Supporting Information for:

Flexibility and Swing Effect on the Adsorption of Energy-Related Gases in ZIF-8: Combined Experimental and Simulation Study

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Section S1. Pore size distribution and partial charges of ZIF-8

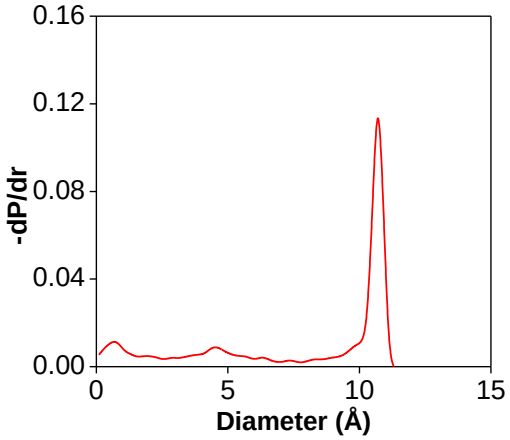

Figure S1. Pore size distribution (PSD) for the ZIF-8 structure.

Table S1: Point charges on Imidazole ligand in ZIF-8 and in isolated molecule, extracted from DFT (PBE) calculation (Mülliken charges).

	Imidazole (fig. A)	Cluster (fig. B)	Periodic (fig.C)
N	-0.358	-0.459	-0.403
N	-0.323	-0.422	-0.403
C_{double}	0.020	0.061	0.004
C_{double}	-0.003	0.019	0.004
C_{NN}	0.277	0.374	0.317
C_{methyl}	-0.304	-0.302	-0.358
H_{double}	0.070	0.050	0.107
H_{double}	0.076	0.078	0.107
H_{methyl}	0.105	0.102	0.147
H_{methyl}	0.109	0.100	0.147
H_{methyl}	0.131	0.148	0.147
$H_{(N)}$	0.200	-	-
Zn	-	0.361	0.367
Zn	-	0.378	0.367

