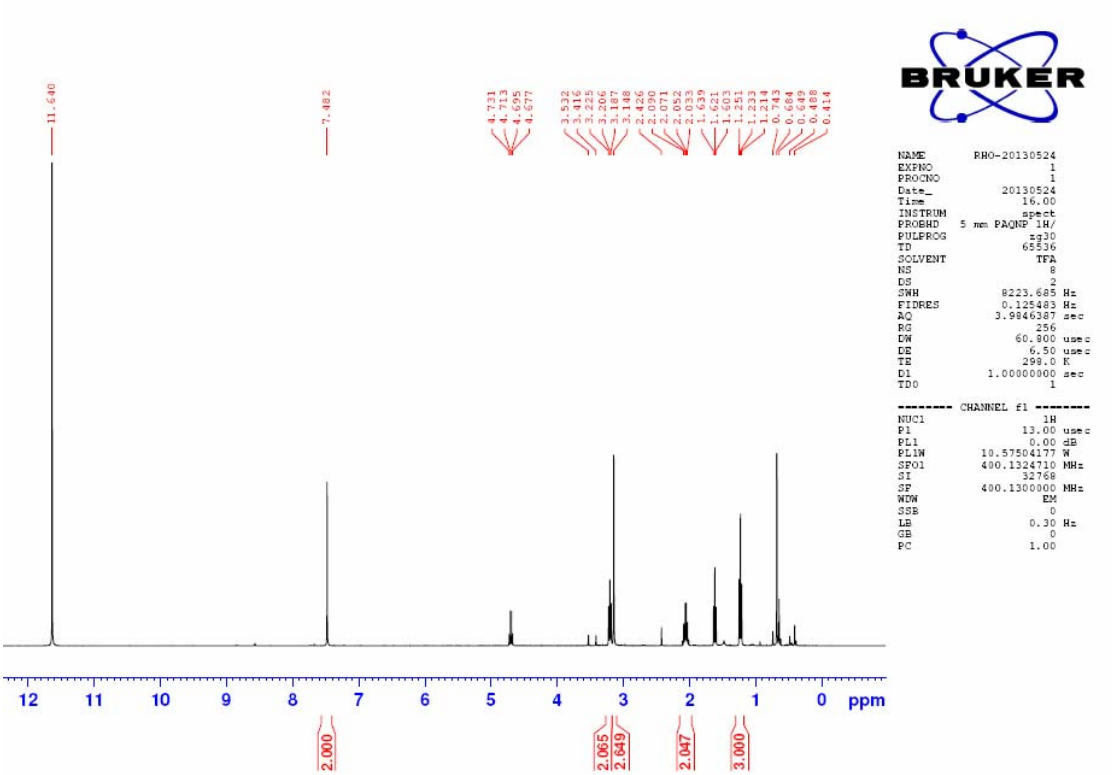

Figure s2. The ^{1}HNMR spectra of **ZTIF-2** in CF_3COOD solvent.

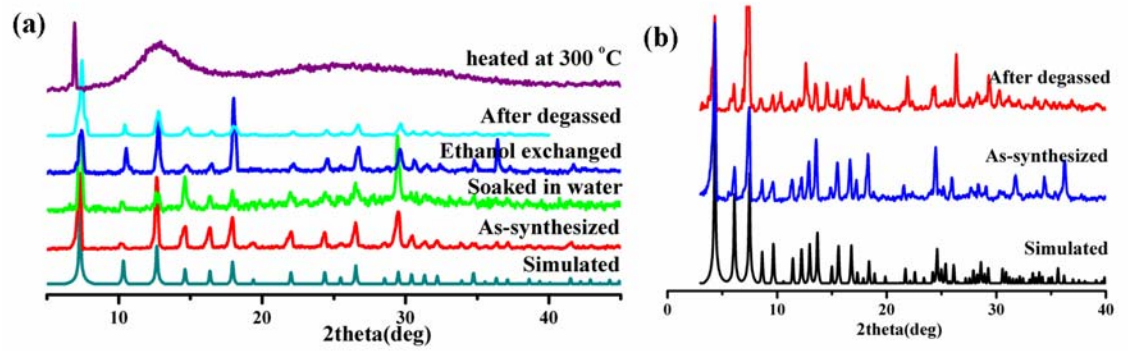

Figure s3. The Powder XRD patterns of **ZTIF-1** (a) and **ZTIF-2** (b).

