

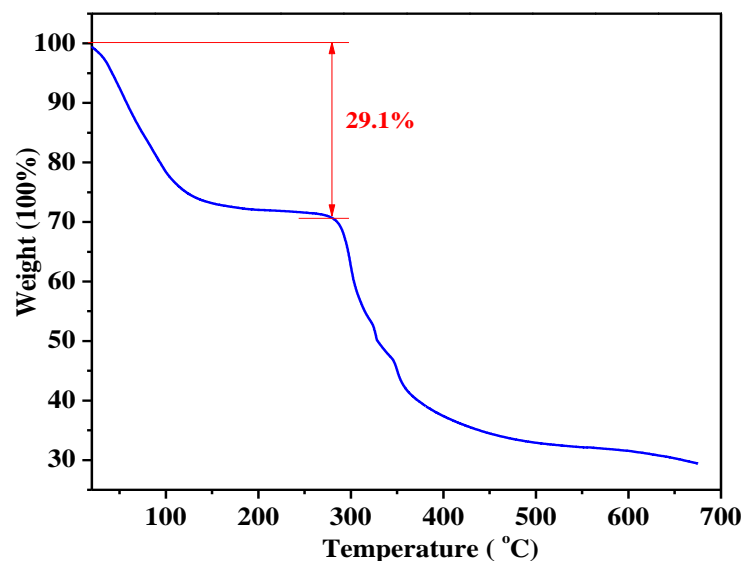
## Supporting Information

### **A highly porous 4,4-paddlewheel-connected NbO-type metal–organic framework with large gas-uptake capacity**

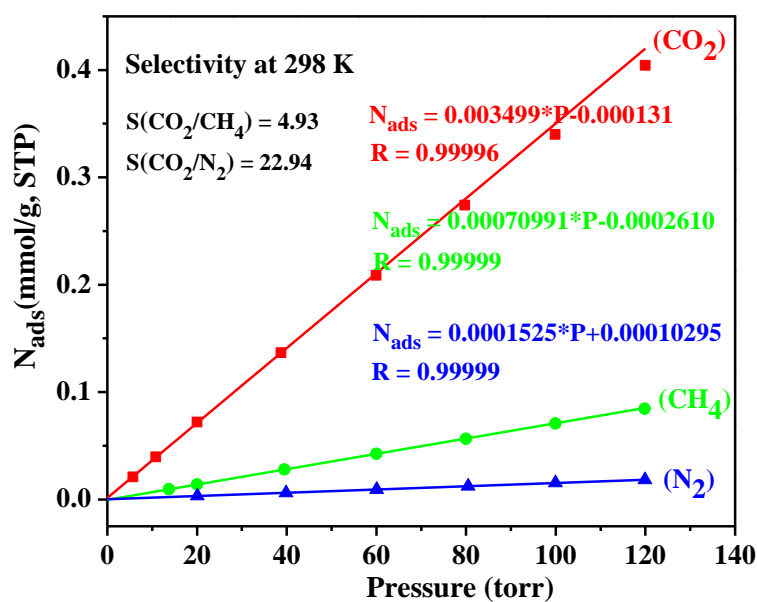
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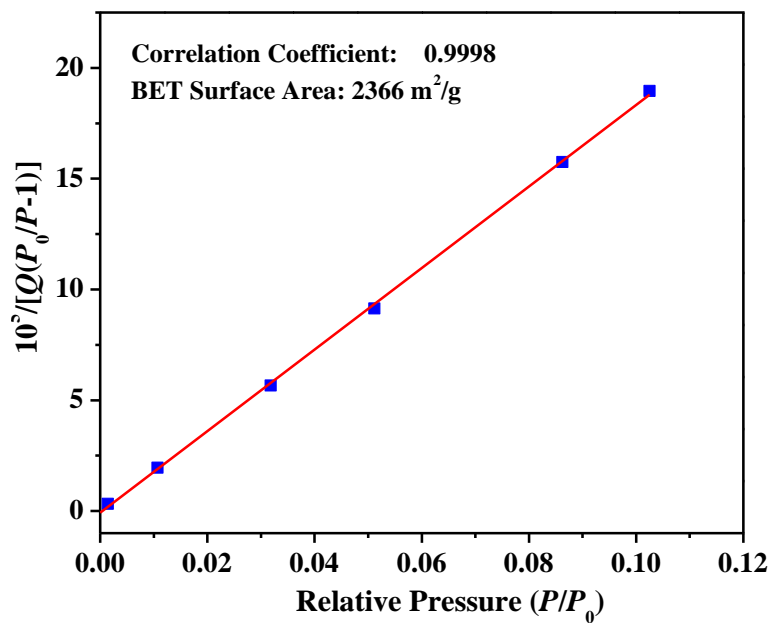
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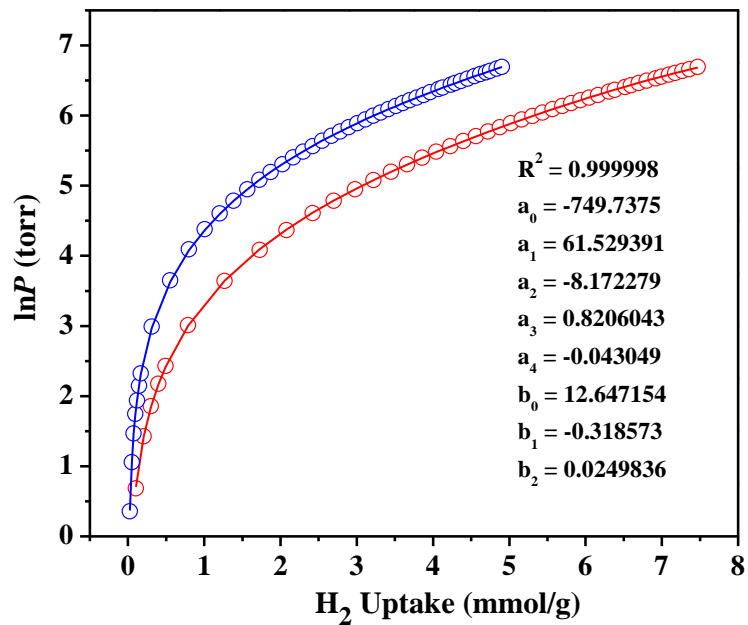
**Fig. S1** TGA data of acetone-exchanged sample of HNUST-2.



