Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Shape Selective Properties of the Al-Fumarate Metal-Organic Framework in the Adsorption and Separation of *n*-Alkanes, iso-Alkanes, cyclo-Alkanes and Aromatic Hydrocarbons

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Supporting Information

1. Powder X-ray diffraction

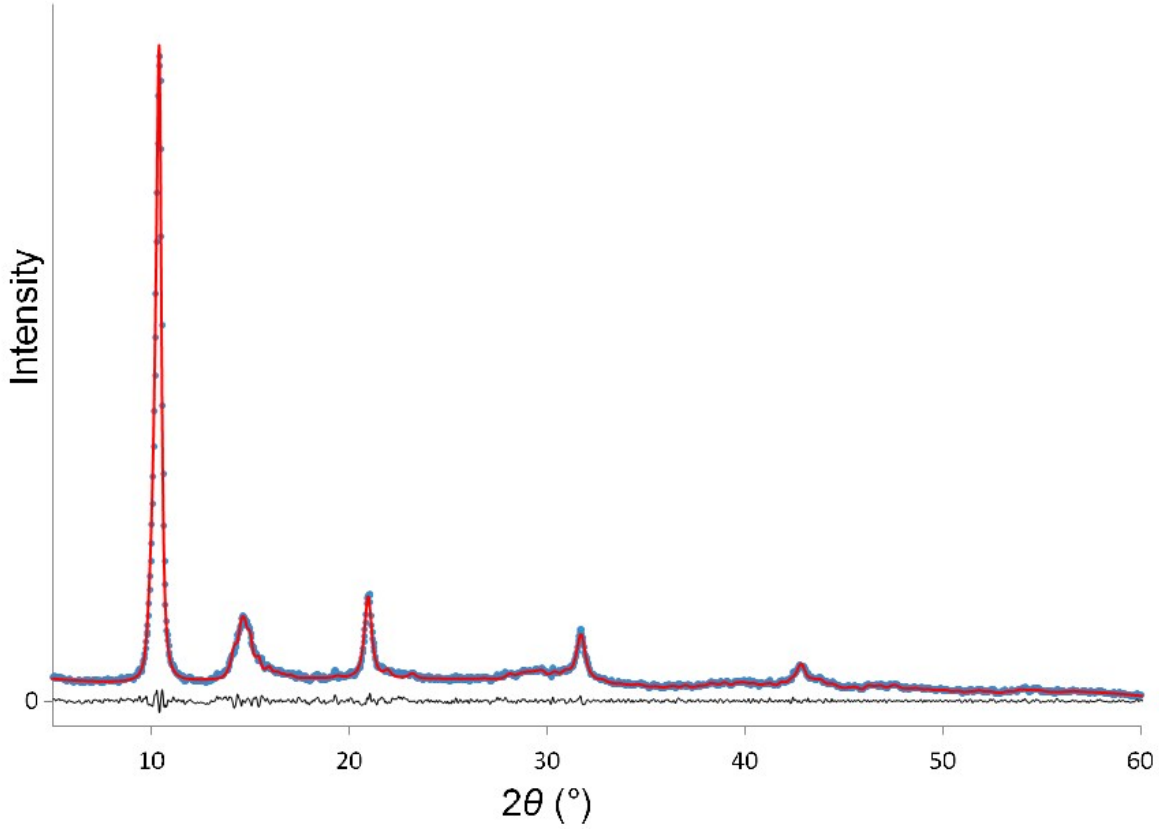

Fig.S0: Experimental (blue) and calculated (red) PXRD profiles and difference (black) plot of the Pawley refinement of Al-Fumarate.

The synthesized Al-fumarate was solvent exchanged with ethanol after synthesis and dried at room temperature. PXRD data were acquired of the hydrated sample since acquisition is performed at room temperature. Powder XRD patterns were recorded on a STOE STADI-P Combi instrument in the Debye–Scherrer geometry (Cu-$K_{\alpha 1,}$ λ = 1.5418 Å) using an IP position-sensitive detector (2θ = 0-60°; Δ2θ = 0.03°). Lattice parameters (a = 6.923 Å, b = 12.121 Å, c = 14.258 Å, β = 124.36 °; Rwp = 5.748) were obtained through Pawley refinement in the monoclinic space group $P2_1/c$ [39] using TOPAS-Academics (Topas Academics 4.2, Coelho Software, 2007).