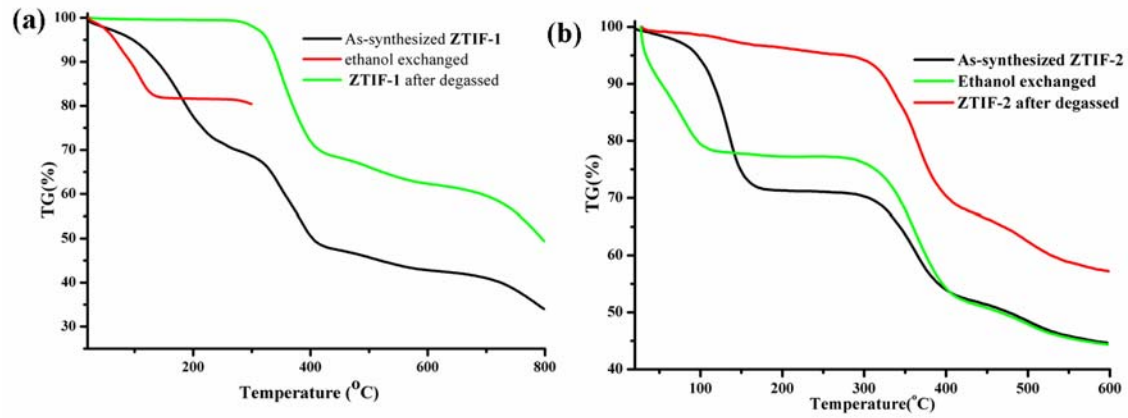

Figure s4. The TG plots of **ZTIF-1** (a) and **ZTIF-2** (b).

The TGA traces of the as-synthesized **ZTIF-1 and 2** samples and the samples after being immersed in dry ethanol solvents at ambient temperature for three days are shown in Figure s4, showing effective solvent-exchange. In particular, in the TGA trace of ethanol-exchanged samples of **ZTIF-1**, the initial gradual weight-loss step of 31.5% till 300 ^{o}C were replaced by a small initial step (17.6% of weight loss) at 135 °C temperature, a plateau to ca. 290 °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-2**, the initial gradual weight-loss step of 28.1% till 170 ^{o}C were replaced by a small initial step (21.0% of weight loss) at 100 °C temperature, a plateau to ca. 290 °C and a sharp weight loss from that point onwards indicates the decomposition of the material.

Isosteric heat of gas adsorption

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

$$\ln(p) = \ln(n) + 1/T(A_0 + A_1 n + A_2 n^2 + ...) + (b_0 + b_1 n + b_2 n^2 + b_3 n^3 + \ldots) \quad (1)$$

Where P is pressure, N is amount adsorbed, T is temperature, A_0, A_1 and A_2 ... and b_0 b_1 b_2 … are temperature independent empirical parameters.

The isosteric heat of adsorption was estimated from the following equation (**2**) as a function of CO_2 uptake.

$$Q_{st} = -R(A_0 + A_1 n + A_2 n^2 + \ldots) \quad (2)$$

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

Henry's constant (KH) is calculated from where T is temperature.

