Supporting Information

Synthesis of Highly Crystalline NH_2-MIL-125 (Ti) with S-Shaped Water Isotherms for Adsorption Heat Transformation

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Materials

Terephthalic acid (H_2BDC), 2-aminoterephthalic acid (NH_2-BDC) (99% purities each) and titanium butoxide, titanium isopropoxide (97% purities each) were purchased from TCI. Anhydrous methanol (MeOH) and anhydrous N,N-dimethylformamide (with 99.8% purities each) were purchased from Sigma Aldrich. These chemicals were used without any further purification. The nitrogen gas was of ultra-high purity (99.999%).

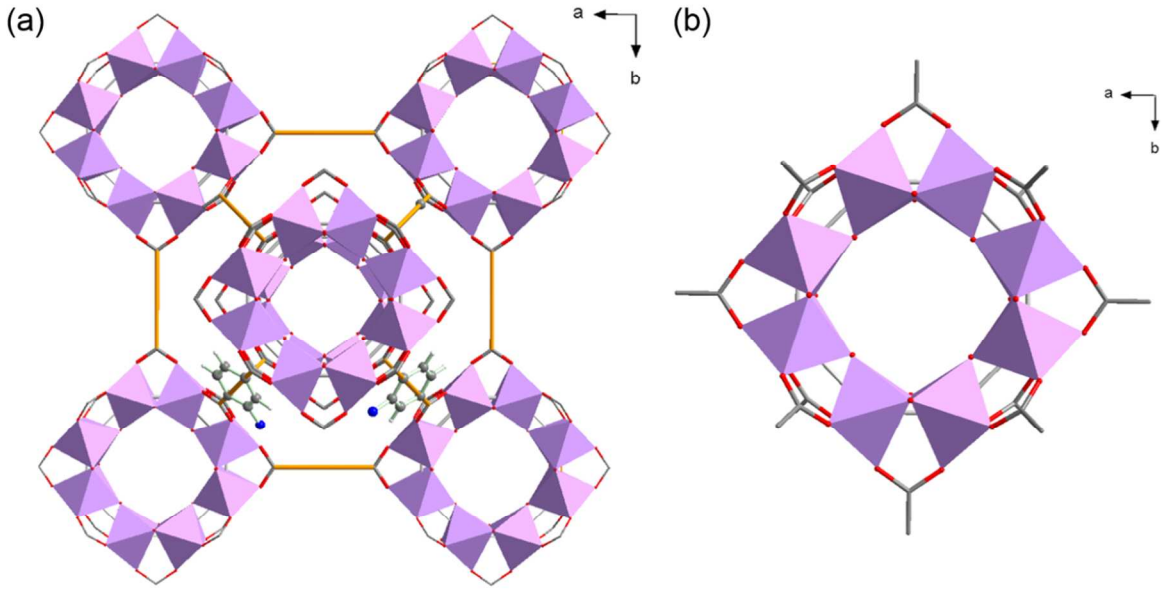

Figure S1. Polyhedral structures of NH_2-MIL-125 along the *c* axis

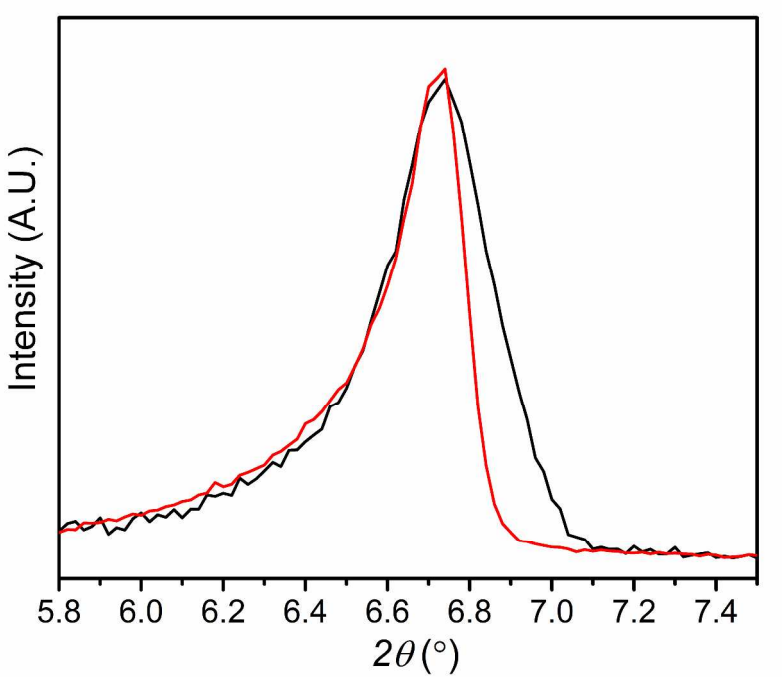

Figure S2. Normalized powder XRD profiles of NH_2-MIL-125 synthesized using $Ti(BuO)_4$ (red line) and $Ti(iPrO)_4$ (black line) by a reflux method.

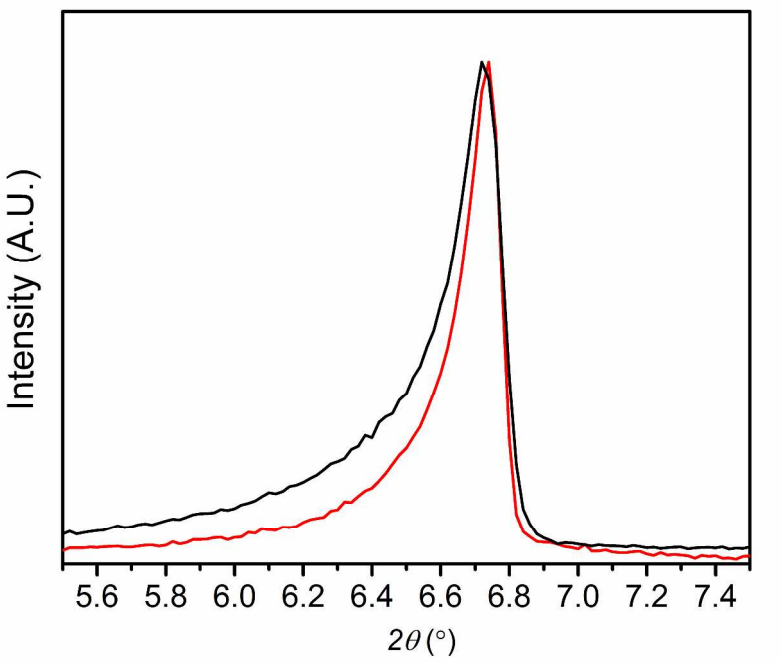

Figure S3. Normalized powder XRD profiles of NH_2-MIL-125 synthesized using $Ti(BuO)_4$ (red line) and $Ti(iPrO)_4$ (black line) by a solvothermal method.

