The Effect of Atomic Point Charges on Adsorption Isotherms of CO_2 and Water in Metal Organic Frameworks – Supporting Information

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Additional details about the calculations of point charge sets used in the main paper

Table S1 – Point charge calculation details for cluster methods.

Charge Set	Charge Method	Functional	Basis set metals	Basis Set non-metals	Cluster details	Saturation	DOI
Yang and Zhong (2006)	CHELPG	B3LYP	LAND2DZ	6-31+G*	1 cluster centred on linker	methyl	10.1021/jp062723w
Yazaydin et al. (2009) (1)	CHELPG	B3LYP	6-31+G*	6-31+G*	1 cluster centred on linker	methyl	10.1021/ja9057234
Sagara et al. (2004)	CHELPG	PBE	6-31+G*	6-31+G*	1 cluster centred on linker	methyl	10.1063/1.1809608
Dubbeldam et al. (2007)	CHELPG	PBE	6-31+G*	6-31+G*	1 cluster centred on linker	methyl	10.1002/anie.200700218
Mu et al. (2010)	CHELPG	B3LYP	LAND2DZ	6-31+G*	1 cluster centred on linker	methyl	10.1016/j.micromeso.2009.10.015
Fischer et al. (2009)	MSK	PBE	DNP	DNP	1 cluster centred on linker	n/a	10.1002/cphc.200900459
Babarao et al. (2007)	RESP	B3LYP	6-31G*	6-31G*	1 large cluster with 4 linkers	hydrogen	10.1021/la062289p
Belof et al. (2009) (1)	MSK	HF	SBKJC	SBKJC	1 cluster centred on metal	hydrogen	10.1021/jp901988e
Belof et al. (2009) (2)	MSK	HF	6-31G*	6-31G*	1 cluster centred on metal	hydrogen	10.1021/jp901988e
Tafipolsky et al. (2007)	MSK	B3LYP	Stuttgart ECP	6-31G**	2 clusters, centred on metal and linker	hydrogen	10.1002/jcc.20648
Finsy et al. (2009)	CHELPG	n/a	n/a	n/a	n/a	n/a	10.1039/b822247a
Yang et al. (2011)	CHELPG	PBE	LAND2DZ	6-31+G*	1 cluster centred on metal-ligand bond	methyl	10.1039/c1cc13543k
Liu et al. (2009) (1)	CHELPG	B3LYP	6-311++G**	6-311++G**	1 cluster centred on metal (30 atoms)	methyl	10.1080/08927020802398926
Liu et al. (2009) (2)	CHELPG	B3LYP	6-311++G**	6-311++G**	1 cluster centred on metal (50 atoms)	methyl	10.1080/08927020802398926
Yazaydin et al. (2009) (2)	CHELPG	PBE	6-31+G*	6-31+G*	1 cluster centred on linker	methyl	10.1021/cm900049x
Babarao et al. (2009)	MSK	B3LYP	LAND2DZ	6-31G*	1 cluster centred on linker	methyl	10.1021/la803074g
Haldoupis et al. (2015)	LoProp	MP2	ANO-RCC	ANO-RCC	several clusters	hydrogen	10.1021/acs.jpcc.5b03700
Pham (CHELPG)	CHELPG	HF	LAND2DZ	6-31G*	several clusters	variable	10.1021/jp402764s
CHELPG (Clusters)	CHELPG	M06L	6-31G**	6-31G**	several clusters	hydrogen	This work
DDEC (Clusters)	DDEC	M06L	6-31G**	6-31G**	several clusters	hydrogen	This work

Table S2 – Point charge calculation details for periodic methods.

Charge Set	Charge Method	Functional	Code	Basis Set		Brillouin Zone Sampling		DOI
				Core Electrons	Valence Electrons[1]	Grid	k-points	
Manz and Sholl (2010)	DDEC	PW91	VASP	PAW	PW, 400 eV	Γ-point	1	10.1021/ct100125x
Manz and Sholl (2010)	DDEC Uncompensated	PW91	VASP	PAW	PW, 400 ev	Γ-point	1	10.1021/ct100125x
Strathclyde	DDEC	PBE	CP2K	GTH	GPW, 6800 eV, DZVP	Not used	Not used	This work
Campana et al. (2009)	REPEAT	PBE	CPMD	GTH	PW, 1088 eV	Γ-point	n/a	10.1021/ct9003405
Manz and Sholl (2010)	Hirshfeld	PW91	VASP	PAW	PW, 400 eV	Γ-point	1	10.1021/ct100125x
Manz and Sholl (2010)	ISA	PW91	VASP	PAW	PW, 400 eV	Γ-point	1	10.1021/ct100125x
Manz and Sholl (2010)	Bader	PW91	VASP	PAW	PW, 400 eV	Γ-point	1	10.1021/ct100125x
Nazarian et al. (2016)	DDEC	PBE	VASP	n/a	n/a	variable[2]	1000 points per atom	10.1021/acs.chemmater.5b03836
Wilmer et al. (2012)	REPEAT	PW91	VASP	PAW	PW, 520 eV	Monkhorst-Pack	variable [2]	10.1021/jz3008485
Ramsahye et al. (2007)	Mulliken	PW91	DMol	all-electron	G, DNP	n/a	n/a	10.1007/s10450-007-9025-5
Ghosh et al. (2014)	REPEAT	PW91	VASP	PAW	PW, 550 eV	Monkhorst-Pack	n/a	10.1039/c4cc04945d
Zang et al. (2013)	DDEC	PBE-D2	VASP	PAW	PW, 500 eV	Γ-point	1	10.1021/jp310497u
Haldoupis et al. (2015)	DDEC	PBE+U	VASP	n/a	PW, 520 eV	Γ-point	2×2×2 grid	10.1021/acs.jpcc.5b03700
Mercado et al. (2016)	REPEAT	PBE	VASP	PAW	PW, 1000 eV	Γ-point	single k point	10.1021/acs.jpcc.6b03393
DDEC CP2K	DDEC	PBE	CP2K	GTH	GPW, 6800 eV, DZVP	Not used	Not used	This work
REPEAT VASP	REPEAT	PBE	VASP	PAW	PW, 415 eV	Γ-point	1×1×2	This work
DDEC VASP	DDEC	PBE	VASP	PAW	PW, 415 eV	Γ-point	1×1×2	This work

[1]For calculations with Plane Waves (PW), the energy cut-off in units of eV is given; for calculations with Gaussians (G), the basis set is given; for calculations with Gaussian and Plane Waves (GPW), both the cut-off and the Gaussian basis set is given

[2] Different sampling schemes were used for different MOFs, check original papers

Determination of cluster-based charges for Sifsix-2-Cu-I

DFT calculations were carried out on several clusters carved from the SIFSIX periodic cell, as shown in Figures S1-S4. Whenever necessary, terminal atoms were capped with hydrogen atoms, as shown in the figures. Calculations were done using Gaussian 09 (Frisch et al. 2009), with the M06-L functional and a 6-31G** basis set. All the atomic positions were frozen at their crystallographic sites with the exception of those corresponding to the hydrogen atoms, which were fully relaxed in the calculations.

