Electronic Supplementary Information

Adsorption of CO_2 on a micro-/mesoporous polyimine modified with tris(2-aminoethyl)amine

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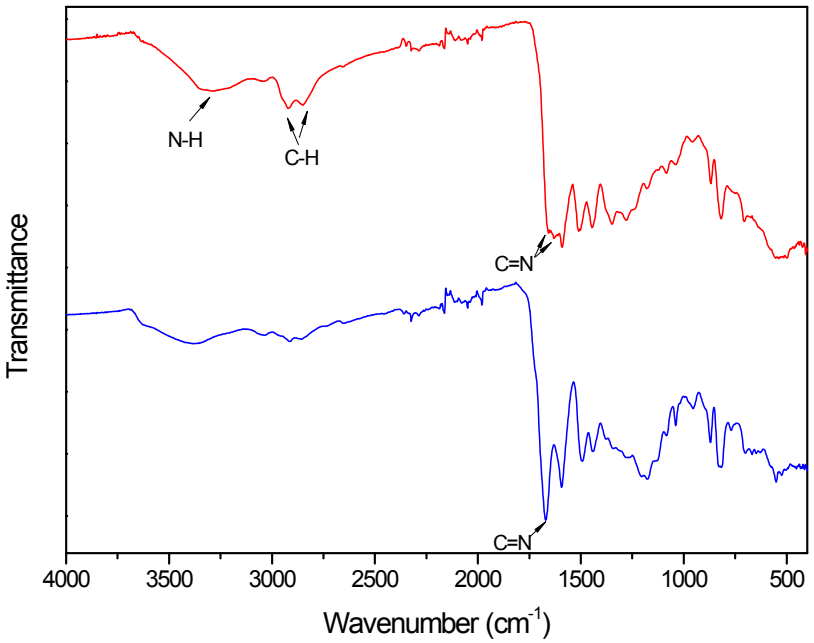

Figure S1. Infrared spectra of PP1-2 (blue line) and PP1-2-tren (red line).

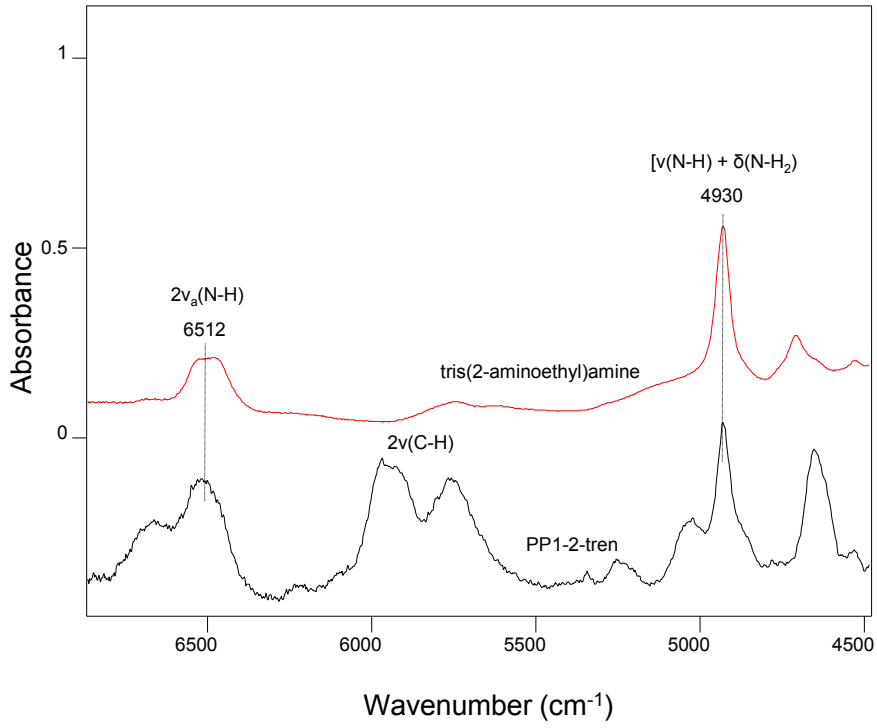

Figure S2. Near infrared spectra of tris(2-aminoethyl)amine (**tren**)and PP1-2-tren.

