

## Electronic Supplementary Information

# A Stable Zinc-4-carboxypyrazole Framework with High Uptake and Selectivity of Light Hydrocarbons

Hong-Ru Fu<sup>†,‡</sup>, Fei Wang<sup>†</sup>, and Jian Zhang<sup>†,\*</sup>

<sup>†</sup>State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian, 35002, China.

<sup>‡</sup>University of Chinese Academy of Sciences, 100049, Beijing, P. R. China

*\* Corresponding Author  
E-mail: zhj@fjirsm.ac.cn  
Fax: +86-591-83715030  
Tel: +86-591-83715030*

**Virial Equation Analysis.** The virial equation can be written as follows:

$$\ln\left(\frac{n}{p}\right) = A_0 + A_1n + A_2n^2 + \dots \quad (\text{S1})$$

where  $n$  is the amount adsorbed (mol g<sup>-1</sup>) at pressure  $p$  (Pa). At low surface coverage, the  $A_2$  and higher terms can be neglected and the equation becomes

$$\ln\left(\frac{n}{p}\right) = A_0 + A_1n \quad (\text{S2})$$

A linear graph of  $\ln(n/p)$  versus  $n$  is obtained at low surface coverage and this is consistent with neglecting higher terms in equation (S2).  $A_0$  quantifies the adsorbate-adsorbent interactions while  $A_1$  is related to adsorbate-adsorbate interactions. This equation has been used extensively in probe molecule studies of adsorption on porous carbons and MOFs.

**Gas sorption Measurements.** Before the measurements, the freshly prepared sample was exchanged with methanol for 3 days. The methanol-exchanged sample was activated under vacuum at 80 °C for 10 hours.

**Ion exchange.** The typical procedure makes use of 100 mg of the compound which is suspended in 20 mL of a 0.1 M aqueous solution of the corresponding inorganic salt: LiNO<sub>3</sub>. After five days, the exchanged solids were subsequently filtered, washed with distilled water and later on suspended during 4 hours in distilled water in order to remove the eventual adsorbed ion pairs. Afterwards, the materials were filtered again and washed with distilled water. The results are indicative that Li<sup>+</sup> gives rise to exchange of 61% H<sub>3</sub>O<sup>+</sup> cations according to the molar ratio of Zn-Li(1:0.21).

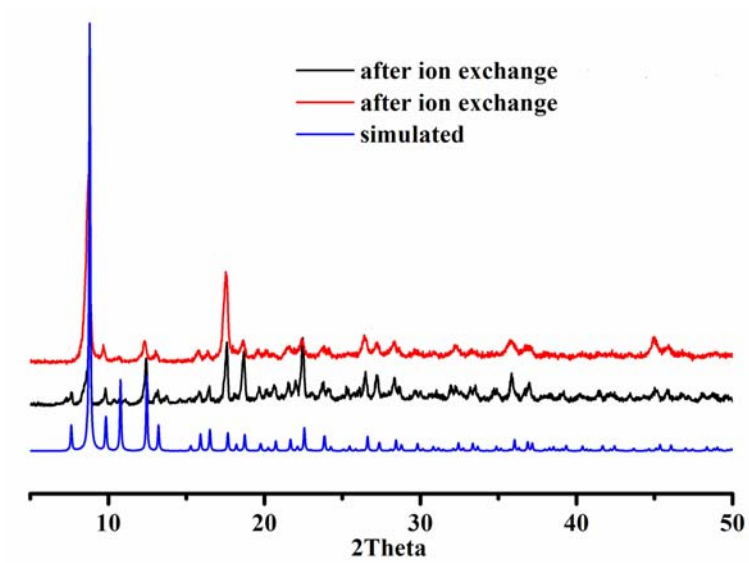


Figure S1. PXRD patterns of as-synthesized **FIR-51** as well as samples treated by ion exchange.