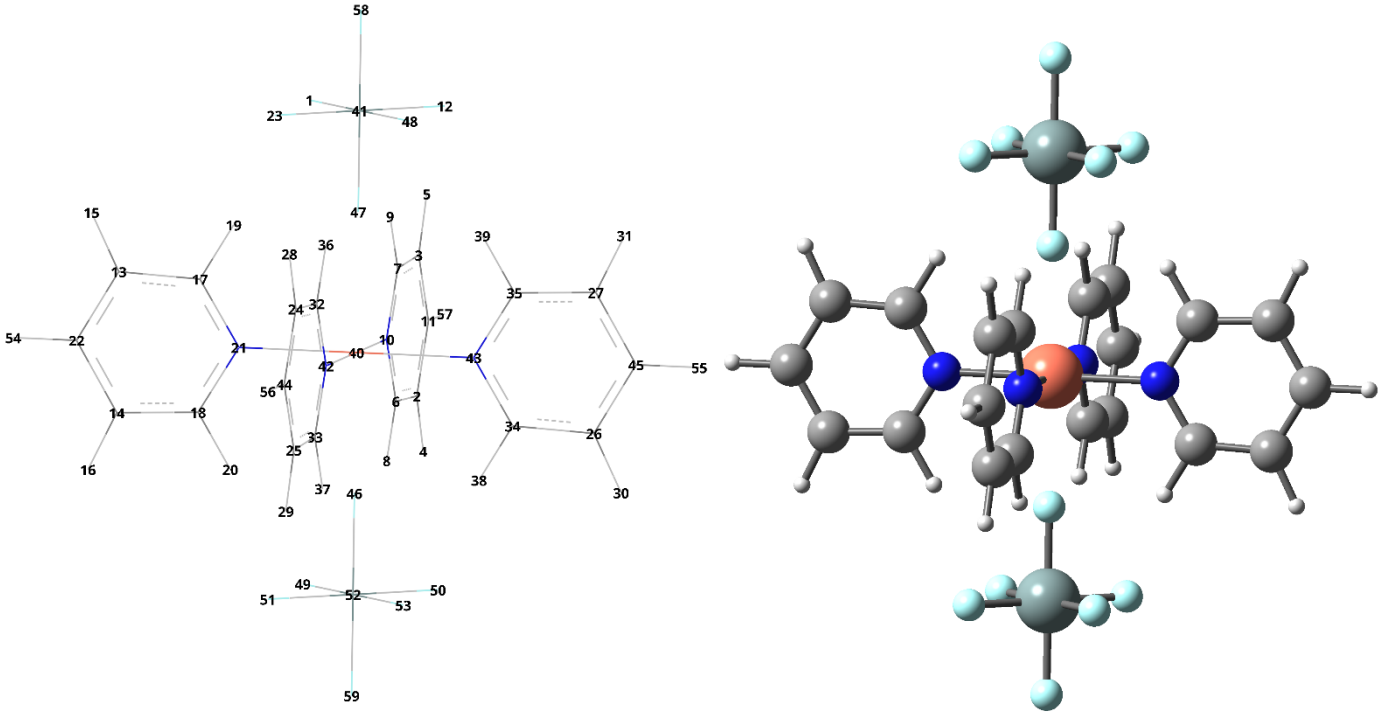

Figure S1 – Structure of cluster 1 used to calculate charges on the SIFSIX MOF (left – wireframe view; right – ball-and-stick view). Atom labels corresponding to the notation used in Tables S7 and S8 are shown in the wireframe view. Color code for the ball-and-stick view is: Carbon – grey; Hydrogen – white; Copper – orange; Silicon – green; Fluorine – teal.

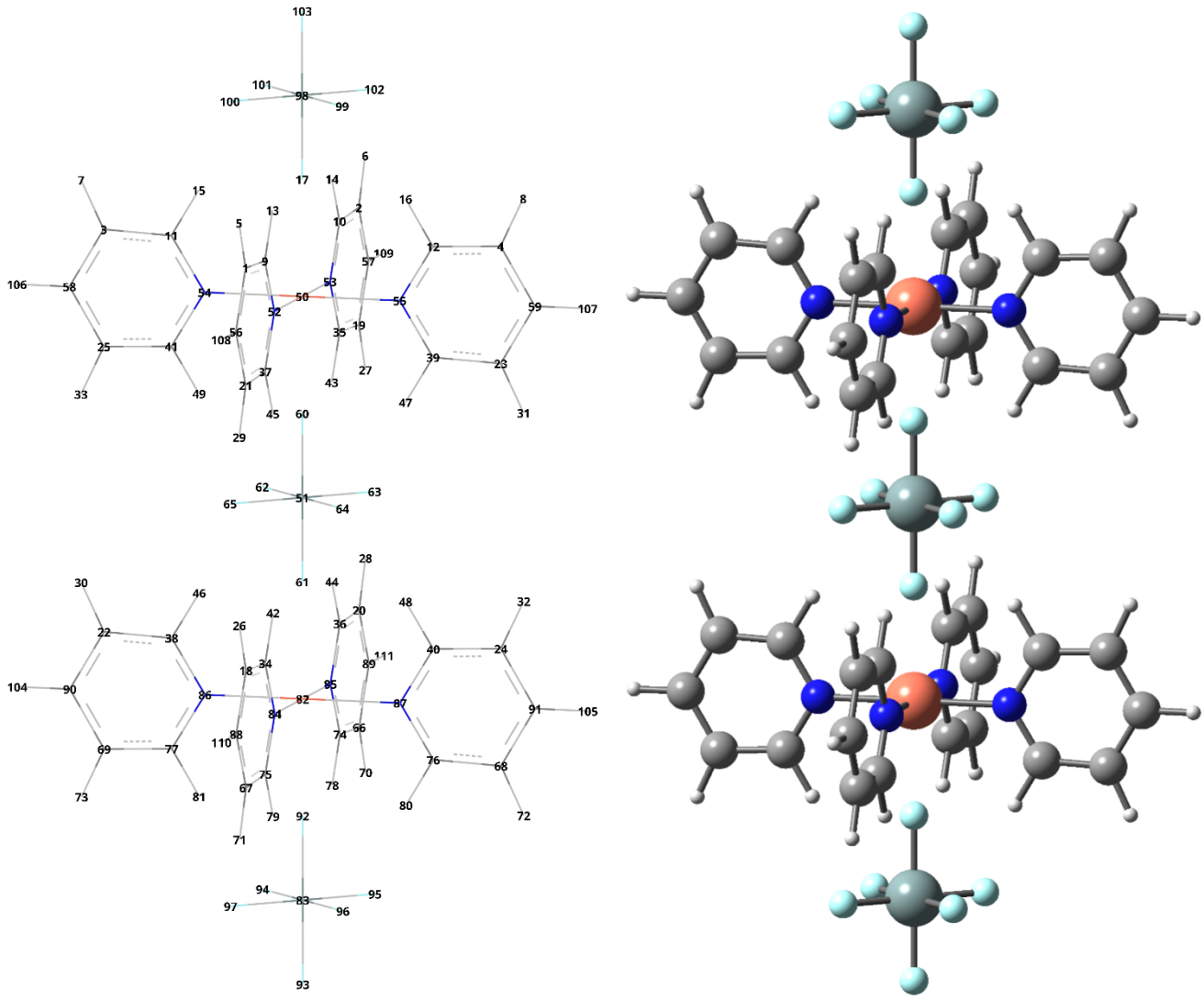

Figure S2 – Structure of cluster 2 used to calculate charges on the SIFSIX MOF (left – wireframe view; right – ball-and-stick view). Atom labels corresponding to the notation used in Tables S7 and S8 are shown in the wireframe view. Color code for the ball-and-stick view is: Carbon – grey; Hydrogen – white; Copper – orange; Silicon – green; Fluorine – teal.