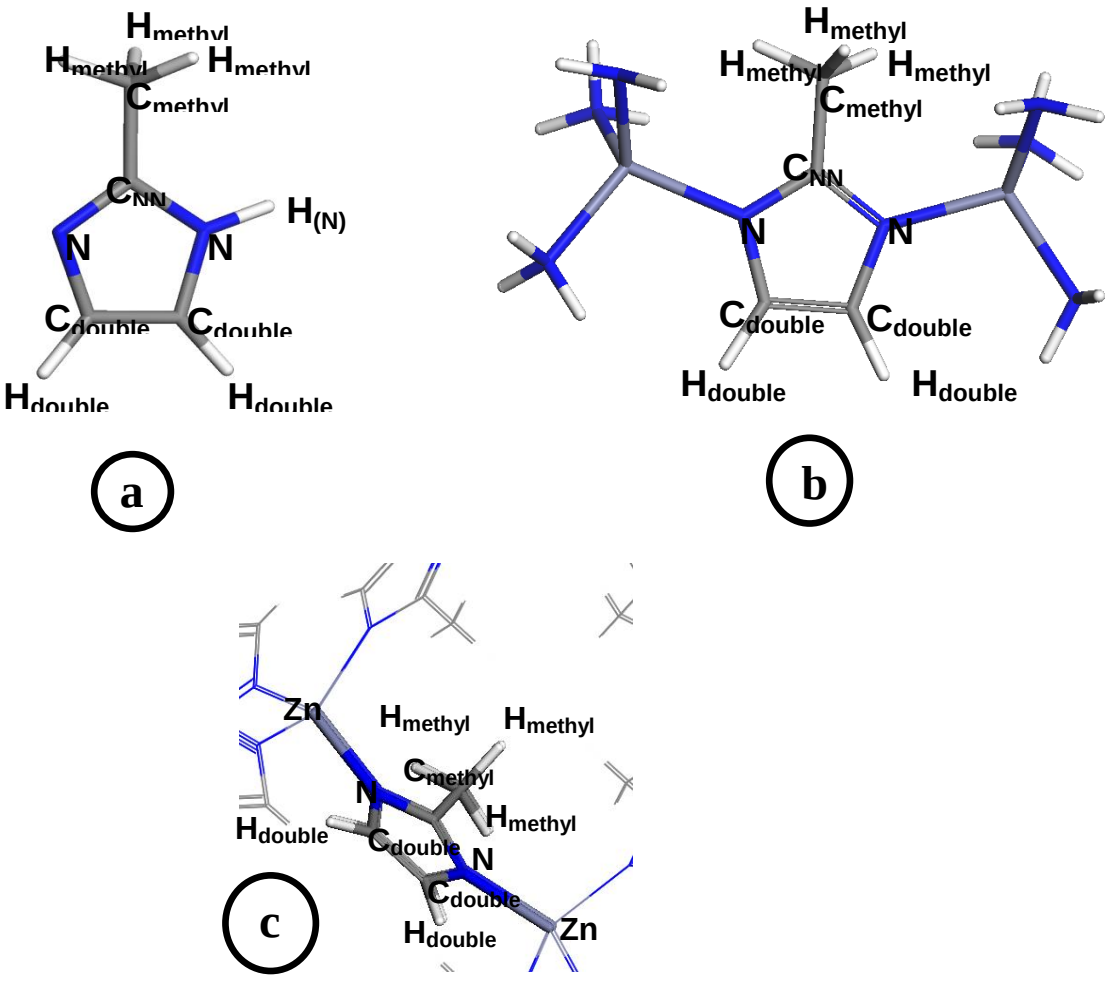

Figure S2: a) Imidazole, **b)** cluster and **c)** periodic boundary conditions representations for the extraction of Mulliken charges.

Section S2. Gas adsorption on ZIF-8.

