Electronic Supplementary Material (ESI) for CrystEngComm

SUPPORTING INFORMATION

Interaction of hydrogen and carbon dioxide with sod-type zeolitic imidazolate frameworks: A periodic DFT-D study

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1) Additional results: ZIF-8

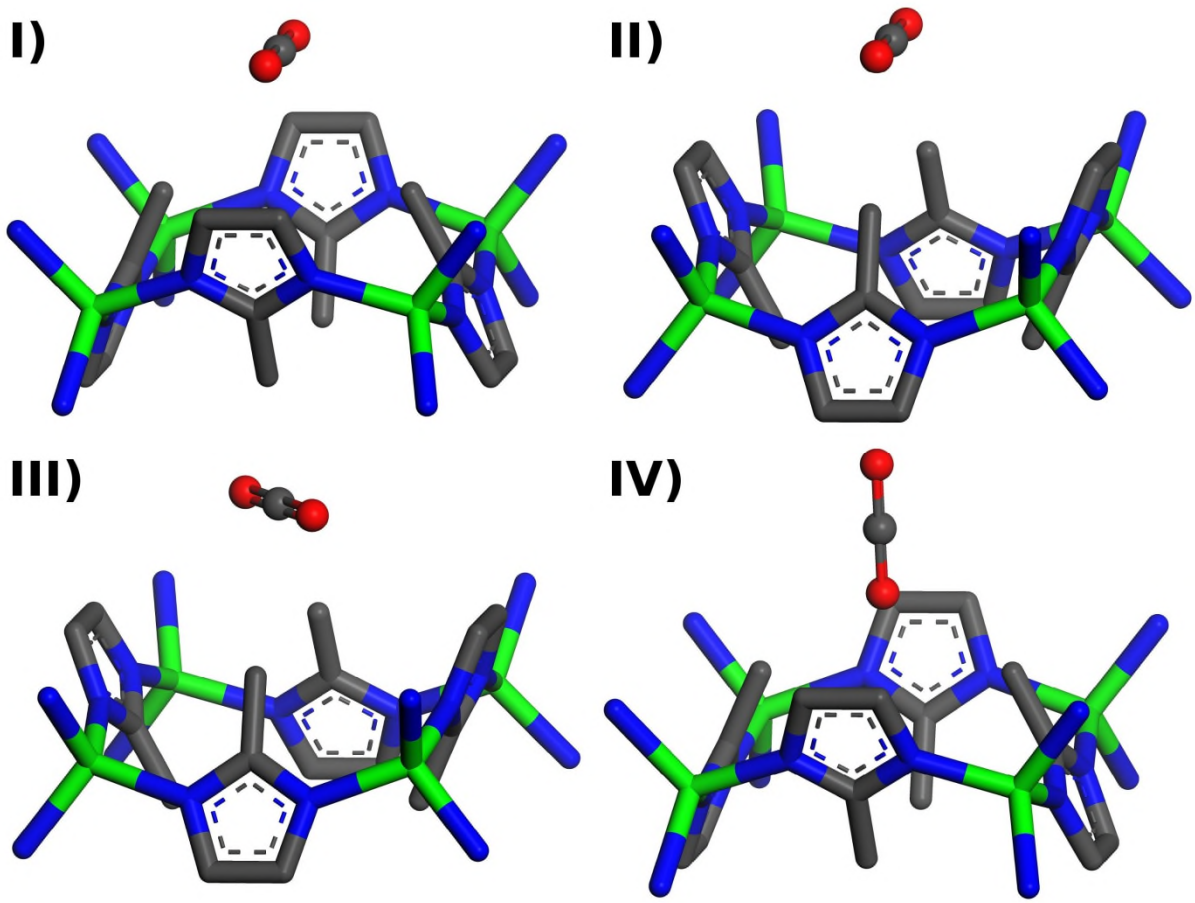

Figure S1: Visualisation of the different orientations of the CO_2 molecule considered in the starting geometries for calculations for site CO_2_D. It should be noted that calculations using different initial orientations may converge to (essentially) the same final configuration. For ZIF-8_CHO, an additional orientation IIIb) was used, where the CO_2 molecule is rotated by 90 degrees about the axis perpendicular to the four-ring. The same set of orientations was used for calculations involving hydrogen at site H_2_4.

Table S1: Calculated interaction energy at sites H_2_4 and CO_2_D in ZIF-8, obtained with different initial orientations of the guest molecule (see figure S1). Only the best value, highlighted in bold, is given in the main paper.

