

Supporting Information

Polymers of intrinsic microporosity chemical sorbents utilizing primary amine appendage through acid-base and hydrogen bonding interactions

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Materials, preparation and experimental methods

All chemicals were purchased from Sigma Aldrich and were used without any further purification. Gas adsorption and surface area measurements were collected using UHP gases via a gas sorption analyzer from Quantachrome: Adsorption and desorption isotherms were collected at 298 K and 313 K. Regeneration of sample was performed at 258 K under vacuum. Fourier transform infrared (FT-IR) spectra were collected using a Bruker Vertex. CO₂ adsorption-desorption cycling was conducted in a lab-scale, custom built packed bed reactor. Approximately 0.16 g sorbent was loaded into a stainless-steel tube (3/8 O.D.) and held in place using quartz wool plugs. The sorbent was first pretreated at 358 K under helium flow (100 cc/min). Then, CO₂ sorption was carried out at 308 K using a gas mixture of 10 vol.% CO₂/He at 100 sccm. Performance under wet conditions was also determined using a gas mixture 10 % CO₂-3% H₂O/He at 100 sccm at 308 K. For both cases, desorption was carried out in two steps: first, isothermal pressure swing desorption at 308 K and second a temperature swing desorption during which the sample was heated to 358 K. The sample was then tested under dry cycle conditions to determine its performance after exposure to steam. The gas effluent was monitored with a ThermoStar[®] mass spectrometer.

Synthesis of PIM-1

3,3,3',3'-tetramethyl-1,1''-spirobisindane-5,5',6,6'-tetrol (27.4 mmol, 9.1 g) and 2,3,5,6-tetrafluorophthalonitrile (27.4 mmol, 5.3 g) were dissolved in dry dimethylformamide (DMF) (240 mL). K₂CO₃ was added in the solution and the reaction was stirred at 58 °C for 40 hr. Water was added after cooling the reaction mixture and the product was separated by filtration. Further purification was performed by reprecipitation from CHCl₃ solution with MeOH and a bright yellow solid product was produced (12.1 g, yield 95 %) after thermal activation at 120 °C.

Synthesis of PIM-1-C

Sodium hydroxide (20g) was added to solution of water (40 mL)/ethanol (50ml). As-synthesized PIM-1 (500 mg) was placed in the solution. Reaction time and temperatures were 24 hr at 25 °C, 1hr at 120 °C, and 3.5 hr at 120 °C for PIM-1-C1, PIM-1-C2 and PIM-1-C3, respectively. Products were filtered and placed in pH 4 water for stirring overnight at ambient conditions and at 105 °C for 1 hr. After washing with water and methanol, polymers were thermally activated for the amine loading step.

Preparation of PIM-1-C-TA sorbent

PIM-1-C (100 mg) was added in 20 mL methanol solution of tris(2-aminoethyl)amine (TAEA) and stirred for 24 hr at ambient conditions. The sorbent was filtered and washed with hexane. The product was thermally activated at 85 °C under vacuum prior to characterization studies.



Figure S1: Model reaction of PIM-1-C-TA sorbent and images of PIM-1, PIM-1-C3 and PIM-1-C3-TA.

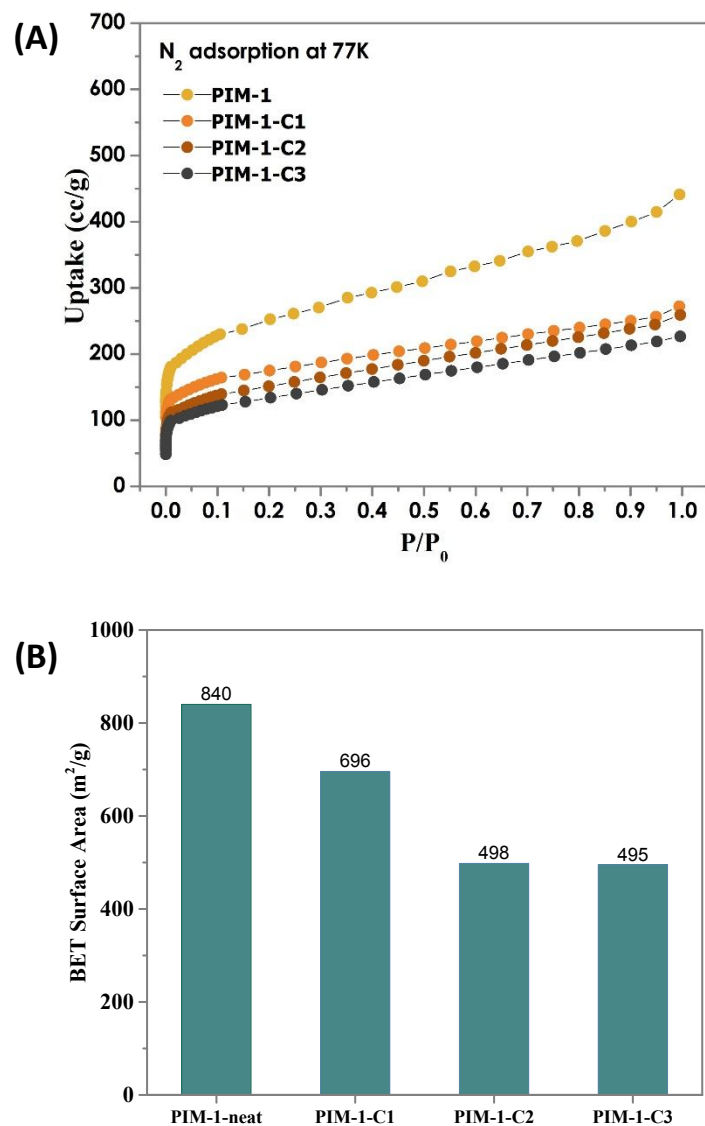


Figure S2: (A) N_2 adsorption isotherms (77 K) of PIM-1, PIM-1-C1, PIM-1-C2 and PIM-1-C3, (B) BET surface area of PIM-1, PIM-1-C1, PIM-1-C2 and PIM-1-C3.