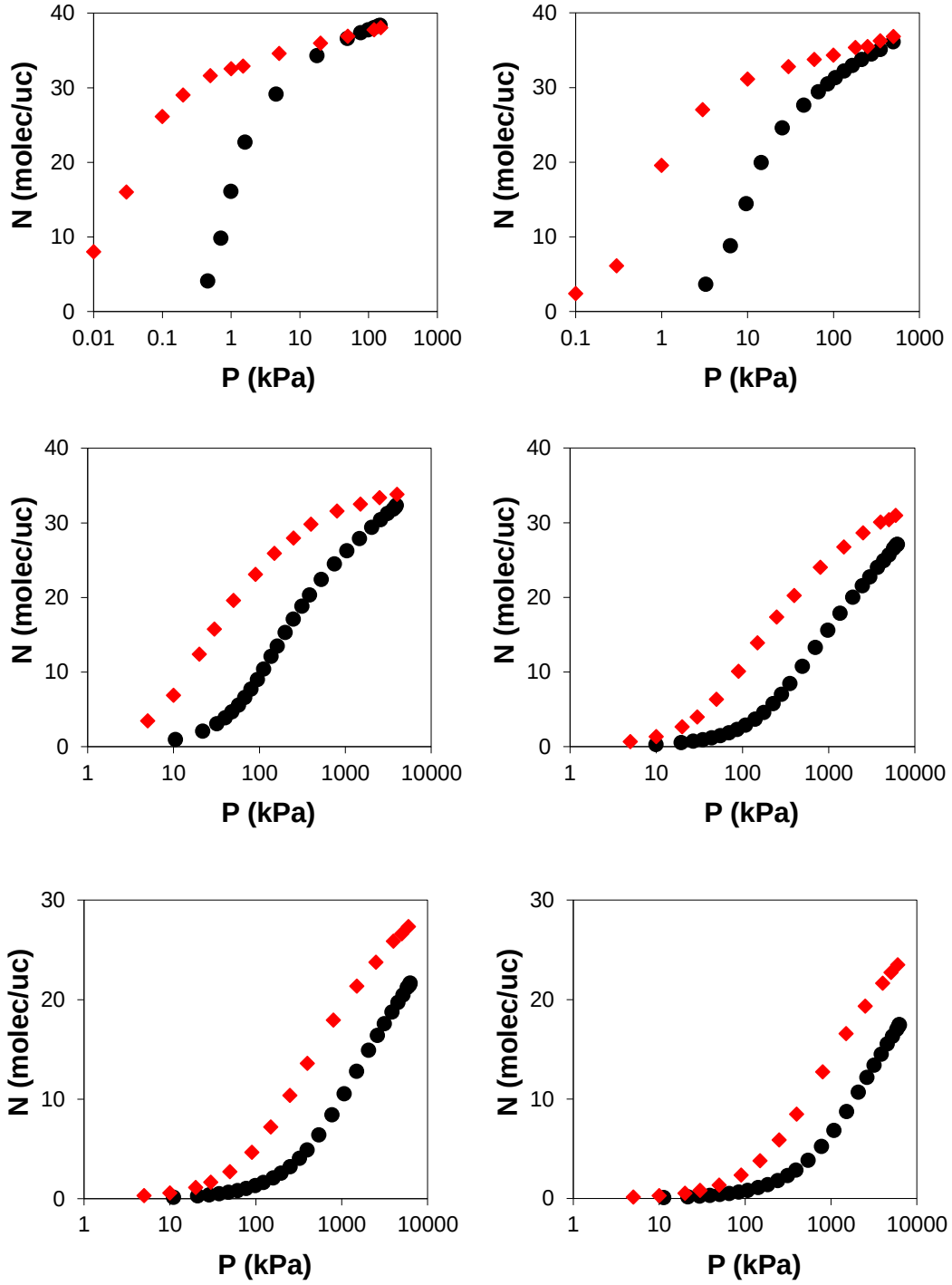

Figure S3. Adsorption isotherms of methane on ZIF-8 at *(from top-left to bottom-right)* 125, 150, 200, 240, 270 and 300 K. Experiments, black circles; UFF simulations on ZIF-8AP, red diamonds.

Table S2. Scaling factors (ϕ) applied to UFF-simulated isotherms of methane on ZIF-8AP in order to match experimental maximum amount adsorbed for isotherms at different temperatures.

