Unravelling the origin of enhanced CO_2 selectivity in amine-PIM-1 during mixed gas permeation

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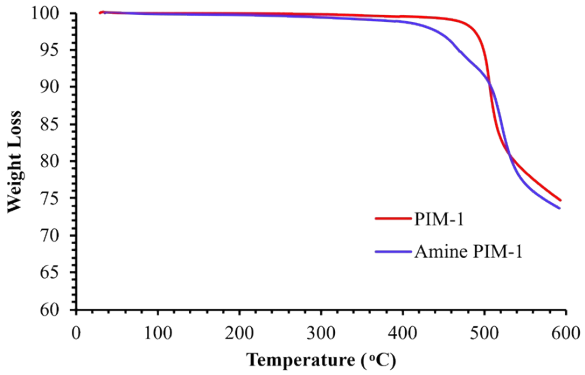
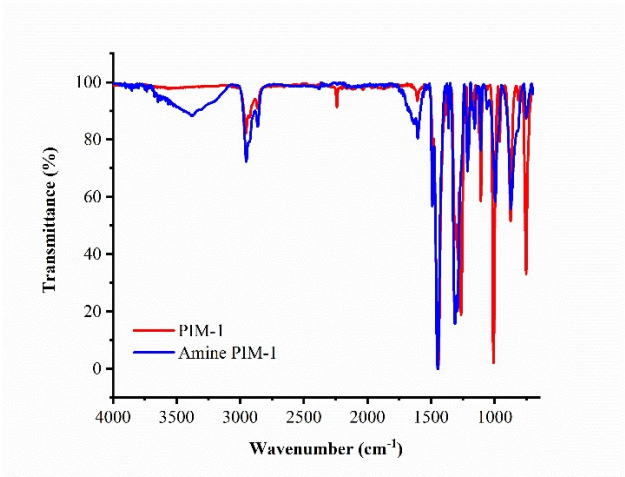
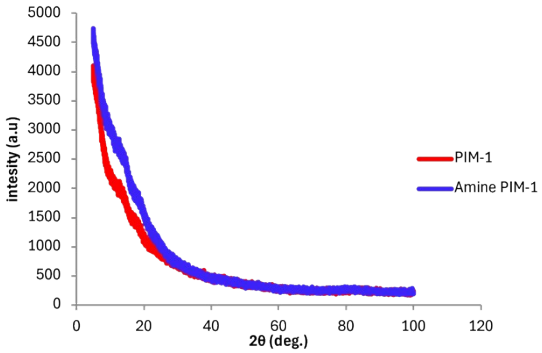


ESI Figure 1 TGAs of PIM-1 (red) and amine-PIM-1 (blue).

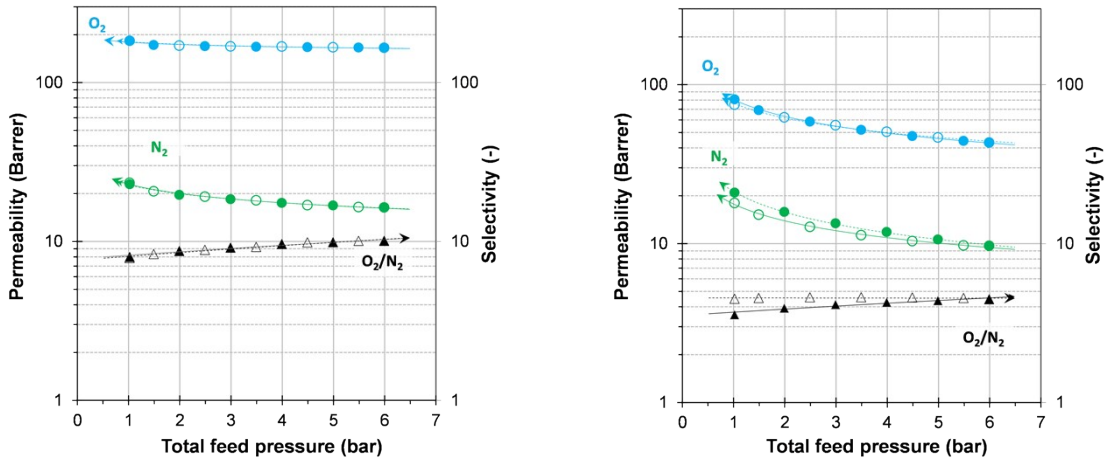


ESI Figure 2 FT-IR spectra of PIM-1 (red) and amine-PIM-1 (blue).



