Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information

Enhancing CO_2 Adsorption enthalpy and Selectivity via Amino Functionalization of a Tetrahedral Framework Material

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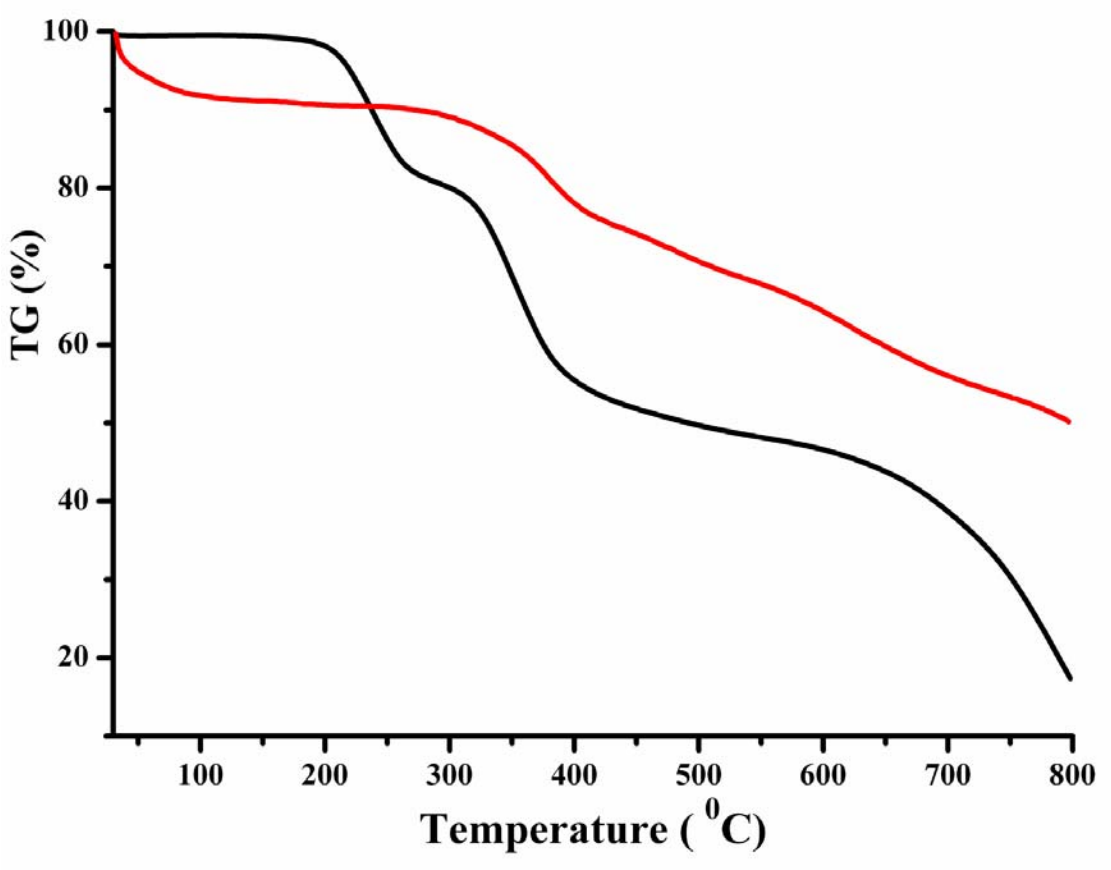

Figure S1. The TGA diagram of **1** (a, black) and methanol exchanged sample (b, red).

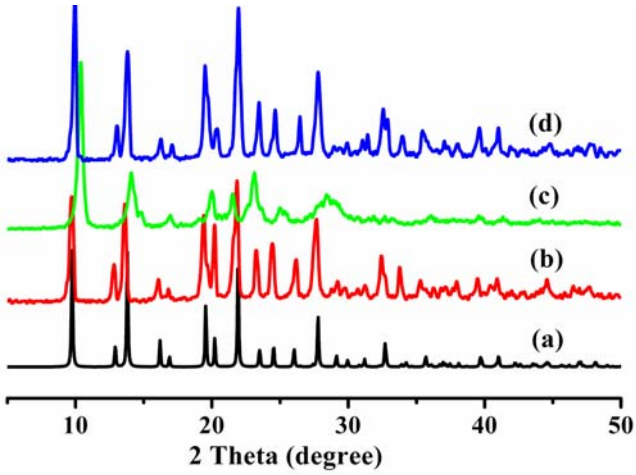

Figure S2. The powder XRD patterns of **1**: (a) simulated; (b) experimental; (c) the activated samples after adsorption; (d) the activated samples soaked in DMF.