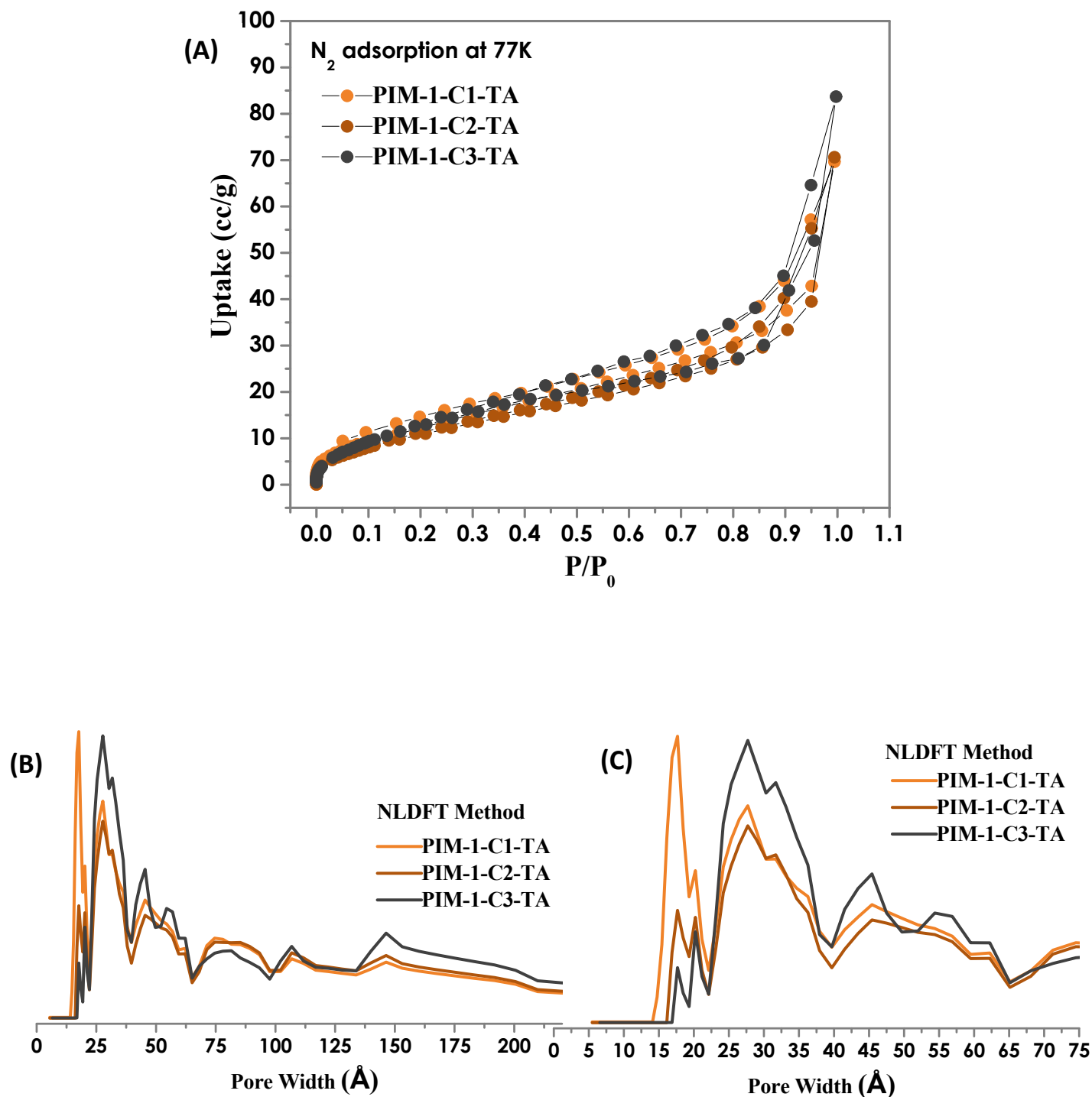


Figure S3: (A) N_2 adsorption isotherms (77 K) of PIM-1-C1-TA, PIM-1-C2-TA and PIM-1-C3-TA, (B) full range (0-22 nm) pore size distribution calculated by the NLDFT method, and (C) zoomed-in (0-7.5 nm) pore size distribution.

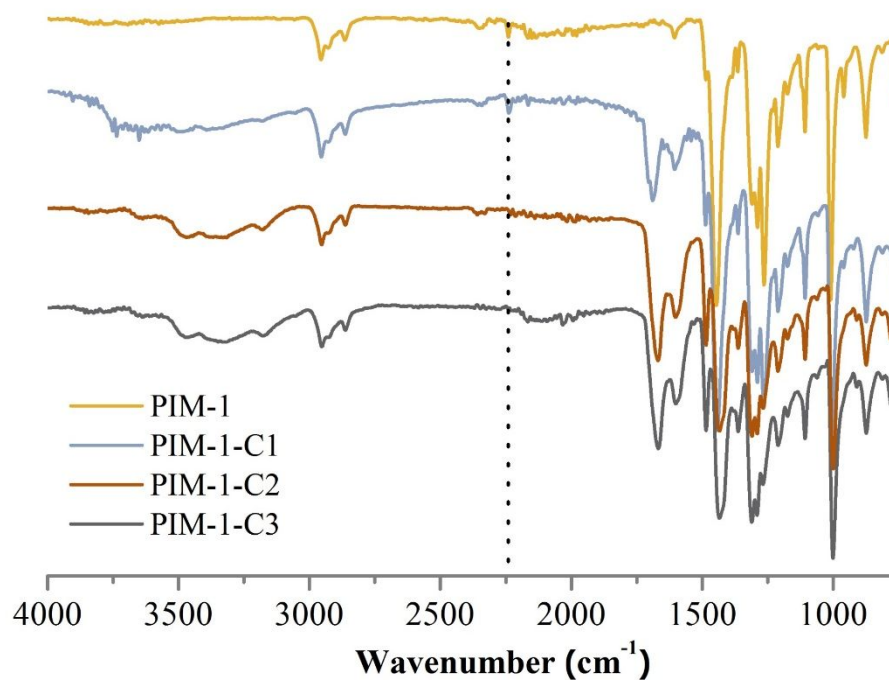


Figure S4: FT-IR spectra of PIM-1, PIM-1-C1, PIM-1-C2 and PIM-1-C3.

<i>Polymer</i>	I_{CN}/I_{CH}^*	<i>Degree of conversion (%)</i>
<i>PIM-1</i>	0.050	0%
<i>PIM-1-C1</i>	0.047	6%
<i>PIM-1-C2</i>	0.026	48%
<i>PIM-1-C3</i>	0.004	92%

Table S1: Degree of nitrile functionalization based on FT-IR spectra of PIM-1, PIM-1-C1, PIM-1-C2 and PIM-1-C3.