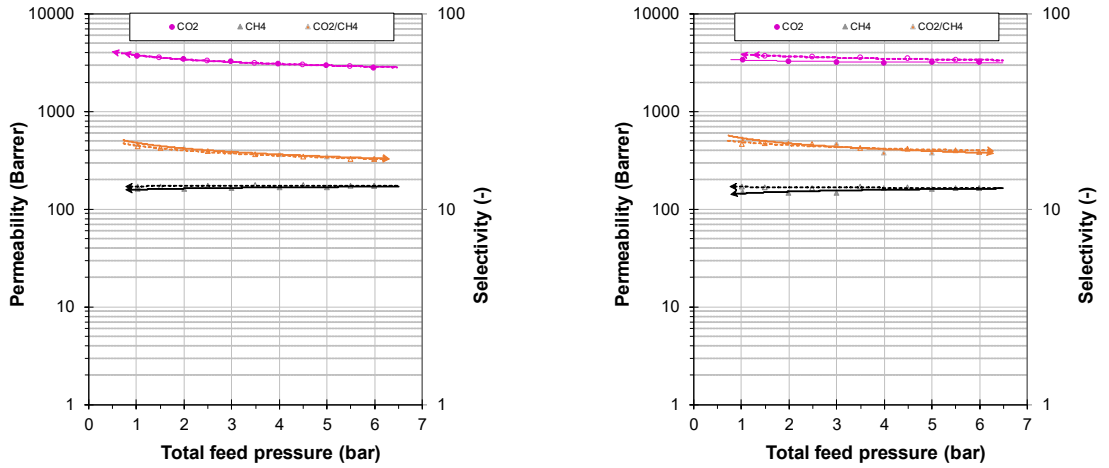
ESI Figure 3 X-ray diffractograms of PIM-1 (red) and amine-PIM-1 (blue).

(a) (b)

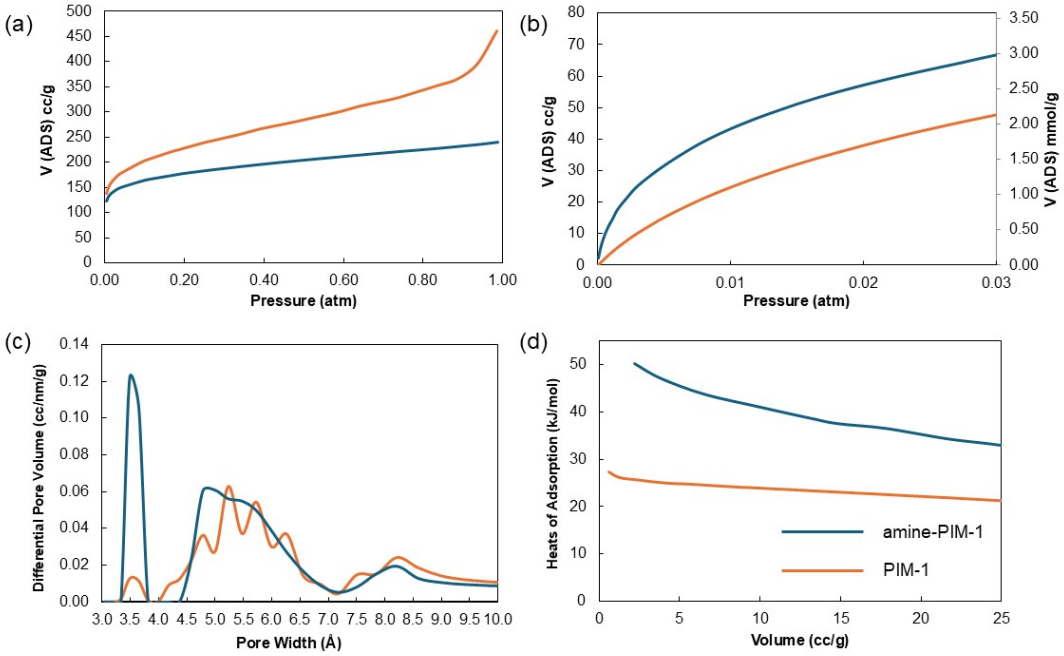


ESI Figure 4 Pressure dependence of permeability and selectivity in amine-PIM-1 for (a) pure O_2 and N_2, and (b) their 81.45/18.55 vol% binary mixture. Filled symbols represent the pressure-increase steps and open symbols represent the subsequent pressure-decrease steps.