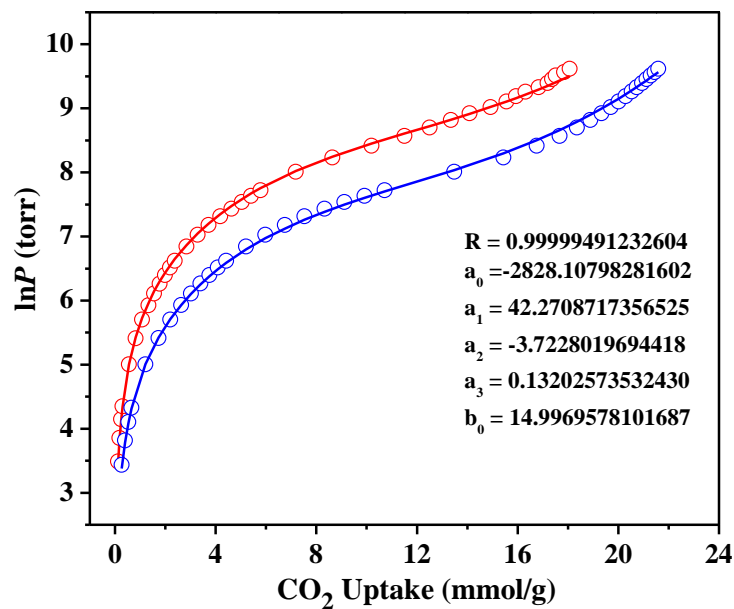
**Fig. S2** The fitting initial slope for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> isotherms for HNUST-2 collected at 298 K ( $N_{\text{ads}}$  = gases uptake;  $R$  = related coefficient). The calculated selectivity of CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/N<sub>2</sub> is 4.9 and 22.9, respectively.