2. Argon porosimetry

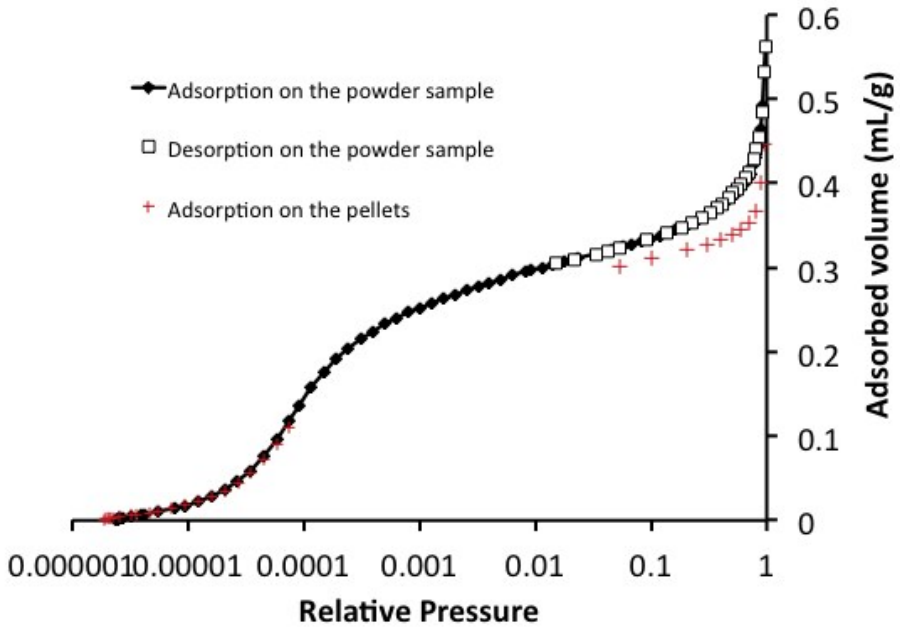

Fig. S1: Argon isotherm of the Al-Fumarate powder sample and the pellets retrieved from the column, activated at 250 °C. Amount adsorbed is expressed in adsorbed volume at 87.45 K

Fig.S1 shows the Argon isotherm on the fresh powder and the pellets retrieved from the column after use. Until a relative pressure of 0.01, the isotherms of the used sample (was kept for more than 6 months in the column) and the fresh sample (with Al-Fumarate structure as confirmed by XRD) completely coincide, demonstrating that the Al-Fumarate structure is fully retained. At higher pressure, a modest decrease of 7 % (at the relative pressure of 0.2) in pore volume was observed, but this is rather due to a change in experimental parameters during the Ar isotherm measurement and the shaping procedure of powder into pellets (binderless).

3. Pulse gas chromatography

The linearity of the graph of the first moment of each chromatogram obtained at different flow rates shows that the experiments were performed in absence of mass transport limitations.