* I_{CN}/I_{CH} : the ratio of the area under -CN and -CH absorption stretching.

The degree of conversion was calculated with respect to I_{CN}/I_{CH} of PIM-1 (0.050).

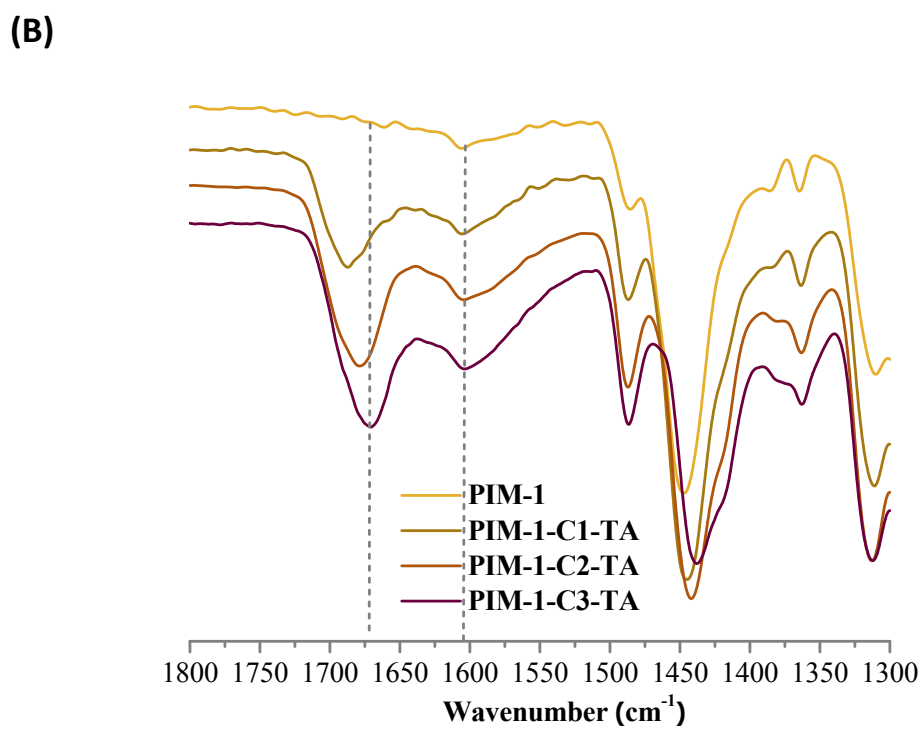
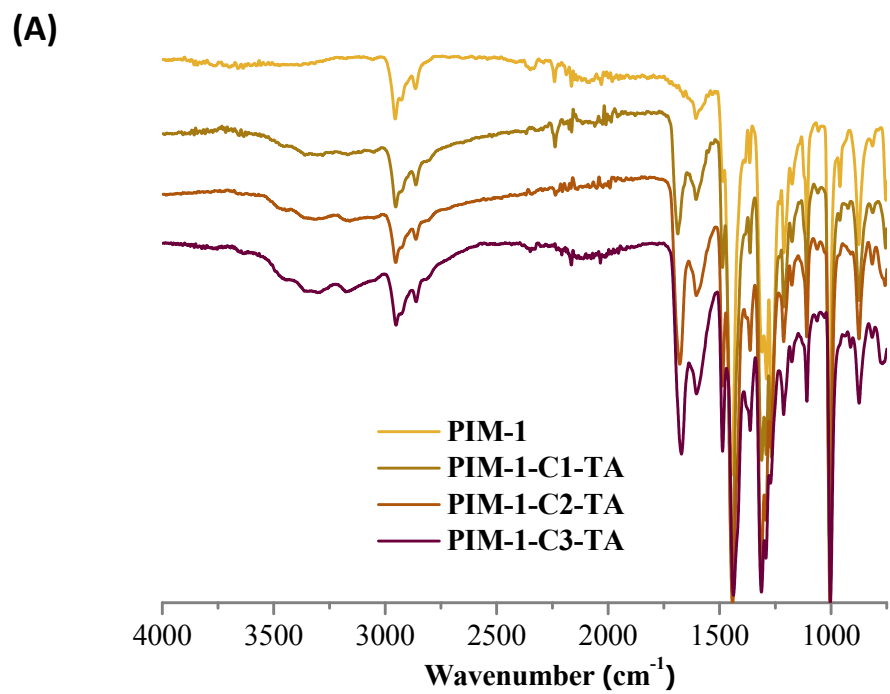


Figure S5: (A) Full range (4000-750 cm^{-1}) and (B) expanded (1800-1300 cm^{-1}) FT-IR spectra of PIM-1-TA, PIM-1-C1-TA, PIM-1-C2-TA and PIM-1-C3-TA.

