# *Electronic Supporting Information for*

# Constuction and Adsorption Properties of Microporous Tetrazine-Based Organic Frameworks

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## Experimental procedures

**Chemicals and Physical Measurements.** All the chemicals used for synthesis were commercially available and used as received. Tetrakis(4-cyanatophenyl)methane (TCPM) was prepared according to the reported methods.[1] Solid-state NMR experiment was carried on a Varian Infinityplus-400 wide-bore (89 mm) NMR spectrometer at a proton frequency of 399.7 MHz using a 4 mm double-resonance HX CP/MAS NMR probe. IR spectra were measured on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Thermogravimetric analyses (TGA) was carried out on a Rigaku standard TG-DTA analyzer with a heating rate of 10 °C $min^{-1}$ from room temperature to 800 °C. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C analyzer. The X-ray powder diffraction spectra (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100mA for a Cu-target tube and a graphite. Scanning electron microscope (SEM) images were recorded using a Hitachi S4800 Type II FE-SEM at 3.0 kV. Gas adsorption measurements were performed using an ASAP 2020 M gas adsorption analyzer.

**Synthesis of the TzFs.** These materials were obtained from TCPM by similar procedures, so only the synthesis of TzF-1 will be described in detail and other details are listed in Table S1. Also, the possible scheme of these reactions is shown in Scheme S1[2].

**Synthesis of TzF-1.** Tetrakis(4-cyanatophenyl)methane (300 mg, 0.71 mmol) and sulfur (0.3 g, 9.37 mmol) were placed in a 25 mL round flask, followed by the addition of hydrazine (5 mL). The reaction mixture was magnetically stirred and heated to reflux for 4 days. After cooling, the solvent was removed by filtration and the resulting light yellow solid was washed by hydrazine, water and ethanol. Subsequent suspension of the solid into a mixture of glacial acetic acid (60 mL) and water (40 mL) was cooled to 0 °C, and followed by the addition of sodium nitrite (1.81 g) in cold water (5 mL), the reaction mixture turned red-violet in color. The mixture was then filtrated and collected after soxhlet extracted over night with tetrahydrofuran (THF) (yield: 65% ~ 75%).

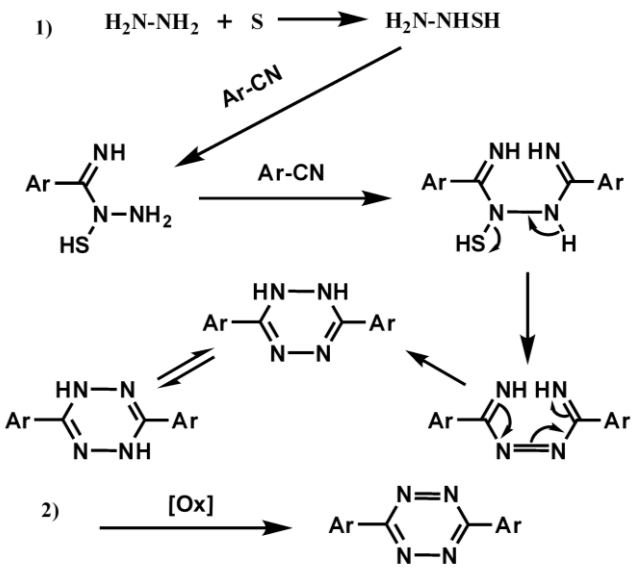
1. M. Grimm, B. Kirste and H. Kurreck, *Angewandte Chemie*, 1986, **98**, 1095-1099.
2. G. Clavier and P. Audebert, *Chemical Reviews*, 2010, **110**, 3299-3314.

**Table S1.** Details for the synthesis of the tetrazine-based framework materials

| TzFs | Hydrazine/mL | Sulphur/g | Reaction time | Temperature | Added solvent |
|---|---|---|---|---|---|
| TzF-1 | 5 | 0.3 | 4 days | reflux | none |
| TzF-2 | 5 | 0.3 | 2 days | reflux | THF 10mL |
| TzF-3 | 10 | 0.8 | 4 days | reflux | THF 10mL ethanol 10ml |
| TzF-4 | 6 | 0.4 | 4 days | reflux | 1,4-dioxane 5mL DMSO 5mL |
| TzF-5 | 5 | 0.4 | 3 days | 60℃ | DMSO 10mL |
| TzF-6 | 16 | 0.6 | 3 days | 90℃ | none |
| TzF-7 | 18 | 0.6 | overnight | 90℃ | Ethane-1,2-diol 10mL |

