

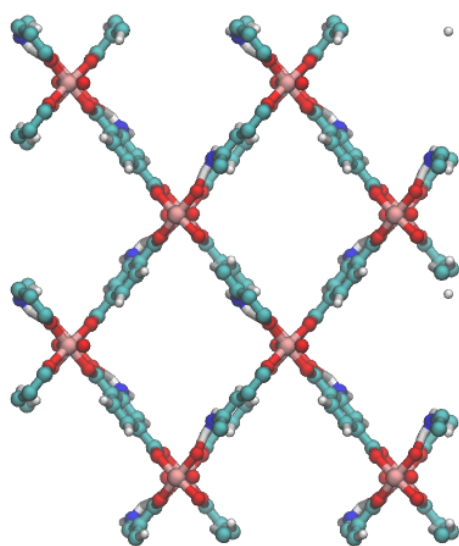
# Supporting Information for: Understanding and Solving Disorder in Substitution Pattern of Amino Functionalized MIL-47(V)

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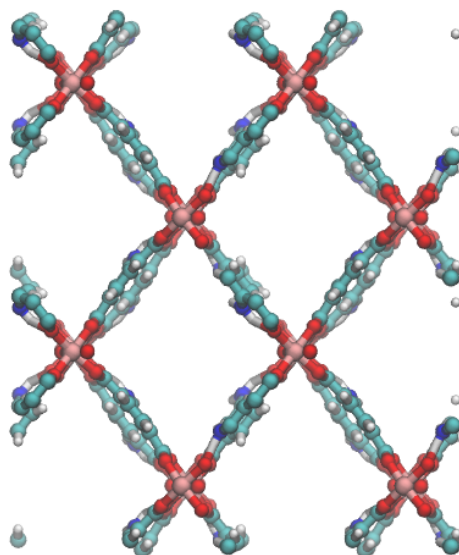
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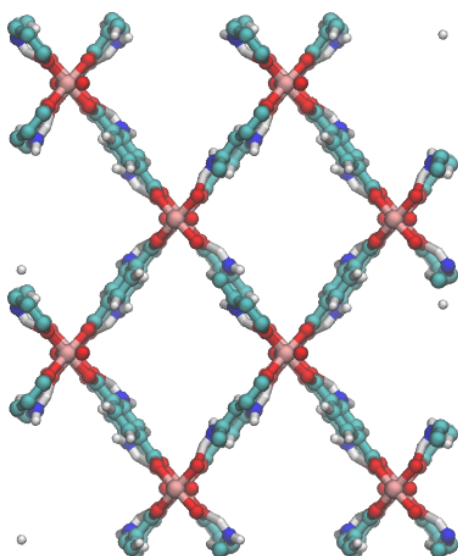
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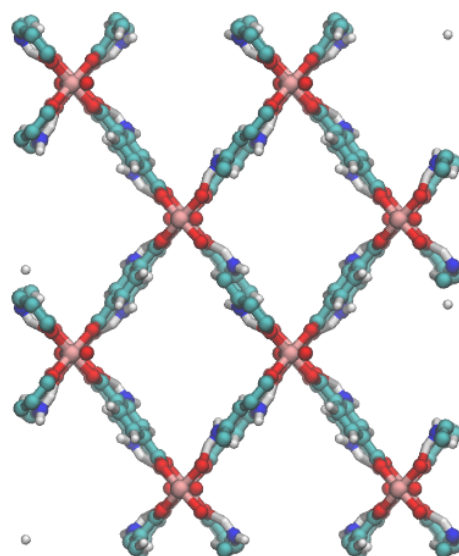
A2B2