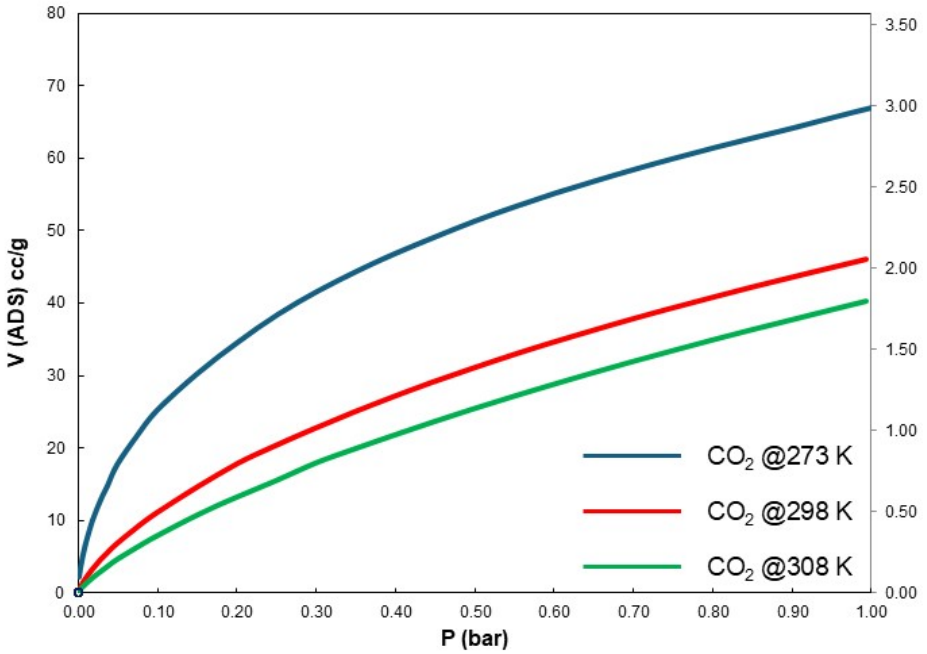
(a) (b)



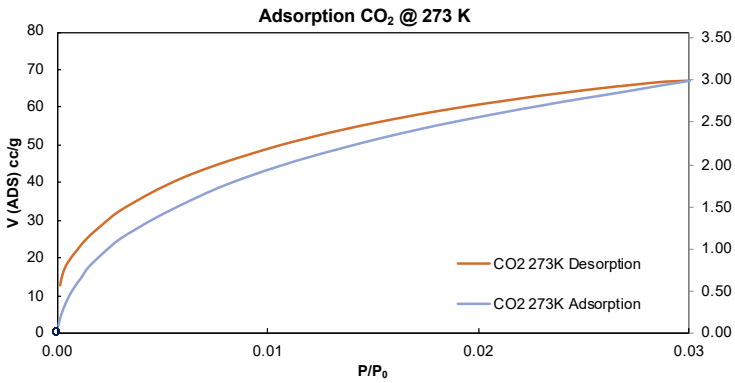
ESI Figure 5 Pressure dependence of permeability and selectivity of PIM-1 for (a) pure CO_2 and CH_4, and (b) for a CO_2/CH_4 mixture (52.11/47.89 vol%). The PIM-1 sample was methanol treated, dried in a vacuum oven for 4h at 373 K and aged for 2144 days.