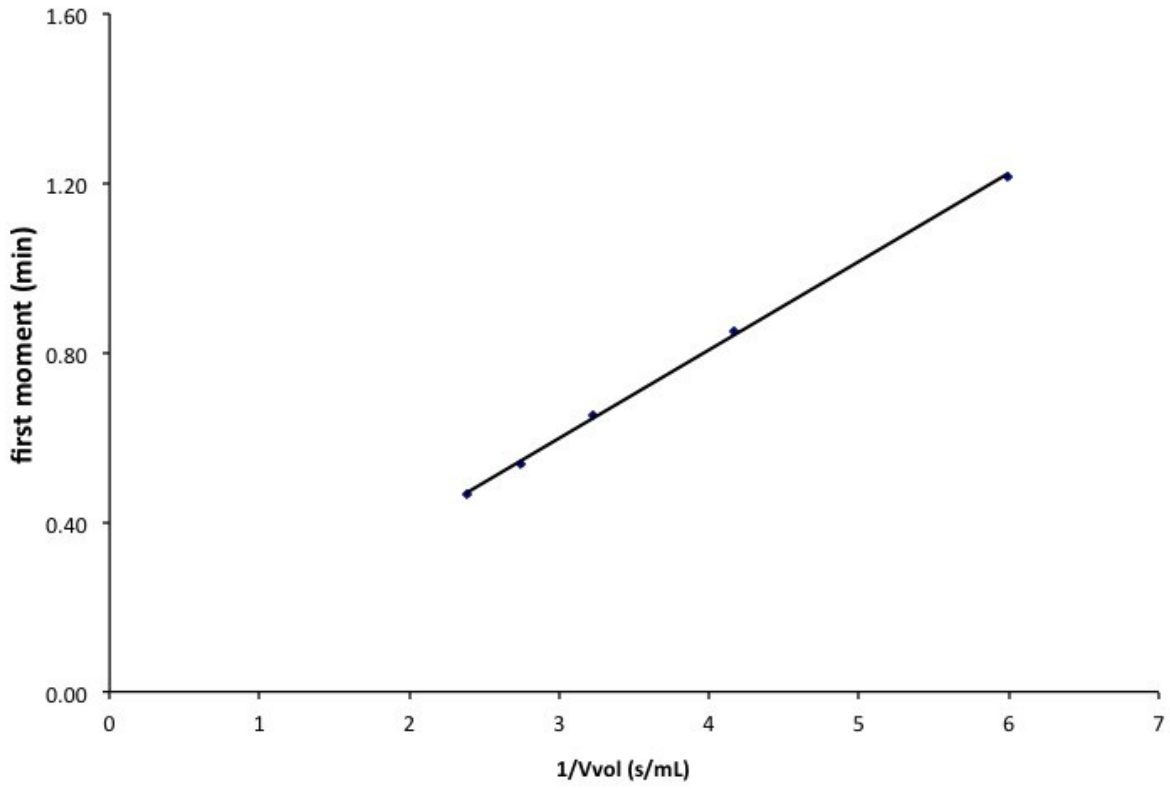

Fig. S2: Flow rate dependency of the first moment of *n*-C5 on Al-Fumarate at 250 °C