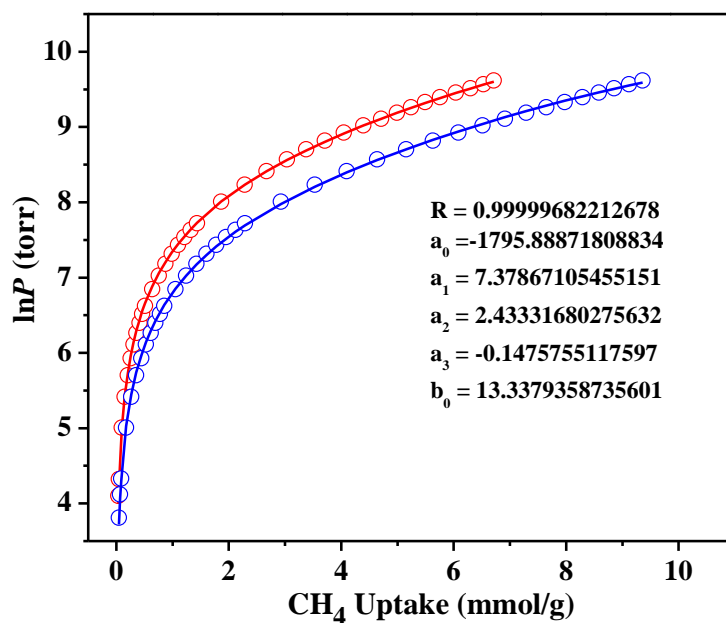
**Fig. S3** The BET plots for HNUST-2 in the chosen range ( $P/P_0 = 0.001 - 0.1$ ).



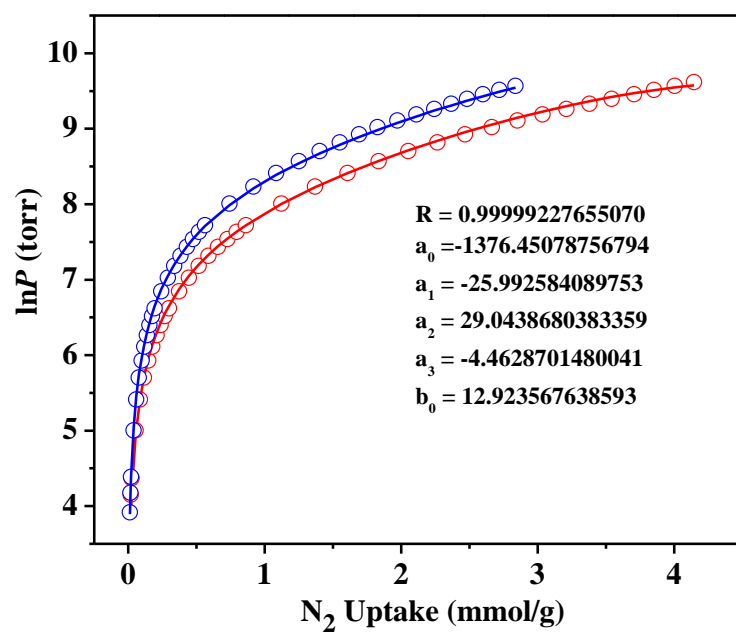
**Fig. S4** The H<sub>2</sub> isotherms at 77 K and 87 K (red and blue symbols) and the virial equation fits (red and blue lines) for HNUST-2.



**Fig. S5** The CO<sub>2</sub> isotherms at 273 K and 298 K (blue and red symbols, respectively) and the corresponding Virial equation fits (blue and red lines, respectively) for HNUST-2.



**Fig. S6** The CH<sub>4</sub> isotherms at 273 K and 298 K (blue and red symbols, respectively) and the corresponding Virial equation fits (blue and red lines, respectively) for HNUST-2.



**Fig. S7** The N<sub>2</sub> isotherms at 273 K and 298 K (red and blue symbols, respectively) and the corresponding Virial equation fits (red and blue lines, respectively) for HNUST-2.