$$K_{(H)} = \exp(-b_0) \cdot \exp(-a_0/T) \quad (3)$$

The Henry's Law selectivity (Sij) for gas i over j at certain temperature is calculated from the following equation (**4**)

$$S_{ij} = K_{Hi} / K_{Hj} \quad (4)$$

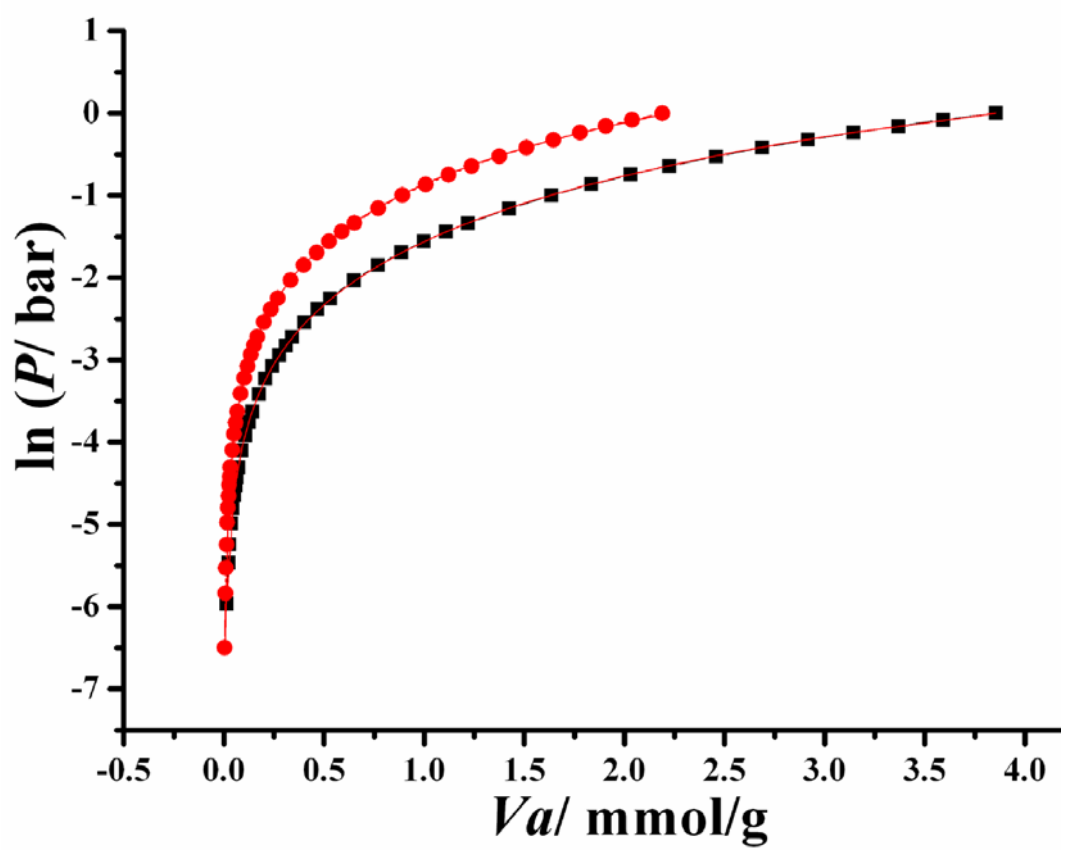

Figure s5. The CO_2 sorption isotherms for Z**TIF-1** fitting by virial method.