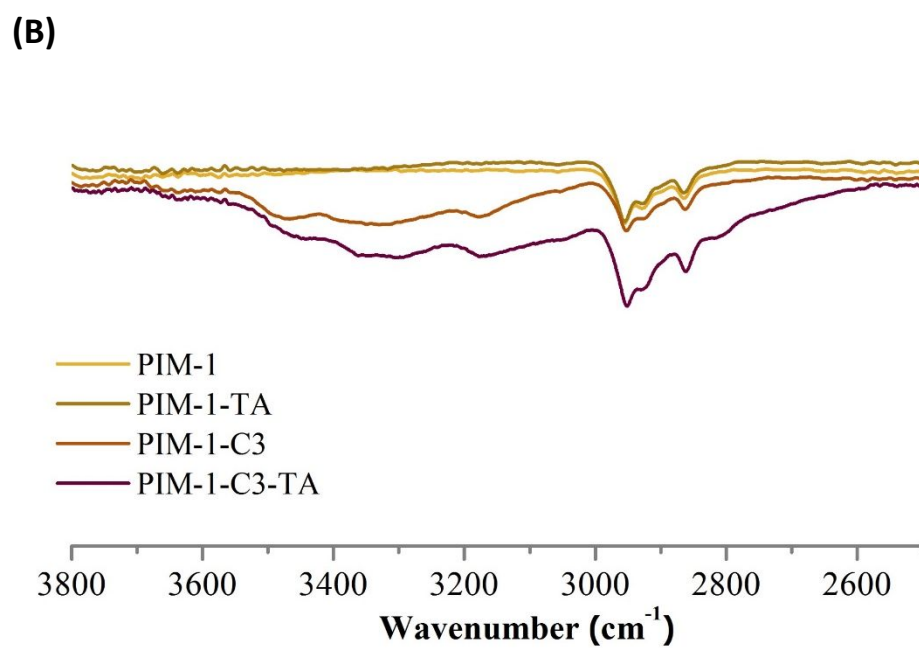
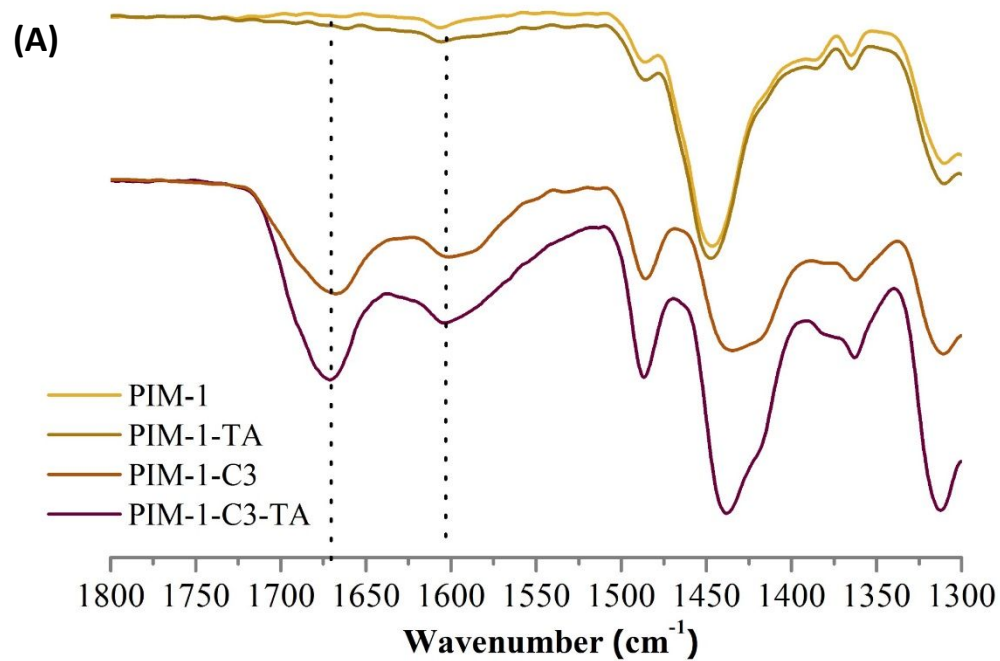


Figure S6: Expanded FT-IR spectra of PIM-1, PIM-1-TA, PIM-1-C3 and PIM-1-C3-TA. (A) 1800-1300 cm^{-1} , and (B) 3800-2500 cm^{-1}

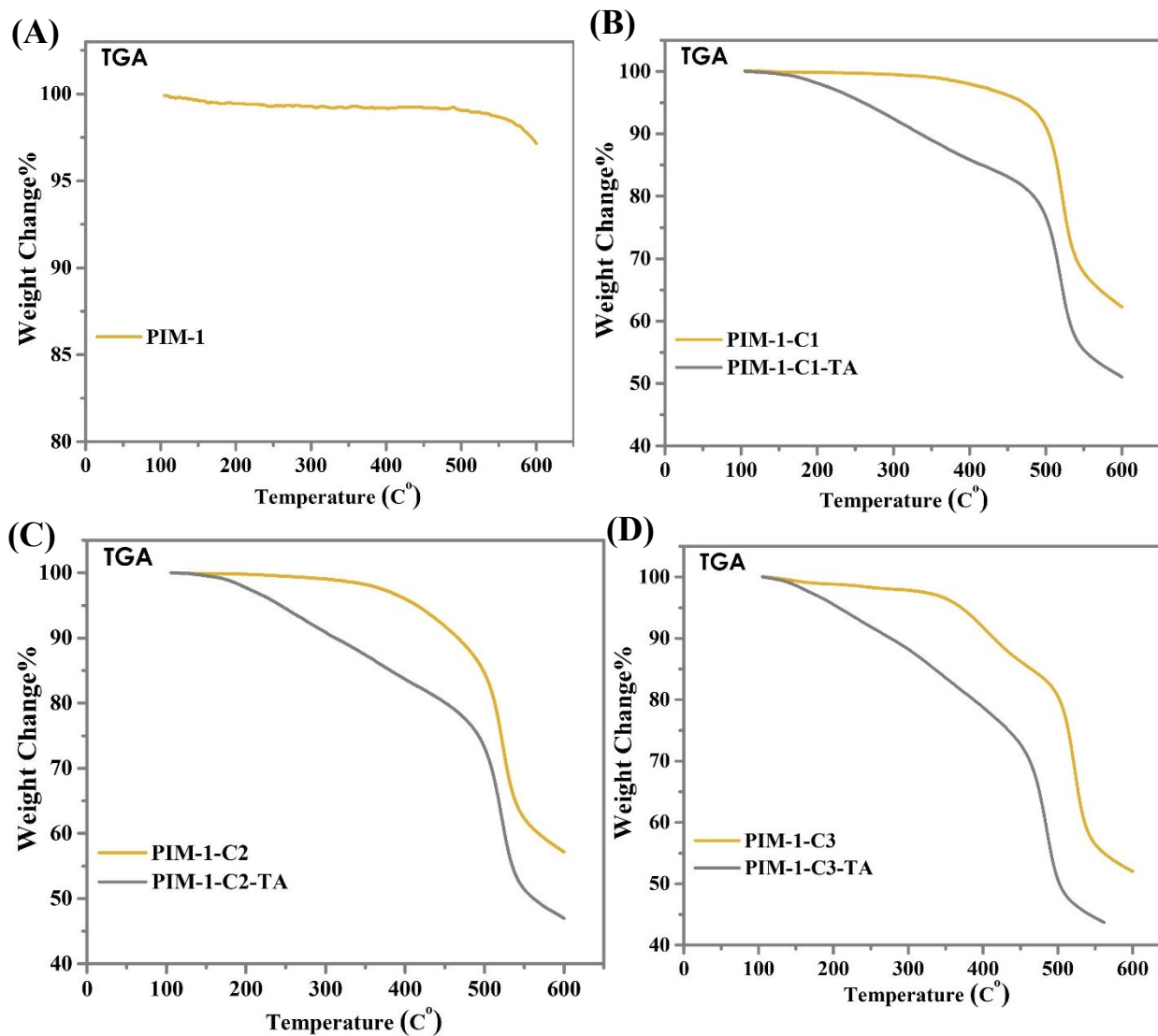


Figure S7: Thermogravimetric analysis of (A) PIM-1, (B) PIM-1-C1 and PIM-1-C1-TA, (C) PIM-1-C2 and PIM-1-C2-TA, (D) PIM-1-C3 and PIM-1-C3-TA.