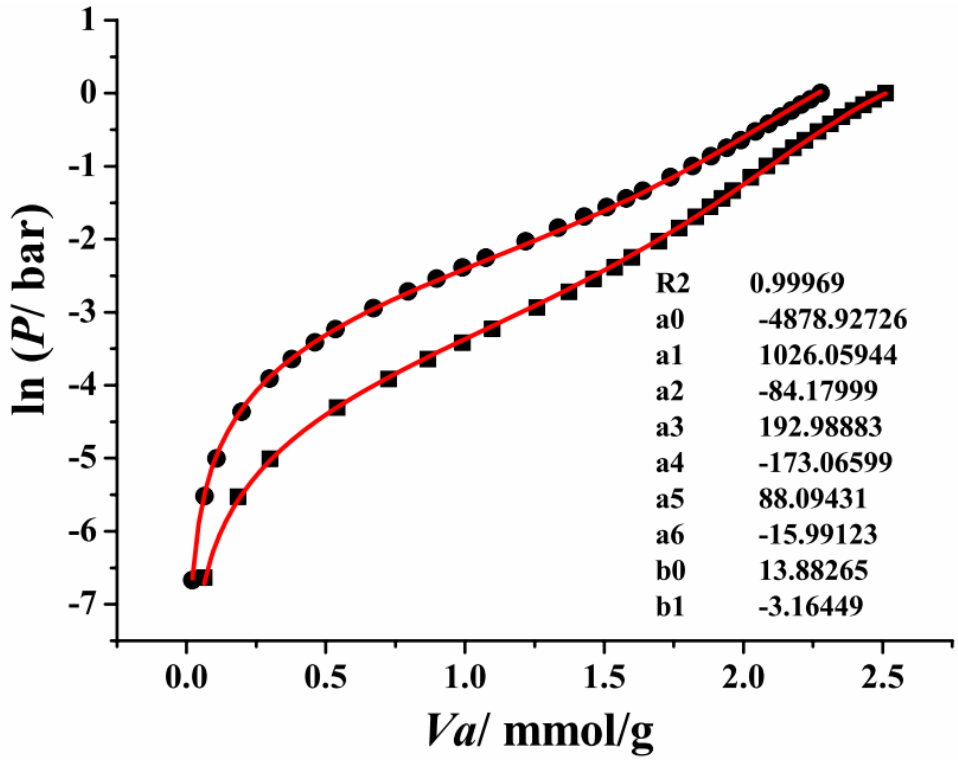

Figure S3. CO_2 adsorption isotherms for **1** fitting by virial method.

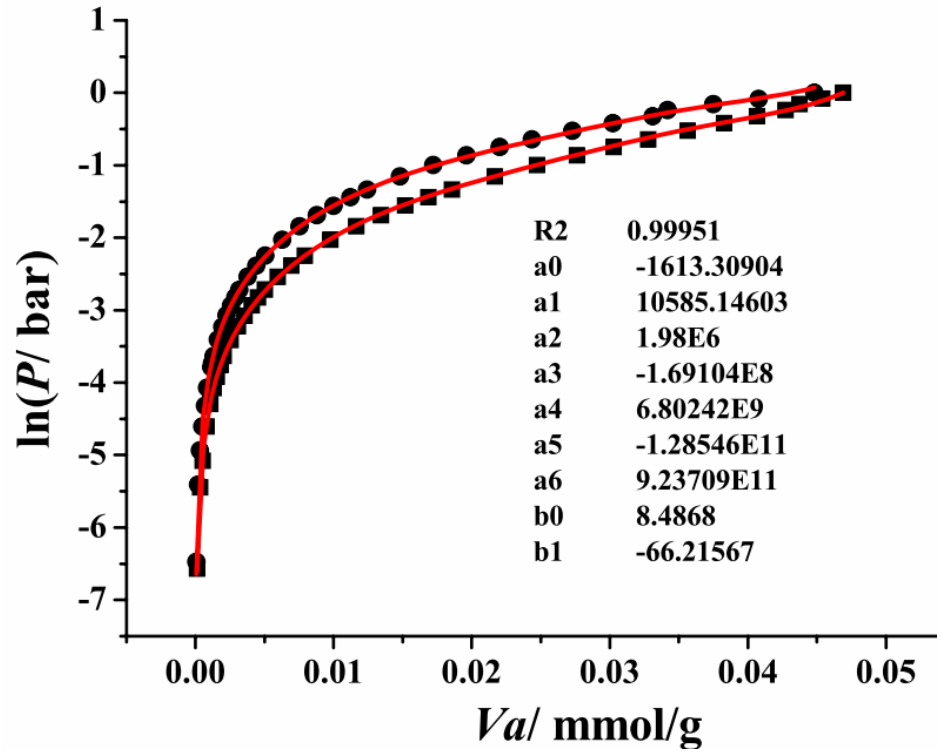

Figure S4. N_2 adsorption isotherms for **1** fitting by virial method.