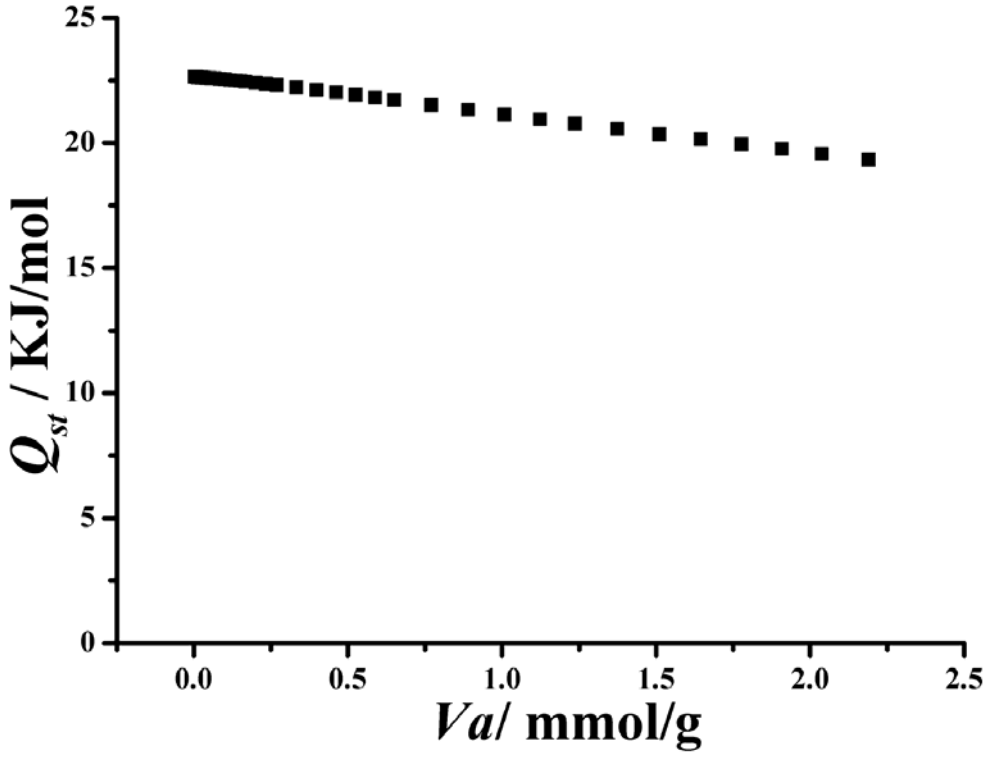

Figure s6. The isosteric heat of CO_2 adsorption for **ZTIF-1** estimated by the virial equation.