A2B3

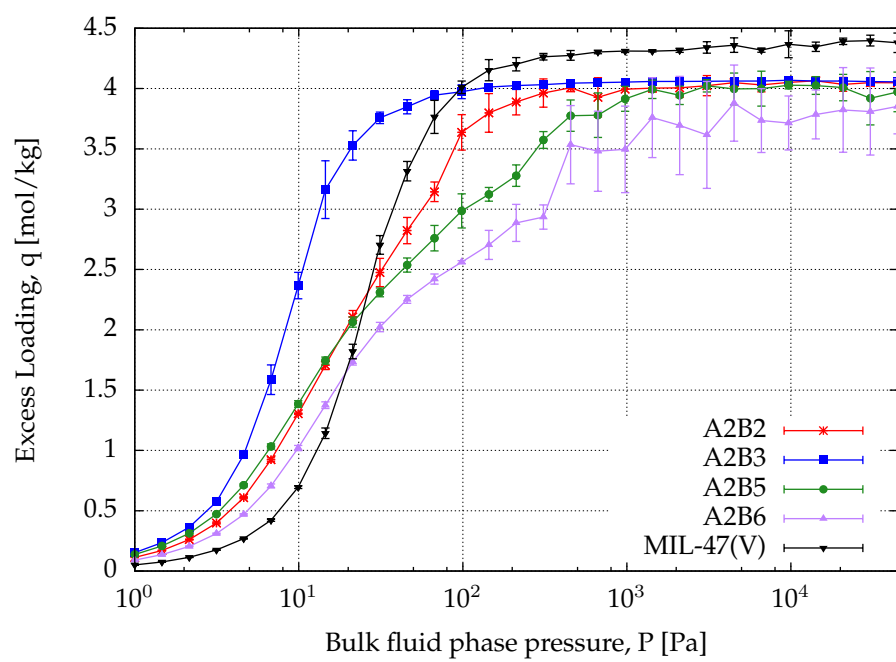


A2B5

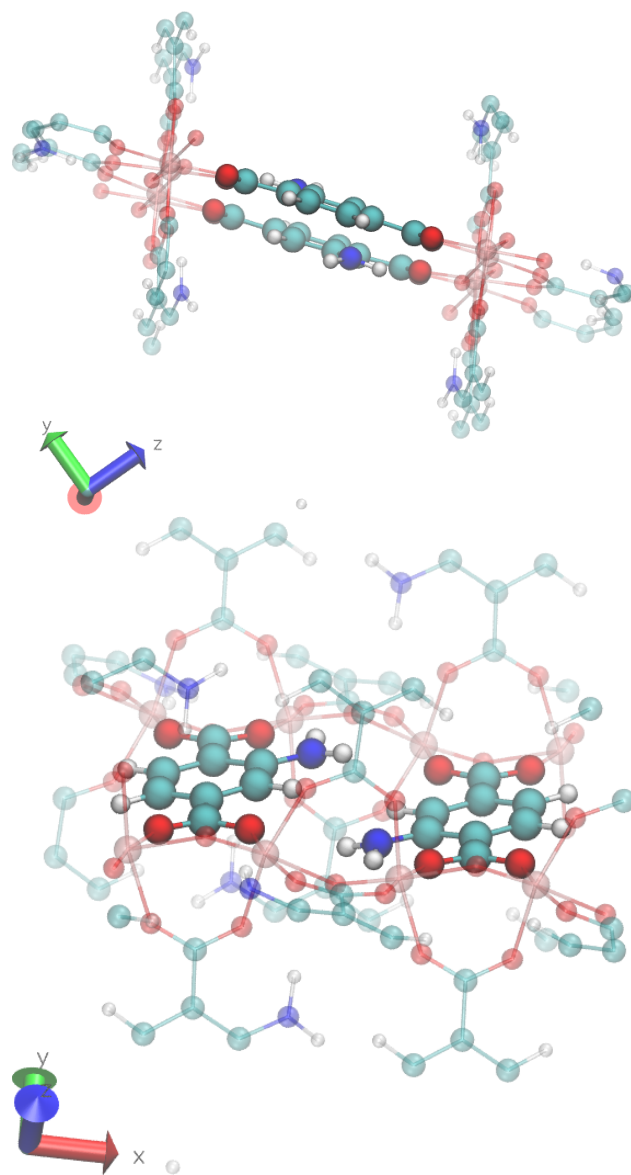


A2B6

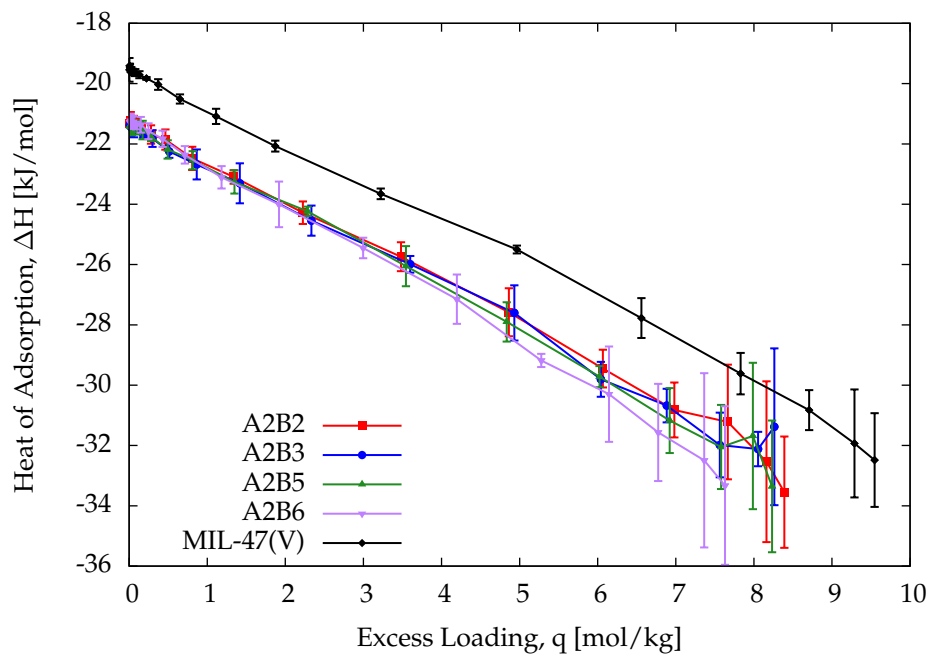
**Figure S1:** Channels of four amino functionalized MIL-47(V) viewed along the a-axis.



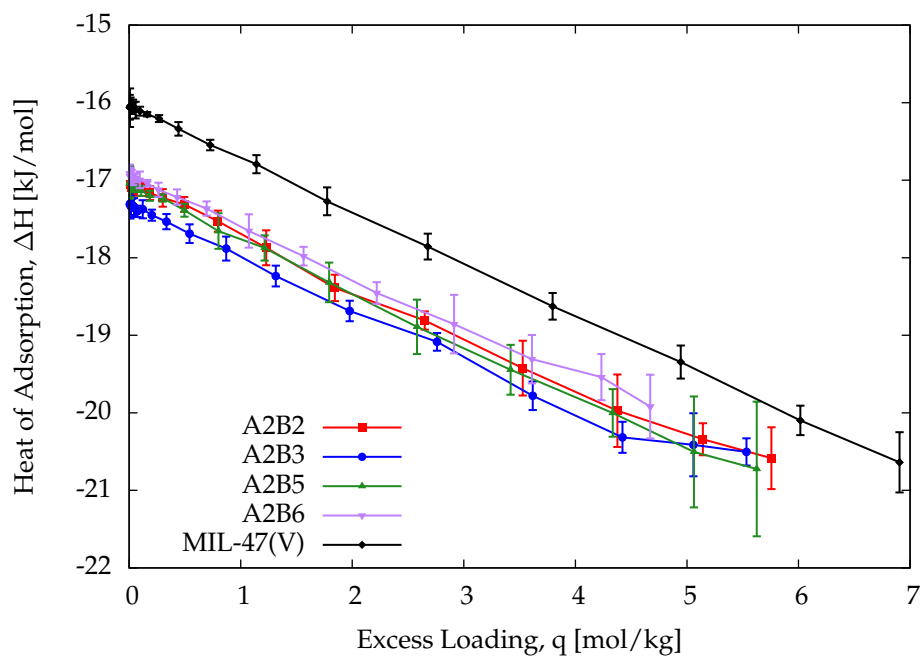
**Figure S2:** CB-GCMC adsorption isotherm of benzene for MIL-47(V) and NH<sub>2</sub>-MIL-47(V) at T = 328 K.



**Figure S3:** A2B5 NH<sub>2</sub>-MIL-47(V) supercell with adjacent BDC-linkers highlighted to illustrate repulsive behaviour of the nitrogens when constrained along the b-axis.