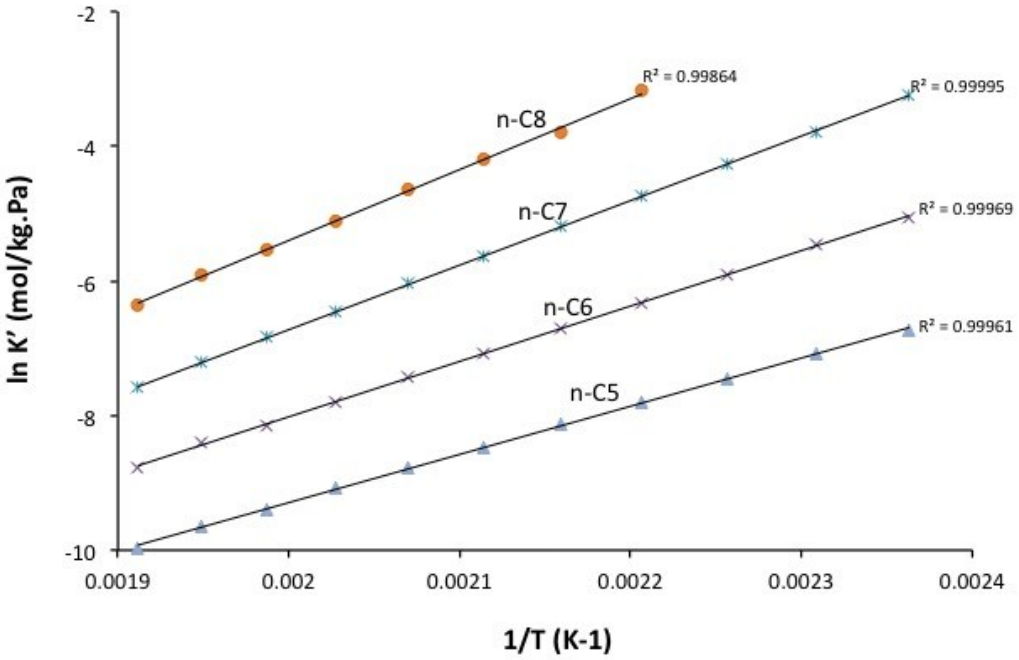

Fig. S3: van 't Hoff plots of *n*-alkanes on Al-Fumarate MOF

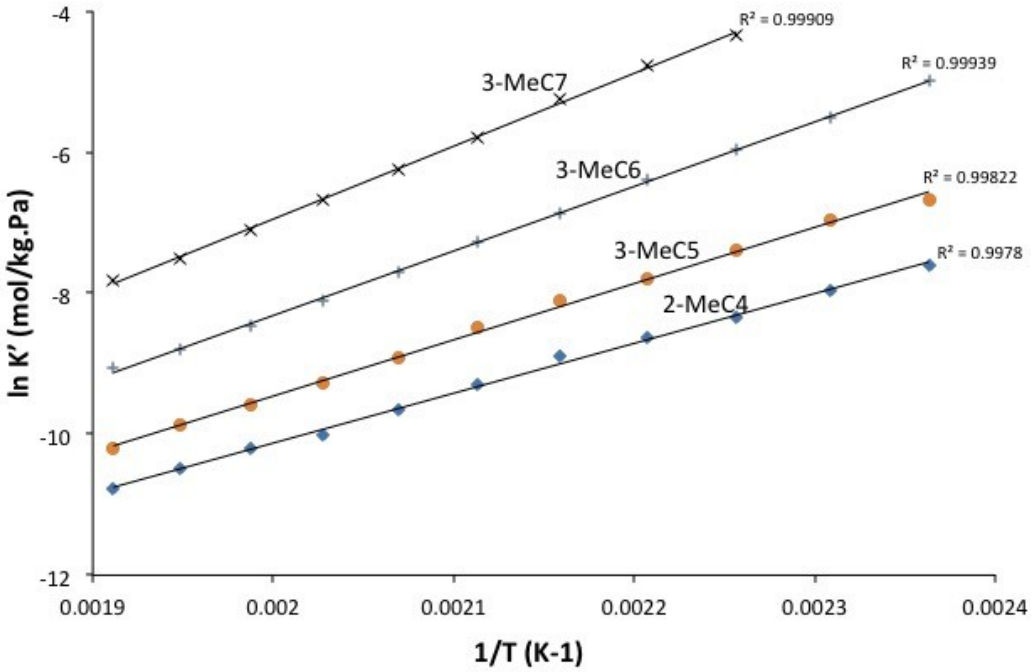

Fig. S4: van 't Hoff plots of mono-branched alkanes on Al-Fumarate

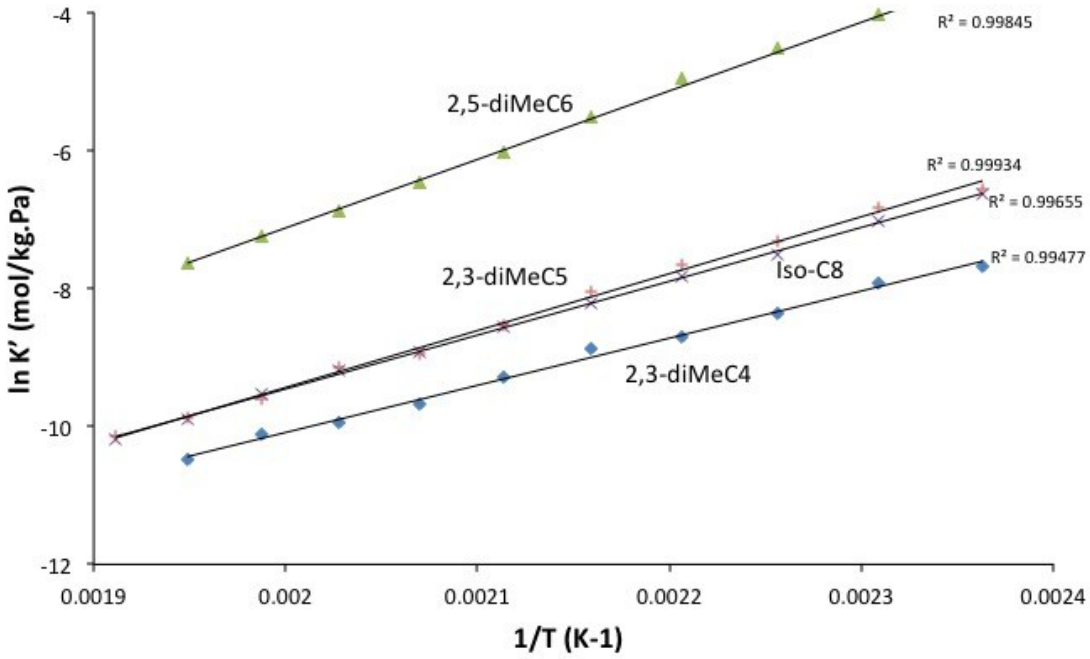

Fig. S5: van 't Hoff plots of di-branched and tri-branched alkanes on Al-Fumarate