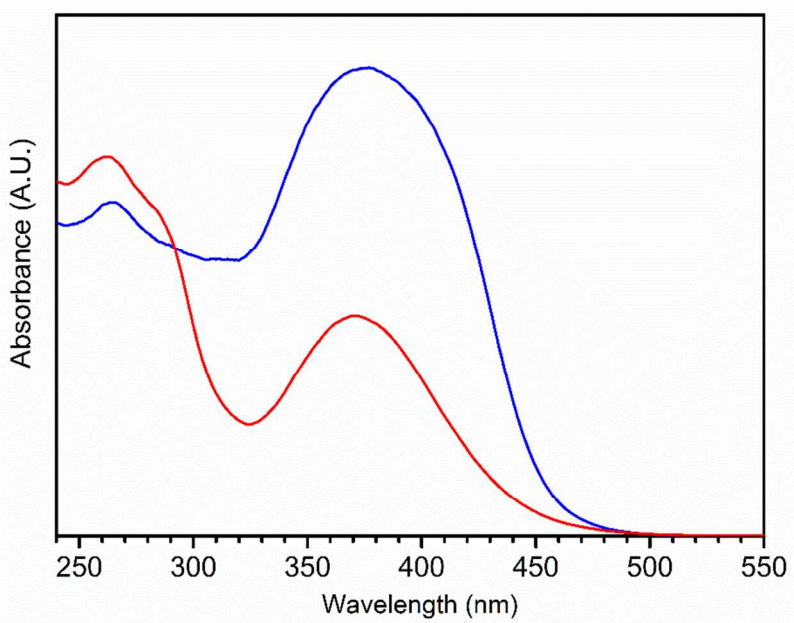

Figure S4. Diffuse reflectance UV-vis absorption spectra of NH_2-MIL-125 (blue line; solvothermal method, red line; reflux method)

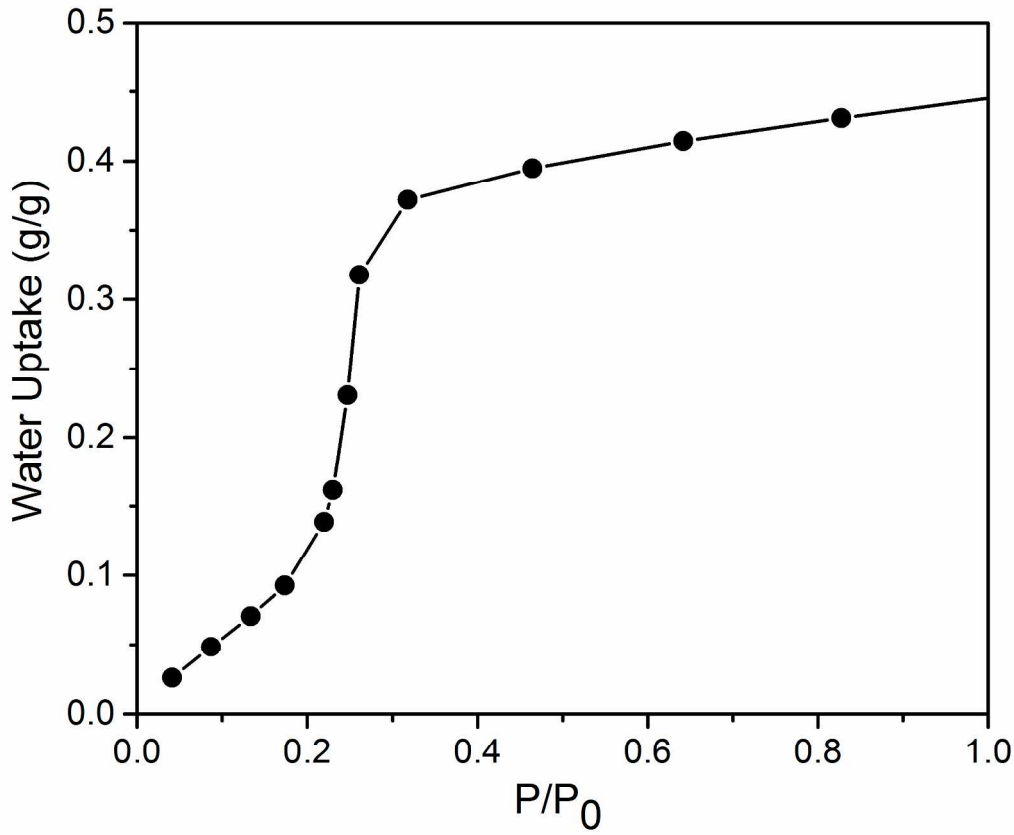

Figure S5. Water adsorption isotherm of Ti(*i*PrO)$_4$-derived NH_2-MIL-125 at 308.15

