Electronic Supplementary Material (ESI) for Chemical Science.

Cutting-Edge Molecular Modelling to Unveil New Microscopic Insights into the Guest-Controlled Flexibility of Metal-Organic Frameworks

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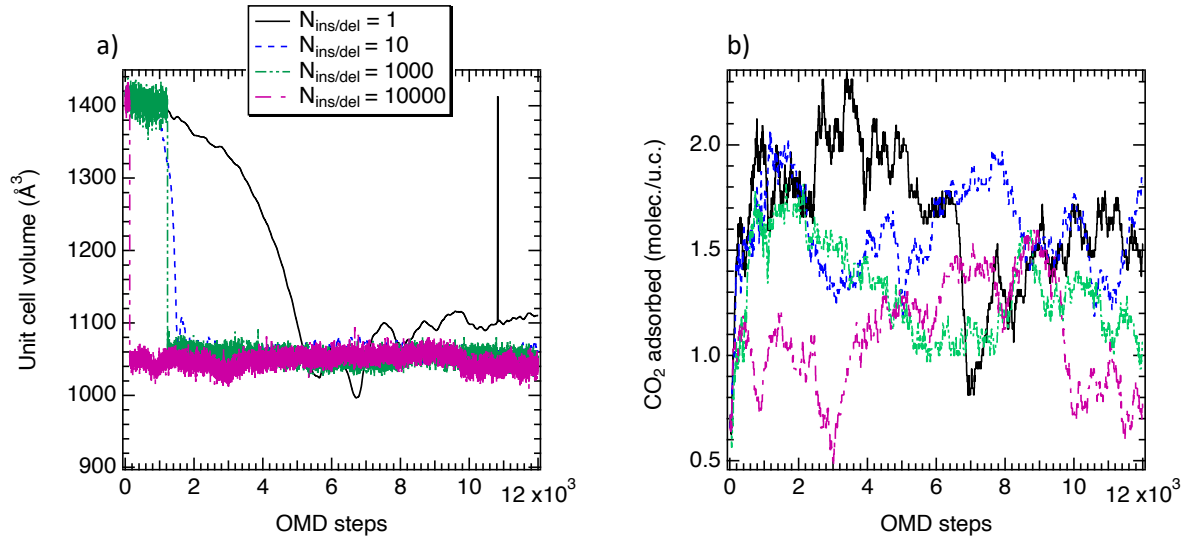

Figure S1: a) Unit cell volume a) and b) CO_2 adsorbed as a function of the time for four $N_{ins/del}$) corresponding to the time interval ($t_{ins/del}$). Gas pressure is 0.5 bar and temperature corresponds to 298 K.

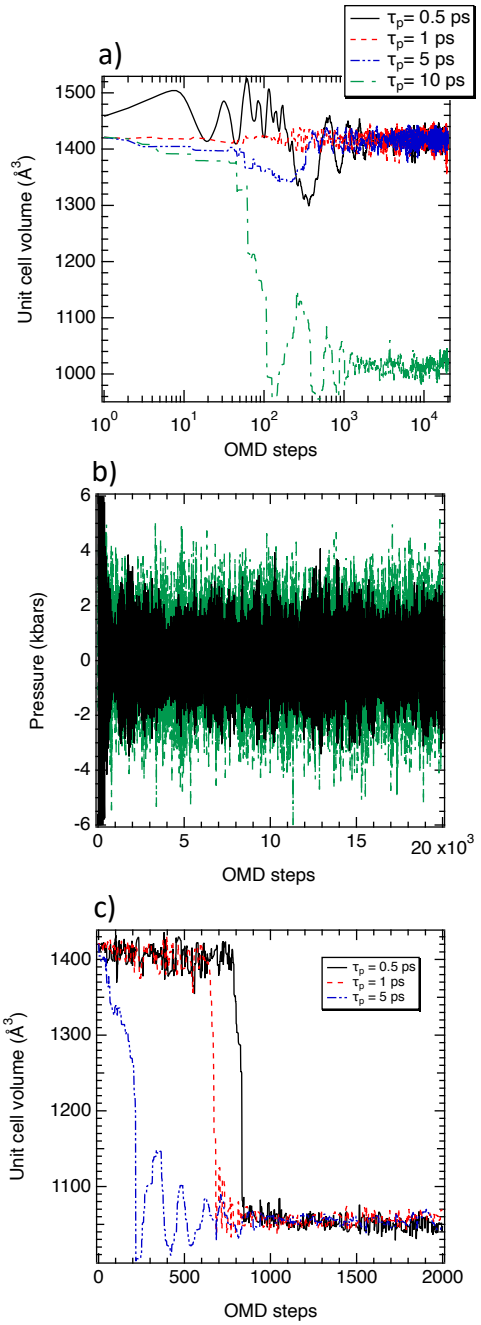

Figure S2: a) Unit cell volume of MIL-53(Cr)@CO_2 and b) total pressure for a CO_2 fugacity of 0.1 bar at 298 K. c) unit cell volume of MIL-53(Cr)@CO_2 for a CO_2 fugacity of 0.5 bar at 298 K. Three parts are provided for several relaxation times (τ_p) controlling the pressure fluctuations through the barostat.

