Electronic Supporting Information

Computationally aided design of defect-appended aliphatic amines for CO₂ activation within UiO-66

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1. MOF functionalization benchmark

Table S1. Total Energy of the optimised geometries. Several geometries were optimised starting from different initial configurations of the amino acid chain to simulate different configurations produced by thermal motion. Values in kcal mol^{-1}.

UiO-66_gly	Total E	UiO-66_gaba	Total E
Configuration 1	-1964185.48	Configuration 1	-1989973.09
Configuration 2	-1964186.92	Configuration 2	-1989970.83
Configuration 3	-1964185.92	Configuration 3	-1989970.77
Configuration 4	-1964184.23	Configuration 4	-1989975.98
Configuration 5	-1964184.98	Configuration 5	-1989976.17
Configuration 6	-1964188.56	Configuration 6	-1989976.42
UiO-66_ala	**Total E**	**UiO-66_ava**	**Total E**
Configuration 1	-1977079.22	Configuration 1	-2002866.40
Configuration 2	-1977077.47	Configuration 2	-2002876.12
Configuration 3	-1977082.36	Configuration 3	-2002861.00
Configuration 4	-1977090.08	Configuration 4	-2002870.54
Configuration 5	-1977086.63	Configuration 5	-2002861.06
Configuration 6	-1977082.55	Configuration 6	-2002857.99

2. CO₂ activation.

Table S2. Binding energy (BE) and geometrical parameters for the adsorption of CO_2 of the unprotonated systems. Energies in kcal·mol^{-1}; Bond distances in Angstrom; Angles in degrees. CO_2 is considered activated when there is an elongation of the CO bond compared to the calculated value for isolated CO_2 = 1.18 Ang. Calculated C-N distance for isolated carbamic acid = 1.37 Ang.

System	BE	N1··C	N2··C	N3··C	C-O1	C-O2	O1-C-O2	CO₂ act
UiO-66_gly	-3.85	4.24	2.71	6.29	1.18	1.18	176	N
UiO-66_gly_2	-0.52	4.57	4.23	6.02	1.18	1.18	180	N
UiO-66_gly_3	-3.90	3.97	2.76	6.76	1.18	1.18	176	N
UiO-66_gly_4	-3.75	3.82	3.32	5.27	1.18	1.18	178	N
UiO-66_gly_5	0.15	5.14	4.76	5.35	1.18	1.18	180	N
UiO-66_gly_6	-4.07	5.00	2.85	6.67	1.18	1.18	176	N
AVERAGE	-2.66						178	0%
UiO-66_ala	-3.33	4.80	2.96	5.15	1.18	1.18	177	N
UiO-66_ala_2	-3.91	4.39	2.83	7.38	1.18	1.18	175	N
UiO-66_ala_3	-6.21	4.20	2.64	3.66	1.18	1.18	173	N
UiO-66_ala_4	-4.69	4.75	2.64	7.81	1.18	1.18	172	N
UiO-66_ala_5	-7.23	3.56	2.54	4.09	1.18	1.18	170	N
UiO-66_ala_6	-3.06	4.10	3.06	3.75	1.18	1.18	178	N
AVERAGE	-4.74						174	0%
UiO-66_gaba	-5.07	3.50	2.77	3.78	1.18	1.18	174	N
UiO-66_gaba_2	-4.08	3.73	2.78	7.13	1.18	1.18	175	N
UiO-66_gaba_3	-4.66	3.84	2.74	7.24	1.18	1.18	175	N
UiO-66_gaba_4	-38.06	3.13	1.71	5.44	1.22	1.23	142	Y
UiO-66_gaba_5	-39.81	3.15	1.71	5.20	1.22	1.23	142	Y
UiO-66_gaba_6	-43.14	3.08	1.68	4.02	1.22	1.24	141	Y
UiO-66_gaba_7	-40.90	3.29	1.71	3.53	1.23	1.22	142	Y
AVERAGE	-25.10						156	57%
UiO-66_ava	-6.76	2.89	2.88	4.72	1.18	1.18	174	N
UiO-66_ava_2	-49.19	3.05	1.66	3.39	1.23	1.24	139	Y
UiO-66_ava_3	-6.08	4.30	2.58	5.20	1.18	1.18	171	N
UiO-66_ava_4	-35.95	3.26	1.75	5.12	1.23	1.22	144	Y
UiO-66_ava_5	-5.88	4.11	2.62	5.06	1.18	1.18	172	N
UiO-66_ava_6	-8.24	2.87	2.63	3.39	1.18	1.18	172	N
AVERAGE	-18.68						162	33%