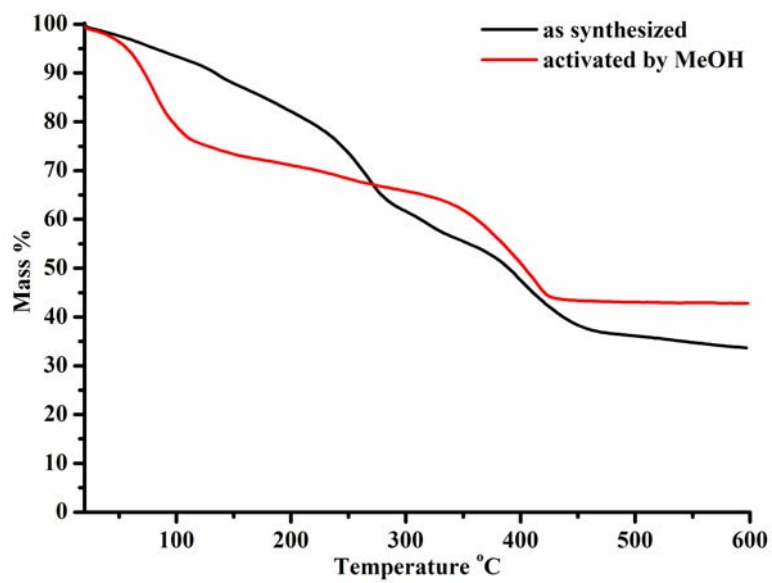
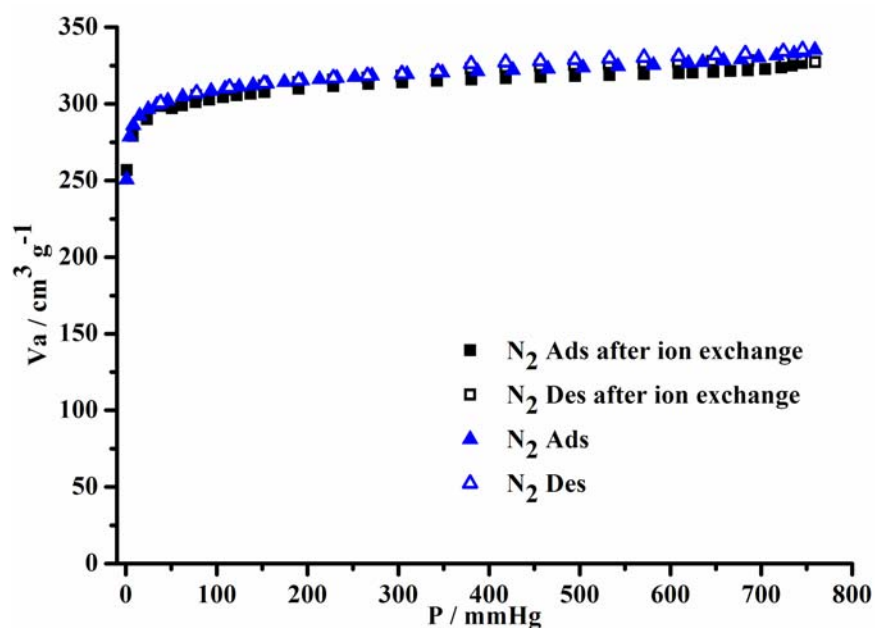
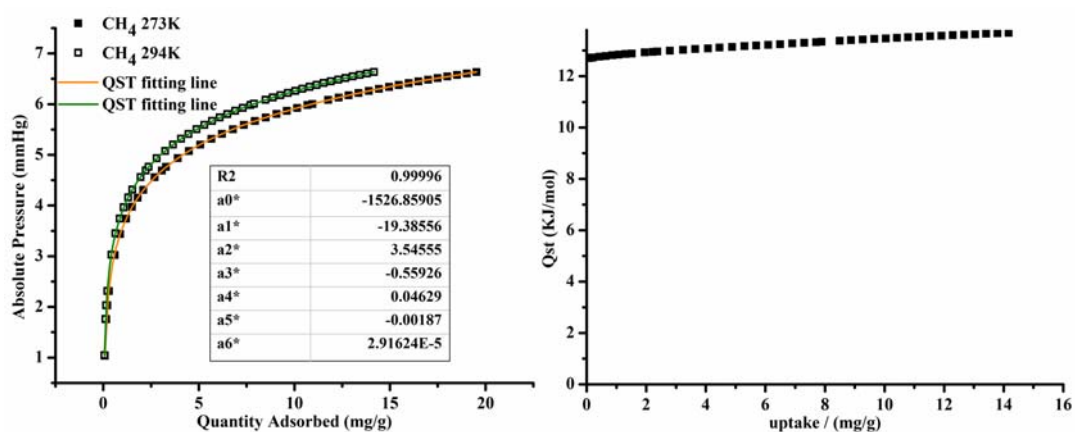