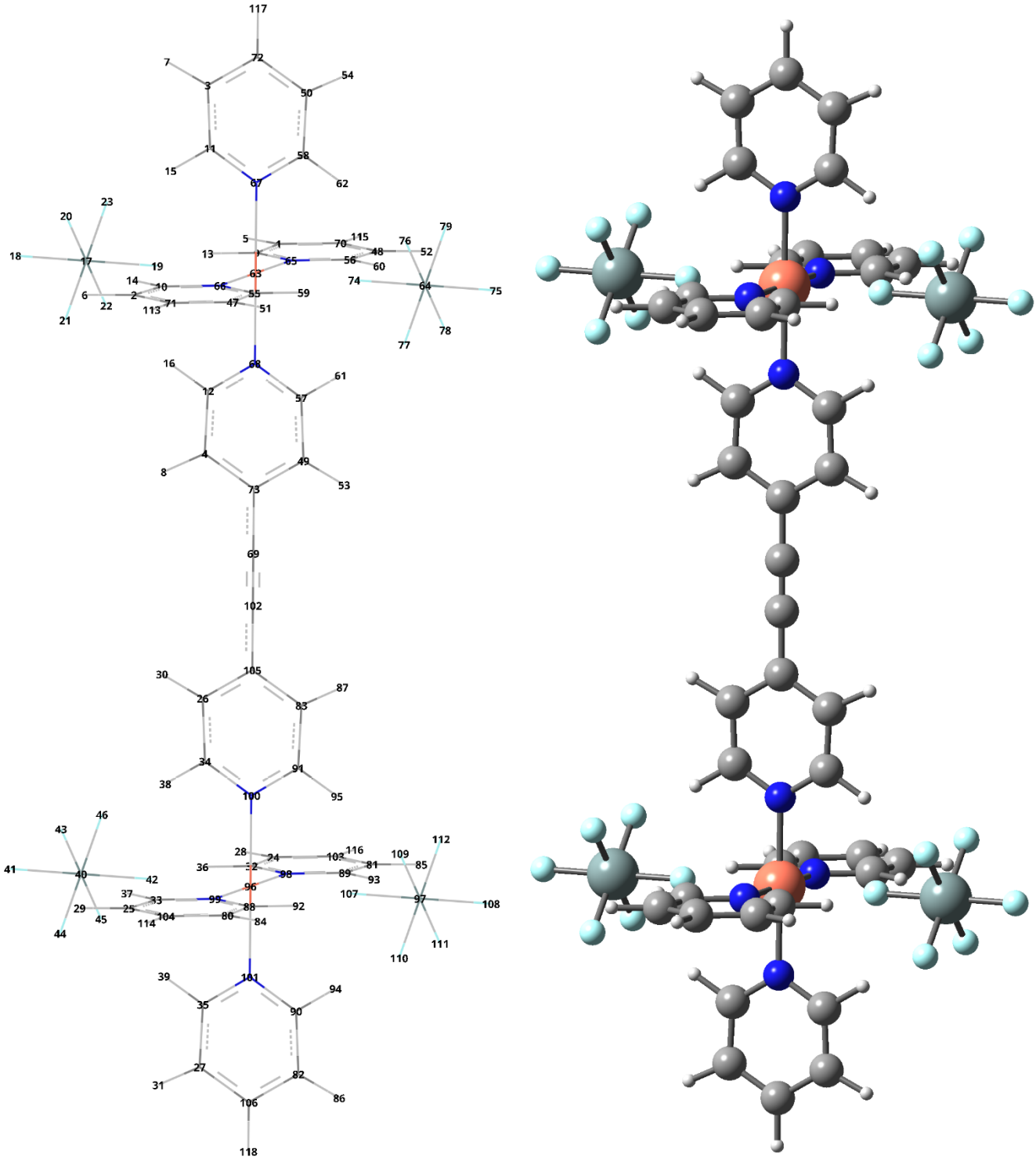

Figure S3 – Structure of cluster 3 used to calculate charges on the SIFSIX MOF (left – wireframe view; right – ball-and-stick view). Atom labels corresponding to the notation used in Tables S7 and S8 are shown in the wireframe view. Color code for the ball-and-stick view is: Carbon – grey; Hydrogen – white; Copper – orange; Silicon – green; Fluorine – teal.