3. Beyond the ideal situation.

Table S3. Binding energies in kcal·mol^{-1} for the CO_2 activated system with different amount of defect functionalisation for the active configurations of unprotonated UiO-66_gaba and UiO-66_ava.

| System	% of functionalised sites in the pore	
	42	**8**
UiO-66_gaba_4	-33.86	-3.11
UiO-66_gaba_5	-36.75	-3.38
UiO-66_gaba_6	-35.26	-3.41
UiO-66_gaba_7	-32.85	-4.70
UiO-66_ava_2	-31.72	-4.54
UiO-66_ava_4	-31.16	-4.9

Table S4. Relative energies for the active unprotonated UiO-66_gaba and UiO-66_ava with only 42% of defect functionalisation for the hydrogen transfer. Values in kcal·mol^{-1}.

UiO-66_gaba configurations	Relative Energy
UiO-66_gaba_4_42%	0.0
UiO-66_gaba_4_42%_H-tran	-8.69
UiO-66_gaba_5_42%	0.0
UiO-66_gaba_5_42%_H-tran	-8.31
UiO-66_gaba_6_42%	0.0
UiO-66_gaba_6_42%_H-tran	-8.45
UiO-66_gaba_7_42%	0.0
UiO-66_gaba_7_42%_H-tran	-8.17
UiO-66_ava configurations	**Relative Energy**
UiO-66_ava_2_42%	0.0
UiO-66_ava_2_42%_H-tran	-4.80
UiO-66_ava_4_42%	0.0
UiO-66_ava_4_42%_H-tran	-6.48

Table S5. Geometrical data of UiO-66_ava systems with only 16% of defect functionalisation. Distances in Angstrom. Angles in degree. Binding Energy in kcal mol^{-1}. H··N represent the distance between the two amine groups. CO_2 is considered activated when there is an elongation of the CO bond compared the calculated value for isolated CO_2 = 1.18 Ang. Calculated CN distance for isolated carbamic acid = 1.37 Ang.

System	Binding Energy	C··N	C-O1	C-O2	O1-C-O2	CO_2 Activated	H··N

Configuration B_2	-	-	-	-	-		7.29
Configuration B_3	-	-	-	-	-		7.43
Configuration B_4	-	-	-	-	-		7.29
Configuration C_1	-5.36	2.63	1.18	1.18	172.71	N	3.42
Configuration C_2	-5.91	2.51	1.18	1.18	170.43	N	5.11
Configuration C_3	-14.02	2.08	1.20	1.20	156.07	Y	4.09
Configuration C_4	-6.51	2.63	1.18	1.18	170.42	N	2.28
Configuration C_5	-21.50	2.00	1.20	1.21	151.64	Y	2.05
Configuration C protonated	-64.34	1.61	1.22	1.25	136.00	Y	-
Configuration D	-	-	-	-	-		17.22
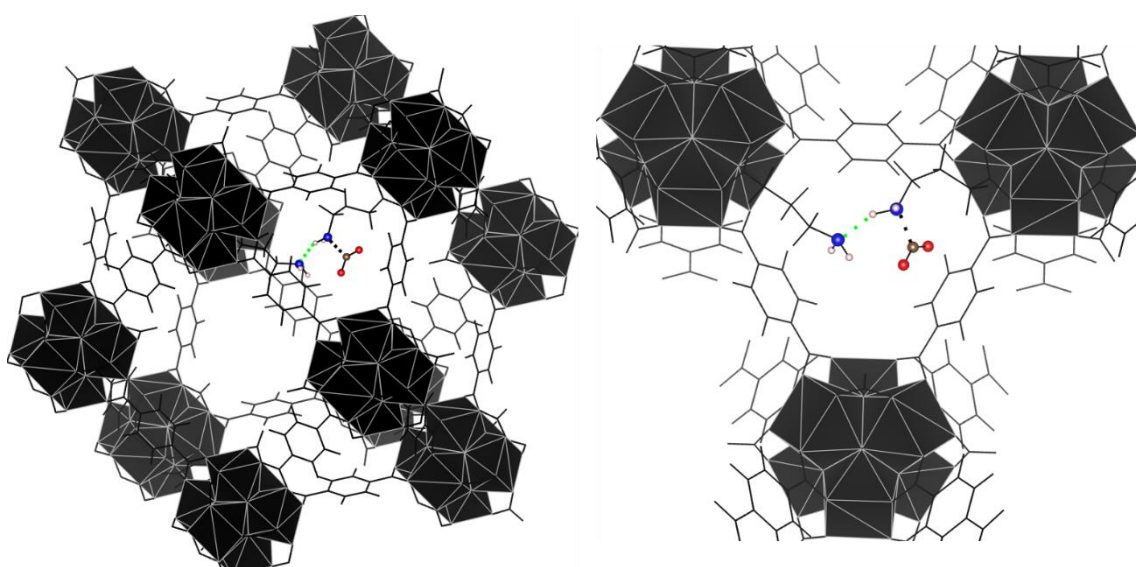
Figure S1. Snapshot showing the CO_2 adsorption for unprotonated UiO-66_ava with a functionalisation of 16%. Atom colours: N = blue, C = brown, O = red, H beige. Hydrogen bond is highlighted with green dashed lines. N··C interaction is the black dashed line.