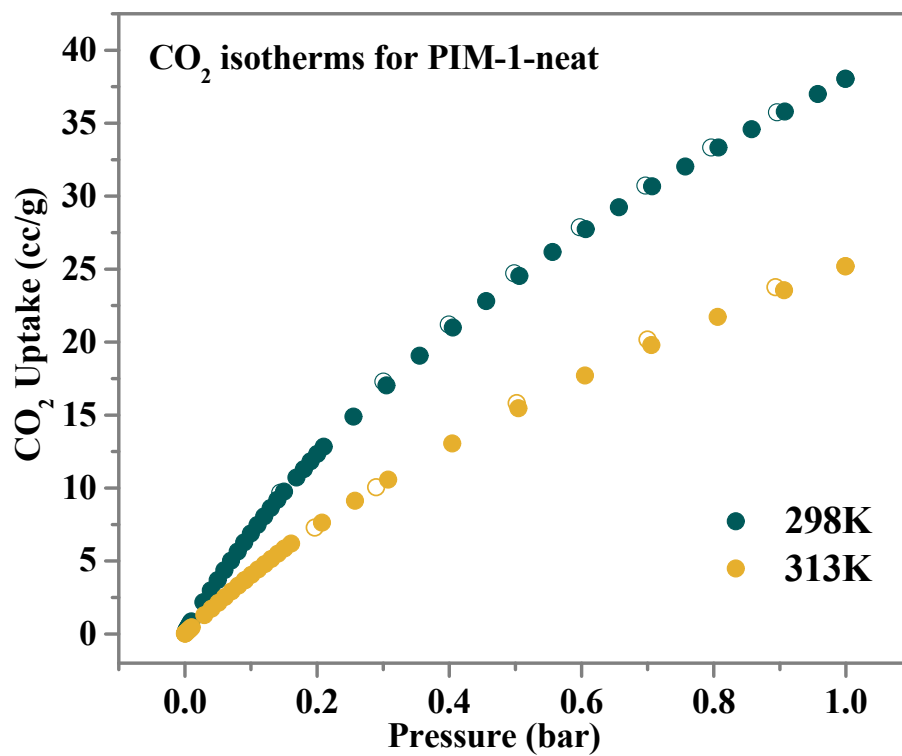


Figure S8: CO₂ adsorption/desorption isotherms (at 298 K and 313 K) of PIM-1.

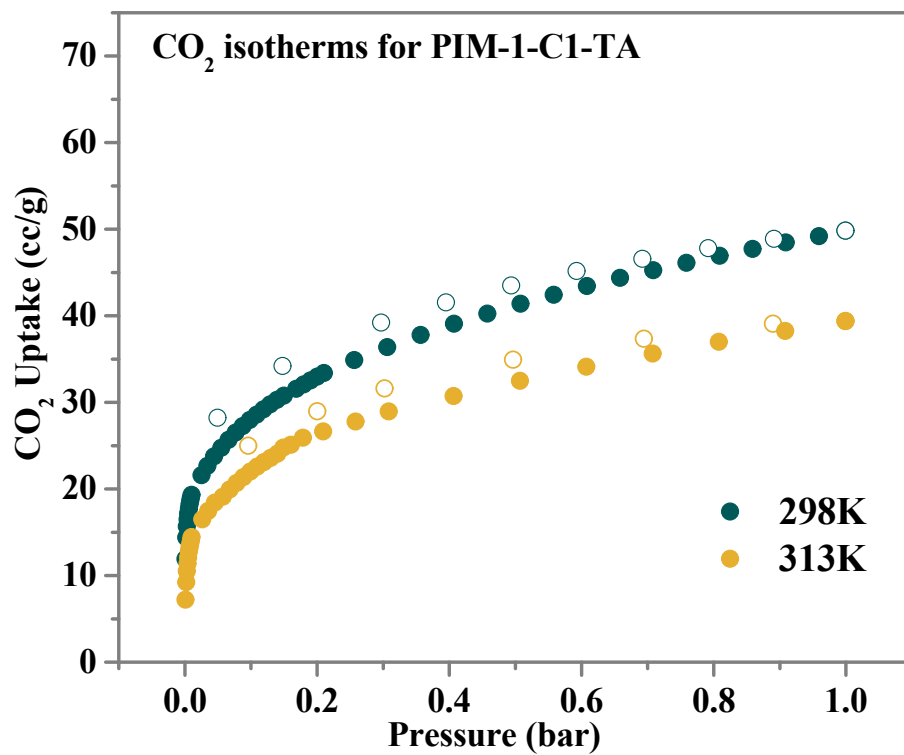


Figure S9: CO₂ adsorption/desorption isotherms (at 298 K and 313 K) of PIM-1-C1-TA.

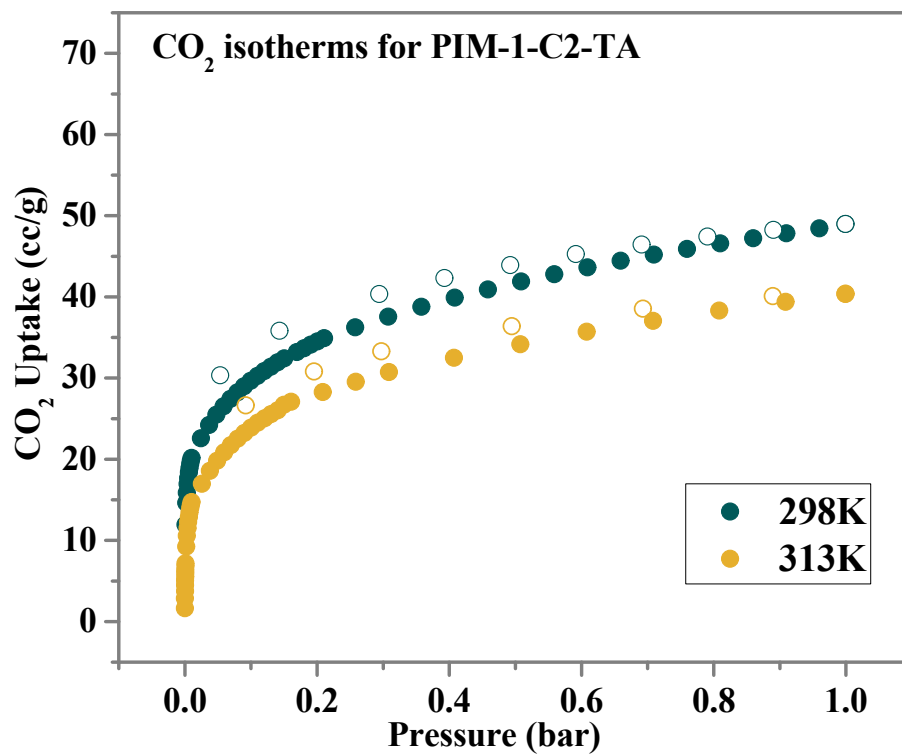


Figure S10: CO₂ adsorption/desorption isotherms (at 298 K and 313 K) of PIM-1-C2-TA.