Site	E_{int} / kJ mol^{-1}	Site	E_{int} / kJ mol^{-1}
H_2_4, I	**-7.7**	CO_2_D, I	-14.6
H_2_4, II	-5.2	CO_2_D, II	-15.7
H_2_4, III	-7.5	CO_2_D, III	**-15.9**
H_2_4, IV	-7.2	CO_2_D, IV	-12.3

Table S2: Comparison of experimental hydrogen adsorption sites[a)] and DFT-derived sites in ZIF-8. The coordinates of the centre of mass are given. The length of the difference vector Δ is also given, assuming the cell parameters of the DFT-optimised structure.

Site	*Experiment*			*DFT*			Δ / Å
	x	*y*	*z*	*x*	*y*	*z*	
H_2_1	0.2297	0.2297	0.0089	0.2359	0.2421	0.0039	0.25
H_2_2	0.3089	0.3089	0.3089	0.3200	0.3202	0.3162	0.30
H_2_3	0.2008	0.2008	0.2008	0.1855	0.2012	0.1887	0.33
H_2_4	0.2540	0	0	0.2605	0.0022	0.0015	0.11

a) Experimental adsorption sites from:
H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* **2007**, *129*, 5314-5315.

2) Additional results: BIF-3_Li and BIF-3_Cu

Table S3: Calculated interaction energies at hydrogen and carbon dioxide adsorption sites in BIF-3_Li and BIF-3_Cu. For sites H_2_4 and CO_2_D, results obtained with different initial orientations of the guest molecule are listed (see figure S1).

Site	*BIF-3_Li* E_{int} / kJ mol^{-1}	*BIF-3_Cu* E_{int} / kJ mol^{-1}	Site	*BIF-3_Li* E_{int} / kJ mol^{-1}	*BIF-3_Cu* E_{int} / kJ mol^{-1}
H_2_1	-12.0	-13.4	CO_2_A	-27.1	-27.9
H_2_2	-11.1	-9.9	CO_2_B	-22.8	-23.3
H_2_3	-11.4	-11.0	CO_2_C	-19.0	-19.9
H_2_4, I	-8.8	-9.1	CO_2_D, I	-17.1	-17.7
H_2_4, II	-7.8	-8.6	CO_2_D, II	-16.6	-15.9
H_2_4, III	-8.7	-9.0	CO_2_D, III	-17.4	-17.3
H_2_4, IV	-8.8	-8.8	CO_2_D, IV	-12.6	-13.6

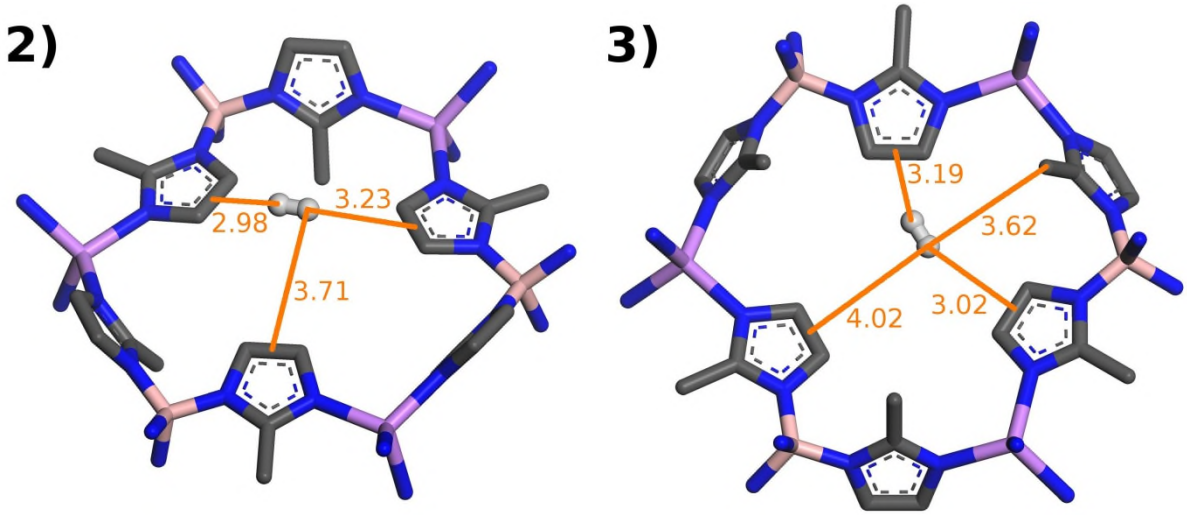

Figure S2: DFT-optimised adsorption geometries of sites H_2_2 (left) and H_2_3 (right) in BIF-3_Li.