**Table S2.** Resulting BET and Langmuir surface areas and pore volume of the obtained materials

| TzFs | $S_{BET}$ /$m^2 \cdot g^{-1}$ | $S_{Langmuir}$ /$m^2 \cdot g^{-1}$ | H-K Maxium Pore Volume/ $cm^3 \cdot g^{-1}$ |
|---|---|---|---|
| TzF-1 | 458 | 611 | 0.50 |
| TzF-2 | 514 | 682 | 0.31 |
| TzF-3 | 233 | 308 | 0.14 |
| TzF-4 | 171 | 227 | 0.12 |
| TzF-5 | 348 | 468 | 0.49 |
| TzF-6 | 444 | 593 | 0.46 |
| TzF-7 | 571 | 764 | 1.09 |




**Scheme S1** The possible mechanism for the fomation of TzFs.

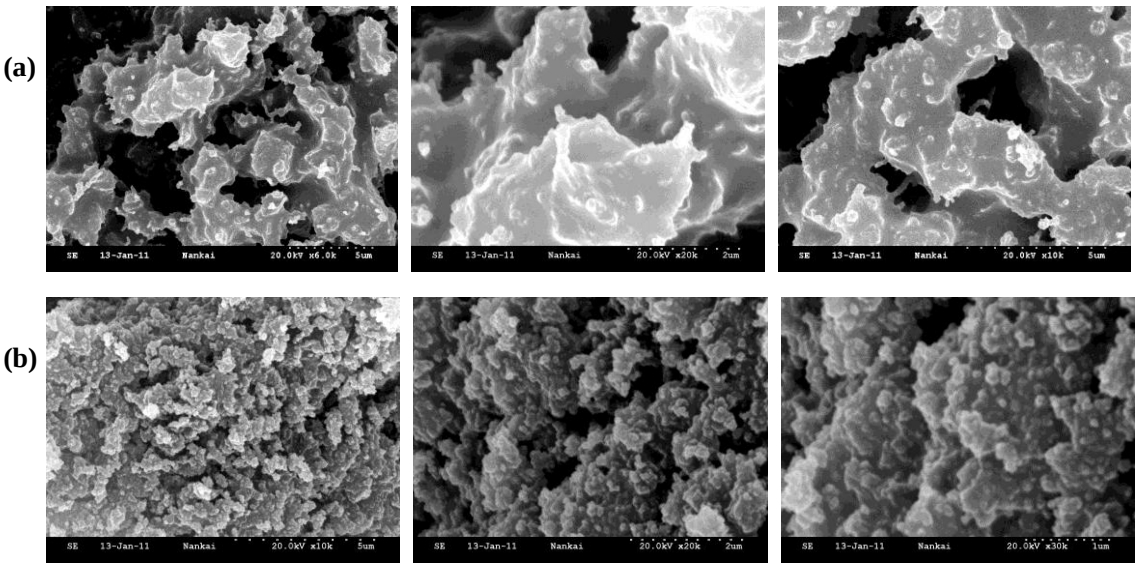