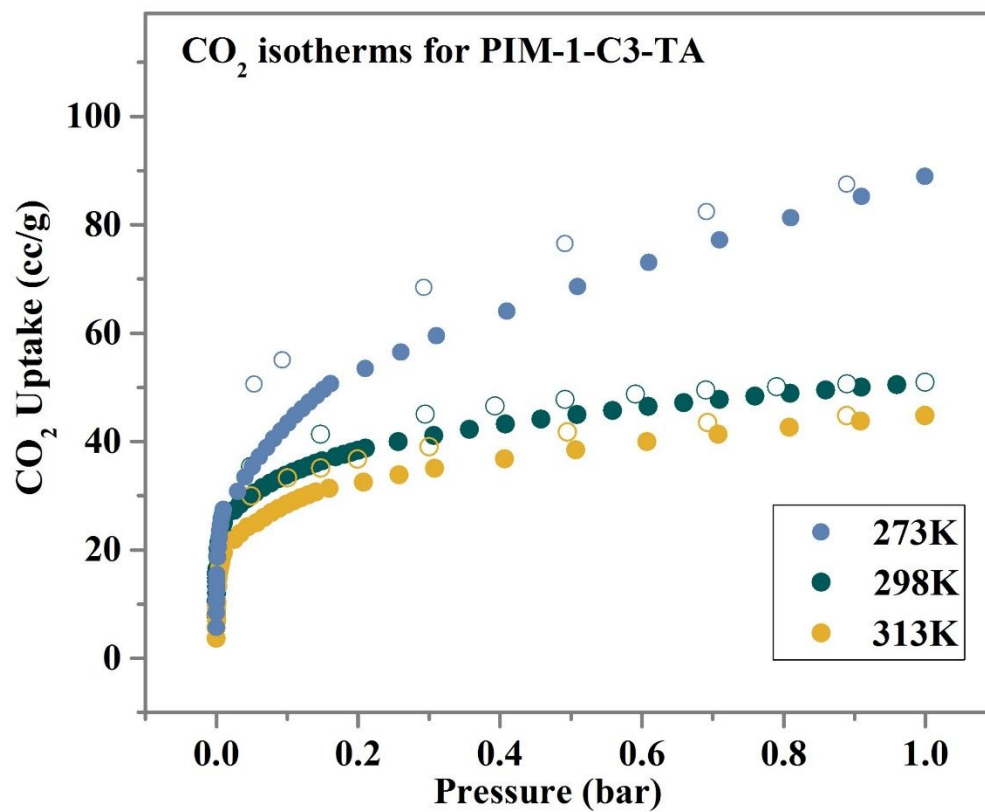


Figure S11: CO₂ adsorption/desorption isotherms (at 273K, 298 K and 313 K) of PIM-1-C3-TA.