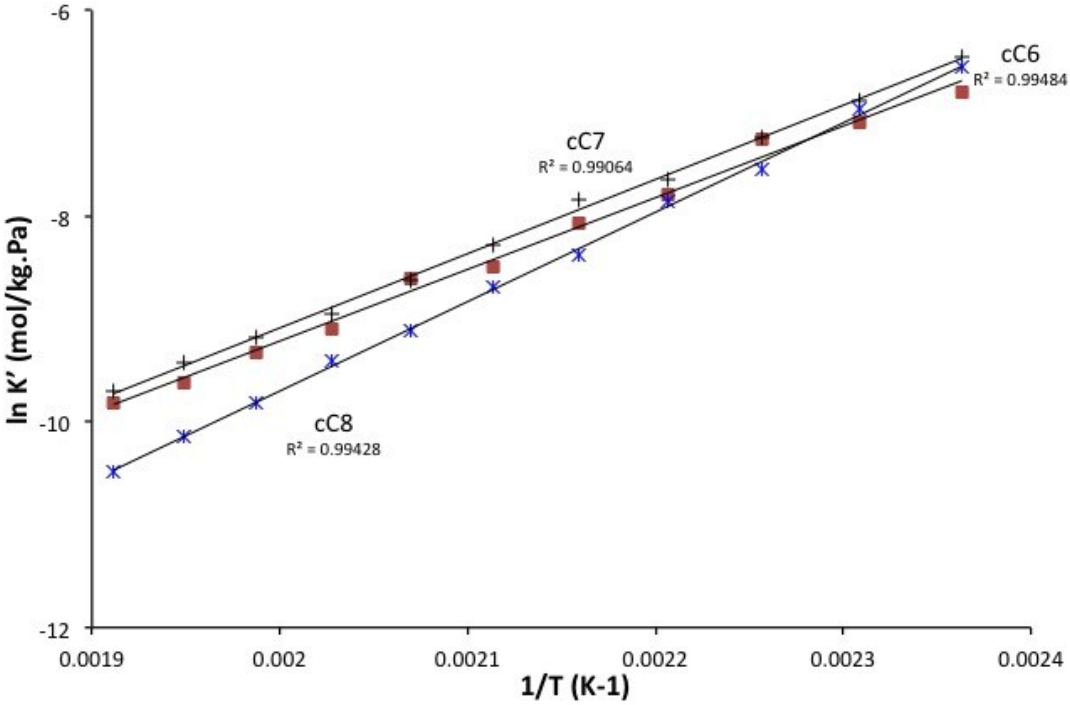

Fig. S6: van 't Hoff plots of cyclic alkanes on Al-Fumarate

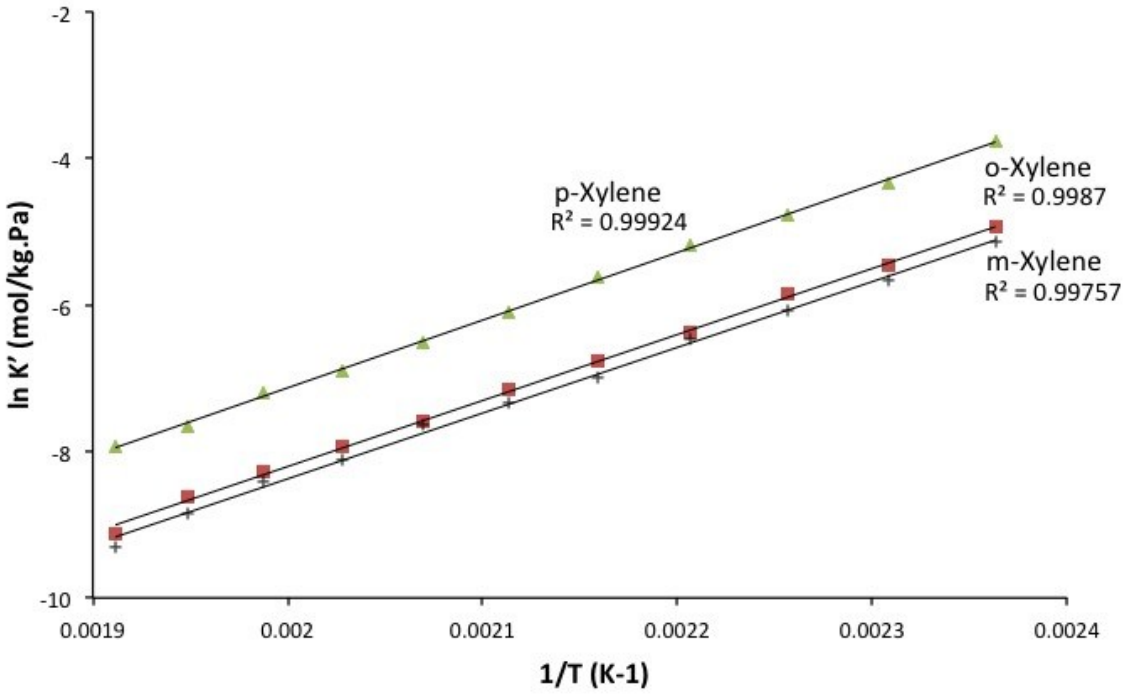

Fig. S7: van 't Hoff plots of aromatics on Al-Fumarate