**Figure S1.** SEM images for the TzFs: (a) TzF-6 showing an amorphous forms; (b) TzF-7 displaying a more loose surface.

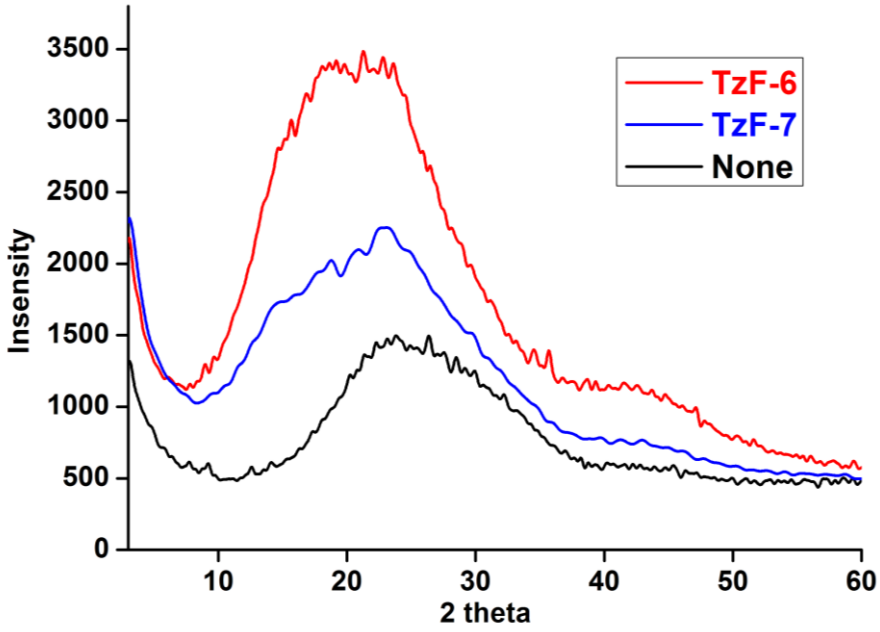



**Figure S2.** X-ray powder diffraction patterns of TzF-7 (blue), TzF-6 (red), and an empty pan (black).

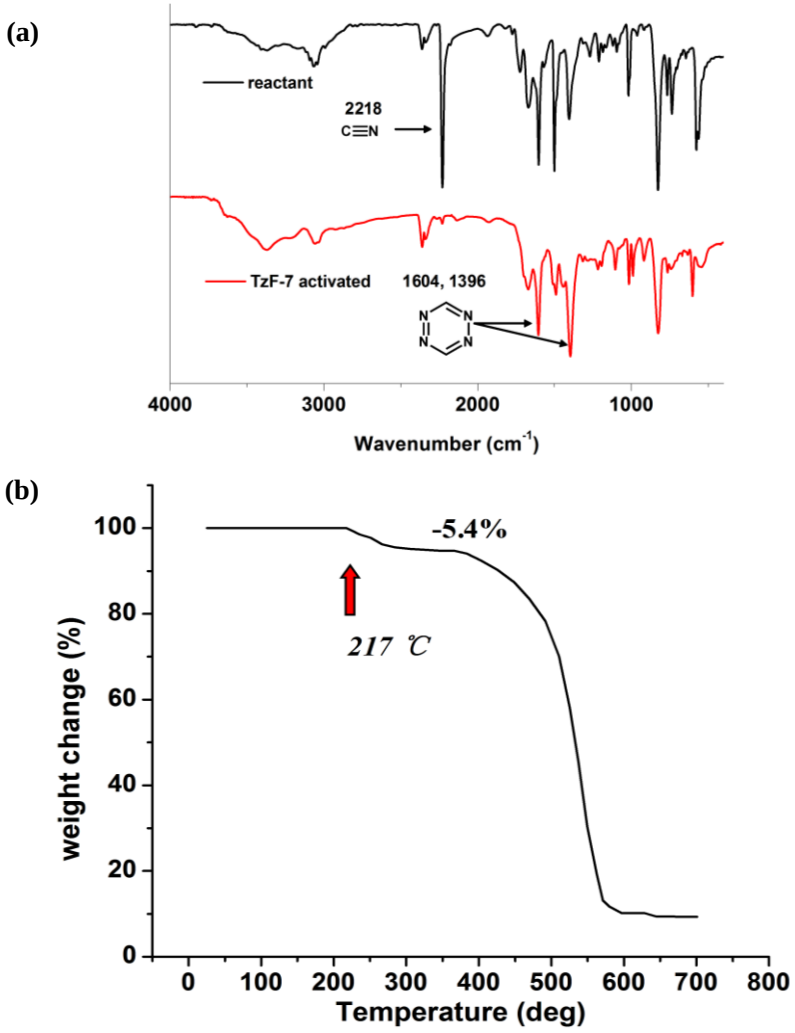



**Figure S3** (a) FT-IR spectra of the reactant TCPM and the TzF-7 prepared from TCPM; (b) TGA curve of TzF-1 under air atmosphere and heating rate of 10℃ $min^{-1}$.