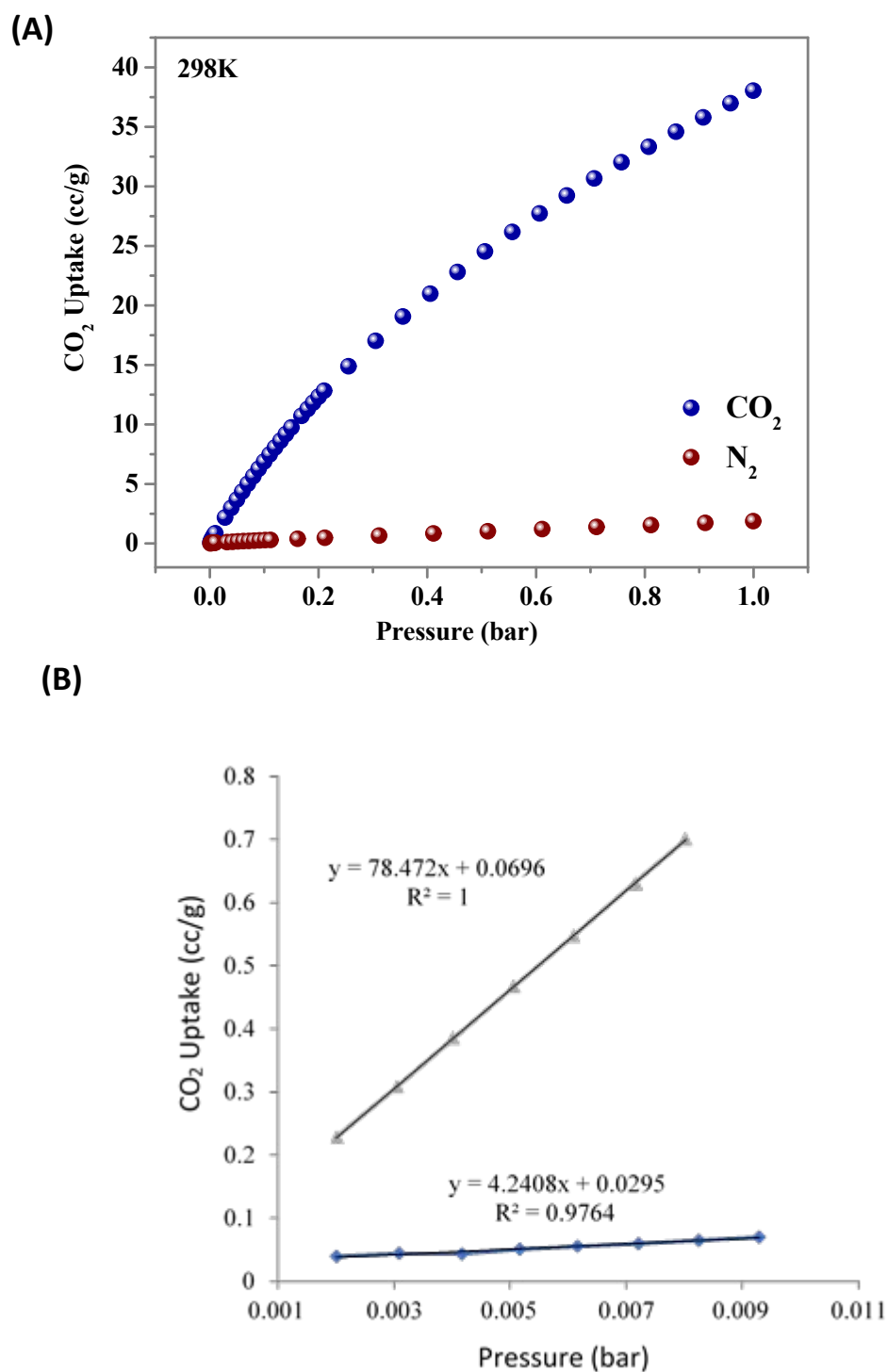


Figure S12: (A) CO₂ and N₂ adsorption isotherms at 298 K of PIM-1 and (B) initial slopes of isotherms.

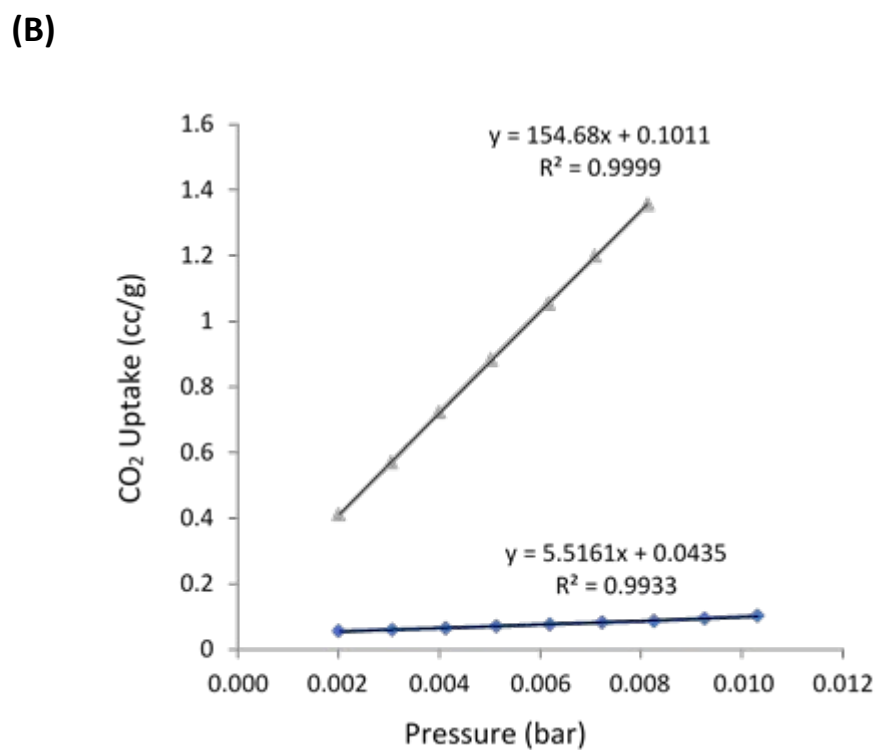
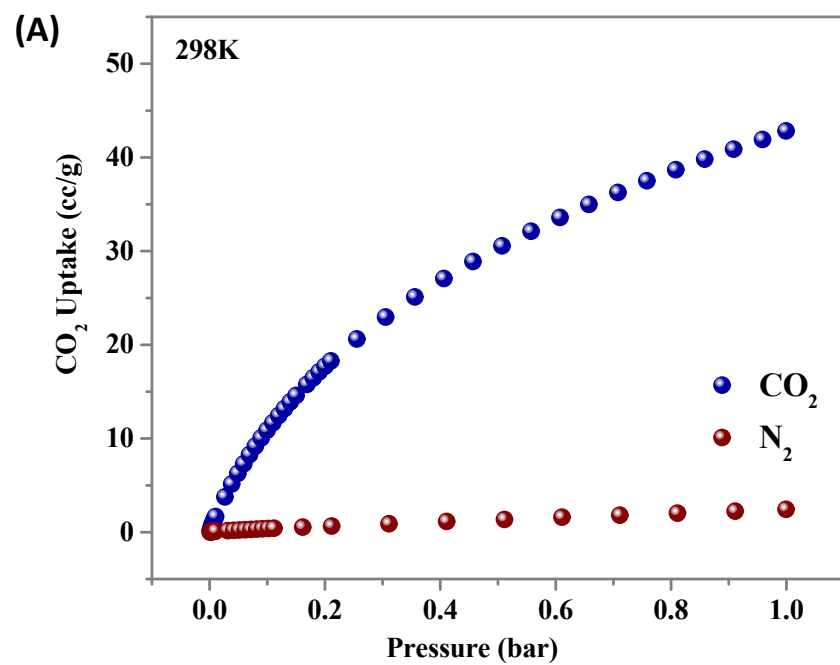


Figure S13: a) CO₂ and N₂ adsorption isotherms (at 298K) PIM-1-C3 and b) initial slopes of isotherms.