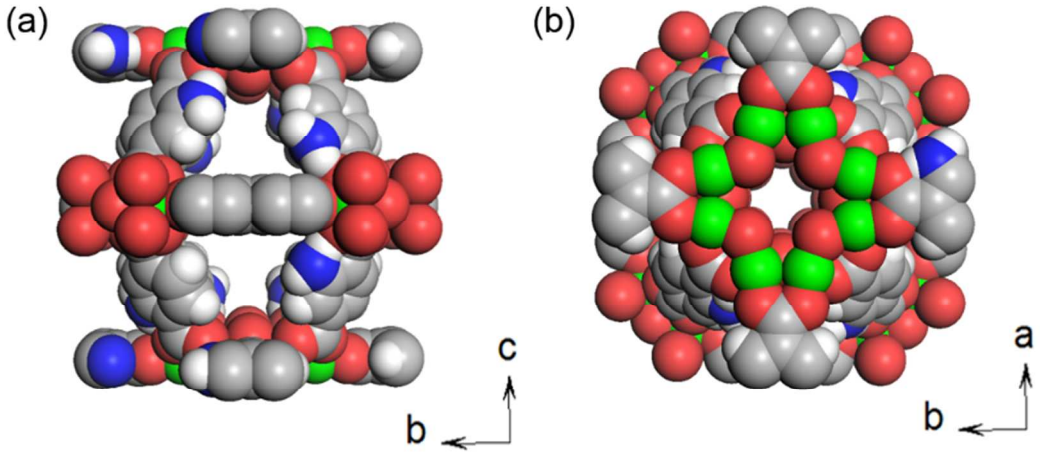

Figure S6. Space-filling models of NH_2-MIL-125(Ti) (a) along *a* axis and (b) along *c* axis.

Synthesis of MIL-125:

For the synthesis of MIL-125 by reflux reaction, BDC (3.85 g, 21.2 mmol) was dissolved in DMF (50 ml) by stirring it in a 500 ml round bottom flask under heating in an oil bath at 110 ºC for 1 hour. Then, MeOH (14 ml) was dissolved in this solution under stirring for 1 hour under reflux condition while heating at 100 ºC in the oil bath. Then, $Ti(BuO)_4$ (4.2ml) was also added into this solution and the new mixture solution was stirred for 72 hours while heating at 108 ºC under reflux condition. After cooling to room temperature, the white crystalline product was collected by filtration. This product was twice washed with DMF to remove the excess unreacted ligand and then twice washed with MeOH to replace DMF with MeOH.

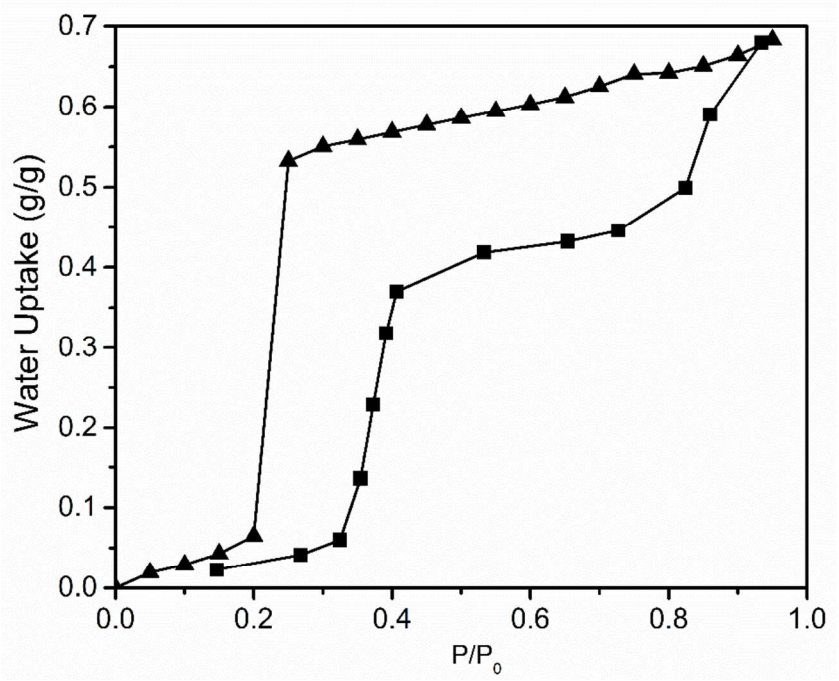

Figure S7. The water adsorption isotherms of NH_2-MIL-125 (triangles) and MIL-125 (squares) at 308.15 K