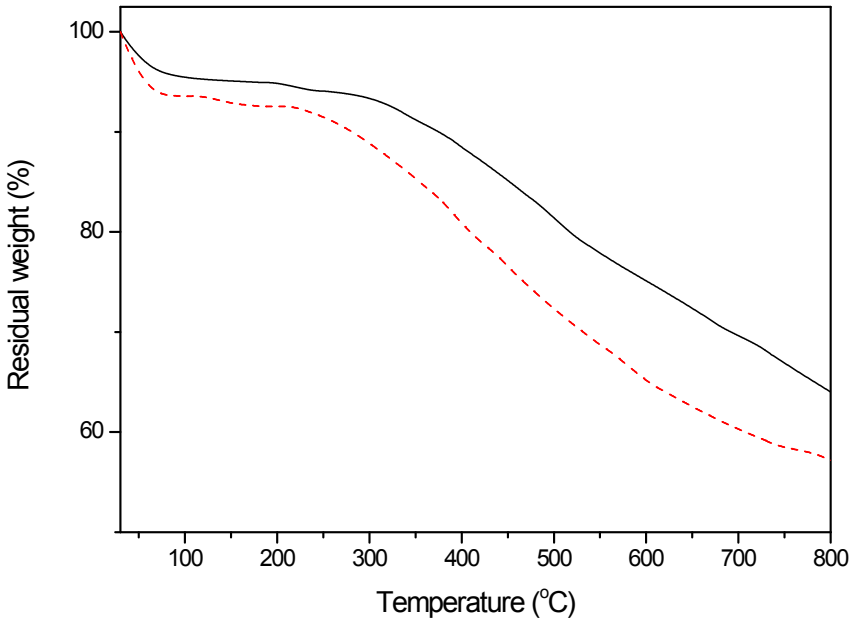

Figure S3. Thermal gravimetric analysis (TGA) curves of PP1-2 (solid line) and PP1-2-tren (dashed line).

Regression analyses of CO_2 adsorption isotherms

The CO_2 adsorption isotherms of PP1-2 and PP1-2-tren recorded at 273 K and 293 K adhered well with a dual-site Langmuir model

$$q = q_A + q_B = \frac{q_{sat,A} b_A p}{1 + b_A p} + \frac{q_{sat,B} b_B p}{1 + b_B p} \quad (1)$$

where A and B are two distinct adsorption sites, q_{sat} is saturation loading in mol kg^{-1}, b is temperature dependent Langmuir constant (Pa^{-1}) expressed as

$$b = b_0 exp(\frac{E}{RT}) \quad (2)$$

Calculation of isosteric heat of adsorption (Q_{st})

The Q_{st} was determined by using the Clausius-Clapeyron equation

$$Q_{st} = RT^2 \left(\frac{\partial \, lnp}{\partial \, T}\right)_q \quad (3)$$

The details for the calculation of Q_{st} in the dual-site Langmuir model are given by Mason *et al.*[1] The regression analysis results are presented in Table S1-2, Figure S4-5. The heat of adsorption of CO_2 for PP1-2-tren determined by this method is shown in Figure S6.

The Qst for PP1-2 and PP1-2-tren were also calculated directly from the experimental isotherms recorded at 273 K and 293 K by using equation (3). The value of Q_{st} was directly obtained from a plot of lnp against the reciprocal of the temperature, as presented in Figure S7-8.

[1] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, **2011**, *4*, 3030-3040.