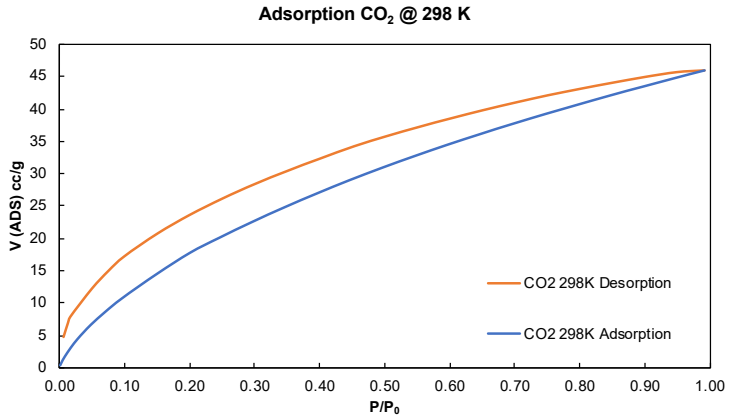


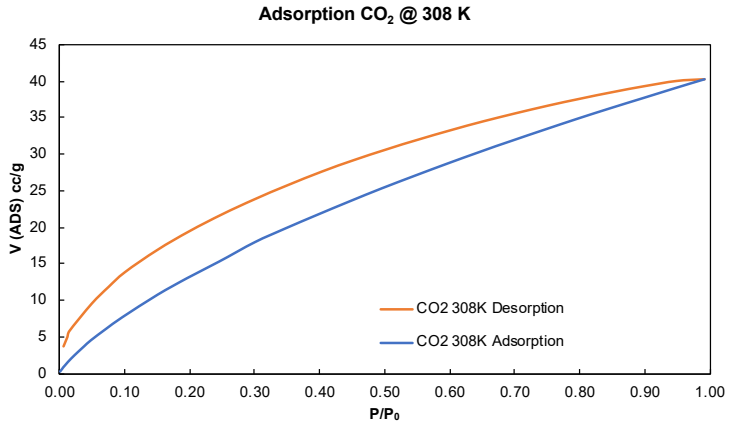
ESI Figure 6 (a) Isothermal N_2 adsorption at 77 K; (b) CO_2 adsorption at 273 K; (c) pore size distribution (CO_2); (d) heat of CO_2 adsorption of PIM-1 (orange lines) and amine-PIM-1 (blue lines).



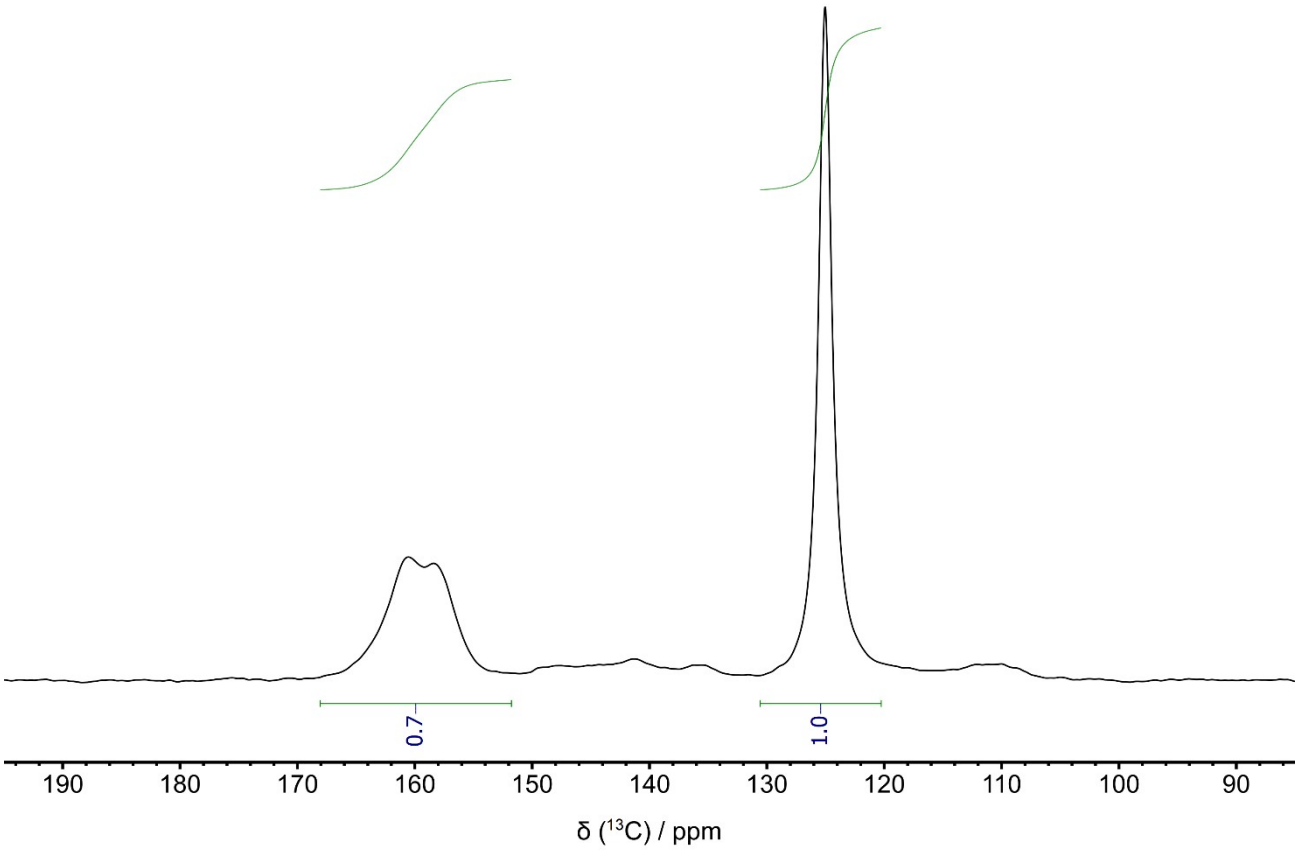
ESI Figure 7CO_2 uptakes of amine-PIM-1 at 273, 298, and 308 K used for the calculation of the isosteric heat of adsorption (Q_{st}).







ESI Figure 8 CO_2 adsorption and desorption isotherms of amine-PIM-1 at 273, 298, and 308 K showing hysteresis in desorption.