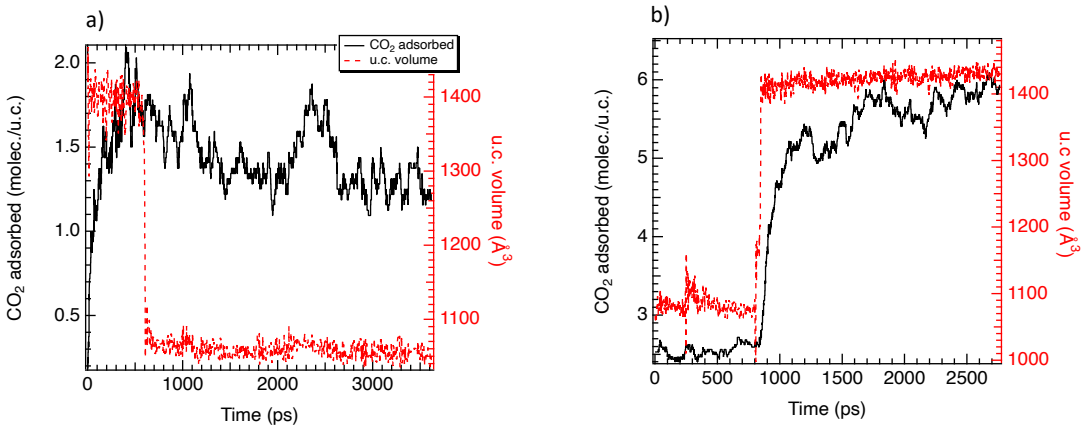

Figure S3: Unit cell volume of MIL-53(Cr)@CO_2 (right axis) and CO_2 adsorbed (left axis) for a CO_2 fugacity of a) 0.5 bar and b) 5.0 bar at 298 K.

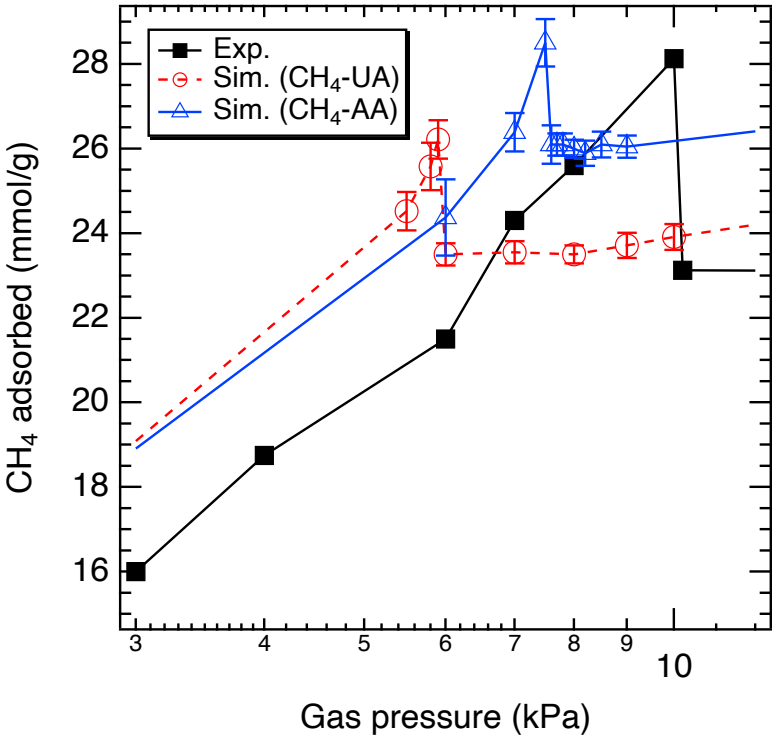

Figure S4: Simulated and experimental CH_4 adsorption isotherm at 111 K on DUT-49 as semi-logarithmic scale. CH_4 molecules were described from the all atoms (AA) and united atom (UA) force fields.