Table S1. Parameters for the dual-site Langmuir model for adsorption of CO_2 in PP1-2. The parameters were determined by regression analyzes using the adsorption isotherms recorded at temperatures of 273 K and 293 K. (Figure S4)

$q_{sat,A} = 0.70\ mol\ kg^{-1}$

$q_{sat,B} = 2.57\ mol\ kg^{-1}$

$b_A = b_{A0} exp(\frac{E_A}{RT})$

$b_{A0} = 3.85 \times 10^{-10} Pa^{-1}$

$E_A = 29.5\ kJ\ mol^{-1}$

$b_B = b_{B0} exp(\frac{E_B}{RT})$

$b_{B0} = 5.67 \times 10^{-10} Pa^{-1}$

$E_B = 22.2\ kJ\ mol^{-1}$

Table S2. Parameters for the dual-site Langmuir model for adsorption of CO_2 in PP1-2-tren. The parameters were determined by regression analyzes using the adsorption isotherms recorded at temperatures of 273 K and 293 K. (Figure S5)

$q_{sat,A} = 0.85\ mol\ kg^{-1}$

$q_{sat,B} = 1.84\ mol\ kg^{-1}$

$b_A = b_{A0} exp(\frac{E_A}{RT})$

$b_{A0} = 4.28 \times 10^{-18} Pa^{-1}$

$E_A = 80.6\ kJ\ mol^{-1}$

$b_B = b_{B0} exp(\frac{E_B}{RT})$

$b_{B0} = 4.76 \times 10^{-13} Pa^{-1}$

$E_B = 40.8\ kJ\ mol^{-1}$

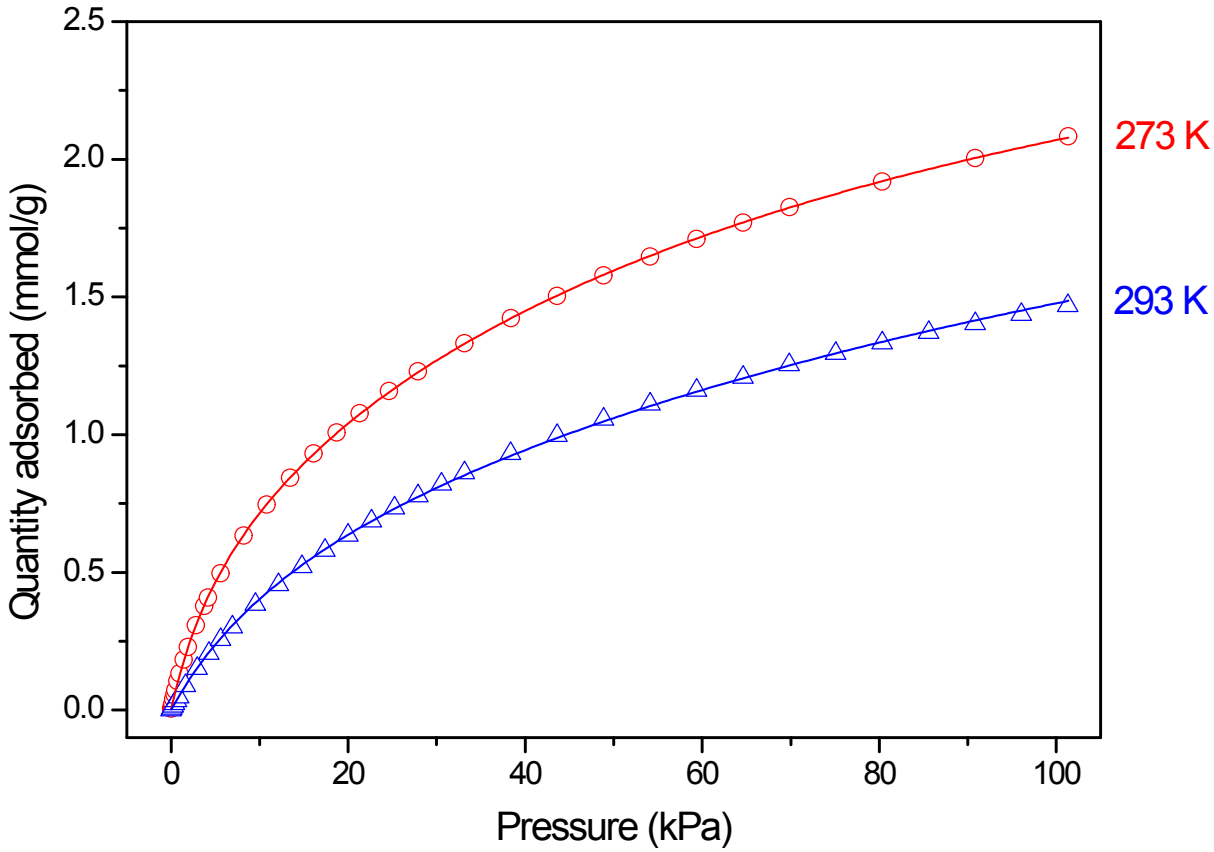

Figure S4. CO_2 adsorption isotherms of the substrate PP1-2 recorded at temperatures of 273 K (circle) and 293 K (triangle) and the corresponding isotherms (solid line) in a dual-site Langmuir model.