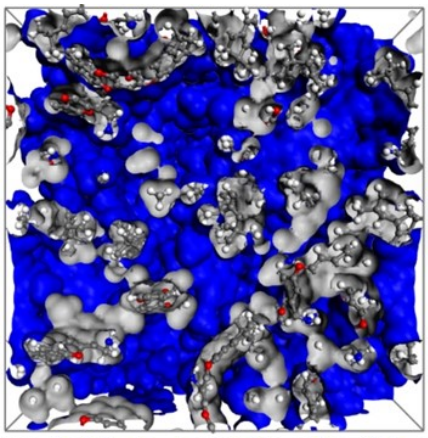


ESI Figure 9 Quantitative ^{13}C DE MAS spectrum of amine-PIM-1 loaded with $^{13}CO_2$ with integrals of chemisorbed and physisorbed CO_2 signals.

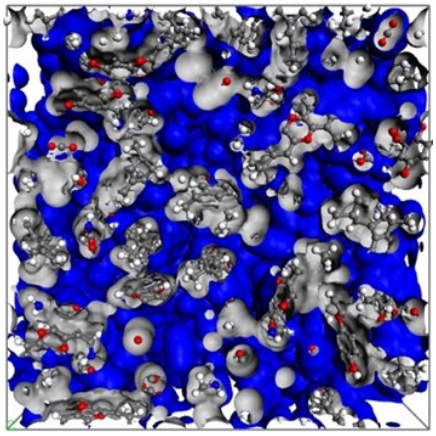
ESI Table 1 Gas surface accessible area (for BET evaluation) calculated for O_2, CO_2, N_2, and CH_4 using Teplyakov-Meares' radii. The accessible area was calculated by using a probe centre that rolls over a scaled van der Waals surface. Teplyakov-Meares' radii are 1.44 Å (O_2), 1.51 Å (CO_2), 1.52 Å (N_2), and 1.59 Å (CH_4).

Gas	**Gas surface accessible area (m^2g^{-1}) in chemisorbed-amine-PIM-1**	**Gas surface accessible area (m^2g^{-1}) in amine-PIM-1**
O_2	695.0±0.1	860.8±0.2
CO_2	609.0±0.1	744.5±0.3
N_2	602.6±0.15	732.6±0.8
CH_4	551.0±0.2	652.2±0.3

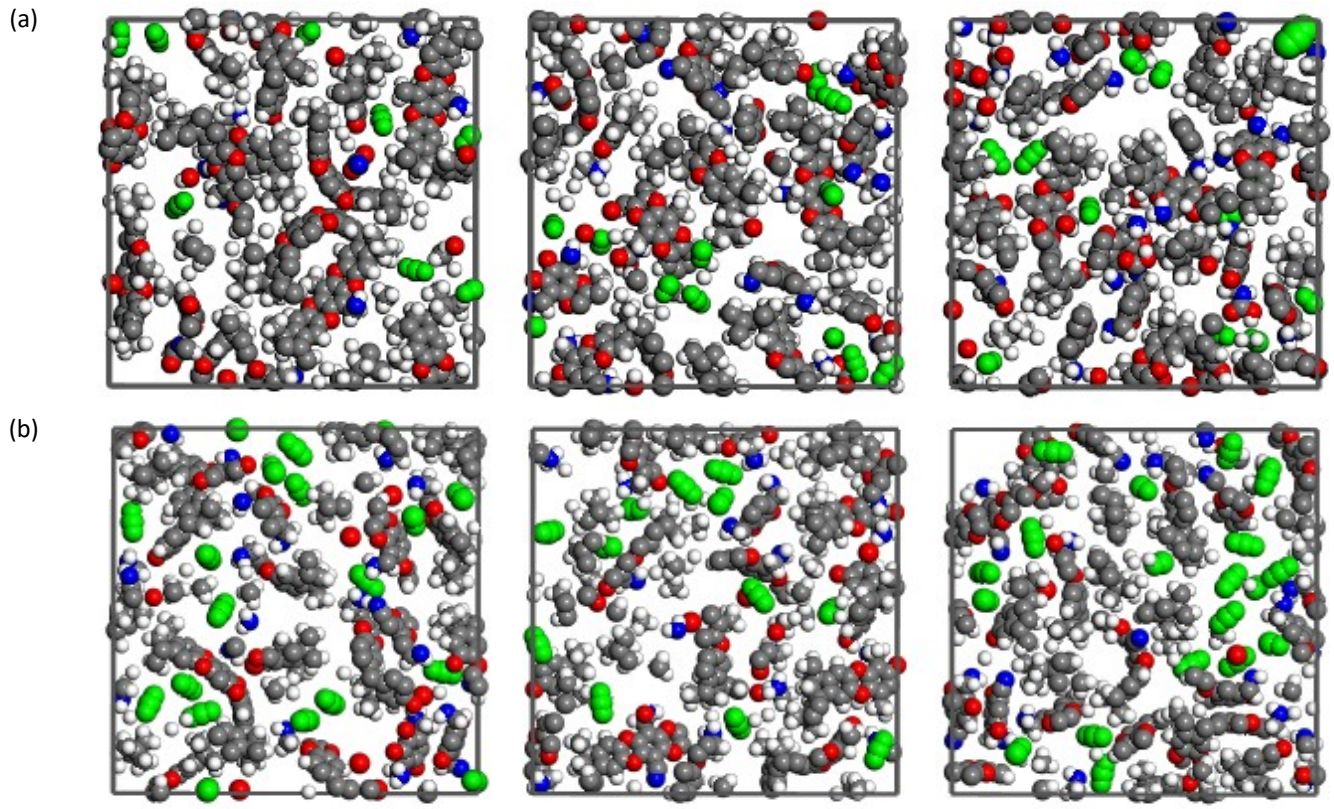
(a)