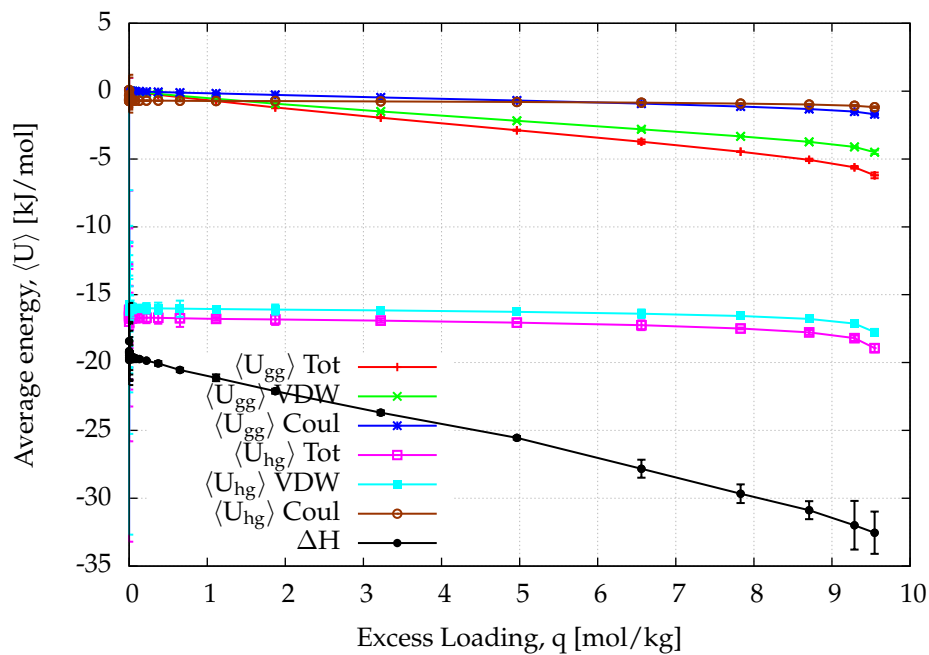


(a)  $\text{CO}_2$

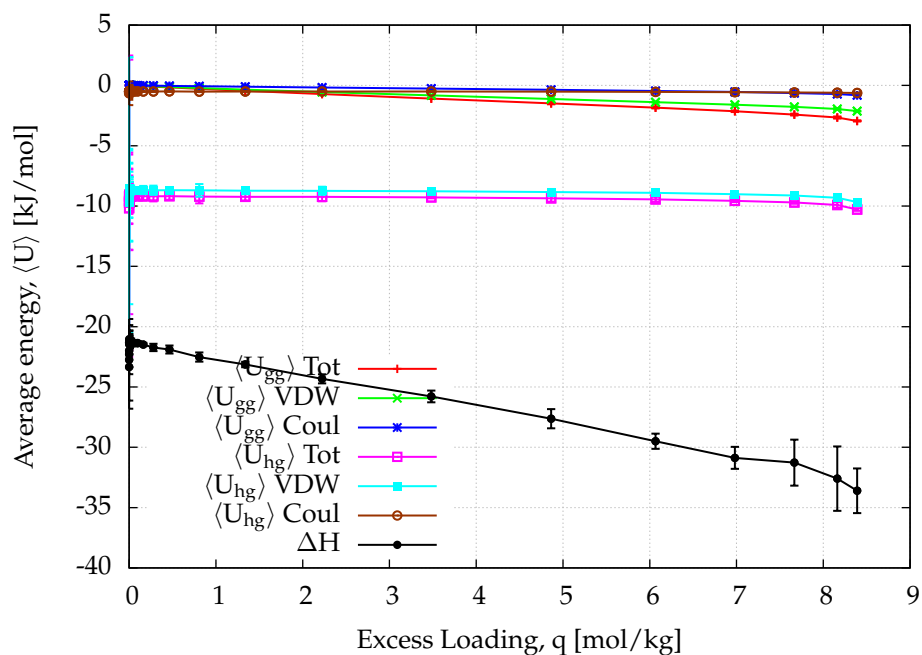


(b) methane

**Figure S4:** Heat of adsorption  $\Delta H$  in [kJ/mol] at 303 K as function of excess loading in [mol/kg] for  $\text{NH}_2$ -MIL-47(V) and MIL-47(V) computed from fluctuation formula.



(a) MIL-47(V)



(b) A2B2 NH<sub>2</sub>-MIL-47(V)

**Figure S5:** Heat of adsorption  $\Delta H$  and average guest-guest (gg) and host-guest (hg) energy in [kJ/mol] per adsorbate expressed in electrostatics (Coul) and Van der Waals (VDW) contributions as function of the excess loading for (a) MIL-47(V) and (b) A2B2 NH<sub>2</sub>-MIL-47(V) for CO<sub>2</sub> adsorption at 303 K.