Temperature (K)	125	150	200	230	270	300
ϕ	1.01	0.98	0.96	0.88	0.79	0.74

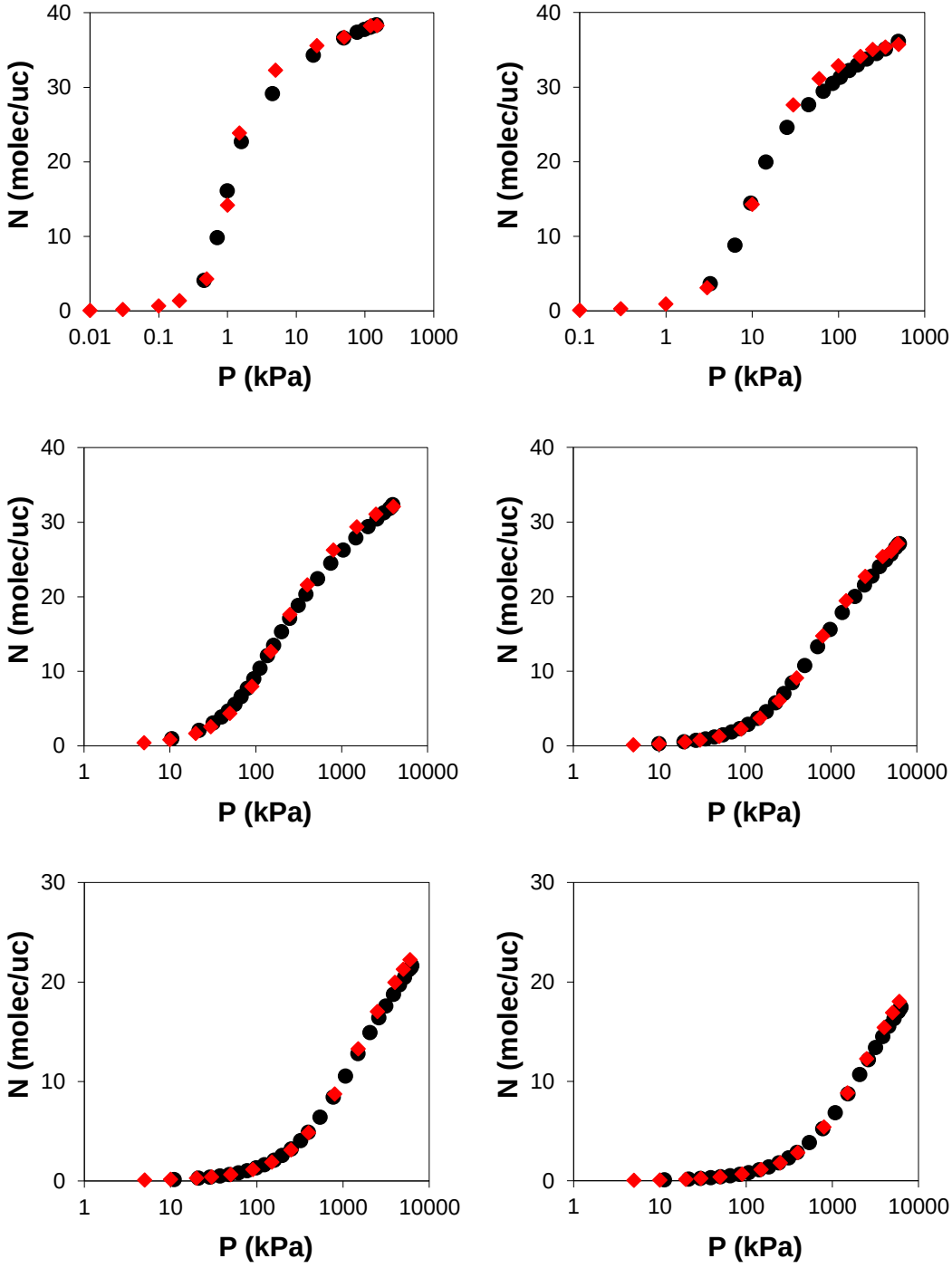

Figure S4. Adsorption isotherms of methane on ZIF-8 at *(from top-left to bottom-right)* 125, 150, 200, 240, 270 and 300 K. Experiments, black circles; UFF(*) simulations on ZIF-8AP, red diamonds.