Figure S2. TGA curves of compound **FIR-51** under  $N_2$  atmosphere.



**Figure S3.** a)  $N_2$  sorption isotherms of **FIR-51** at 77 K, b)  $N_2$  sorption isotherms of **FIR-51** at 77 K after ion-exchange.



**Figure S4.** The Isosteric heat of  $CH_4$  adsorption for **FIR-51** estimated by the virial equation.

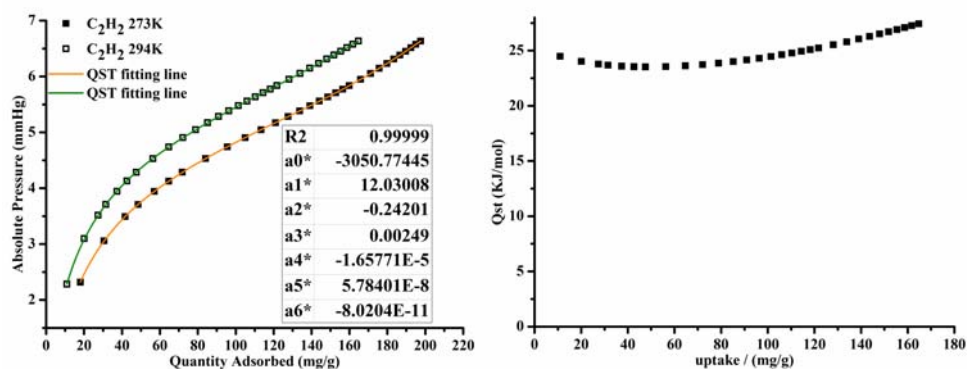


Figure S5. The Isosteric heat of C<sub>2</sub>H<sub>2</sub> adsorption for **FIR-51** estimated by the virial equation.

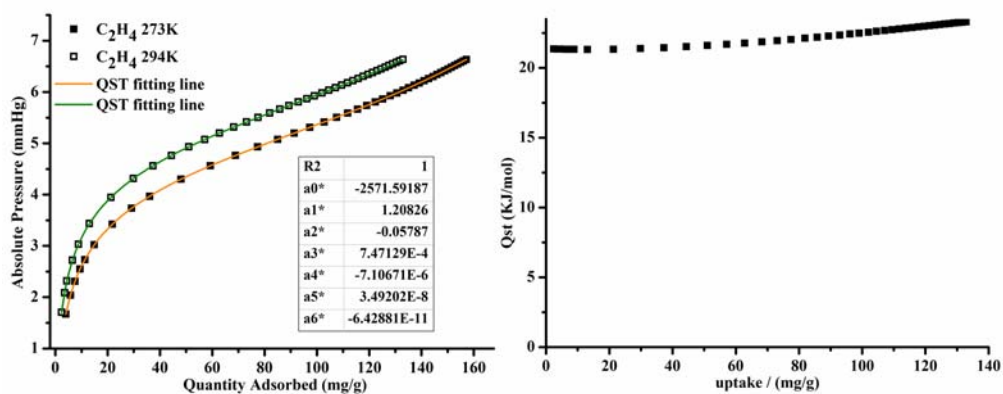


Figure S6. The Isosteric heat of C<sub>2</sub>H<sub>4</sub> adsorption for **FIR-51** estimated by the virial equation.