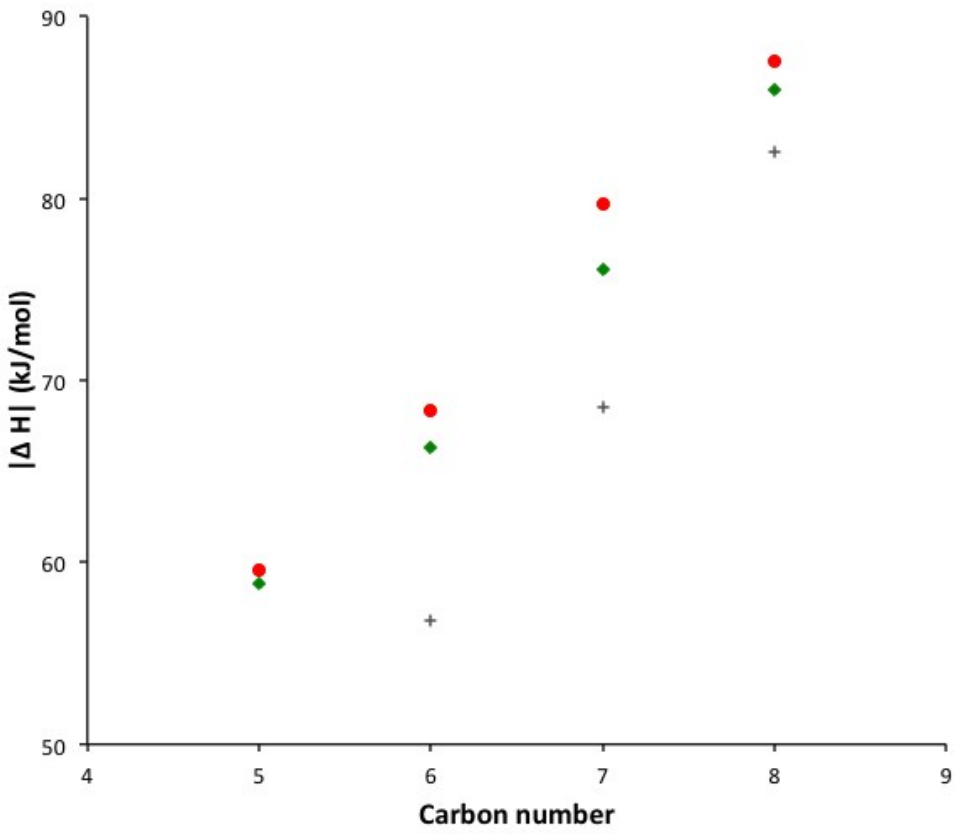

Fig.S8: Absolute value of the adsorption enthalpy of •Linear, ◆ Mono-branched and + Di-branched alkanes on Al-Fumarate