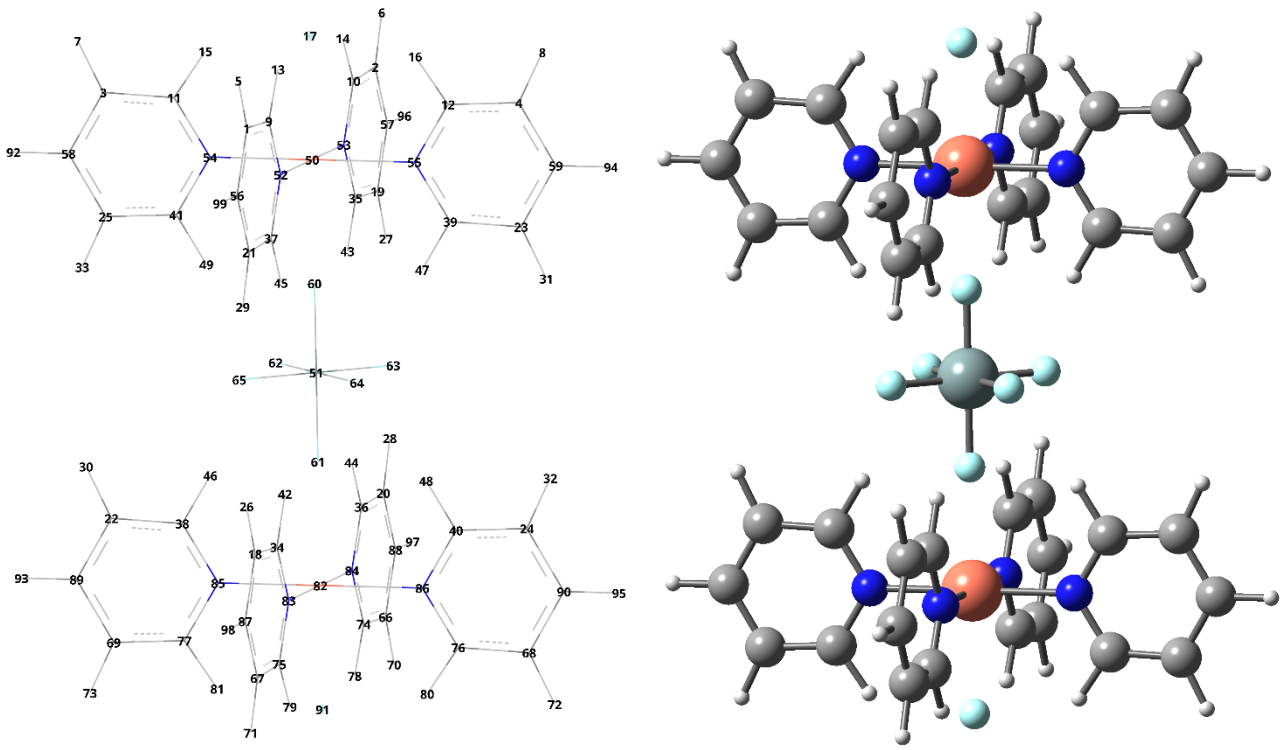

Figure S4 – Structure of cluster 4 used to calculate charges on the SIFSIX MOF (left – wireframe view; right – ball-and-stick view). Atom labels corresponding to the notation used in Tables S7 and S8 are shown in the wireframe view. Color code for the ball-and-stick view is: Carbon – grey; Hydrogen – white; Copper – orange; Silicon – green; Fluorine – teal.

Point charges were calculated on each cluster using both CHELPG and DDEC methods, and the values are reported in Tables S7 and S8. In an attempt to emulate the procedure of Pham et al. (2013), we have selected the atoms of each type that were surrounded by a chemical environment that was most representative of the fully periodic MOF framework (shown in bold in Tables S7 and S8), and calculated the average charge for each atom type. This led to a framework with non-zero overall charge, therefore the remaining charge was uniformly distributed over all atoms, leading to the final charge sets shown in Table 6 of the main paper.

Table S3 – Point charges for the SIFSIX MOF obtained on the clusters shown in Figures S1-S4 using the DDEC method. Atom labels correspond to the notation used in the figures. Charges shown in bold were used to calculate the average framework charges to use in the GCMC simulations.

cluster 1			cluster 2			cluster 3			cluster 4		
label	atom	charge	label	atom	Charge	label	atom	charge	label	atom	charge
1	F	-0.501	1	C	-0.10857	1	C	-0.10162	1	C	-0.13998
2	C	-0.11832	2	C	-0.10937	2	C	-0.10198	2	C	-0.14052
3	C	-0.11832	3	C	-0.10951	3	C	-0.09839	3	C	-0.13989
4	H	0.121666	4	C	-0.10777	**4**	**C**	**-0.14438**	4	C	-0.14039
5	H	0.121666	5	H	0.132769	5	H	0.139104	5	H	0.105406
6	C	0.112357	6	H	0.132558	6	H	0.139034	6	H	0.105746
7	C	0.112357	7	H	0.132894	7	H	0.137233	7	H	0.105496
8	H	0.09155	8	H	0.132444	**8**	**H**	**0.14927**	8	H	0.10543
9	H	0.09155	9	C	0.115866	9	C	0.107106	9	C	0.102308
10	N	-0.27712	10	C	0.118986	10	C	0.111225	10	C	0.102618
11	C	-0.01916	11	C	0.116076	11	C	0.112668	11	C	0.102338
12	F	-0.50189	12	C	0.120272	**12**	**C**	**0.120751**	12	C	0.103164

13	C	-0.10187	13	H	0.123095	13	H	0.126142	13	H	0.095579
14	C	-0.10187	14	H	0.120089	14	H	0.118527	14	H	0.095594
15	H	0.123855	15	H	0.123645	15	H	0.118526	15	H	0.095671
16	H	0.123855	16	H	0.115588	**16**	**H**	**0.120288**	16	H	0.095653
17	C	0.129391	**17**	**F**	**-0.63514**	17	Si	1.978334	17	F	-0.72518
18	C	0.129391	18	C	-0.1222	18	F	-0.46949	18	C	-0.13319
19	H	0.094181	19	C	-0.12287	19	F	-0.64045	19	C	-0.13155
20	H	0.094181	20	C	-0.12182	20	F	-0.54267	20	C	-0.13199
21	N	-0.27449	21	C	-0.12192	21	F	-0.54325	21	C	-0.13315
22	C	-0.02395	22	C	-0.12266	22	F	-0.55088	22	C	-0.13298
23	F	-0.50189	23	C	-0.12415	23	F	-0.54887	23	C	-0.13188
24	C	-0.11832	24	C	-0.12186	24	C	-0.10178	24	C	-0.13184
25	C	-0.11832	25	C	-0.12274	25	C	-0.10157	25	C	-0.13336
26	C	-0.10187	26	H	0.118945	**26**	**C**	**-0.14446**	26	H	0.113462
27	C	-0.10187	27	H	0.118647	27	C	-0.0986	27	H	0.11204
28	H	0.121666	28	H	0.119478	28	H	0.139008	28	H	0.112078
29	H	0.121666	29	H	0.119058	29	H	0.139131	29	H	0.113482
30	H	0.123855	30	H	0.119299	**30**	**H**	**0.149147**	30	H	0.113445
31	H	0.123855	31	H	0.120959	31	H	0.137406	31	H	0.112136
32	C	0.112357	32	H	0.119116	32	C	0.107458	32	H	0.112126
33	C	0.112357	33	H	0.119078	33	C	0.111975	33	H	0.113444
34	C	0.129391	34	C	0.110781	**34**	**C**	**0.123054**	34	C	0.116141
35	C	0.129391	35	C	0.111409	35	C	0.112774	35	C	0.115936
36	H	0.09155	36	C	0.111795	36	H	0.12545	36	C	0.111511
37	H	0.09155	37	C	0.111208	37	H	0.119845	37	C	0.115912
38	H	0.094181	38	C	0.111275	**38**	**H**	**0.120238**	38	C	0.115102
39	H	0.094181	39	C	0.110891	39	H	0.119227	39	C	0.116729
40	Cu	0.919084	40	C	0.1112	40	Si	1.980905	40	C	0.116734
41	Si	1.928124	41	C	0.111732	41	F	-0.4753	41	C	0.111768
42	N	-0.27712	42	H	0.107043	42	F	-0.64018	42	H	0.1039
43	N	-0.27449	43	H	0.106614	43	F	-0.56233	43	H	0.103262
44	C	-0.01916	44	H	0.107085	44	F	-0.54345	44	H	0.110384
45	C	-0.02395	45	H	0.107017	45	F	-0.54935	45	H	0.103931
46	F	-0.56966	46	H	0.107173	46	F	-0.53206	46	H	0.103715
47	F	-0.56966	47	H	0.106853	47	C	-0.10179	47	H	0.104083
48	F	-0.501	48	H	0.107148	48	C	-0.10155	48	H	0.104079
49	F	-0.501	49	H	0.106705	**49**	**C**	**-0.14429**	49	H	0.10998
50	F	-0.50189	50	Cu	0.947216	50	C	-0.09851	50	Cu	0.85961
51	F	-0.50189	**51**	**Si**	**2.031855**	51	H	0.138861	**51**	**Si**	**2.027532**
52	Si	1.928124	52	N	-0.23855	52	H	0.139092	52	N	-0.24403
53	F	-0.501	53	N	-0.24165	**53**	**H**	**0.149136**	53	N	-0.24454
54	H	0.104079	54	N	-0.24048	54	H	0.137264	54	N	-0.24491
55	H	0.104079	55	N	-0.23935	55	C	0.11248	55	N	-0.2462
56	H	0.100758	56	C	-0.01397	56	C	0.107329	56	C	-0.03049
57	H	0.100758	57	C	-0.01483	**57**	**C**	**0.120763**	57	C	-0.03083
58	F	-0.32797	58	C	-0.01453	58	C	0.112952	58	C	-0.03108
59	F	-0.32797	59	C	-0.01459	59	H	0.117609	59	C	-0.03017
			60	**F**	**-0.62891**	60	H	0.127066	**60**	**F**	**-0.62867**
			61	**F**	**-0.62914**	**61**	**H**	**0.120098**	**61**	**F**	**-0.629**