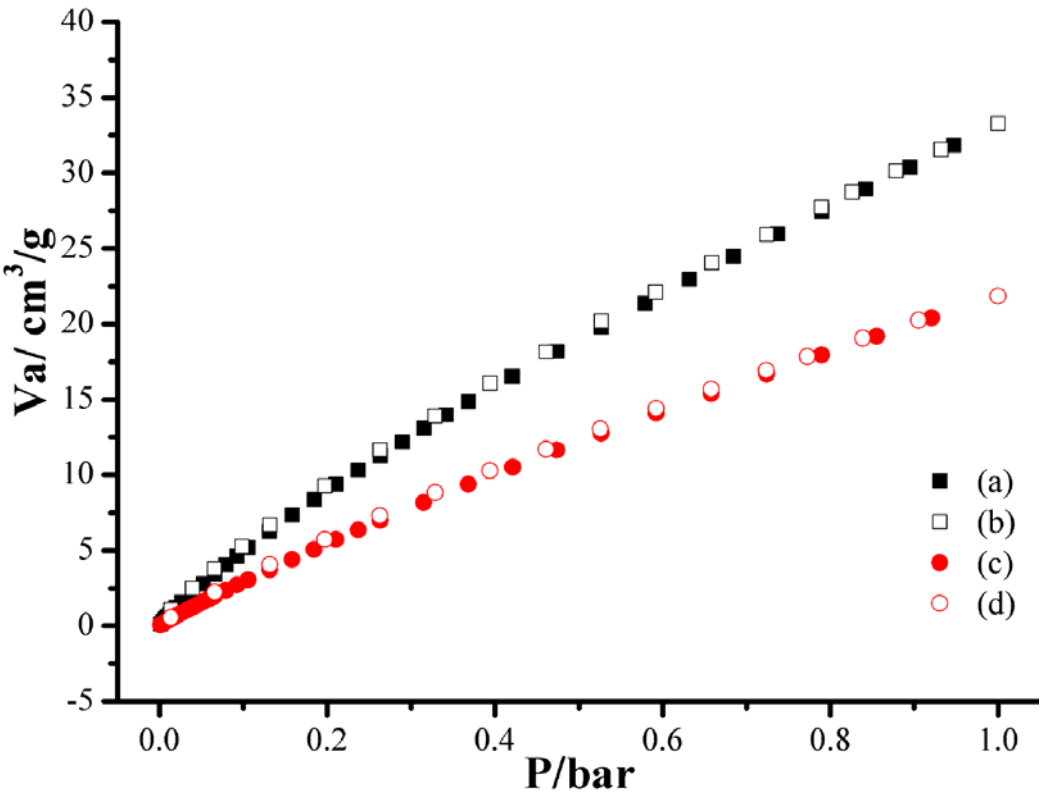

Figure s7. The CO_2 sorption isotherms of **ZTIF-2**. Adsorption (a) and desorption (b) at 273K; Adsorption (c) and desorption (d) at 295K.

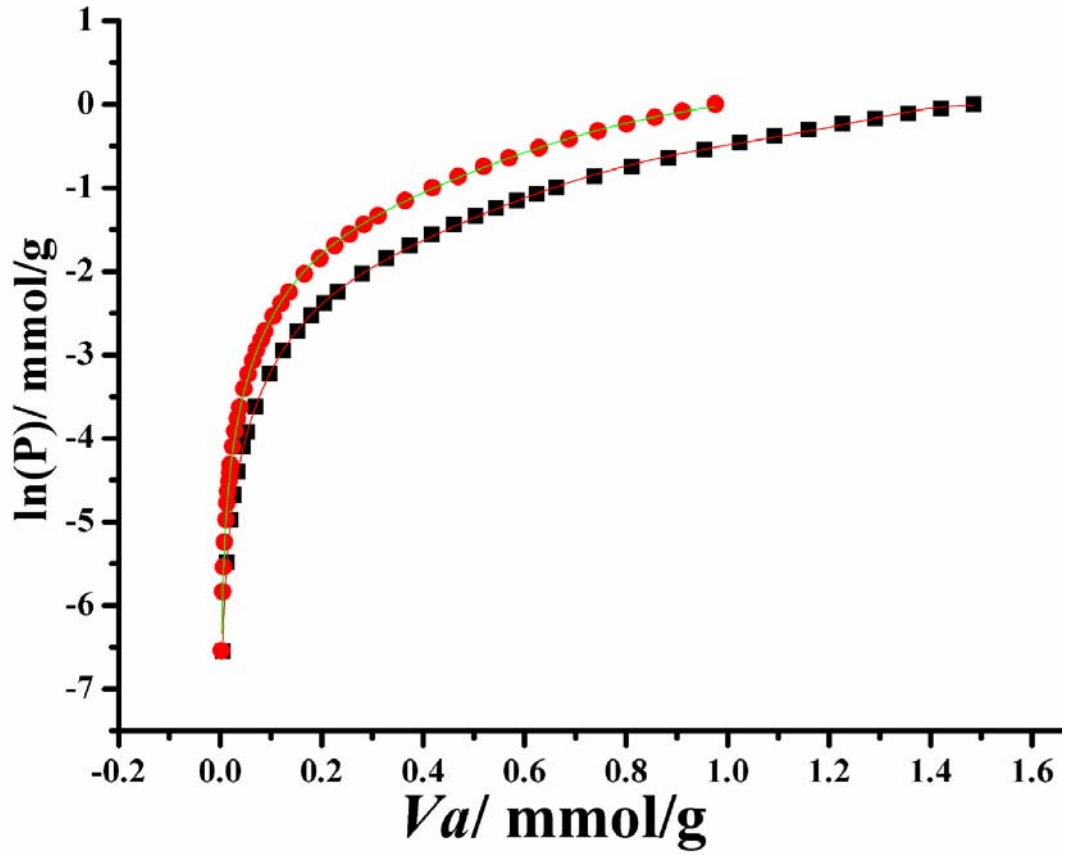

Figure s8. The CO_2 sorption isotherms for Z**TIF-2** fitting by virial method.