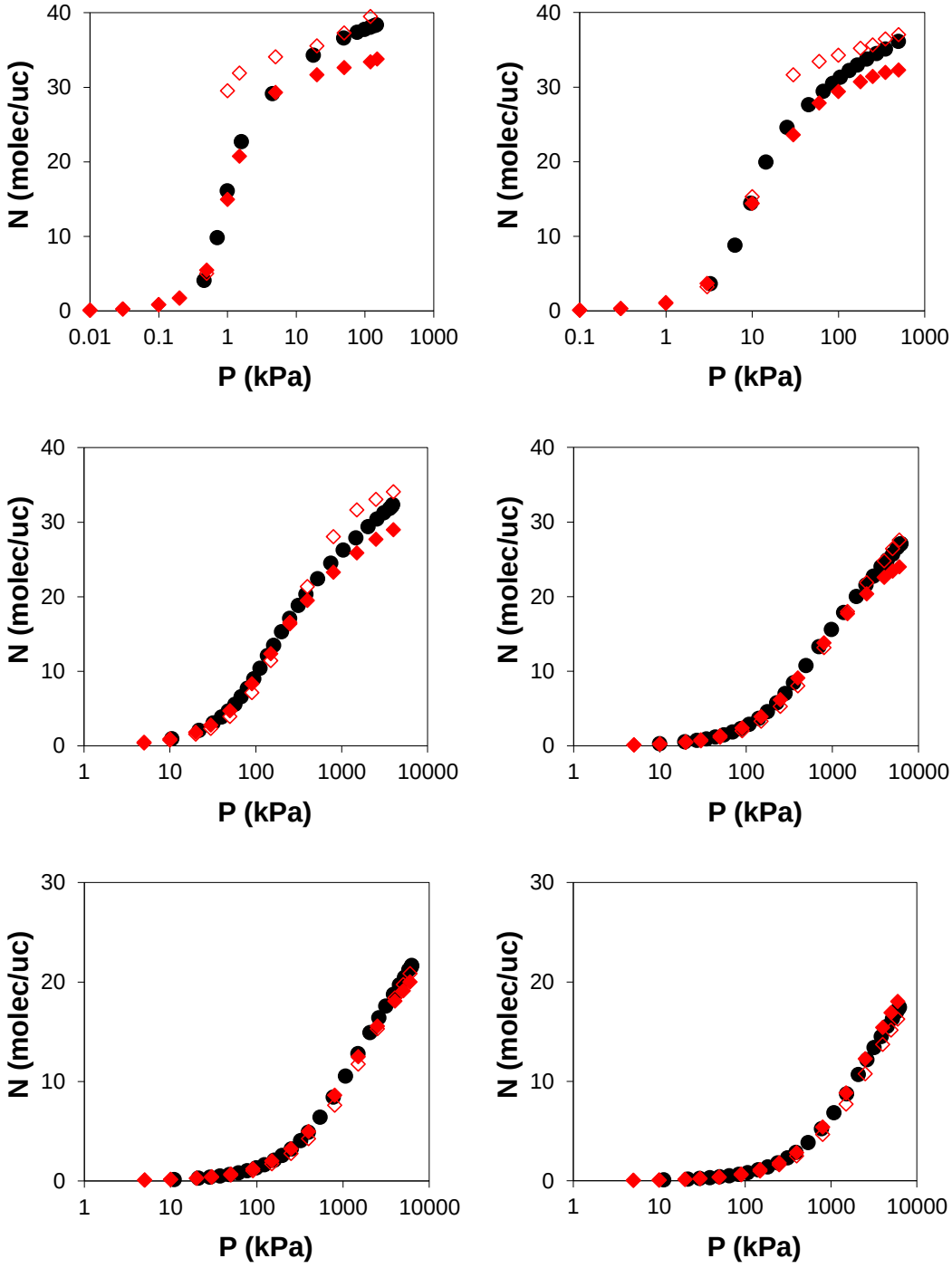

Figure S5. Adsorption isotherms of methane on ZIF-8 at *(from top-left to bottom-right)* 125, 150, 200, 240, 270 and 300 K. Experiments, black circles UFF(+) on ZIF-8AP, closed red diamonds; UFF(+) on ZIF-8HP, open red diamonds