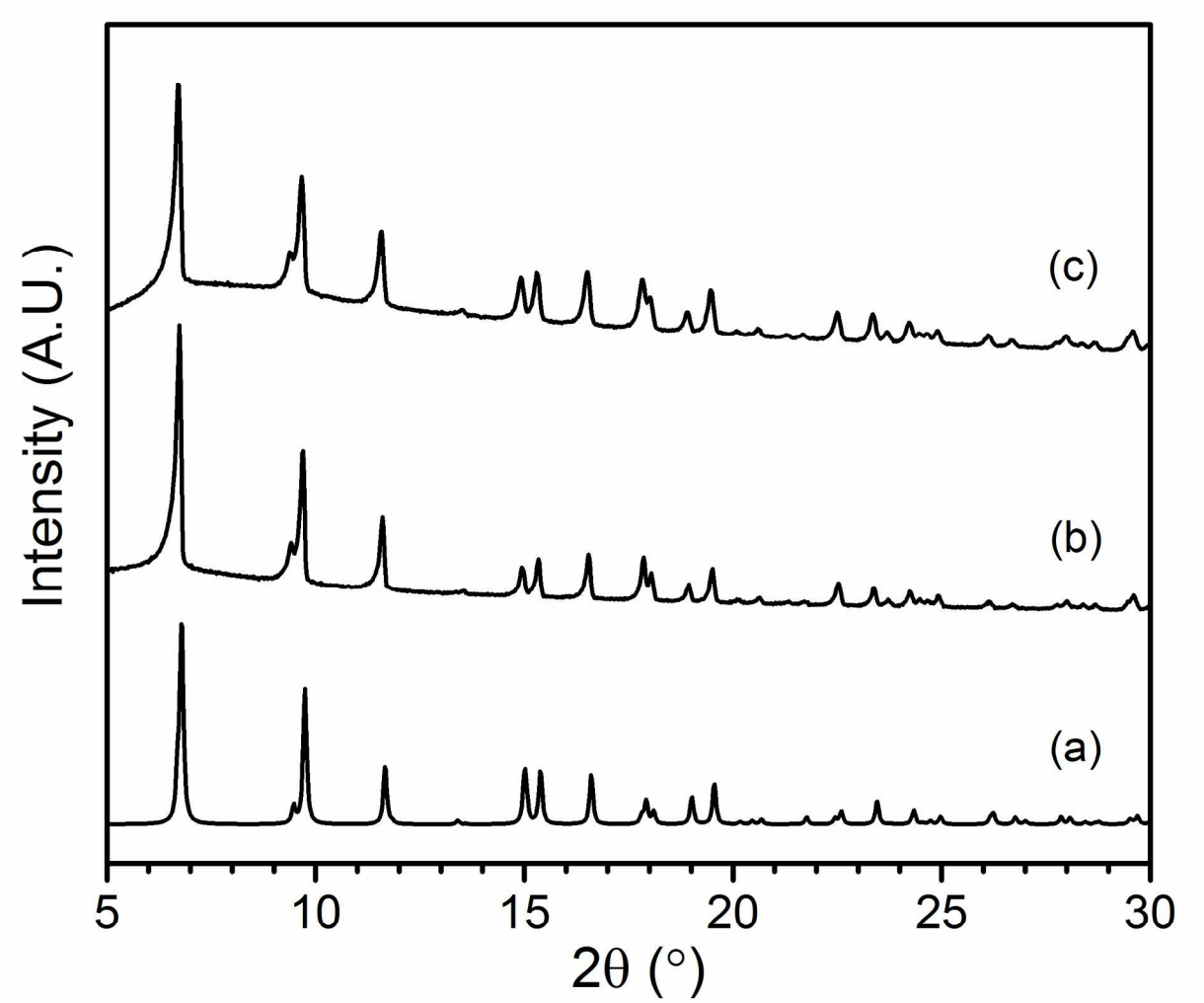

Figure S8. (a) Simulated PXRD profile, (b) experimental PXRD profiles of as-synthesized NH_2-MIL-125 and activated NH_2-MIL-125 after 10 water adsorption-desorption cycles