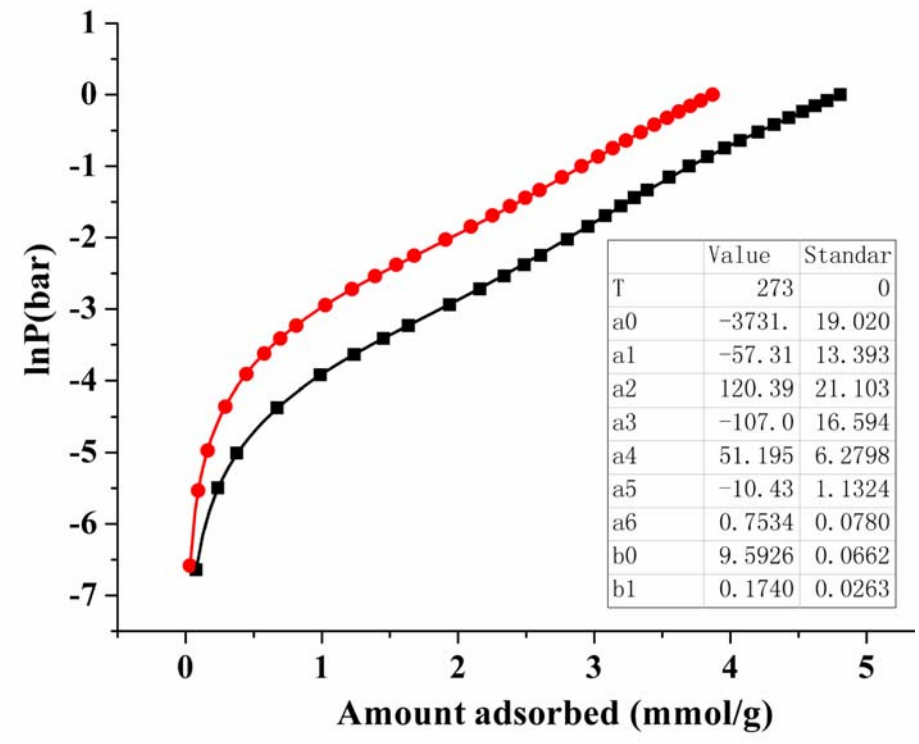

Figure S5. The CO_2 sorption isotherms for **TIF-A1** fitting by virial method.

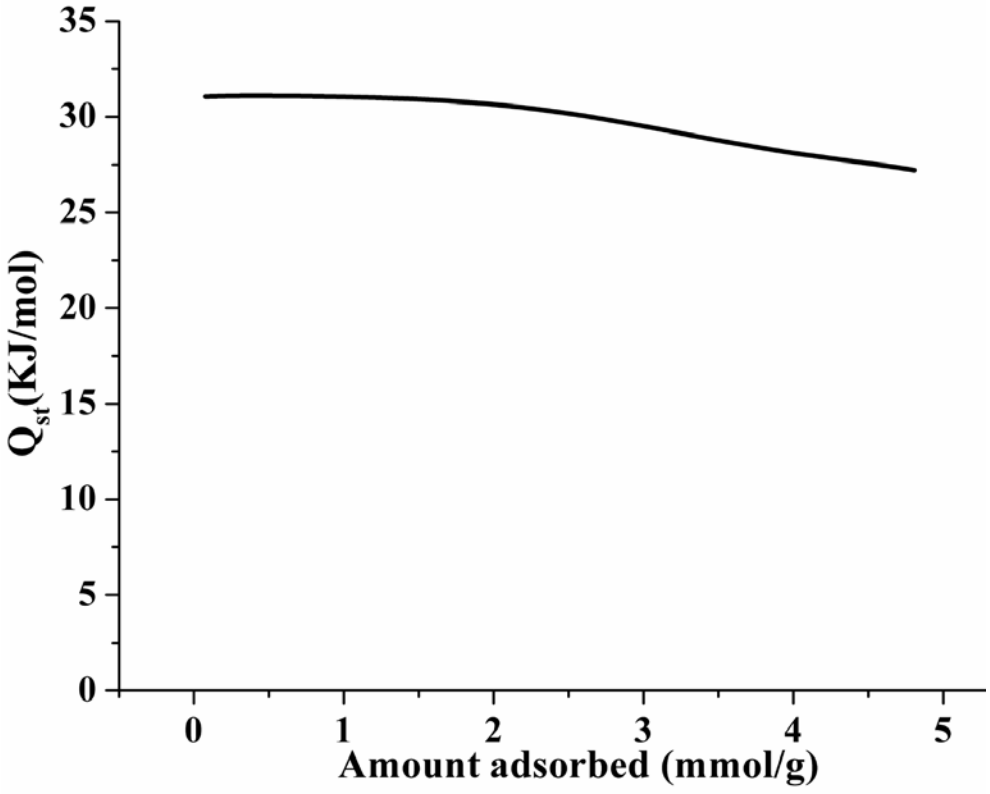

Figure S6. The isosteric heat of CO_2 adsorption for **TIF-A1** estimated by the virial equation.