			62	**F**	**-0.61769**	62	H	0.119372	**62**	**F**	**-0.61067**
			63	**F**	**-0.61752**	**63**	**Cu**	**0.984735**	**63**	**F**	**-0.6226**
			64	**F**	**-0.61716**	64	Si	1.980385	**64**	**F**	**-0.6206**
			65	**F**	**-0.61759**	65	N	-0.22512	**65**	**F**	**-0.6224**
			66	C	-0.10871	66	N	-0.22464	66	C	-0.14047
			67	C	-0.10813	67	N	-0.22404	67	C	-0.14
			68	C	-0.10807	**68**	**N**	**-0.22725**	68	C	-0.14042
			69	C	-0.10865	**69**	**C**	**-0.07841**	69	C	-0.13988
			70	H	0.132916	70	C	-0.00732	70	H	0.105743
			71	H	0.132485	71	C	-0.00648	71	H	0.105409
			72	H	0.132622	72	C	-0.0085	72	H	0.105428
			73	H	0.132848	**73**	**C**	**0.199724**	73	H	0.105488
			74	C	0.116395	74	F	-0.63847	74	C	0.102722
			75	C	0.120602	75	F	-0.46784	75	C	0.102298
			76	C	0.12042	76	F	-0.54087	76	C	0.103186
			77	C	0.120839	77	F	-0.54336	77	C	0.102372
			78	H	0.123136	78	F	-0.54898	78	H	0.095623
			79	H	0.115715	79	F	-0.56036	79	H	0.095581
			80	H	0.115658	80	C	-0.10182	80	H	0.095639
			81	H	0.115574	81	C	-0.10134	81	H	0.095654
			82	Cu	0.95044	82	C	-0.09858	82	Cu	0.859652
			83	Si	1.998066	**83**	**C**	**-0.14455**	83	N	-0.24405
			84	N	-0.24042	84	H	0.139007	84	N	-0.24511
			85	N	-0.23852	85	H	0.138844	85	N	-0.24445
			86	N	-0.23879	86	H	0.137421	86	N	-0.24615
			87	N	-0.23899	**87**	**H**	**0.148919**	87	C	-0.0305
			88	C	-0.01477	88	C	0.109493	88	C	-0.03074
			89	C	-0.01429	89	C	0.112342	89	C	-0.03109
			90	C	-0.01391	90	C	0.112568	90	C	-0.03018
			91	C	-0.01446	**91**	**C**	**0.1224**	91	F	-0.72522
			92	**F**	**-0.63255**	92	H	0.122439	92	H	0.091172
			93	F	-0.46496	93	H	0.117655	93	H	0.09117
			94	F	-0.57701	94	H	0.1184	94	H	0.090872
			95	F	-0.57551	**95**	**H**	**0.11978**	95	H	0.090867
			96	F	-0.5752	**96**	**Cu**	**0.984842**	96	H	0.091082
			97	F	-0.57388	97	Si	1.978731	97	H	0.091094
			98	Si	1.996667	98	N	-0.22546	98	H	0.090873
			99	F	-0.57718	99	N	-0.2237	99	H	0.09088
			100	F	-0.57856	**100**	**N**	**-0.22991**			
			101	F	-0.57667	101	N	-0.22471			
			102	F	-0.57657	**102**	**C**	**-0.07584**			
			103	F	-0.46517	103	C	-0.00744			
			104	H	0.103633	104	C	-0.00711			
			105	H	0.103776	**105**	**C**	**0.198948**			
			106	H	0.10375	106	C	-0.00781			
			107	H	0.103416	107	F	-0.63918			
			108	H	0.103566	108	F	-0.47273			
			109	H	0.103498	109	F	-0.54998			
			110	H	0.103622	110	F	-0.54779			

			111	H	0.103984	111	F	-0.5424			
						112	F	-0.54214			
						113	H	0.114523			
						114	H	0.11441			
						115	H	0.114604			
						116	H	0.114796			
						117	H	0.115366			
						118	H	0.115153			

Table S4 – Point charges for the SIFSIX MOF obtained on the clusters shown in Figures S1-S4 using the CHELPG method. Atom labels correspond to the notation used in the figures. Charges shown in bold were used to calculate the average framework charges to use in the GCMC simulations.

cluster 1			cluster 2			cluster 3			cluster 4		
label	atom	charge	label	atom	charge	label	atom	charge	label	atom	charge
1	F	-0.37595	1	C	-0.22238	1	C	-0.1965	1	C	-0.22572
2	C	-0.20276	2	C	-0.22194	2	C	-0.19381	2	C	-0.22589
3	C	-0.20276	3	C	-0.22422	3	C	-0.20946	3	C	-0.22568
4	H	0.143968	4	C	-0.22365	**4**	**C**	**-0.30204**	4	C	-0.22544
5	H	0.143968	5	H	0.16573	5	H	0.166359	5	H	0.122268
6	C	0.212575	6	H	0.164916	6	H	0.165925	6	H	0.122286
7	C	0.212575	7	H	0.165237	7	H	0.168271	7	H	0.122233
8	H	-0.00393	8	H	0.165361	**8**	**H**	**0.188808**	8	H	0.1222
9	H	-0.00393	9	C	0.242215	9	C	0.242863	9	C	0.156073
10	N	-0.26024	10	C	0.245889	10	C	0.238467	10	C	0.156351
11	C	0.059031	11	C	0.257806	11	C	0.271539	11	C	0.156192
12	F	-0.37633	12	C	0.251577	**12**	**C**	**0.256479**	12	C	0.154192
13	C	-0.19336	13	H	0.002823	13	H	0.001198	13	H	0.04497
14	C	-0.19336	14	H	0.001397	14	H	0.009692	14	H	0.044886
15	H	0.145892	15	H	-0.00788	15	H	0.005259	15	H	0.044967
16	H	0.145892	16	H	-0.00489	**16**	**H**	**0.032156**	16	H	0.045711
17	C	0.27726	17	F	-0.17206	17	Si	1.316719	17	F	-0.55533
18	C	0.27726	18	C	-0.2546	18	F	-0.38	18	C	-0.25299
19	H	-0.0271	19	C	-0.25543	19	F	-0.37468	19	C	-0.25293
20	H	-0.0271	20	C	-0.25226	20	F	-0.40926	20	C	-0.25292
21	N	-0.32581	21	C	-0.2525	21	F	-0.41179	21	C	-0.253
22	C	0.050488	22	C	-0.25544	22	F	-0.41382	22	C	-0.25294
23	F	-0.37633	23	C	-0.25375	23	F	-0.4102	23	C	-0.25228
24	C	-0.20276	24	C	-0.25364	24	C	-0.19606	24	C	-0.25228
25	C	-0.20276	25	C	-0.25618	25	C	-0.19457	25	C	-0.25295
26	C	-0.19336	26	H	0.158466	**26**	**C**	**-0.30302**	26	H	0.143723
27	C	-0.19336	27	H	0.158422	27	C	-0.20919	27	H	0.143717
28	H	0.143968	28	H	0.15827	28	H	0.16654	28	H	0.143719
29	H	0.143968	29	H	0.158049	29	H	0.166107	29	H	0.143722
30	H	0.145892	30	H	0.158961	**30**	**H**	**0.188866**	30	H	0.143711
31	H	0.145892	31	H	0.157967	31	H	0.168026	31	H	0.14338
32	C	0.212575	32	H	0.158253	32	C	0.237398	32	H	0.143382
33	C	0.212575	33	H	0.158817	33	C	0.236852	33	H	0.14371
34	C	0.27726	34	C	0.3104	**34**	**C**	**0.26251**	34	C	0.282897
35	C	0.27726	35	C	0.310985	35	C	0.272198	35	C	0.28283