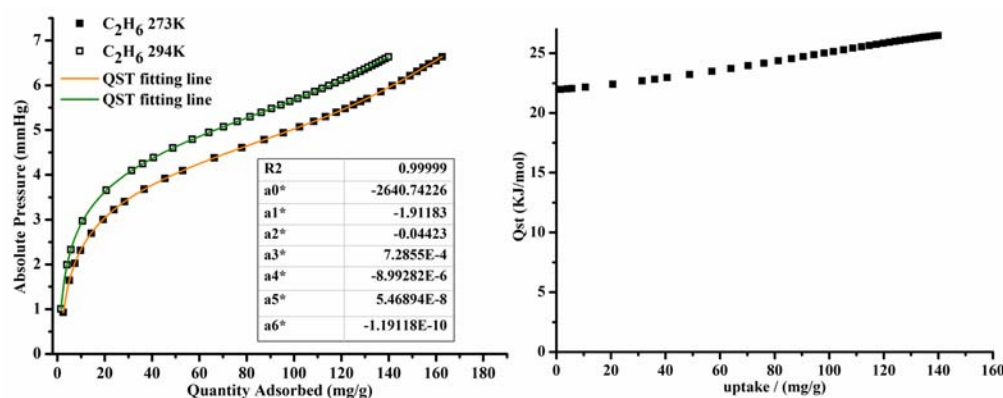


Figure S7. The Isosteric heat of C<sub>2</sub>H<sub>6</sub> adsorption for **FIR-51** estimated by the virial equation.

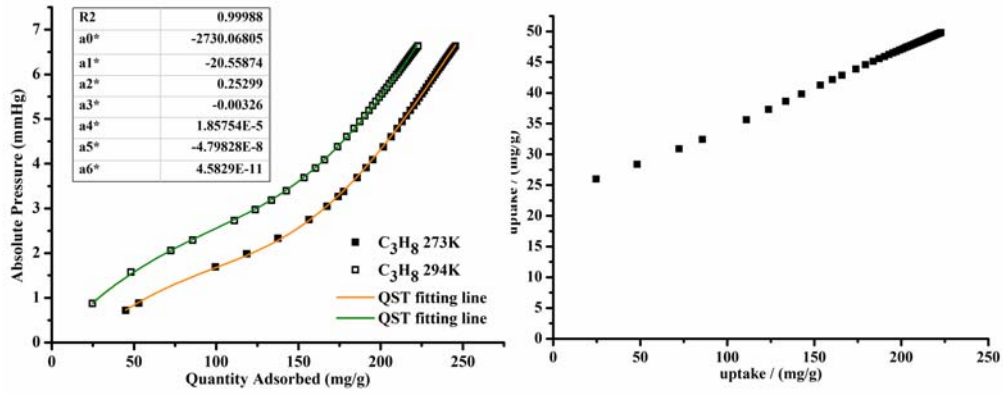


Figure S8. The Isosteric heat of C<sub>3</sub>H<sub>8</sub> adsorption for **FIR-51** estimated by the virial equation.

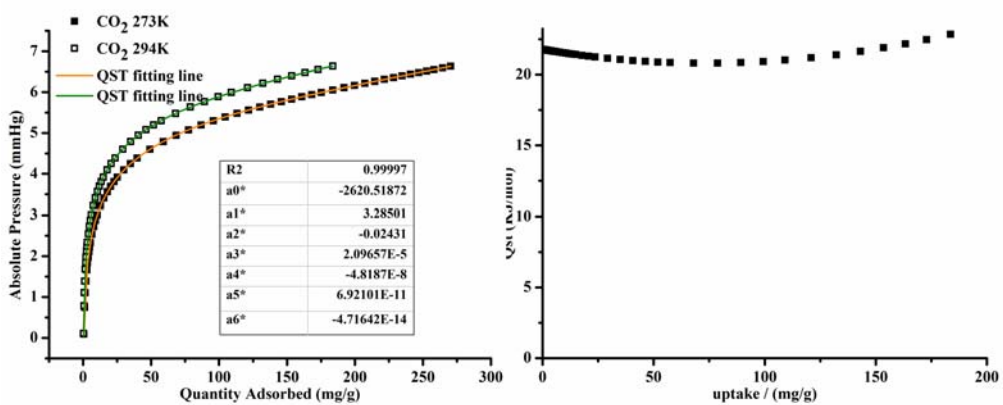


Figure S9. The Isosteric heat of CO<sub>2</sub> adsorption for **FIR-51** estimated by the virial equation.