4. CO_2 activation on the metal node.

Table S4. Binding energy (BE) and geometrical parameters for the adsorption of CO_2 at the inorganic node of UiO-66. SAME NODE refers to CO_2 adsorbed on OH groups of a functionalised corner; OTHER NODE refers to CO_2 adsorbed on OH groups of an unfunctionalized corner. Energies in kcal·mol^{-1}; Bond distances in Angstrom; Angle in degrees. CO_2 is considered activated when there is an elongation of the CO bond compared to 1.18 Ang, the calculated value for isolated CO_2.

System	BE	C-O1	C-O2	O1-C-O2	CO_2 act
UiO-66_ava_SAME_NODE	-1.95	1.18	1.18	180	N
UiO-66_ava_SAME_NODE_2	-1.01	1.18	1.18	180	N

UiO-66_ava_SAME_NODE_3	-0.87	1.18	1.18	180	N
UiO-66_ava_OTHER_NODE	-2.80	1.18	1.18	180	N
UiO-66_ava_OTHER_NODE_2	-2.82	1.18	1.18	180	N
UiO-66_ava_OTHER_NODE_3	-2.75	1.18	1.18	180	N
Average	-2.03	1.18	1.18	180	0%

5. MOF intra-protonation

Table S5. Protonation of the first amine group. Only configurations in which a H bond can be formed between the protonated and the unprotonated amines are favourable. Values are in kcal·mol^{-1}.

System-1	Vacuum	Solvated	System-3	Vacuum	Solvated
UiO-66_gly	0.00	0.00	UiO-66_gaba	0.00	0.00
UiO-66_gly_HIN	19.61	14.16	UiO-66_gaba_HIN	25.02	21.55
UiO-66_gly_HIN_2	6.23	3.07	UiO-66_gaba_HIN_2	30.18	11.31
UiO-66_gly_HIN_3	21.77	18.51	UiO-66_gaba_HIN_3	10.51	4.54
UiO-66_gly_HOUT	35.33	22.42	UiO-66_gaba_HOUT	21.90	15.74
UiO-66_gly_HOUT_2	20.29	7.95	UiO-66_gaba_HOUT_2	50.11	27.23
UiO-66_gly_HOUT_3	19.86	8.16	UiO-66_gaba_HOUT_3	3.44	-4.53
Average	20.52	12.38	Average	23.53	12.64
System-2	**Vacuum**	**Solvated**	**System-4**	**Vacuum**	**Solvated**
UiO-66_ala	0.00	0.00	UiO-66_ava	0.00	0.00
UiO-66_ala_HIN	12.15	6.50	UiO-66_ava_HIN	7.98	-6.98
UiO-66_ala_HIN_2	27.53	9.06	UiO-66_ava_HIN_2	16.38	9.69
UiO-66_ala_HIN_3	15.95	9.06	UiO-66_ava_HIN_3	6.63	-6.88
UiO-66_ala_HOUT	15.29	0.98	UiO-66_ava_HOUT	7.61	-7.60
UiO-66_ala_HOUT_2	49.31	26.50	UiO-66_ava_HOUT_2	7.61	-6.93
UiO-66_ala_HOUT_3	9.84	0.76	UiO-66_ava_HOUT_3	7.01	-19.69
Average	21.68	8.81	Average	8.87	-6.40
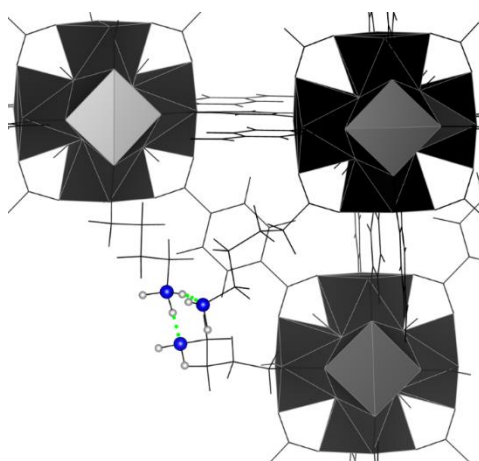
Figure S2. Example of hydrogen bonding network between the amine group (highlighted in

dashed green). This effect stabilizes the protonation of one amine group in UiO-66_ava. Atom colours: N = blue, H = beige

Table S6. Protonation of the 2nd and 3rd amine in UiO-66_ava. The protonation is stabilized by the formation of an H bonding network between the amines. The 3rd protonation was calculated only for the systems in which the 2nd protonation was negative or slightly positive. Energy in kcal·mol^{-1}. Distances in Angstrom.