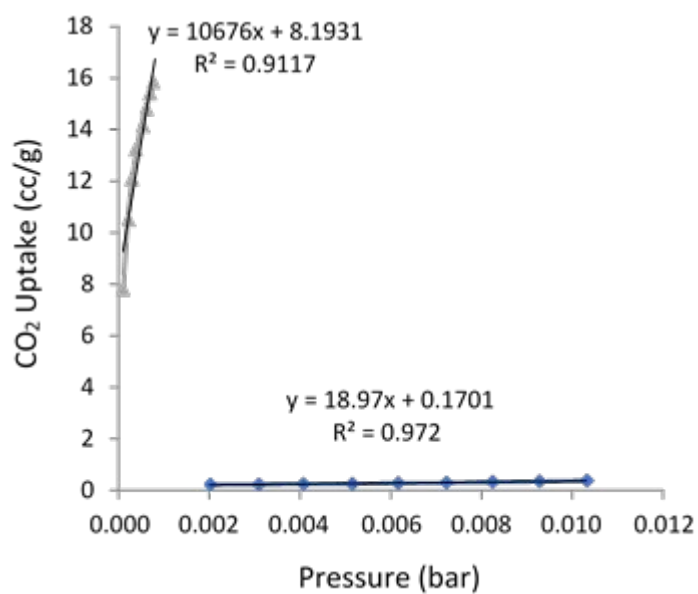
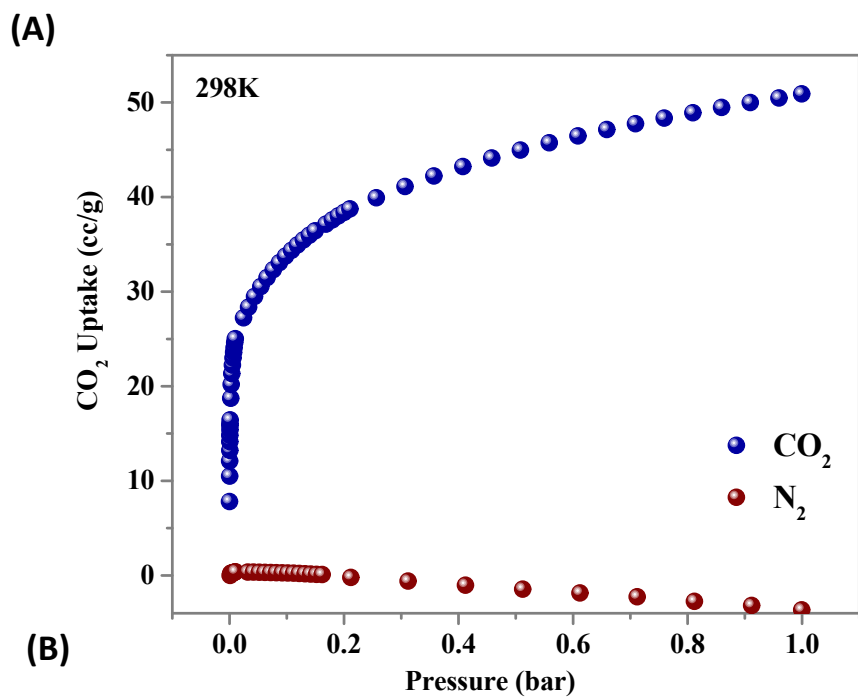


Figure S14: (A) CO₂ and N₂ adsorption isotherms at 298 K for PIM-1-C3-TA and (B) initial slopes of isotherms. Note: At higher pressure range, decreasing N₂ adsorption behavior can be ascribed to low N₂ uptake in the sorbents

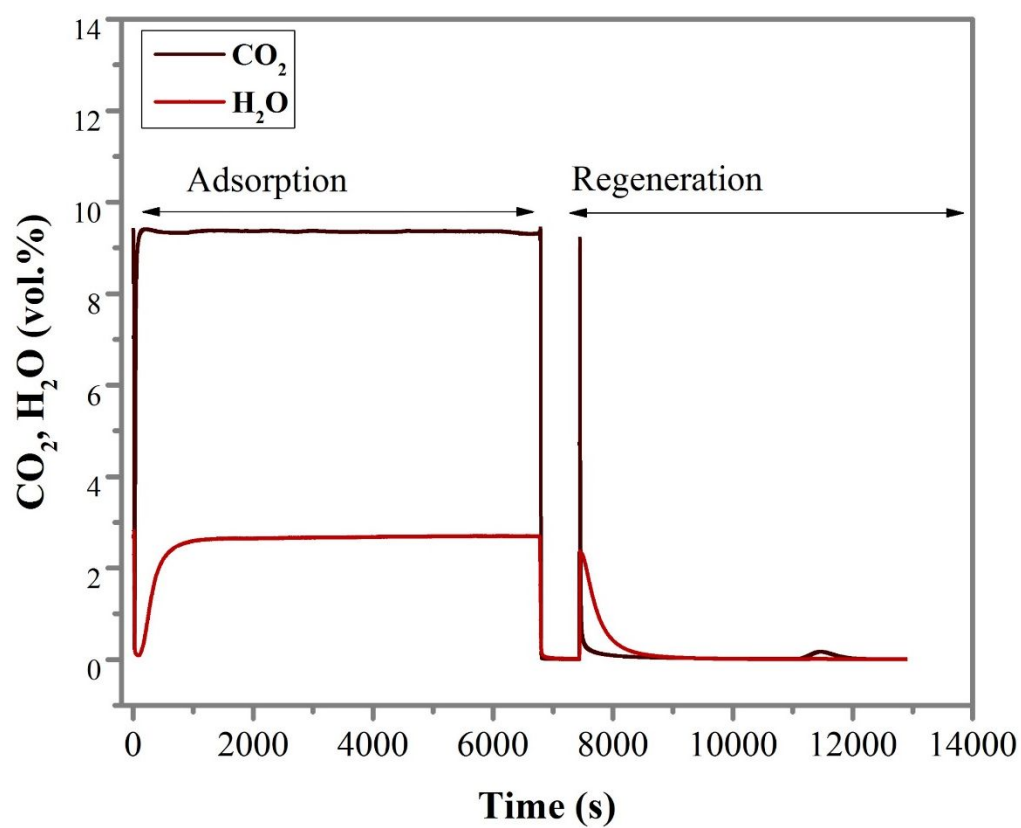


Figure S15: Adsorption and regeneration breakthrough curves of CO₂ and H₂O at 308 K for PIM-1-C3-TA.

Sorbent	CO₂ uptake (cc/g) at 0.15 bar and 298 K	Reference
<i>PIM-1</i>	9	1
<i>PIM-1-TA</i>	1	This work
<i>PIM-1-C1-TA</i>	31	This work
<i>PIM-1-C2-TA</i>	32	This work
<i>PIM-1-C3-TA</i>	36	This work
<i>PIM-1-COOH-360</i>	18	2
<i>DATPIM</i>	12	3
<i>hPIM-1</i>	11	1
<i>14 wt% PEI/PIM-1*</i>	16	4
<i>21 wt% PEI/PIM-1*</i>	28	4
<i>25 wt% PEI/PIM-1*</i>	24	4
<i>Amidoxime-PIM-1</i>	12	5
<i>sPIM-1</i>	6	6
<i>UiO-66-CN@sPIM-1</i>	8	6

Table S2: CO₂ adsorption performance of high-performance PIM-based sorbents in the literature.

*CO₂ isotherm was collected at 318K.

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