In IAST theory, a single-site Langmuir-Freundlich (SSLF)<sup>3</sup> equation was used to fit the adsorption isotherms of pure gas, given by

$$y = \frac{A1 * b1 * x^{c1}}{1 + b1 * x^{c1}}$$

where x is the fugacity of bulk gas at equilibrium with adsorbed phase, A1 is maximum loading in site i (=1), b1 is the affinity constant, and c1 is used to characterize the deviation from the simple Langmuir equation. The fitted parameters then were used to predict adsorption isotherms of each component in the mixture. For CO<sub>2</sub> or CH<sub>4</sub> in each adsorbent, the fitting is nearly perfect. The selectivity of light hydrocarbons were calculated via equalmolar binary mixture. The single-site Langmuir-Freundlich fitting of each gas were listed the below figures.

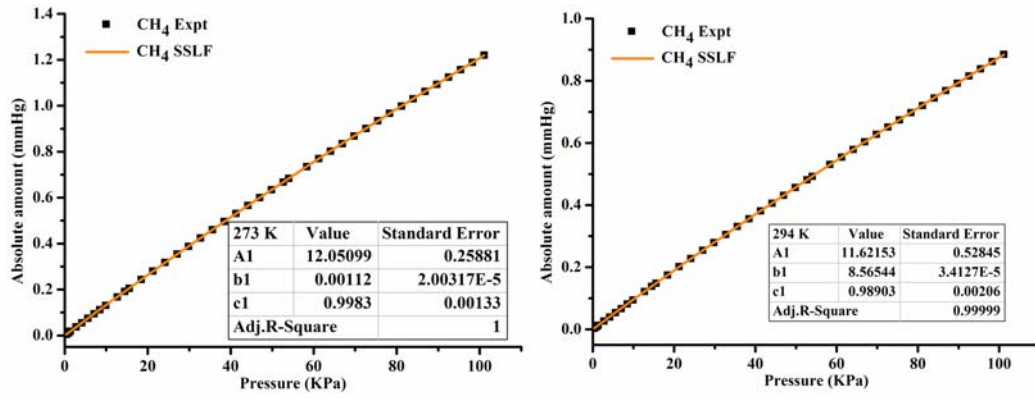


Figure S10. CH<sub>4</sub> adsorption isotherms are fit using the SSLF model (lines).

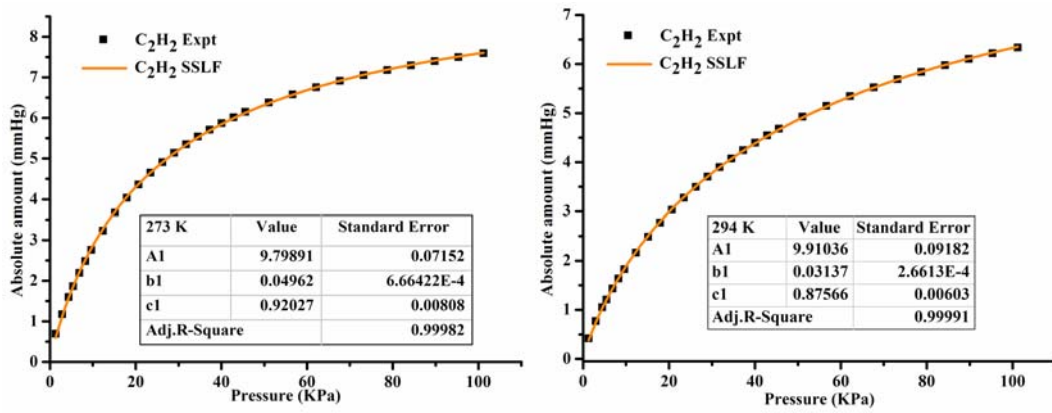


Figure S11. C<sub>2</sub>H<sub>2</sub> adsorption isotherms are fit using the SSLF model (lines).