Figure S9. Optical image of NH_2-MIL-125 pellets

Table S1. Gas adsorption properties of the pellet

NH_2-MIL-125	BET surface area (m^2/g)	Total pore volume (cm^3/g) at P/P_0=0.990	Micropore volume[a] (cm^3/g)	Mesopore Volume[b] (cm^3/g)
1% CMC	955	0.4298	0.3775	0.0282

[a] Determined by t-plot analysis.
[b] Mesopore volume = Total pore volume – micropore volume

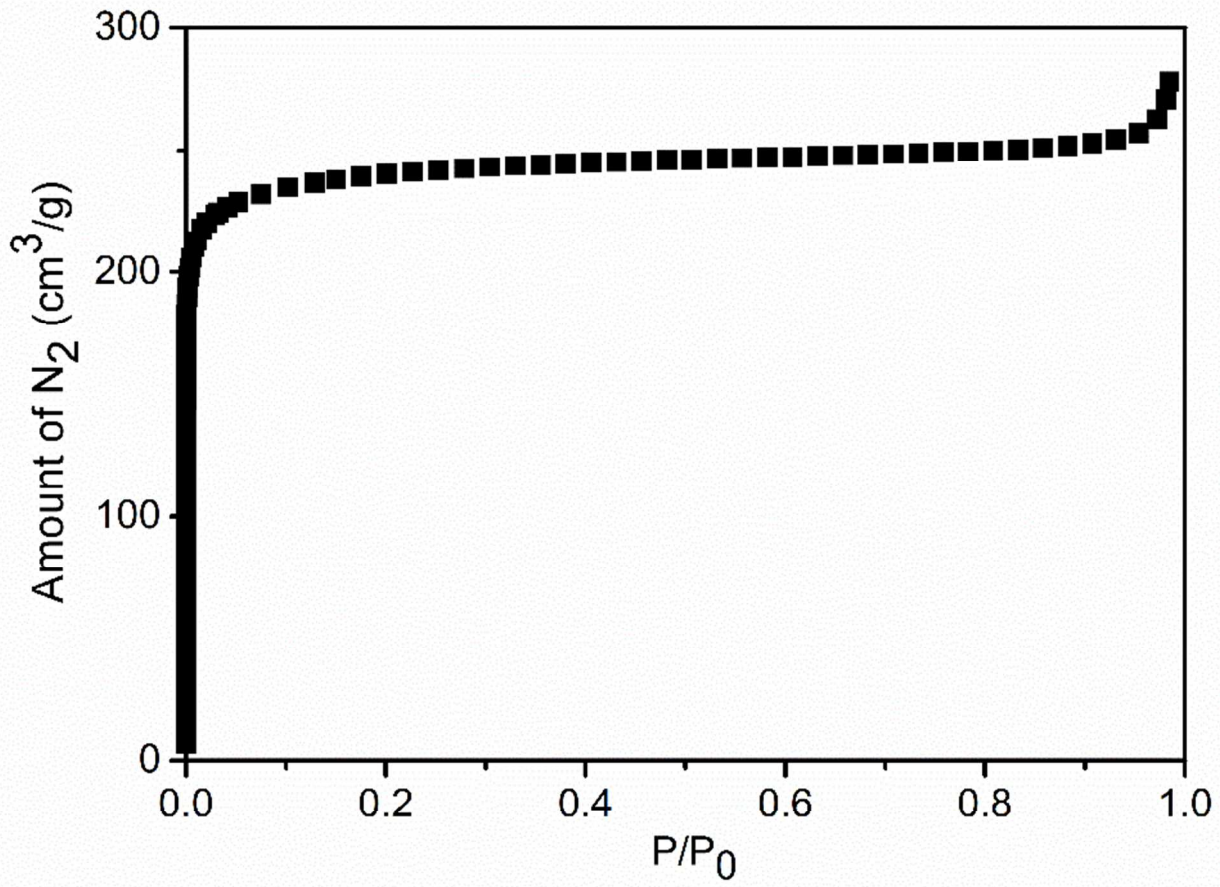

Figure S10. The N_2 adsorption isotherm of NH_2-MIL-125 pellet (NH_2-MIL-125 and 1 wt% CMC) at 77 K