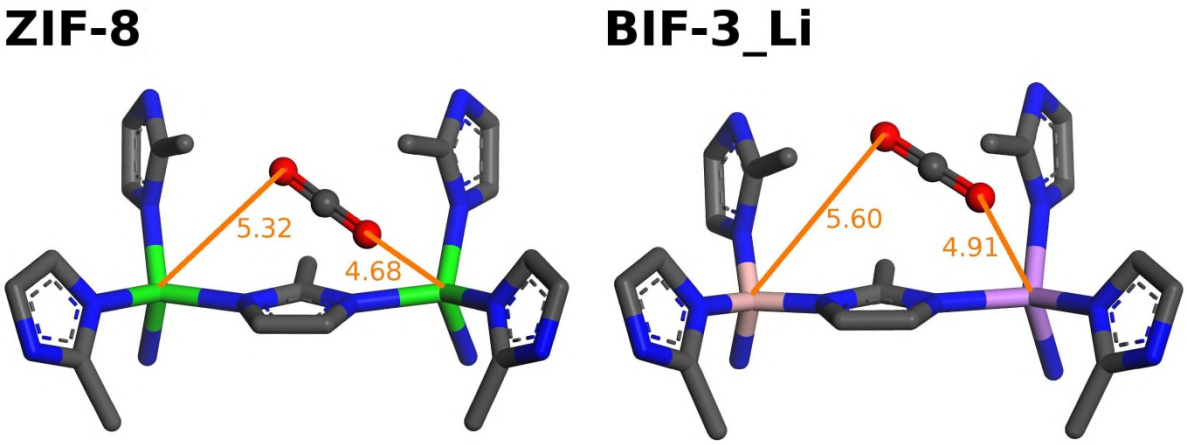

Figure S3: DFT-optimised adsorption geometries of site CO_2_D in ZIF-8 and BIF-3_Li, including the distances to the two nearest T atoms.

3) Additional results: Substituted ZIF-8 derivatives

Table S4: Calculated interaction energies at hydrogen adsorption sites in substituted derivatives ZIF-8. For site H_2_4, results obtained with different initial orientations of the guest molecule are listed (see figure S1).

Site	*ZIF-8*	*ZIF-8_H*	*ZIF_8_NO₂*	*ZIF-8_NH₂*	*ZIF-8_CHO*
	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}
H_2_1	-13.3	-13.2	-12.9	-9.7	-9.2
H_2_2	-8.8	-9.3	-6.6	-6.4	-7.6
H_2_3	-7.6	-8.2	-8.0	-6.8	-7.1
H_2_4, I	-7.7	-8.6	-2.8	-8.2	-8.0
H_2_4, II	-5.2	-2.5	-11.6	-8.0	-8.1
H_2_4, III	-7.5	-7.6	-6.8	-9.5	-8.2
H_2_4, IIIb	-	-	-	-	-7.7
H_2_4, IV	-7.2	-3.6	-3.8	-9.6	-6.7

Table S5: Calculated interaction energies at hydrogen adsorption sites in substituted derivatives ZIF-8. For site CO_2_D, results obtained with different initial orientations of the guest molecule are listed (see figure S1).

Site	*ZIF-8*	*ZIF-8_H*	*ZIF_8_NO₂*	*ZIF-8_NH₂*	*ZIF-8_CHO*
	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}	E_{int} / kJ mol^{-1}
CO_2_A	-26.6	-23.1	-27.1	-24.8	-24.3
CO_2_B	-25.0	-21.6	-15.6	-18.6	-17.0
CO_2_C	-22.3	-20.2	-21.6	-24.8	-23.6
CO_2_D, I	-14.6	-10.4	-21.8	-23.2	-32.8
CO_2_D, II	-15.7	-28.0	-6.5	-13.2	-32.8
CO_2_D, III	-15.9	-28.3	-21.9	-12.1	-33.0
CO_2_D, IIIb	-	-	-	-	-32.9
CO_2_D, IV	-12.3	-20.4	-34.6	-19.7	-32.1