36	H	-0.00393	36	C	0.306597	36	H	0.011228	36	C	0.282822
37	H	-0.00393	37	C	0.306012	37	H	0.005886	37	C	0.282901
38	H	-0.0271	38	C	0.31169	**38**	**H**	**0.027149**	38	C	0.28321
39	H	-0.0271	39	C	0.308484	39	H	0.005963	39	C	0.281947
40	Cu	0.647588	40	C	0.30947	40	Si	1.321001	40	C	0.28194
41	Si	1.25335	41	C	0.312887	41	F	-0.38538	41	C	0.283214
42	N	-0.26024	42	H	-0.12205	42	F	-0.37928	42	H	-0.09297
43	N	-0.32581	43	H	-0.12289	43	F	-0.42758	43	H	-0.09274
44	C	0.059031	44	H	-0.12024	44	F	-0.39645	44	H	-0.09277
45	C	0.050488	45	H	-0.12115	45	F	-0.4191	45	H	-0.09295
46	F	-0.23454	46	H	-0.1216	46	F	-0.39975	46	H	-0.09292
47	F	-0.23454	47	H	-0.12145	47	C	-0.19288	47	H	-0.09263
48	F	-0.37595	48	H	-0.12108	48	C	-0.19667	48	H	-0.09265
49	F	-0.37595	49	H	-0.12288	**49**	**C**	**-0.30232**	49	H	-0.0929
50	F	-0.37633	50	Cu	0.232363	50	C	-0.20939	50	Cu	0.317408
51	F	-0.37633	**51**	**Si**	**2.964441**	51	H	0.165521	**51**	**Si**	**2.872139**
52	Si	1.25335	52	N	-0.17497	52	H	0.166419	52	N	-0.1594
53	F	-0.37595	53	N	-0.18205	**53**	**H**	**0.188793**	53	N	-0.15966
54	H	0.087247	54	N	-0.18864	54	H	0.168233	54	N	-0.16006
55	H	0.087247	55	N	-0.1838	55	C	0.235707	55	N	-0.15867
56	H	0.081397	56	C	0.066738	56	C	0.242786	56	C	0.060252
57	H	0.081397	57	C	0.064502	**57**	**C**	**0.256503**	57	C	0.060296
58	F	-0.23525	58	C	0.06522	58	C	0.271076	58	C	0.060207
59	F	-0.23525	59	C	0.066588	59	H	0.012061	59	C	0.061354
			60	F	-0.30991	60	H	0.001523	**60**	**F**	**-0.4487**
			61	F	-0.31517	**61**	**H**	**0.032543**	**61**	**F**	**-0.44854**
			62	F	-0.69807	62	H	0.005823	**62**	**F**	**-0.6755**
			63	F	-0.69805	**63**	**Cu**	**0.800135**	**63**	**F**	**-0.67548**
			64	F	-0.69819	64	Si	1.318458	**64**	**F**	**-0.67542**
			65	F	-0.69782	65	N	-0.24248	**65**	**F**	**-0.67537**
			66	C	-0.2223	66	N	-0.24559	66	C	-0.22587
			67	C	-0.22085	67	N	-0.30037	67	C	-0.2257
			68	C	-0.22341	**68**	**N**	**-0.30073**	68	C	-0.22542
			69	C	-0.22415	**69**	**C**	**-0.13234**	69	C	-0.22566
			70	H	0.165798	70	C	0.062542	70	H	0.122284
			71	H	0.164902	71	C	0.061199	71	H	0.122265
			72	H	0.165419	72	C	0.072865	72	H	0.122197
			73	H	0.165448	**73**	**C**	**0.400466**	73	H	0.122231
			74	C	0.242771	74	F	-0.3762	74	C	0.156296
			75	C	0.241032	75	F	-0.38016	75	C	0.156017
			76	C	0.251102	76	F	-0.4097	76	C	0.154136
			77	C	0.257899	77	F	-0.4124	77	C	0.156138
			78	H	0.002768	78	F	-0.41409	78	H	0.04494
			79	H	0.004685	79	F	-0.41065	79	H	0.045024
			80	H	-0.00386	80	C	-0.19485	80	H	0.045766
			81	H	-0.00819	81	C	-0.19458	81	H	0.045016
			82	Cu	0.242943	82	C	-0.20976	82	Cu	0.317151
			83	Si	1.334378	**83**	**C**	**-0.30219**	83	N	-0.15933
			84	N	-0.18083	84	H	0.165826	84	N	-0.15958