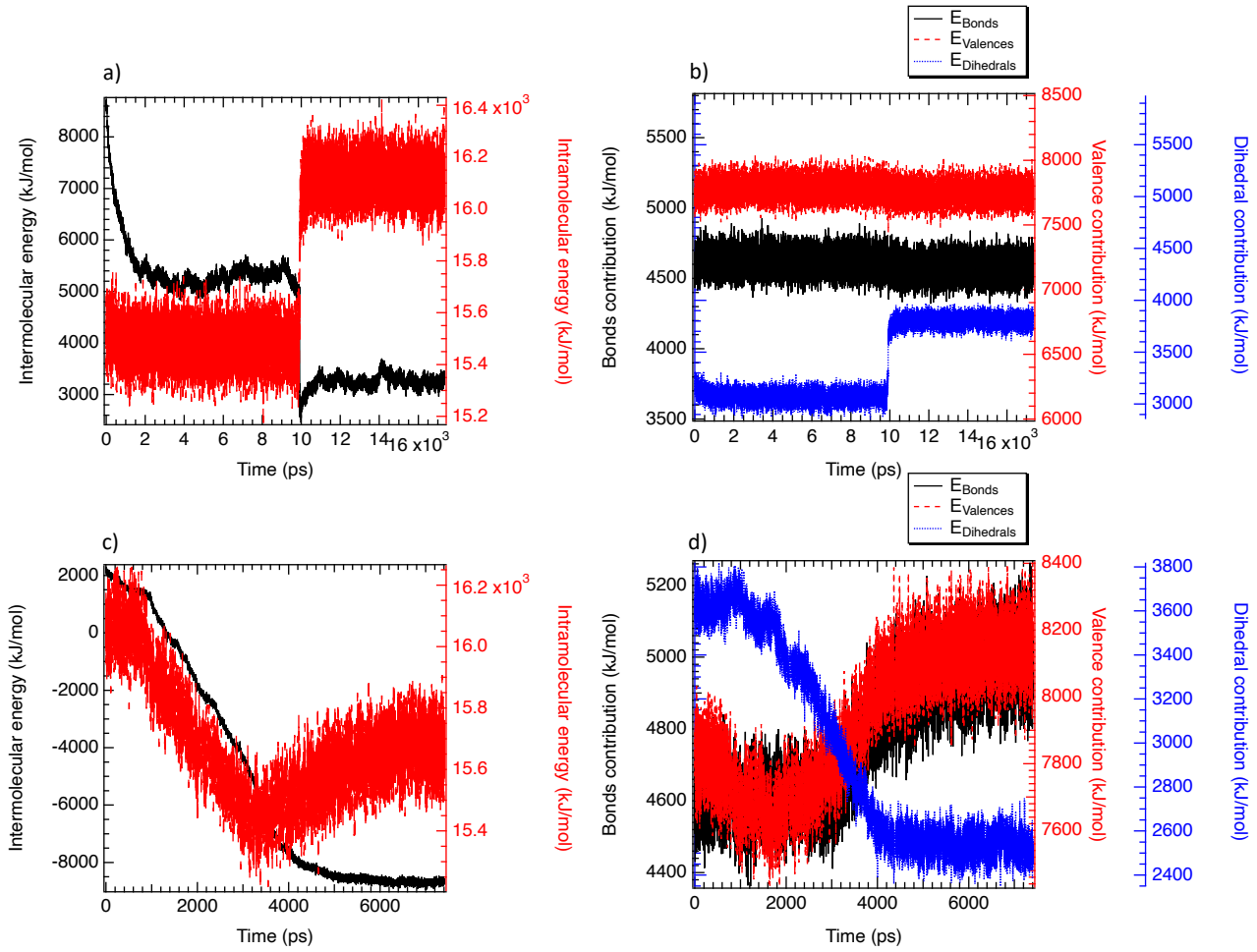

Figure S5: Intermolecular and intramolecular contribution during the *op* → *cp* transition (a) and b)) for a CH_4 fugacity of 6 kPa. and from the reopening (c) and d)) for a CH_4 fugacity of 500 kPa.

Table S1: Unit cell parameters; volume and lengths (a,b,c). The avearge error bar on a, b and c is around 0.4 Å.

DUT-49 form	u.c. volume ($Å^3$)	a=b=c (Å)
1	101298.8	46.6
2	92718.4	45.2
3	89359.1	44.7
4	75980.0	42.4
5	60253.1	39.2
6	45491.1	35.7
7	44954.6	35.6
8	45668.0	35.7
9	104429.5	47.1