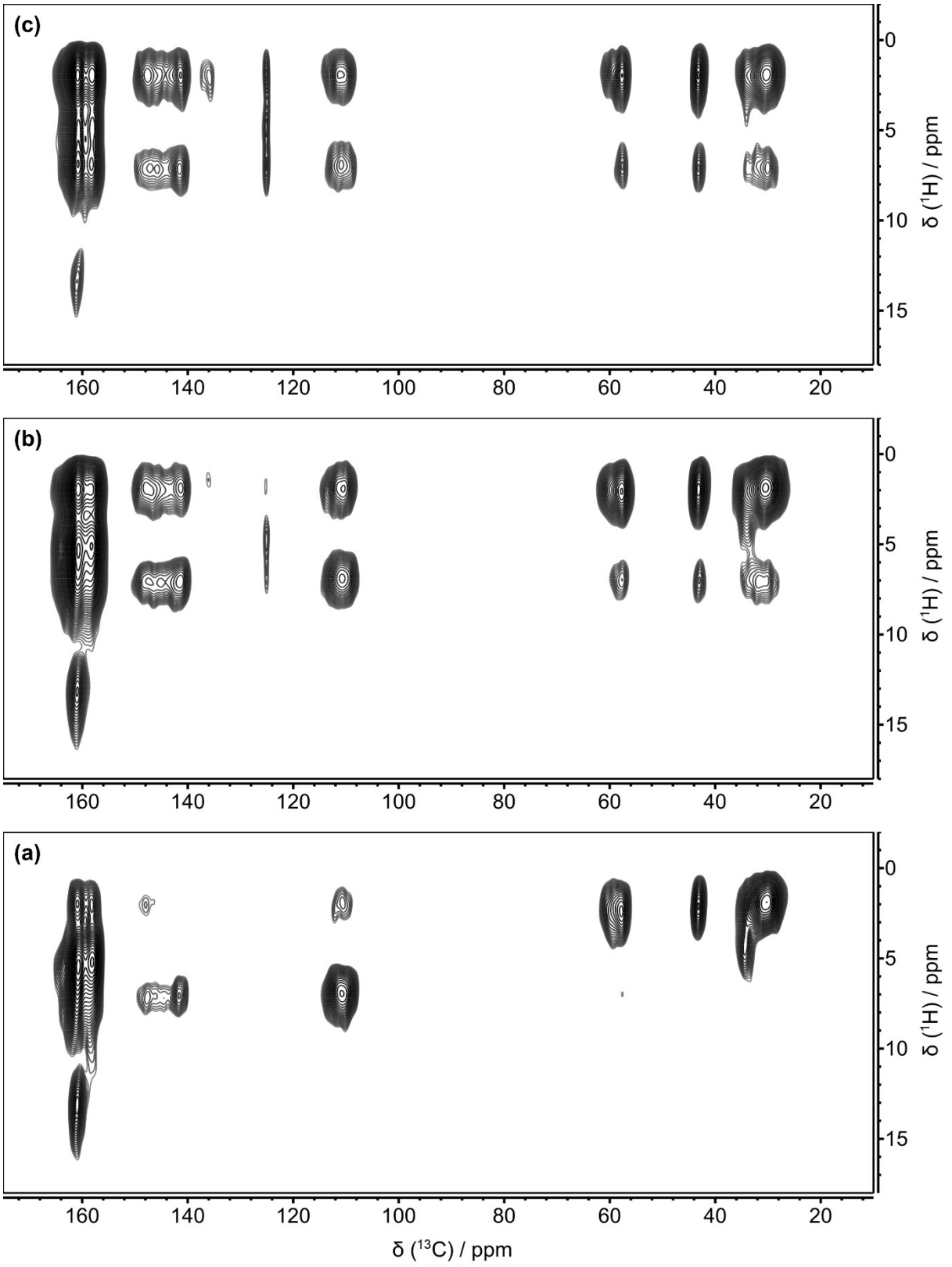
(b)