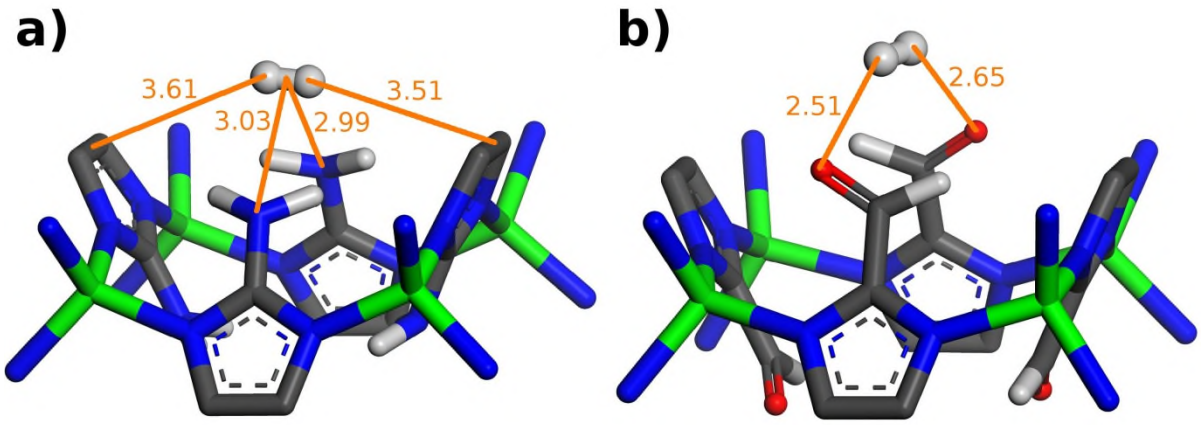

Figure S4: DFT-optimised adsorption geometries of site H_2_4 in ZIF-8_NH_2 (left) and ZIF-8_CHO (right).

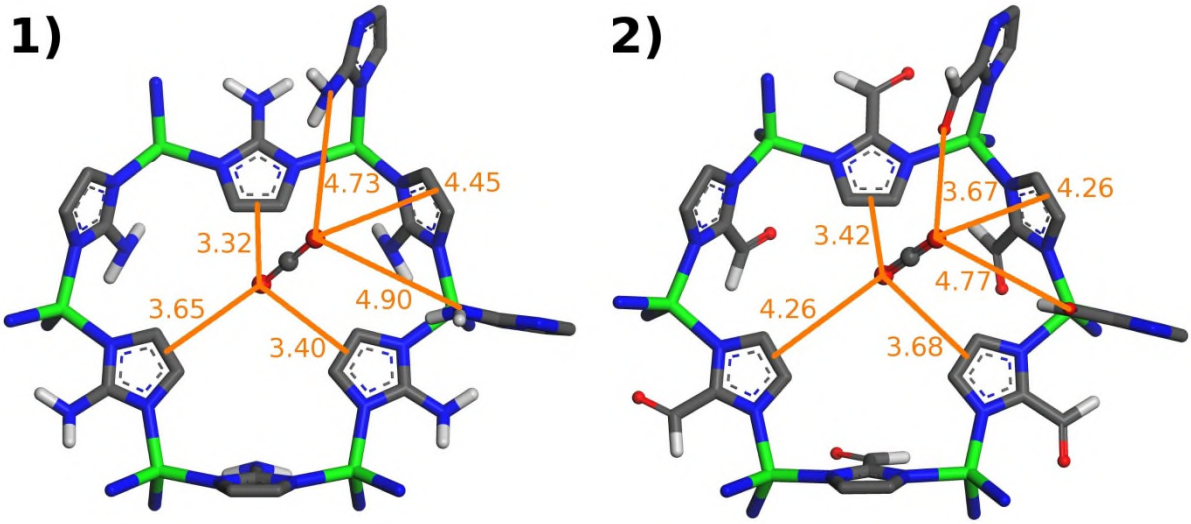

Figure S5: DFT-optimised adsorption geometries of site CO_2_B in ZIF-8_NH_2 (left) and ZIF-8_CHO (right).

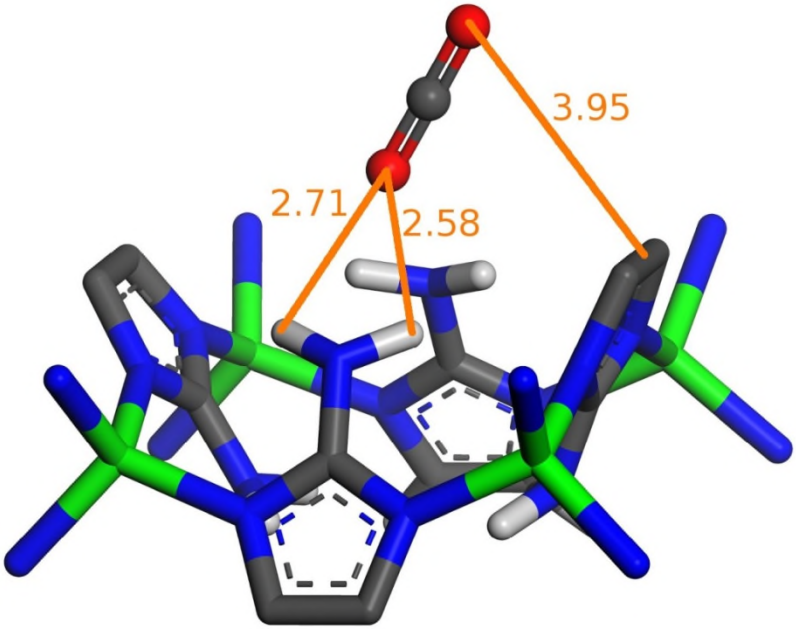

Figure S6: DFT-optimised adsorption geometry of site CO_2_D in ZIF-8_NH_2.