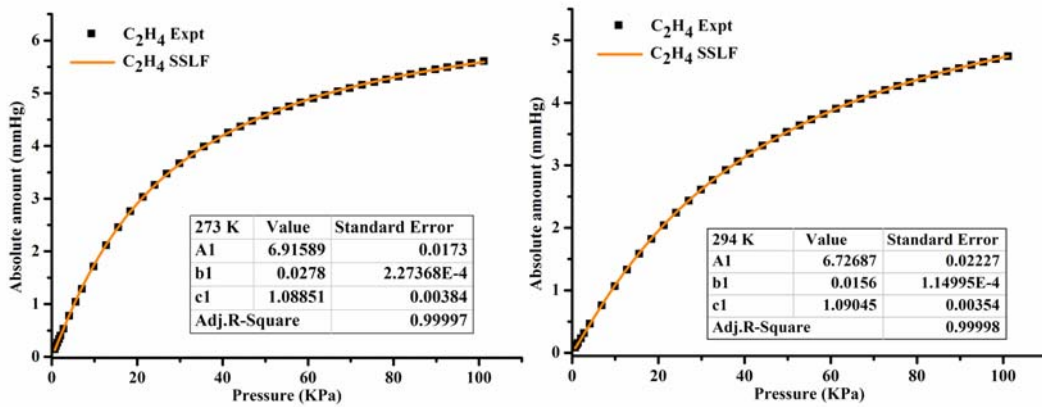


Figure S12. C<sub>2</sub>H<sub>4</sub> adsorption isotherms are fit using the SSLF model (lines).

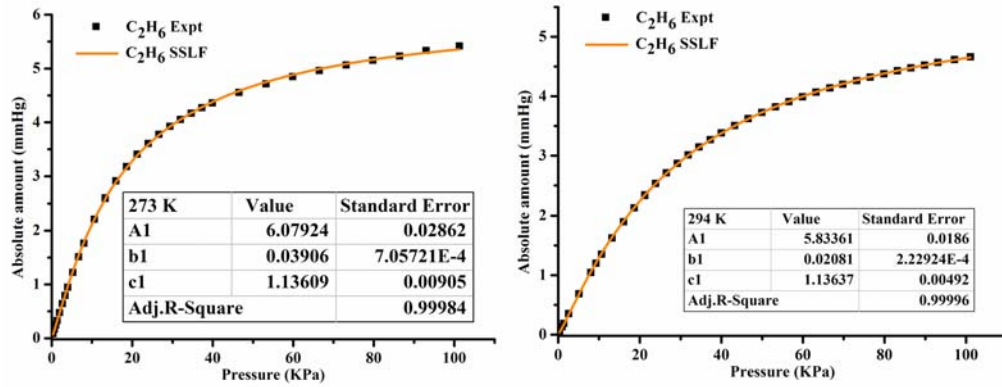


Figure S13. C<sub>2</sub>H<sub>6</sub> adsorption isotherms are fit using the SSLF model (lines).