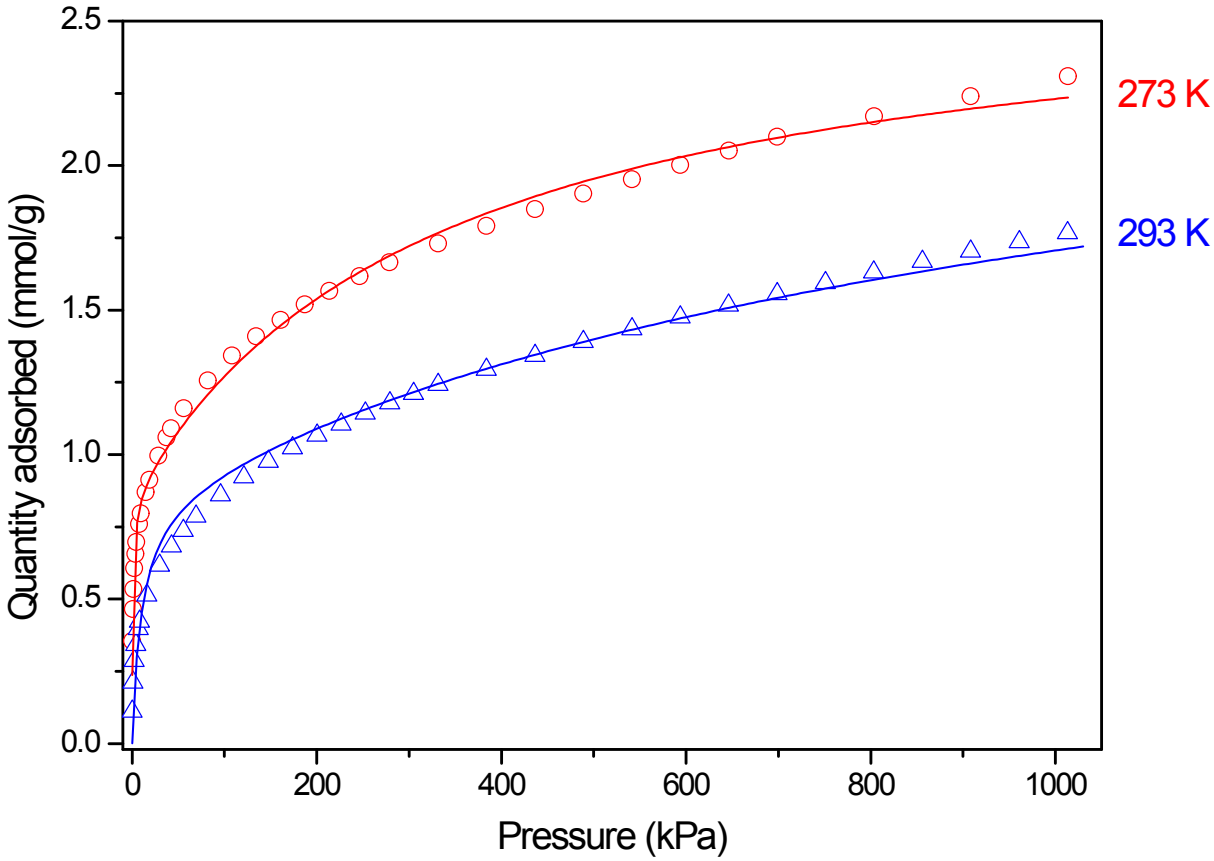

Figure S5. CO_2 adsorption isotherms of PP1-2-tren recorded at 273 K (circle) and 293 K (triangle) and the corresponding isotherms (solid lines) in a dual-site Langmuir model.

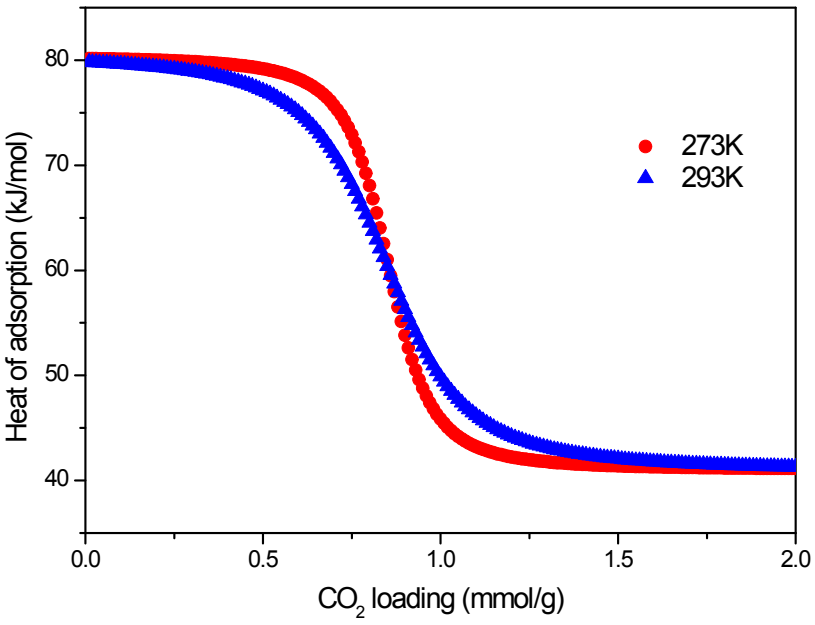

Figure S6. The isosteric heat of adsorption of CO_2 (Q_{st}) for PP1-2-tren at different temperatures determined within a dual-site Langmuir model. The temperature dependence of Q_{st} for CO_2/PP1-2-tren is very weak.