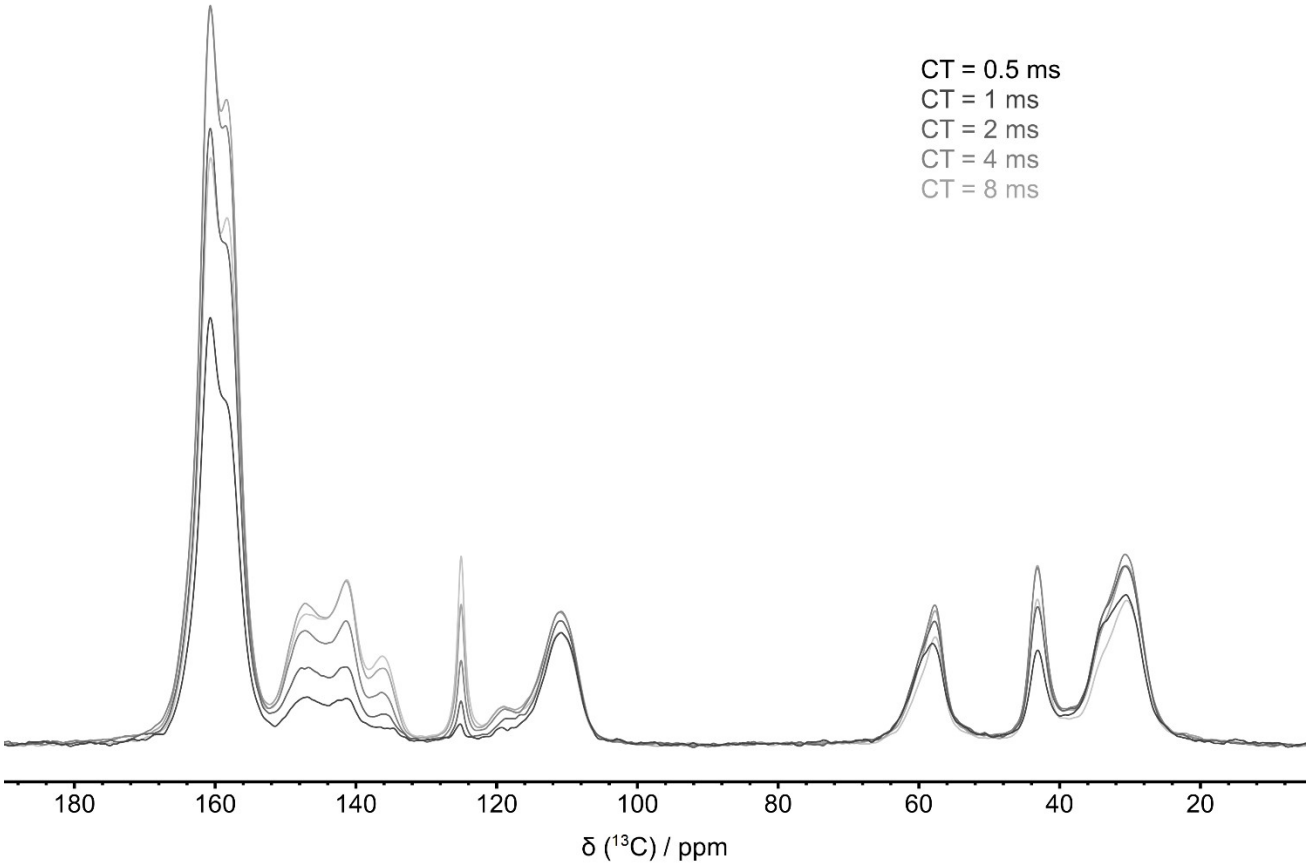
ESI Figure 10 Free volume morphologies in (a) amine-PIM-1 and (b) chemisorbed-amine-PIM-1: the van der Waals isosurface separating the volume "occupied" by chains and the complementary free volume, as perceived by a probe. The isosurface is grey inside (facing polymer) and blue outside. Atoms are reported in CPK style with their van der Waals radii. Colour code: the C atom is grey, the O atom is red, the H atom is white, the N atom is blue.