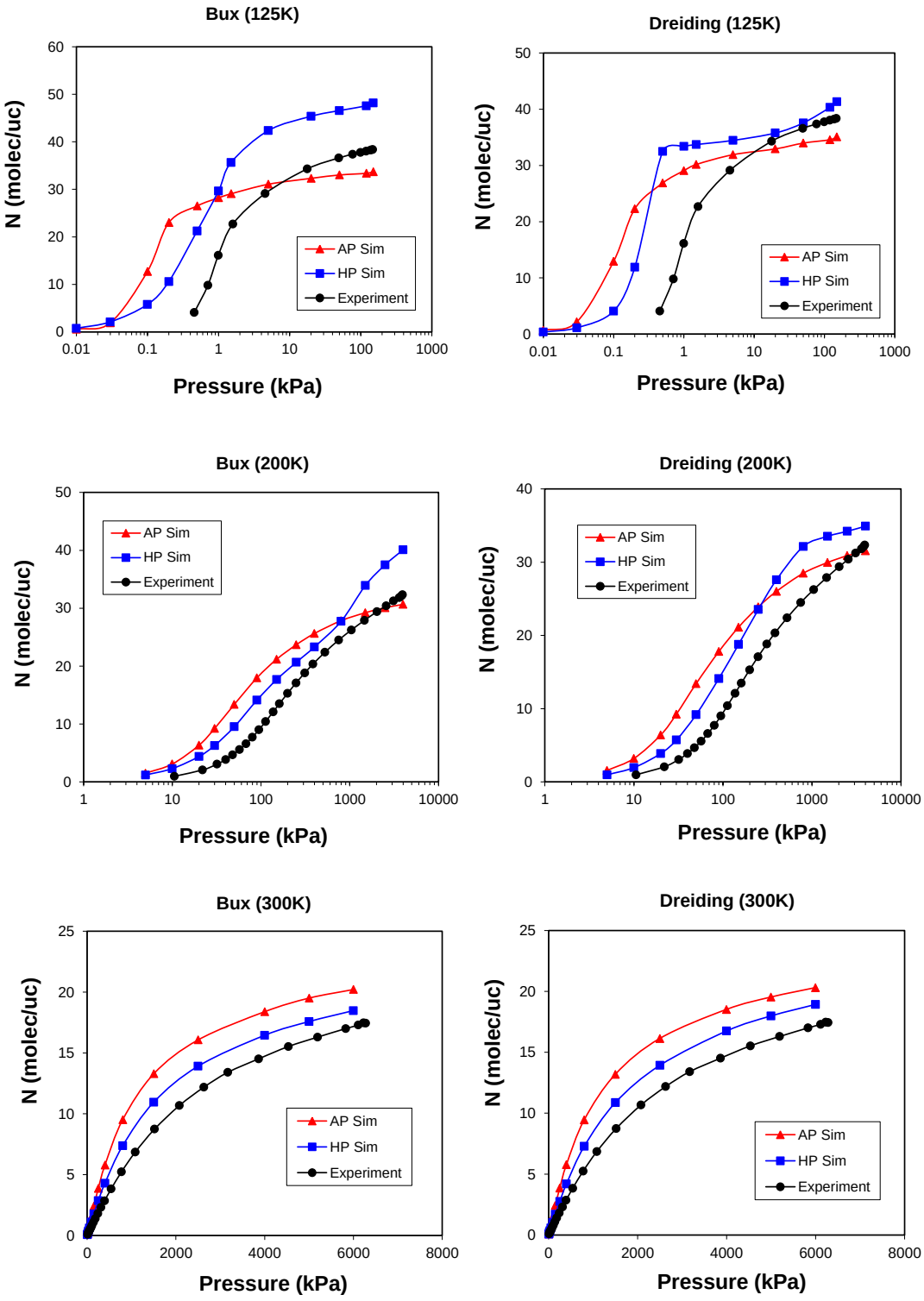

Figure S6. Adsorption isotherms of methane on ZIF-8 at 125, 200 and 300 K. Experiments, black circles; *(left)* Bux et al force field, and *(right)* Dreiding force field. ZIF-8AP, red triangles; ZIF-8HP, blue squares.

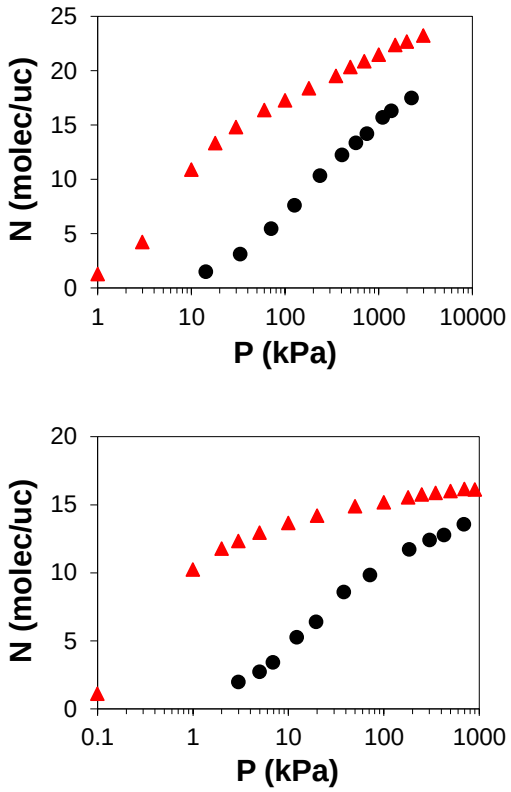

Figure S7. Adsorption isotherms of *(from top to bottom)* ethane and propane on ZIF-8 at 273 K. Experiments, black circles UFF on ZIF-8AP, closed red triangles.