System	Energy	H··N distance NH_3^+··NH_2-a	H··N distance NH_3^+··NH_2-b
UiO-66_ava	0	2.11	3.84
UiO-66_ava_HIN	-6.98	1.65	1.70
UiO-66_ava_HIN_2H	24.56	-	1.37
UiO-66_ava_HIN_3H	-	-	-
UiO-66_ava_HIN_3	-6.88	1.67	1.70
UiO-66_ava_HIN_3_2H	3.92	-	1.51
UiO-66_ava_HIN_3_3H	33.88	-	-
UiO-66_ava_HOUT	-7.6	1.70	1.65
UiO-66_ava_HOUT_2H	-0.86	-	1.41
UiO-66_ava_HOUT_3H	21.27	-	-
UiO-66_ava_HOUT_2	-6.93	1.65	1.70
UiO-66_ava_HOUT_2_2H	20.66		1.43
UiO-66_ava_HOUT_2_2H	-	-	-
UiO-66_ava_HOUT_3	-19.69	1.64	1.69
UiO-66_ava_HOUT_3_2H	13.32	-	1.52
UiO-66_ava_HOUT_3_3H	35.31	-	-

6. CO₂ activation on the protonated systems

Table S7. Binding energy (BE) and geometrical parameters for the adsorption of CO_2 in protonated UiO-66_ala. HIN indicates that the transfer is from an OH group of the same inorganic node where the amino acid is grafted, HOUT that the H is from another node. Energies in kcal·mol⁻¹; Bond distances in Angstrom; Angle in degree. CO_2 is considered activated when there is an elongation of the CO bond compared the calculated value for isolated CO_2 = 1.18 Ang. Calculated C-N distance for isolated carbamic acid = 1.37 Ang.

Structure	BE	N1··C	N2··C	N3··C	C-O1	C-O2	O1-C-O2	CO₂ act
UiO-66_ava_HIN	-98.23	3.12	1.53	3.3	1.27	1.23	131.67	Y
UiO-66_ava_HIN_2	-0.87	3.51	3.48	4.66	1.18	1.18	178.26	N
UiO-66_ava_HIN_3	-0.19	7.12	5.38	5.1	1.18	1.18	179.12	N
UiO-66_ava_HIN_4	-0.33	3.17	3.26	4.6	1.18	1.18	175.96	N
UiO-66_ava_HIN_5	-65.08	3.31	1.63	6.05	1.22	1.25	136.78	Y
UiO-66_ava_HIN_6	-105.27	3.16	1.5	3.39	1.27	1.23	131.27	Y
UiO-66_ava_HOUT	-156.97	3.13	1.43	3.06	1.28	1.26	126.73	Y
UiO-66_ava_HOUT_2	-2.16	3.67	4.86	4.17	1.18	1.17	178.43	N
UiO-66_ava_HOUT_3	-74.18	3.42	1.58	6.21	1.27	1.22	135.89	Y
UiO-66_ava_HOUT_4	-1.08	3.42	3.26	4.73	1.18	1.18	176.75	N
UiO-66_ava_HOUT_5	-67.04	3.24	1.62	5.76	1.22	1.26	136.56	Y
UiO-66_ava_HOUT_6	-108.7	3.14	1.51	3.46	1.23	1.27	131.06	Y
Average	-56.675							58%
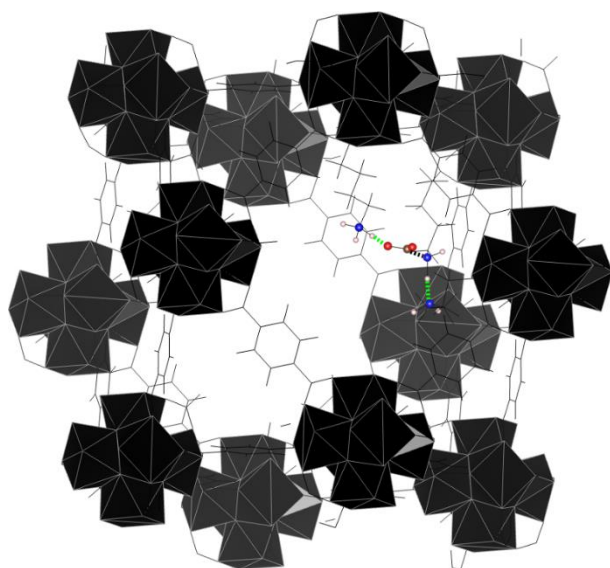
Figure S3. Snapshot showing the CO_2 adsorption for protonated UiO-66_ava (Table S9, UiO-66_ava_HIN_6). Atom colours: N = blue, C = brown, O = red, H beige. Hydrogen bond is highlighted with green dashed lines. N··C interaction is the black dashed line.