			85	N	-0.17666	85	H	0.165777	85	N	-0.15998
			86	N	-0.1879	86	H	0.168188	86	N	-0.1586
			87	N	-0.185	**87**	**H**	**0.188619**	87	C	0.06024
			88	C	0.065049	88	C	0.240256	88	C	0.060285
			89	C	0.066989	89	C	0.23755	89	C	0.060194
			90	C	0.065365	90	C	0.272959	90	C	0.061344
			91	C	0.06684	**91**	**C**	**0.256551**	91	F	-0.5554
			92	F	-0.17525	92	H	0.002058	92	H	0.071278
			93	F	-0.36914	93	H	0.010431	93	H	0.071279
			94	F	-0.45667	94	H	0.005387	94	H	0.070639
			95	F	-0.45432	**95**	**H**	**0.03258**	95	H	0.070639
			96	F	-0.45534	**96**	**Cu**	**0.801621**	96	H	0.071256
			97	F	-0.45219	97	Si	1.31679	97	H	0.071256
			98	Si	1.333462	98	N	-0.24405	98	H	0.071273
			99	F	-0.45696	99	N	-0.23808	99	H	0.071273
			100	F	-0.45566	**100**	**N**	**-0.30344**			
			101	F	-0.45481	101	N	-0.30367			
			102	F	-0.45361	**102**	**C**	**-0.13093**			
			103	F	-0.37337	103	C	0.063275			
			104	H	0.090377	104	C	0.061308			
			105	H	0.089513	**105**	**C**	**0.39968**			
			106	H	0.090176	106	C	0.072882			
			107	H	0.089345	107	F	-0.37655			
			108	H	0.089288	108	F	-0.38003			
			109	H	0.089852	109	F	-0.41355			
			110	H	0.089904	110	F	-0.41024			
			111	H	0.08946	111	F	-0.40902			
						112	F	-0.41186			
						113	H	0.100605			
						114	H	0.100818			
						115	H	0.100723			
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						117	H	0.100253			
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Additional figures

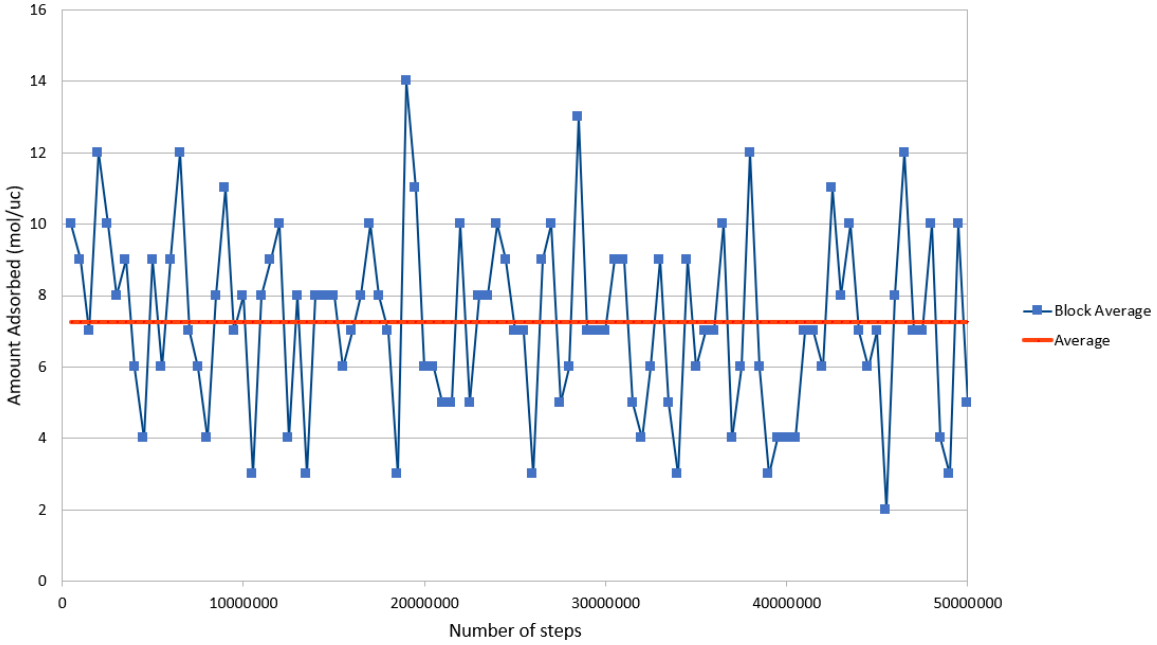

Figure S5 – Plot showing convergence of CO_2adsorbed amountin IRMOF-1 at 298K and 100 kPa compared with overall average. Only data beyond 20×10^6 steps was used for sampling.

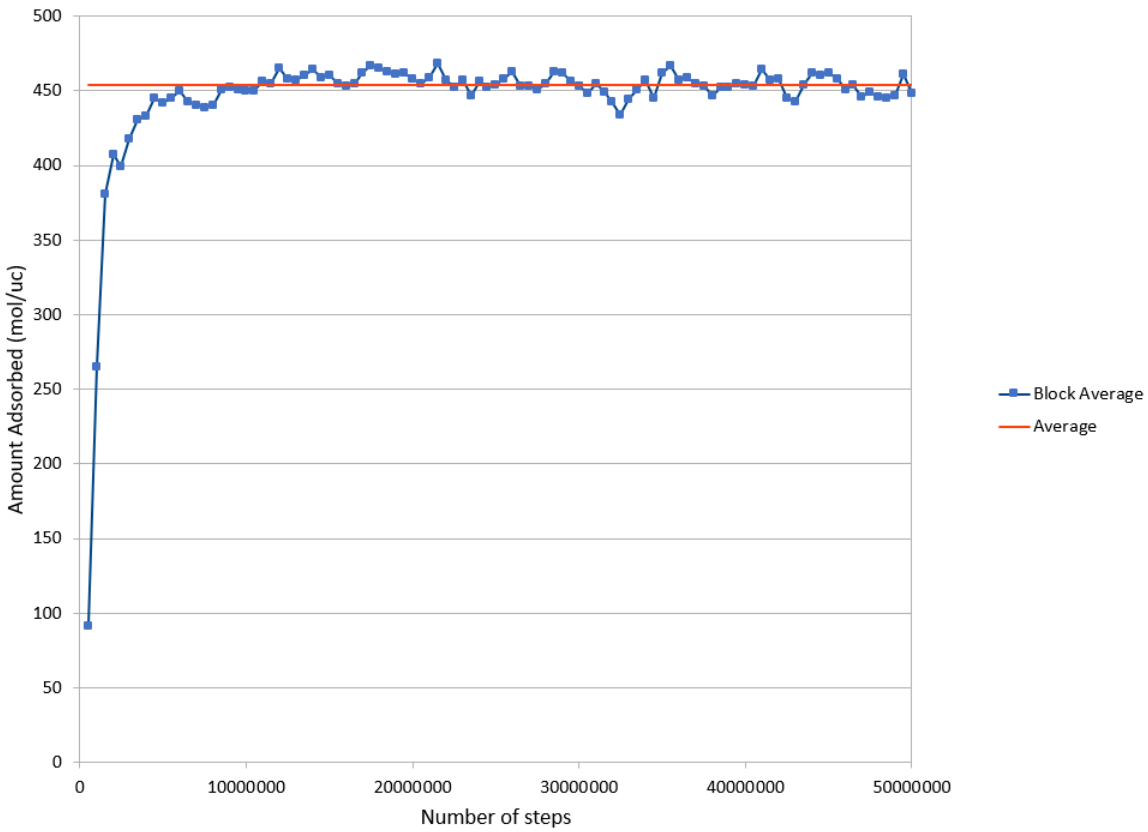

Figure S6 – Plot showing convergence of H_2O adsorbed amount in IRMOF-1 at 298K and 300 kPa compared with overall average. Only data beyond 20×10^6 steps was used for sampling.