Section S3. DFT minimization on CH_4 in ZIF-8AP.

Configuration α_2: The second most stable configuration (Figure S8) has BE of – 17.2 kJ mol^{-1} and it corresponds to CH_4 located on top of the C=C double bond, with $H(CH_4)\cdots C{=}C$ distances of ~2.8 Å, likewise the most stable configuration α_1 (Figure 6).

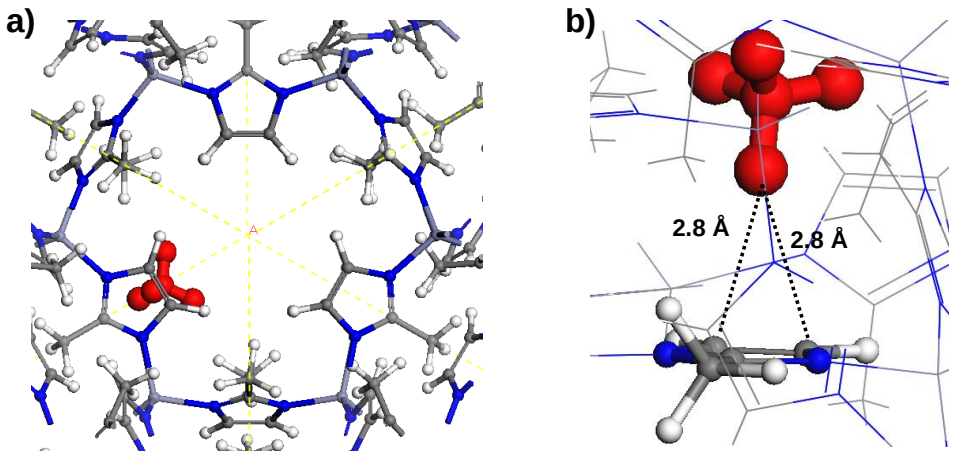

Figure S8 Configuration α_2 for one CH_4 in ZIF-8AP, resulting from energy minimizations with DFT calculations with Grimme dispersive correction.

Configuration α_3: Very similar to the most stable configuration (configuration α_1), with CH_4 on top of C=C double bond of imidazole ligand with one hydrogen pointing towards the double bond, having binding energy BE = -16.4 kJ mol^{-1} (Figure S9). As in configuration α_2, the short $H(CH_4)\cdots C{=}C$ distances are of ~2.8 Å.

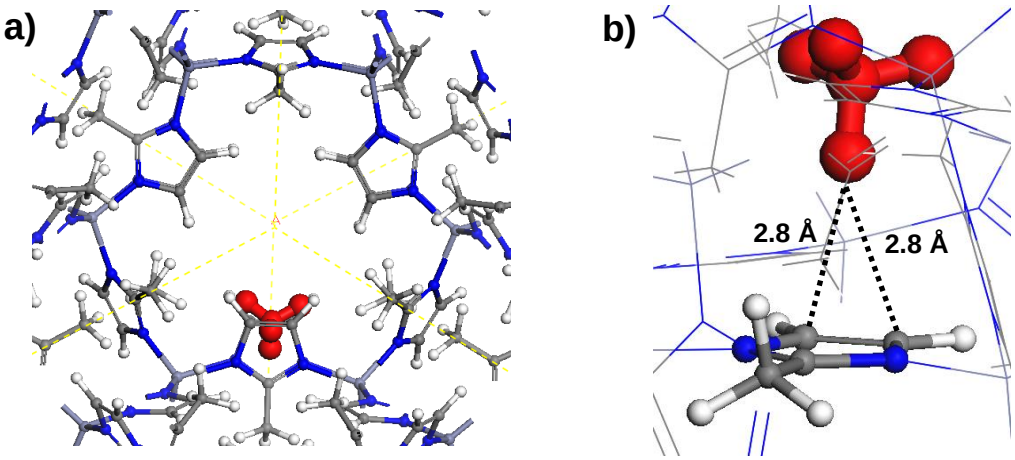

Figure S9: Configuration α_3 for one CH_4 in ZIF-8AP, resulting from energy minimizations with DFT calculations with Grimme dispersive correction.