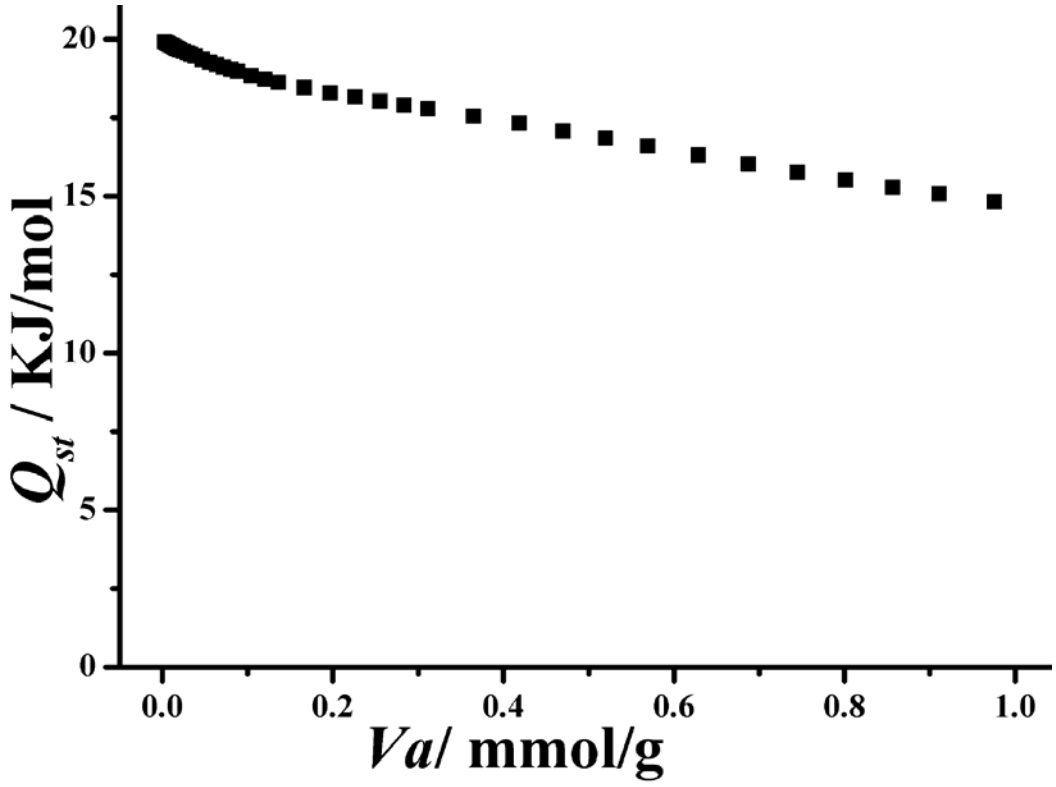

Figure s9. The isosteric heat of CO_2 adsorption for **ZTIF-2** estimated by the virial equation.