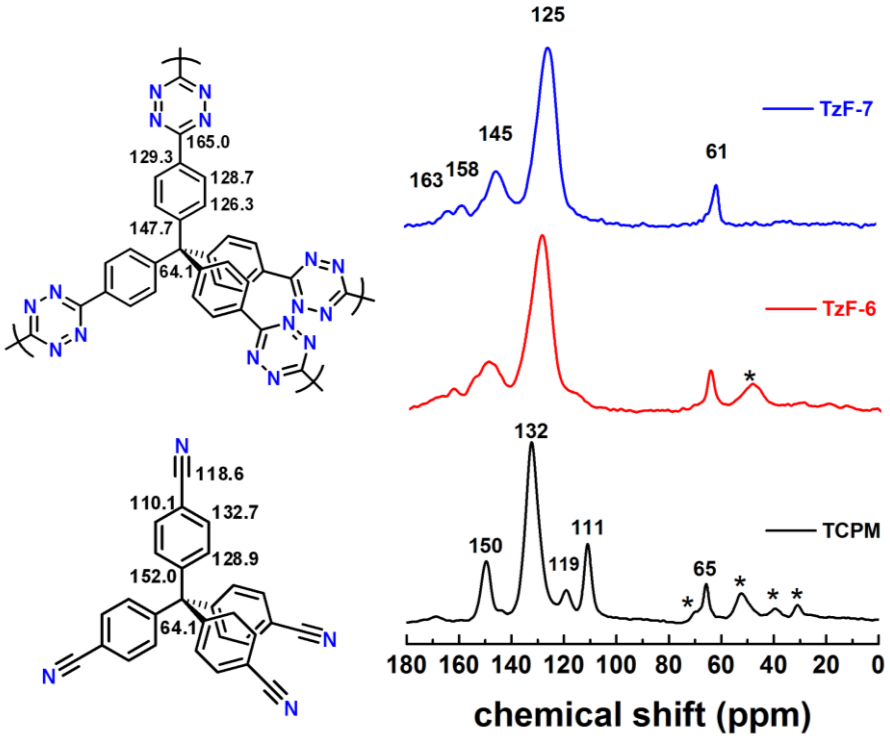



**Figure S4** Solid $^{13}C$ NMR spectra of TCPM (black), TzF-6 (red) and TzF-7 (blue). Asterisks denote spinning sidebands.

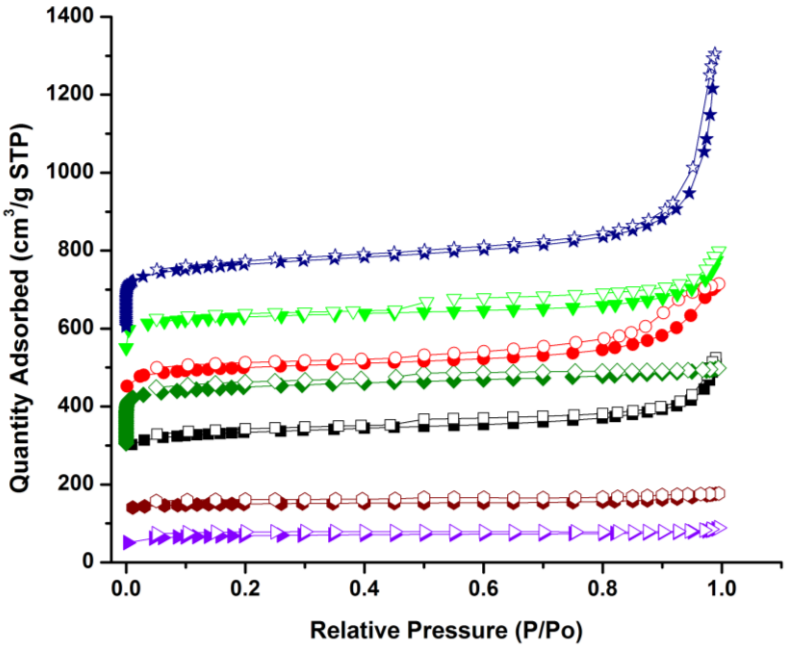



**Figure S5** $N_2$ adsorption and desorption isotherms of the materials obtained at 77 K: TzF-1 (black), TzF-2 (olive), TzF-3 (violet), TzF-4 (wine), TzF-5 (red), TzF-6 (green) and TzF-7 (navy). For clarity, the curves for TzF-7, TzF-6, TzF-5, TzF-2 and TzF-1 were shifted vertically by 600, 500, 400, 300 and 200 $cm^3g^{-1}$, respectively.