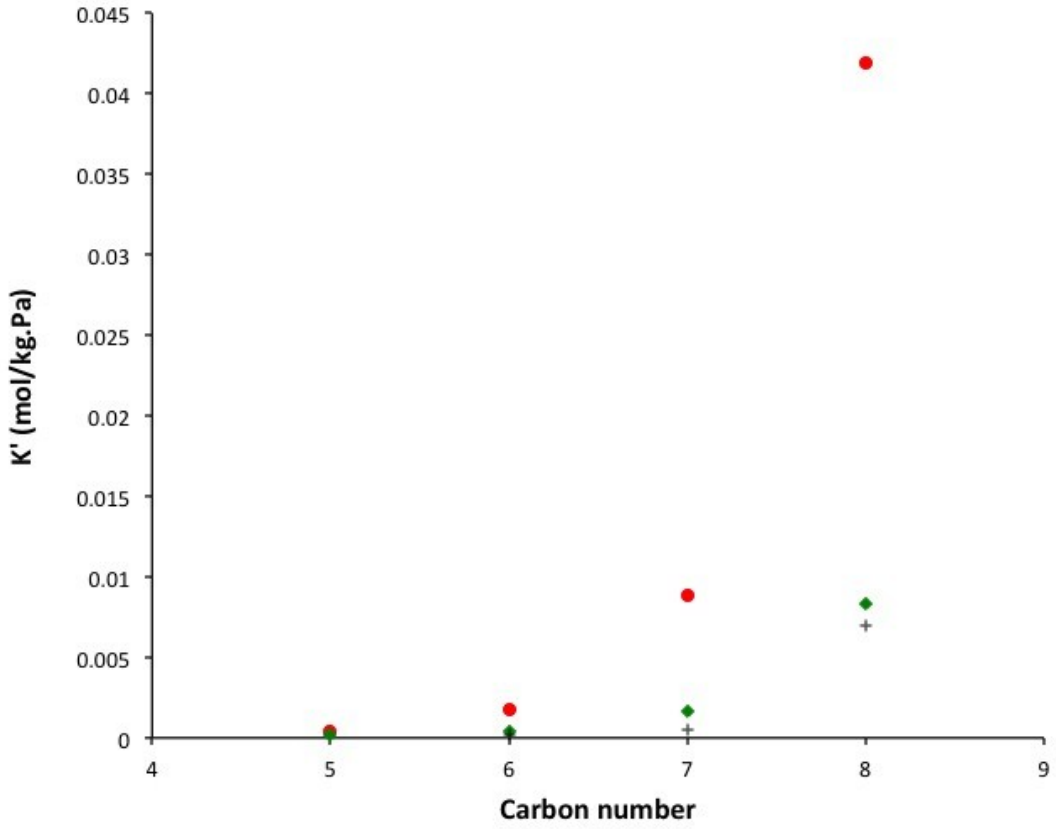

Fig. S9: Absolute value of the Henry constant of • Linear, ◆ Mono-branched and + Di-branched alkanes on Al-Fumarate

To check the stability and the reusability of Al-Fumarate, after a period of more than 6 months, some of the pulse chromatographic experiments were repeated on the same column used for all the experiments. 0.04 μL of n-hexane, 3-methylpentane and 2,3-dimethylbutane were injected (3 times) at 180°C in the column packed with pellets of Al-Fumarate used in the previous experiment. The first moments calculated from the chromatogram of each component at 180°C are nearly identical to the values in the initial experiments, as shown in the Table S1. Separation factors 4.43 and 11.13 for the separation factor of n-hexane versus 3-methylpentane and n-hexane versus 2,3-dimethylbutane respectively at 180°C were obtained. This matches very well the original separation factors (4.38 and 10.93). These data demonstrate the reusability of this material in these experiments.

Table S1: The first moment (μ_1) of each injected component, with a volume of 0.04 μL at 180°C using the column packed with pellets of Al-Fumarate.

Compound	μ_1 (min.) at 180°C Initial measurement	μ_1(min.) at 180°C Measurement after 15 months
n-hexane	21.25	21.66
3-methylpentane	4.93	4.97
2,3-diMethylbutane	2.03	2.03