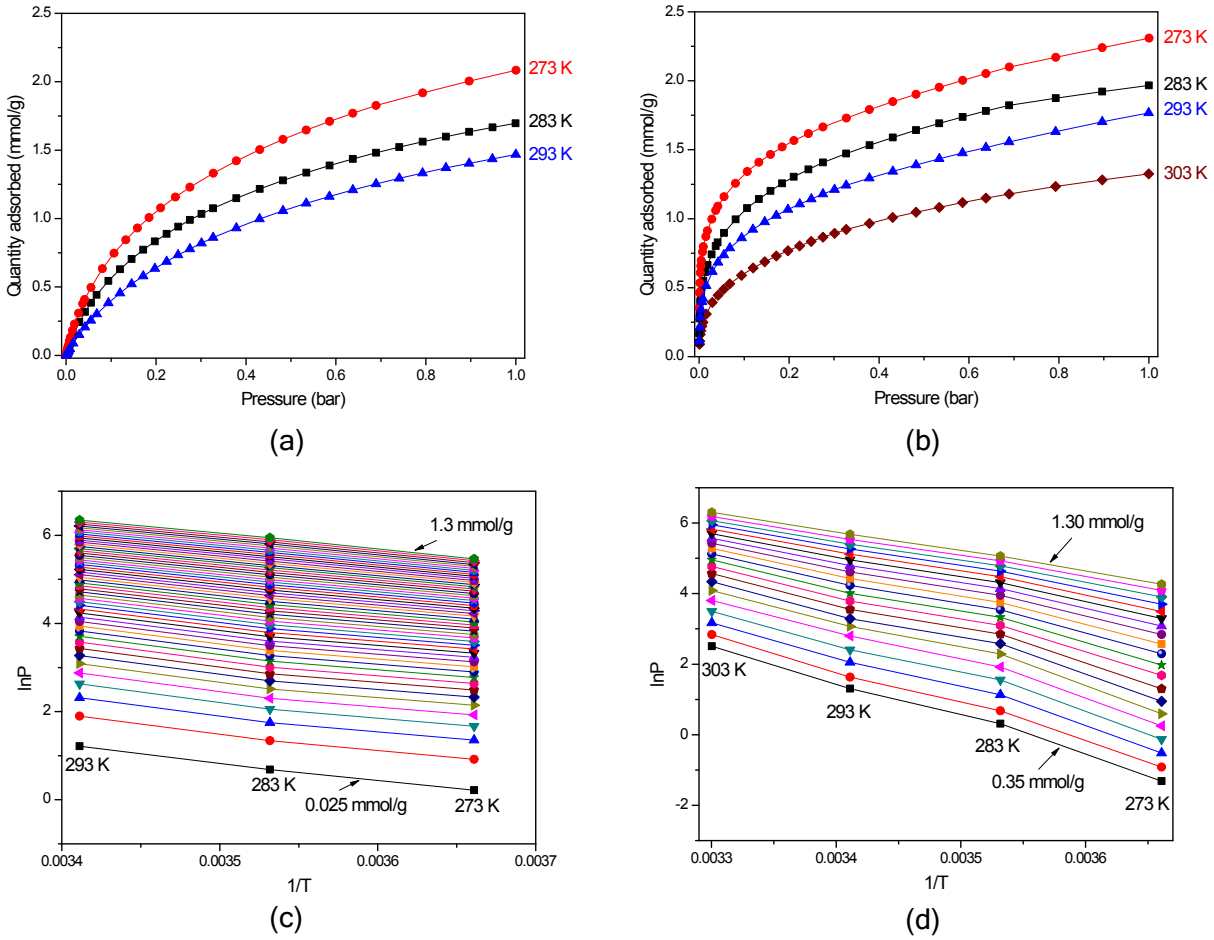

Figure S7. CO_2 adsorption isotherms of (a) PP1-2 (273, 283 and 293 K) (b) PP1-2-tren (273, 283, 293 and 303 K); CO_2 adsorption isosters for (c) PP1-2 and (d) PP1-2-tren. The linearity of the isosters confirmed the accuracy of the Q_{st} calculated from the temperature dependent CO_2 adsorption isotherms.