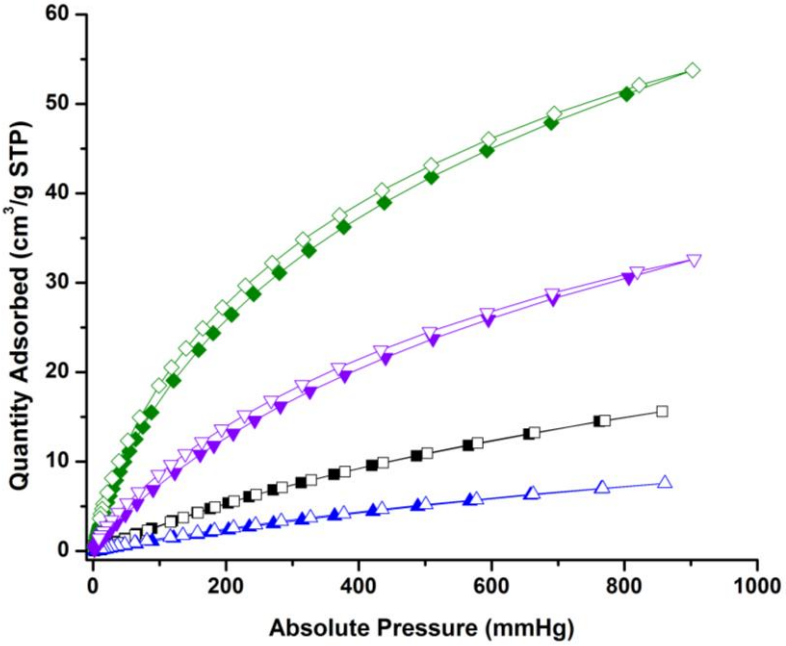



**Figure S6** $CH_4$ adsorption and desorption isotherms of TzF-7 at 273 K (black) and 303 K (blue); $CO_2$ adsorption and desorption isotherms of TzF-7 at 273 K (olive) and 303 K (violet).

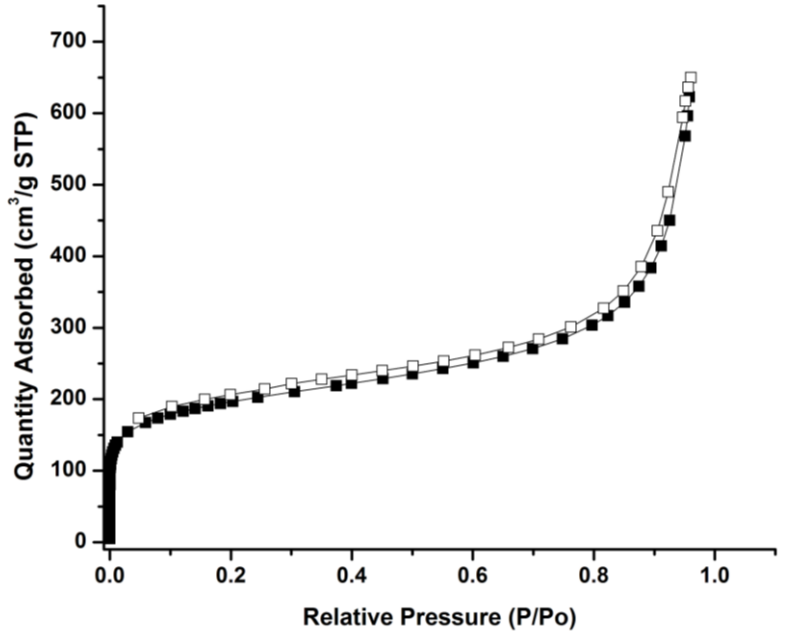



**Figure S7** $O_2$ adsorption and desorption isotherms of TzF-7 at 77 K.

**Estimation of adsorption enthalpies**

A Virial Method model was used for calculating the isosteric enthalpies of adsorption.