Configuration β2: The fifth stable configuration with BE of -16.0 kJ mol^{-1} is characterised by CH_4 located at the centre of the 6-ring pore-window, similar to configuration **β_1**, with H(CH_4)···C=C distance of 2.9Å (Figure S10). The peculiar feature of this configuration when compared with configuration **β_1**, is the absence of weak interactions between H(CH_4) and the -CH_3 groups of imidazolate, as indicated by the relatively long H(CH_4)···C(CH_3) distances of 5.3 Å. Likewise at Site I, the main interaction of CH_4 with the ZIF-8AP framework occurs with the C=C double bond of the imidazolate ring, including an additional contribution of weak interactions with the –CH_3 groups of the imidazolate linker on **β_1,** which are not present on **β_2**. Indeed, this is clearly shown by the DFT calculations, where the differences between **β_1** and **β_2** are about 2 kJ mol^{-1} in BE. Another important difference between the two configurations is the position of CH_4 along the perpendicular axis to the 6-ring window (Figure 7 and S10). In fact, in configuration **β_1**, CH_4 is located above this plane, outside the "sodalite" central cage of ZIF-8AP, facilitating the interaction of the H(CH_4) with the –CH_3 groups of imidazolate linker. On the other hand, in configuration **β_2**, methane is located below the plane, within the "sodalite" central cage of ZIF-8AP, and far from the –CH_3 groups of imidazolate, whose interaction with CH_4 is prevented.

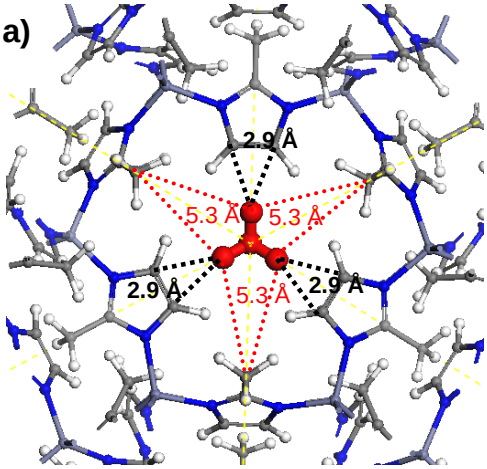

Figure S10: Configuration β_2 for one CH_4 in ZIF-8AP, resulting from energy minimizations with DFT calculations with Grimme dispersive correction.

Section S4. DFT minimization on CH_4 in ZIF-8HP.

Table S3. Mülliken charge (Δq) variation for CH_4 species in the different adsorption sites of ZIF-8AP and ZIF-8HP, with respect to the isolated molecule. Δq = q(CH_4 in ZIF-8HP) – q(CH_4 isolated).

	Δq_{TOT} (CH_4)	Δq(C)	Δq(H)	Δq(H)	Δq(H)	Δq(H)
			ZIF-8AP			
α_1	-0.0025	-0.0074	-0.0041	+0.0128	-0.0025	-0.0013
α_2	+0.0035	+0.0000	-0.0024	-0.0032	+0.0116	-0.0025
α_3	+0.0038	+0.0006	-0.0023	-0.0025	+0.0113	-0.0033
β_1	+0.0146	-0.0041	-0.0049	-0.0041	-0.0041	-0.0041
β_2	-0.0044	+0.0076	-0.0057	+0.0049	-0.0056	-0.0056
γ	+0.0005	+0.0006	-0.0002	+0.0002	+0.0001	-0.0002
			ZIF-8HP			
Θ	-0.0266	+0.0139	+0.0032	+0.0029	+0.0032	+0.0034