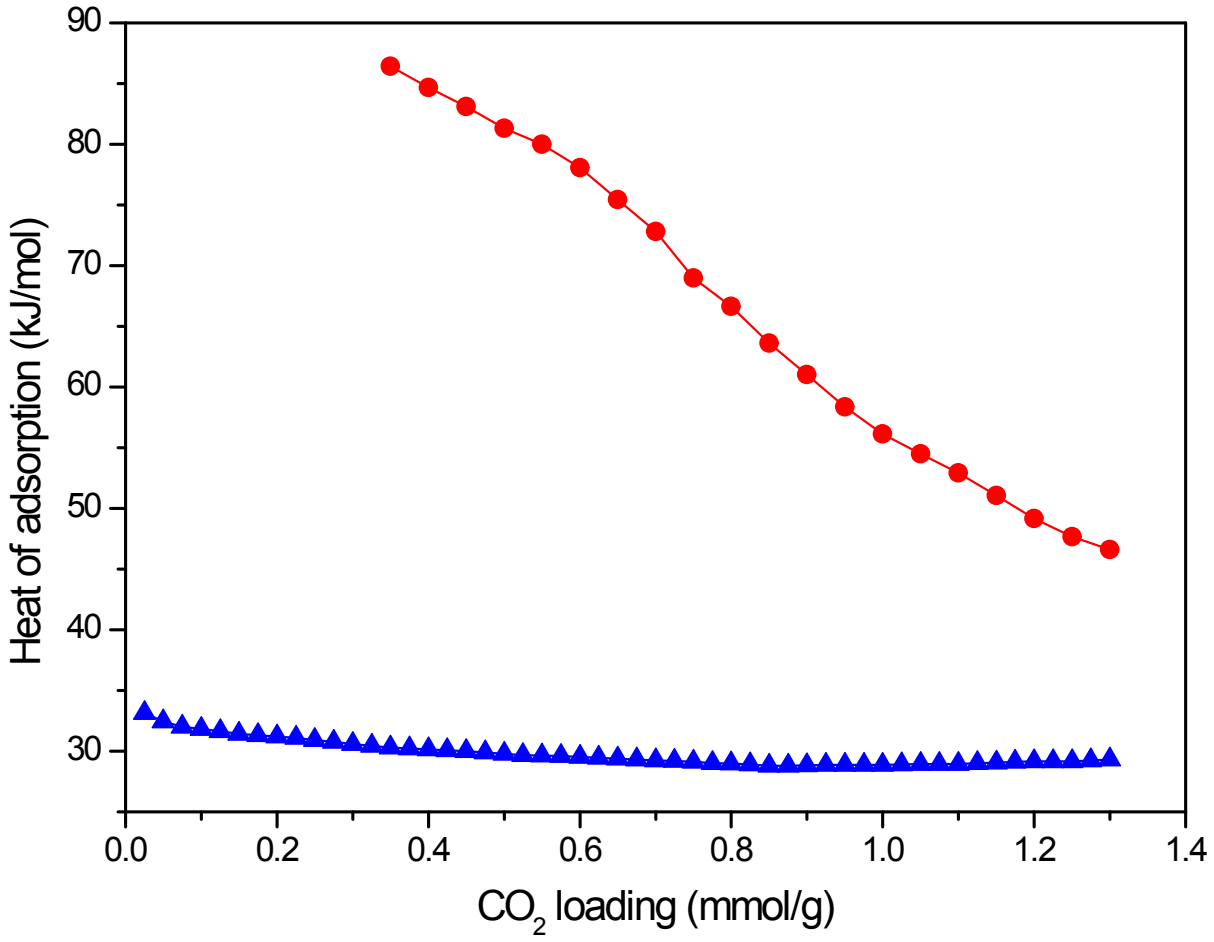

Figure S8. Loading dependent isosteric heat of adsorption of CO_2 for PP1-2 (blue triangles) and PP1-2-tren (red circles). The curves were directly calculated from the experimental CO_2 adsorption isotherms recorded at 273, 283 and 293 K (and also 303 K for PP1-2-tren) using Clausius-Clapeyron equation.

Table S3. Estimated CO_2-over-N_2 selectivities of PP1-2 and PP1-2-tren for two CO_2/N_2 mixtures.

Materials	CO_2/N_2 mixture (15*v*%/85*v*%)			CO_2/N_2 mixture (5*v*%/95*v*%)		
	CO_2 loading at 0.15 bar (mmol/g)	N_2 loading at 0.85 bar (mmol/g)	Selectivity $S=(q_1/q_2)/(p_1/p_2)$	CO_2 loading at 0.05 bar (mmol/g)	N_2 loading at 0.95 bar (mmol/g)	Selectivity $S=(q_1/q_2)/(p_1/p_2)$
PP1-2	0.901	0.1636	31	0.463	0.1815	48
PP1-2-tren	1.446	0.01795	456	1.132	0.02079	1035