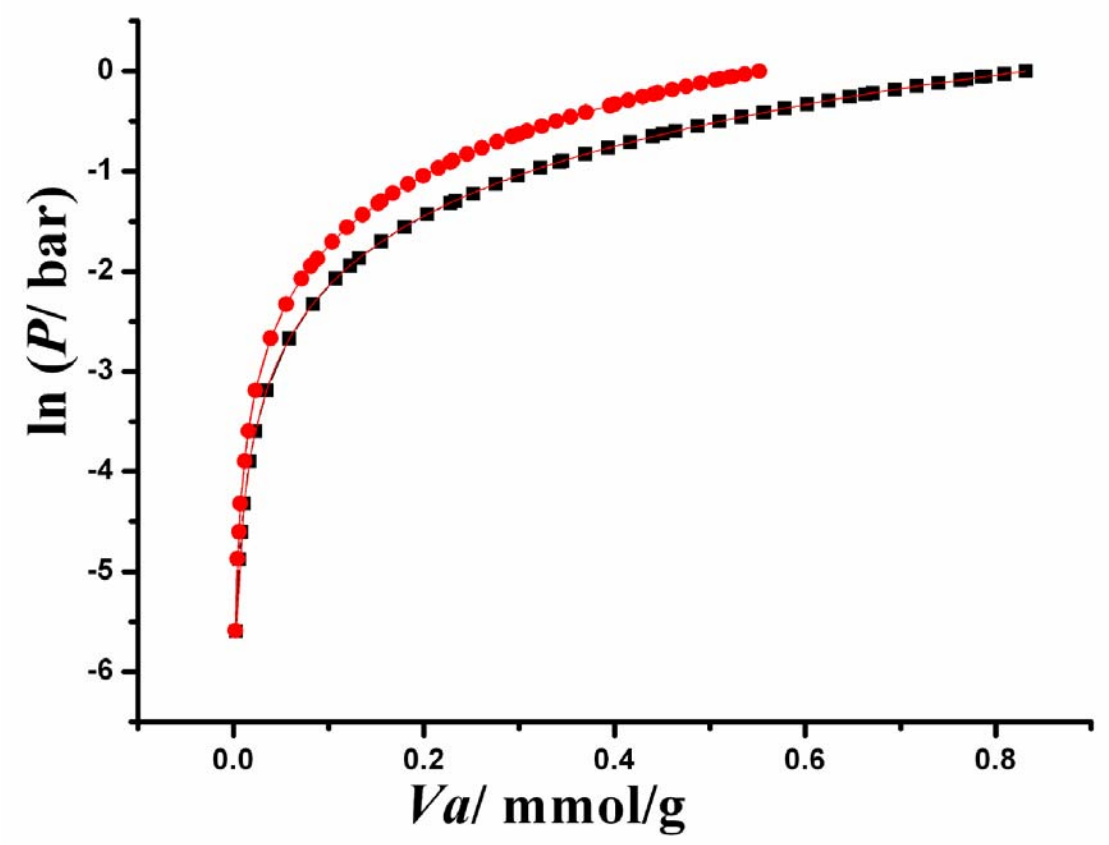

Figure s10. The CH_4 sorption isotherms for Z**TIF-1** fitting by virial method.