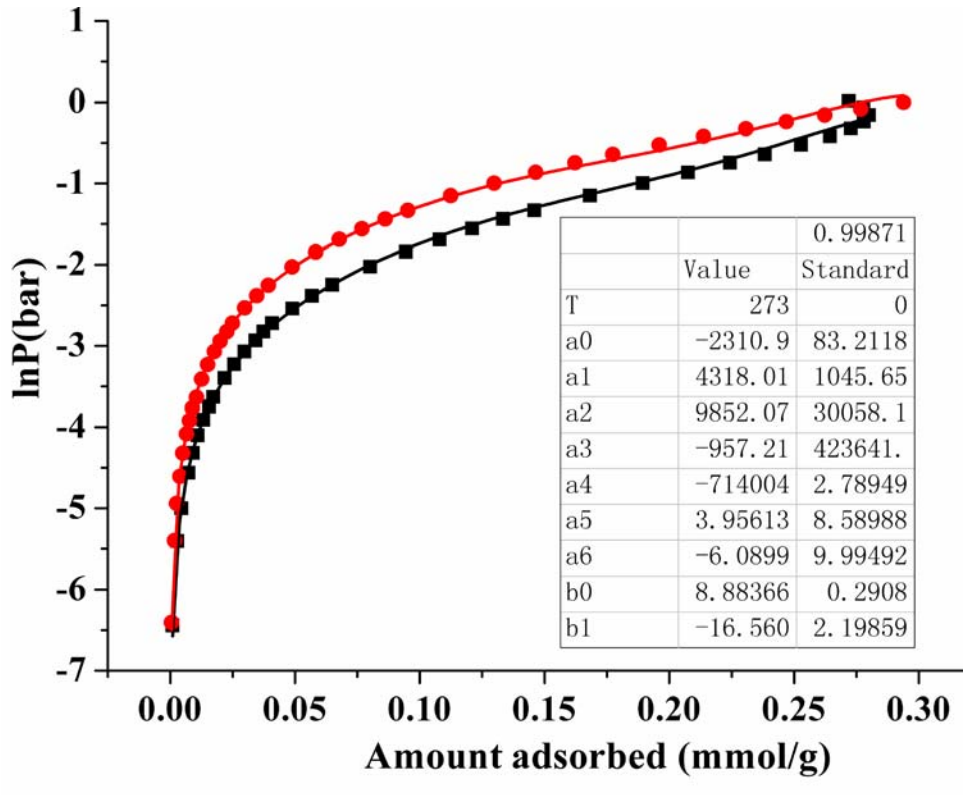

Figure S7. The N_2 sorption isotherms for **TIF-A1** fitting by virial method.

Adsorption selectivity of CO_2/N_2 calculation:

The CO_2 and N_2 sorption data for **1** and **TIF-A1** measured up to 1 bar at 273 K and 298 K were fitted by the virial equation (Figure S3, S4, S5, S7).

$$\ln(P) = \ln(Va)+(a0+a1*Va+a2*Va^2 \ldots + a6*Va^6)/T+(b0+b1*Va) \quad (1)$$

Where ***P*** is pressure, ***Va*** is amount adsorbed, ***T*** is temperature, and **a0**, **a1**, **a2** … , **a6** and **b0**, **b1** are temperature independent empirical parameters.

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

$$K_H = \exp(-b_o)\cdot\exp(-a_o/T) \quad (2)$$

The Henry's Law selectivity (S_{ij}) for gas *i* over *j* at 273K and 298 K is calculated from the following equation.

$$S_{ij} = K_{Hi}/K_{Hj} \quad (3)$$

References:

(a) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, and O. M. Yaghi, High-throughput synthesis of zeolitic imidazolate frameworks and application to CO_2 capture, Science 319 (2008) 939-943;

(b) B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe, and O. M. Yaghi, Colossal cages in zeolitic imidazolate frameworks as selective carbon dioxide reservoirs, Nature 453 (2008) 207-212;

(c) H. Kim, Y. Kim, M. Yoon, S. Lim, S. M. Park, G. Seo and K. Kim, Highly Selective Carbon Dioxide Sorption in an Organic Molecular Porous Materials, J. Am. Chem. Soc. 132 (2010) 12200-12202.