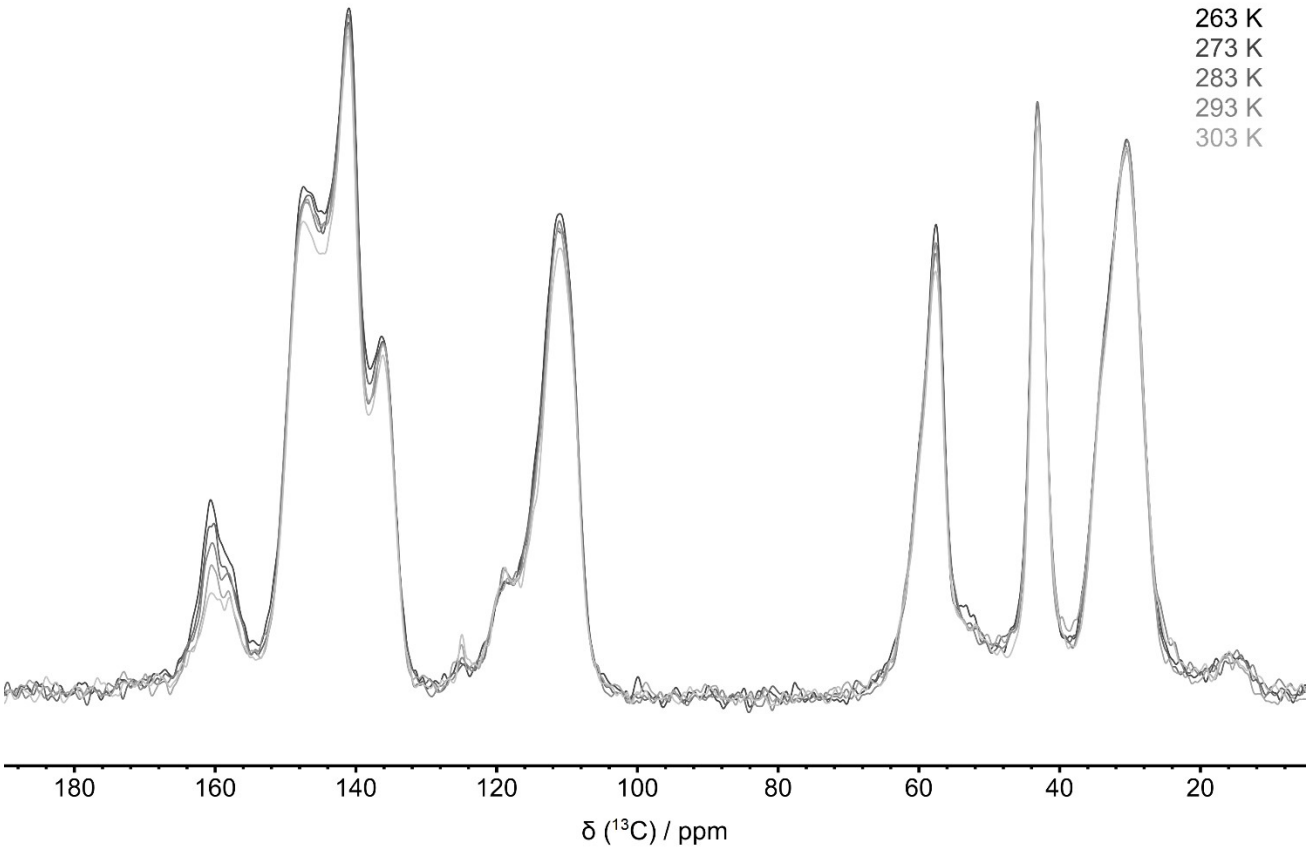
ESI Figure 11A series of three successive slices from: (a) the chemisorbed-amine-PIM-1 and (b) the amine-PIM-1 models, cleaved in the z-direction every 3 Å, corresponding to 1/9th of the total side length. Atoms are reported in CPK style with their van der Waals radii. Colour code: The C atom is grey, the O atom is red, the H atom is white, the N atom is blue, and the CO_2 molecule is green.



ESI Figure 12 ^{1}H-^{13}C HETCOR MAS spectra of amine-PIM-1 loaded with $^{13}CO_2$ recorded with contact time values of 0.5 (a), 1.5 (b), and 3 ms (c).



ESI Figure $13^{1}H$-^{13}C CP MAS spectra of amine-PIM-1 loaded with $^{13}CO_2$ recorded at different contact time (CT) values.



ESI Figure 14 ^{1}H-^{13}C CP MAS spectra of amine-PIM-1 loaded with $^{13}CO_2$ recorded at different temperatures with a contact time of 6 ms.