The following equation is used for this method.

$$\mathbf{In}(n/p) = A_0 + A_1 n + A_2 n^2 \ldots$$

Where $n$ is the amount adsorbed, $p$ is the pressure and $A_0$ and $A_1$ are constants. $A_0$ is related to adsorbate-adsorbent interactions, and $A_1$, adsorbate-adsorbate interactions. These equations were used interpolate between isotherm points to obtain pressures for specific amounts adsorbed. Henry's Law constant ($K_H$) is equal to exp($A_0$). The van't Hoff isochore was used to determine the isosteric enthalpy of adsorption at specific surface coverages. At low surface coverage $A_2$ and higher terms can be neglected. The isosteric enthalpies of adsorption at zero surface coverage were obtained from the $A_0$ values.

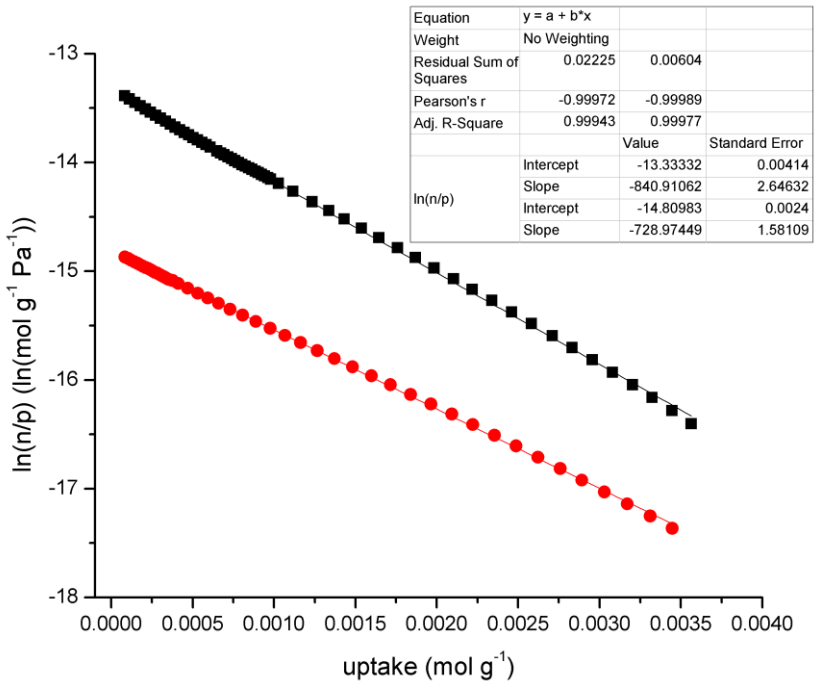



**Figure S8** Analysis of $H_2$ adsorption data of TzF-6 using Virial method.

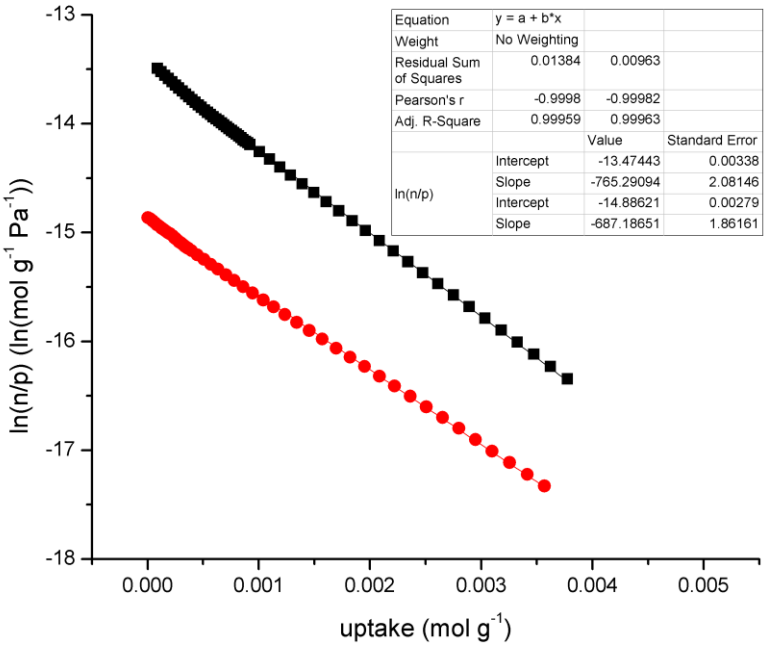



**Figure S9** Analysis of $H_2$ adsorption data of TzF-7 using Virial Method.