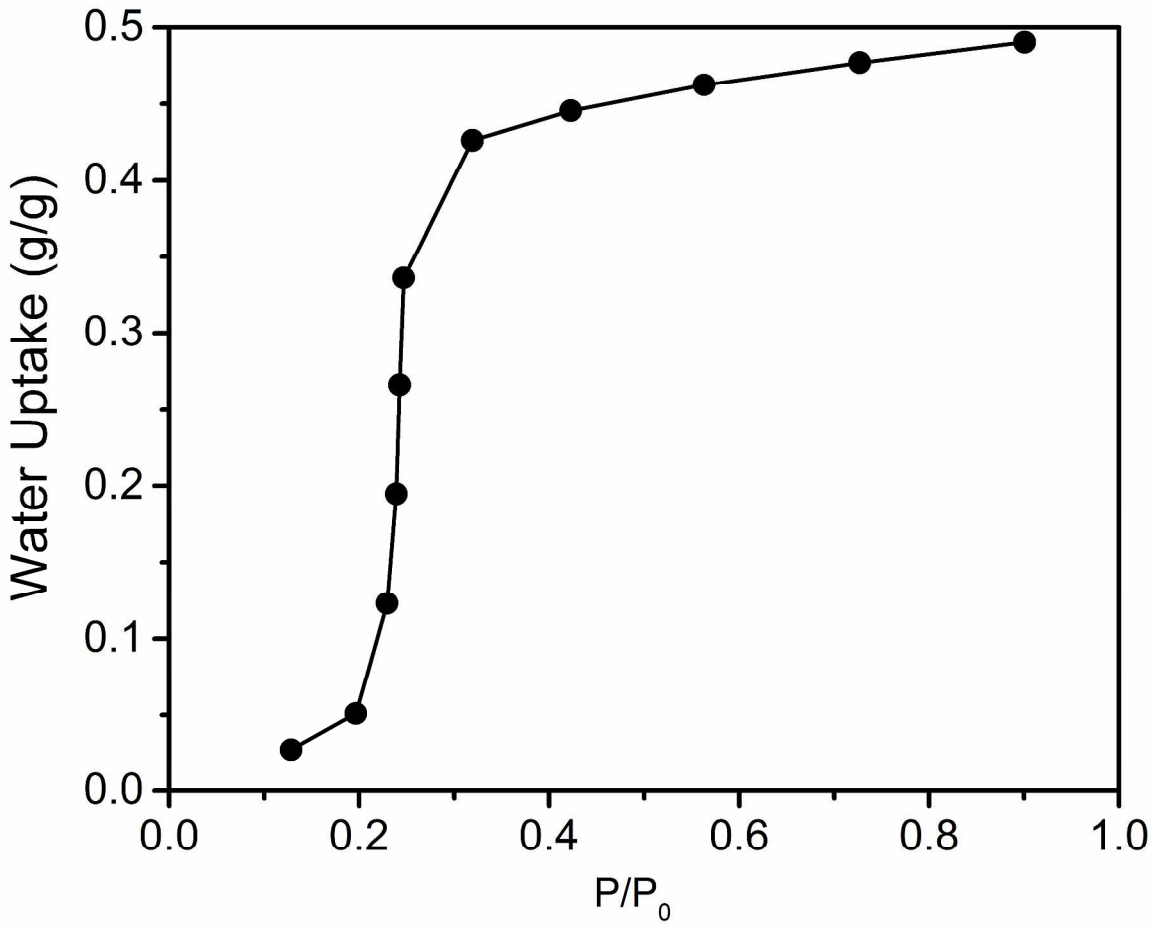

Figure S11. The water adsorption isotherm of NH_2-MIL-125 pellet at 308.15 K