Table S8. Binding energies in kcal·mol^{-1} for the CO$_2$ activated system with different amount of defect functionalisation for the active configurations of protonated UiO-66_ava.

% of functionalised sites in the pore	75	42	8
UiO-66_ava_HIN	-98.23	-61.85	-5.91
UiO-66_ava_HIN_5	-65.08	-65.09	-6.93
UiO-66_ava_HIN_6	-105.27	-64.61	-5.67
UiO-66_ava_HOUT	-156.97	-55.57	-6.38
UiO-66_ava_HOUT_3	-74.18	-74.17	-6.82
UiO-66_ava_HOUT_5	-67.04	-67.24	-7.22
UiO-66_ava_HOUT_6	-108.7	-70.38	-5.28

7. Carbamic acid formation in protonated systems.

Table S10 Hydrogen transfer relative energies for the active unprotonated UiO-66_gaba and UiO-66_ava. Values in kcal·mol^{-1}.

UiO-66_gaba configurations	Relative Energy
UiO-66_gaba_4	0
UiO-66_gaba_4_H-tran	-7.69
UiO-66_gaba_5	0
UiO-66_gaba_5_H-tran	-8.2
UiO-66_gaba_6	0
UiO-66_gaba_6_H-tran	-7.1
UiO-66_gaba_7	0
UiO-66_gaba_7_H-tran	-8.72
UiO-66_ava configurations	**Relative Energy**
UiO-66_ava_2	0
UiO-66_ava_2_H-tran	-1.22
UiO-66_ava_b	0
UiO-66_ava_b_H-tran	-3.89

Table S11 Hydrogen transfer relative energies for the active protonated UiO-66_ava. Values in kcal·mol^{-1}.

Configuration	Relative Energy
UiO-66_ava_2	0
UiO-66_ava_2_H-tran	-2.39
UiO-66_ava_HIN_6	0
UiO-66_ava_HIN_6_H-tran	-8.08
UiO-66_ava_6	0
UiO-66_ava_6_H-tran	-8.24

8. Proton transfer back to the metal node.

Table S 9. Relative energies for the active protonated UiO-66_ava for the hydrogen transfer to reform the hydroxyl group. Values in kcal·mol^{-1}.

System	Relative Energy
UiO-66_ava_HIN	0
UiO-66_ava_HIN_1_H-back	-20.15
UiO-66_ava_HIN_5	0
UiO-66_ava_HIN_5_H-back	-43.7
UiO-66_ava_HIN_6	0
UiO-66_ava_HIN_6_H-back	-23.13
UiO-66_ava_HOUT	0
UiO-66_ava_HOUT_H-back	-30.6
UiO-66_ava_HOUT_5	0
UiO-66_ava_HOUT_5_H-back	-34.16
UiO-66_ava_HOUT_6	0
UiO-66_ava_HOUT_6_H-back	-29.25

Table S 10. Relative energies for the active protonated UiO-66_ava with only two amines for the hydrogen transfer to the hydroxyl group. Values in kcal·mol^{-1}.

System	Relative Energy
UiO-66_ava_HIN_NonFun	0
UiO-66_ava_HIN_NonFun_H-back	-30.6
UiO-66_ava_HIN_5_NonFun	0
UiO-66_ava_HIN_5_NonFun_H-back	-42.96
UiO-66_ava_HIN_6_NonFun	0
UiO-66_ava_HIN_6_NonFun_H-back	-43.12
UiO-66_ava_HOUT_3_NonFun	0
UiO-66_ava_HOUT_3_NonFun_H-back	-42.24
UiO-66_ava_HOUT_5_NonFun	0
UiO-66_ava_HOUT_5_NonFun_H-back	-32.57
UiO-66_ava_HOUT_6_NonFun	0
UiO-66_ava_HOUT_6_NonFun_H-back	-43.21