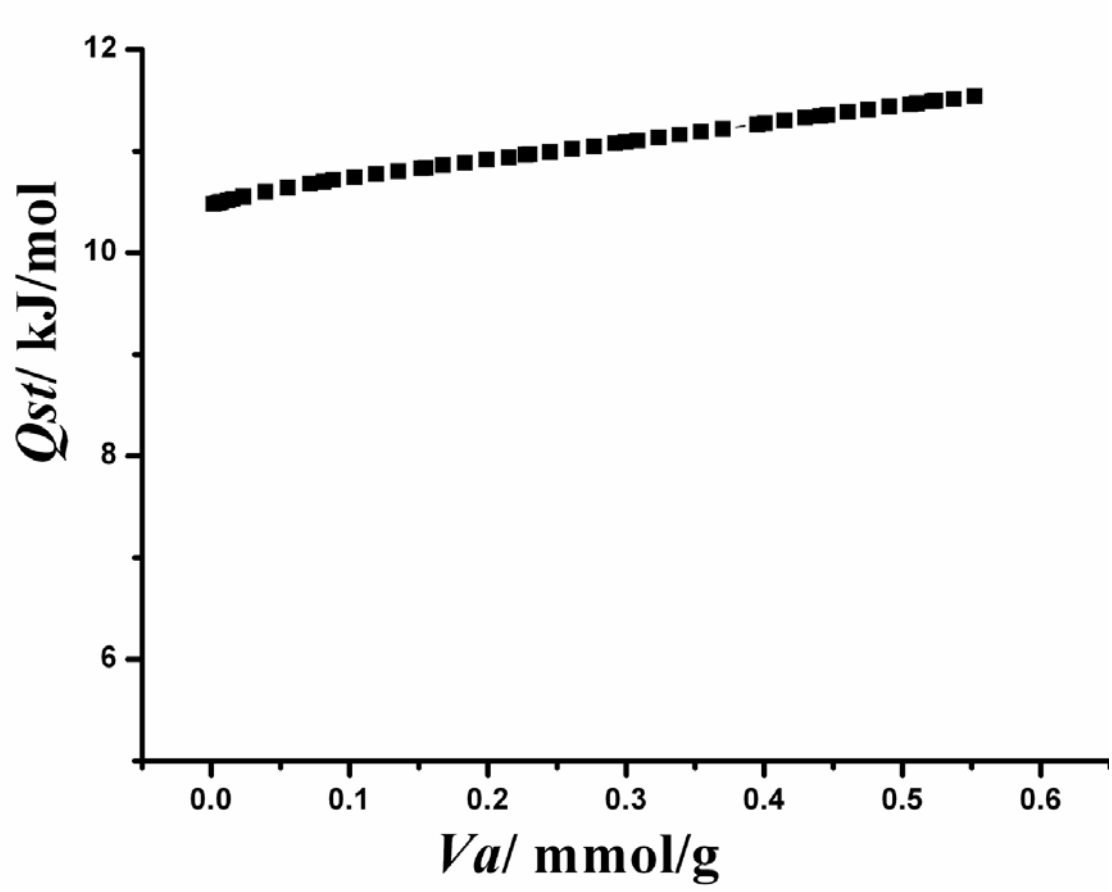

Figure s11. The isosteric heat of CH_4 adsorption for **ZTIF-1** estimated by the virial equation.

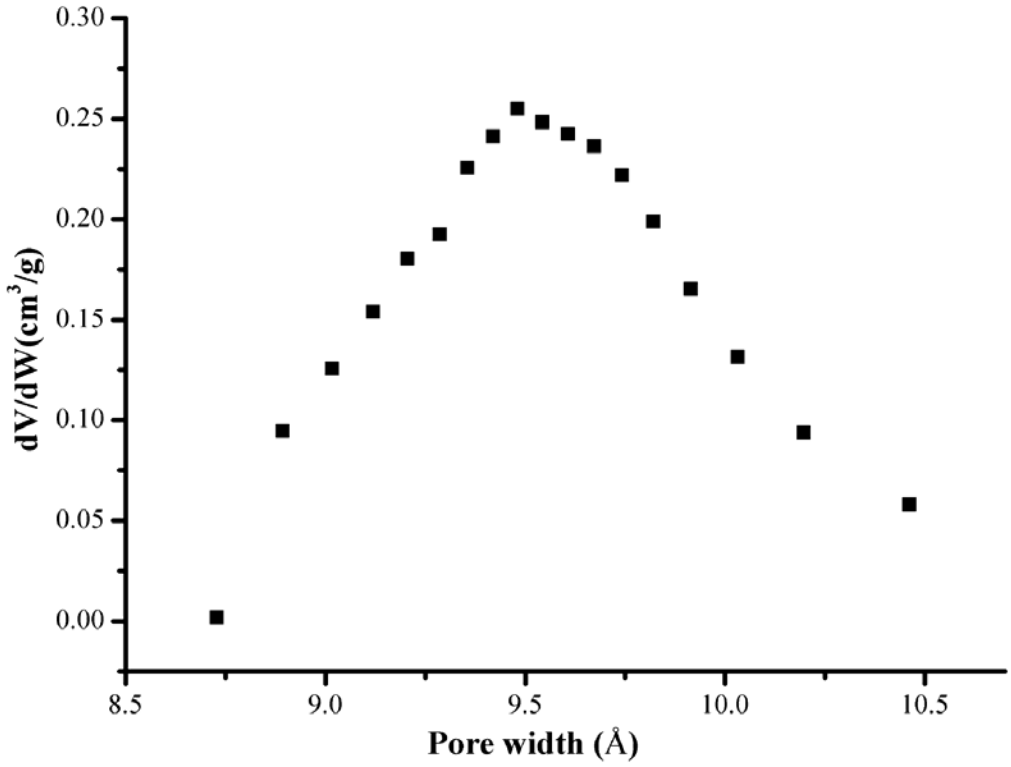

Figure s12. Pore size distribution for **ZTIF-1** by Horvath-Kawazoe method.