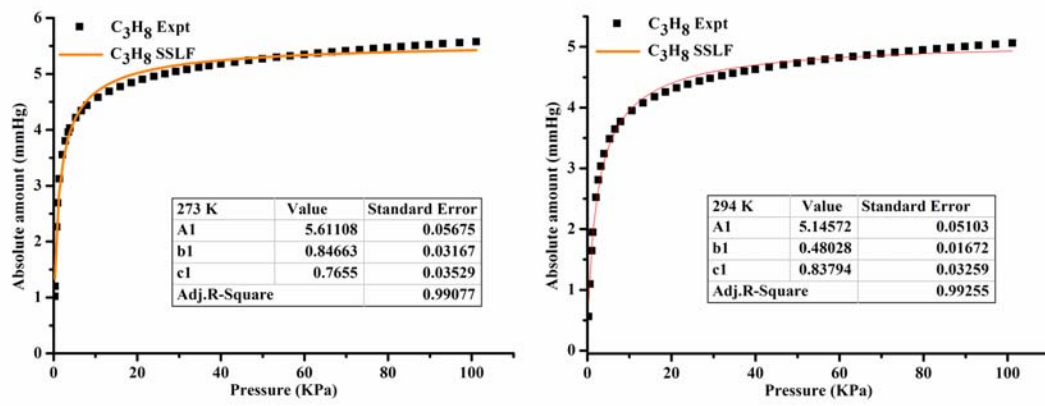


Figure S14. C<sub>3</sub>H<sub>8</sub> adsorption isotherms are fit using the SSLF model (lines).

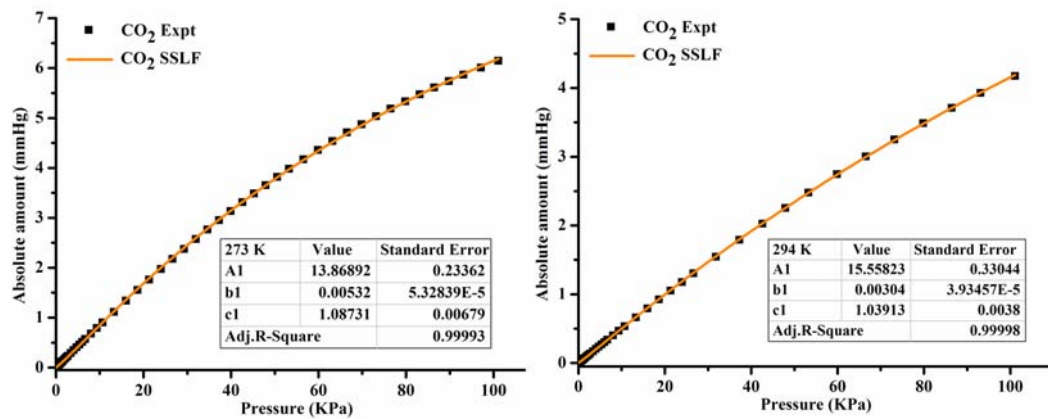
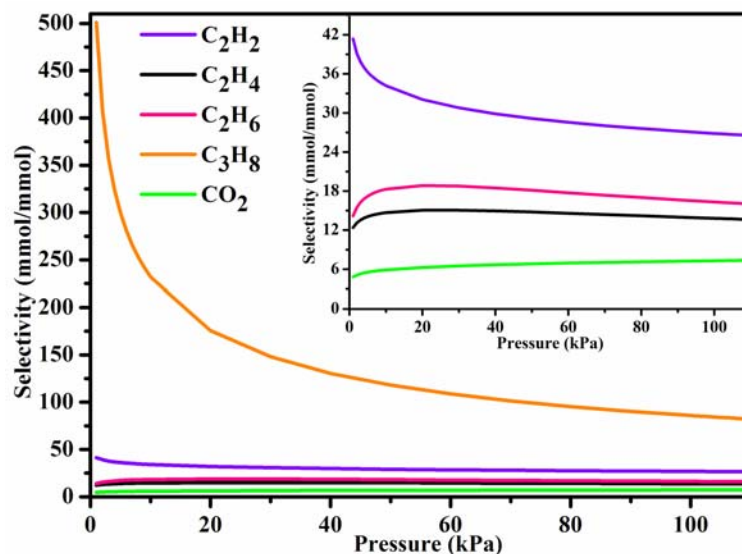


Figure S15. CO<sub>2</sub> adsorption isotherms are fit using the SSLF model (lines).





**Figure S16.** The dynamic selectivity ( $S$ ) for C3, C2s and CO<sub>2</sub> over CH<sub>4</sub> dependent on pressure for **FIR-51** at 273 K. The graph at the top right corner shows more details on the selectivities of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub> over CH<sub>4</sub>.

#### References

1. (a) G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1997. (b) G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112–122.
2. A. L. Spek, Program PLATON, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
3. X. Peng, X. Cheng and D. P. Cao, *J. Mater. Chem.*, 2011, 21, 11259–11270.