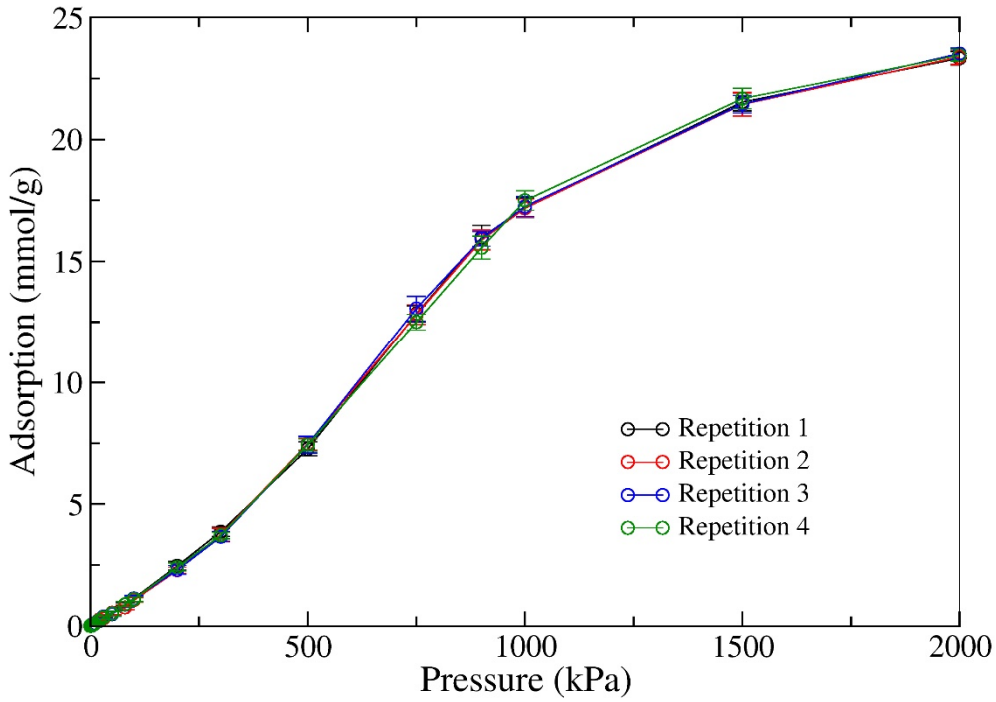

Figure S7 – Plot showing adsorption simulation repetitions of CO_2in IRMOF-1 at 298K using different random seeds. All repetitions are within statistical error of each other.

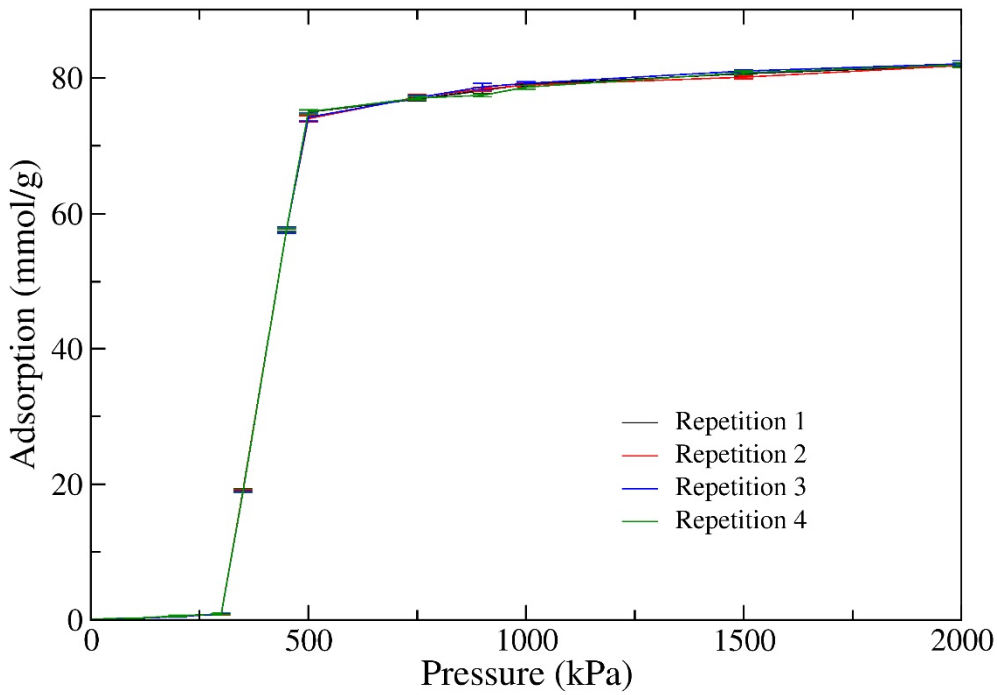

Figure S8 – Plot showing adsorption simulation repetitions of H_2Oin IRMOF-1 at 298K using different random seeds. All repetitions are within statistical error of each other.

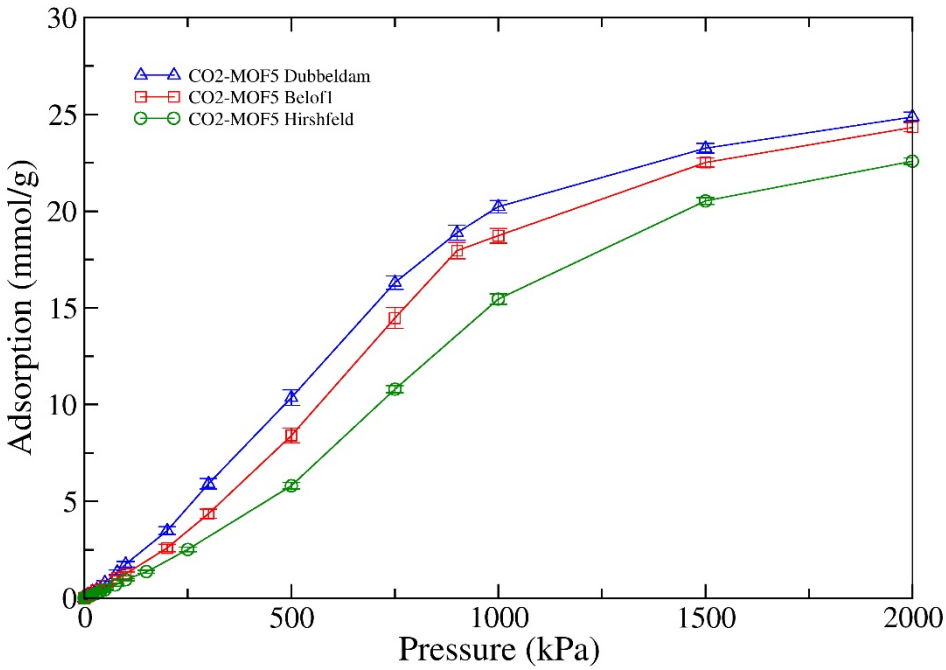

Figure S9 – Plot showing adsorption isotherms of CO_2 in IRMOF-1 at 298K with corresponding error bars. For the vast majority of simulations, the error bars are of the same size as, or smaller than, the symbols used, and are therefore not shown in the main paper to avoid crowding the plots.

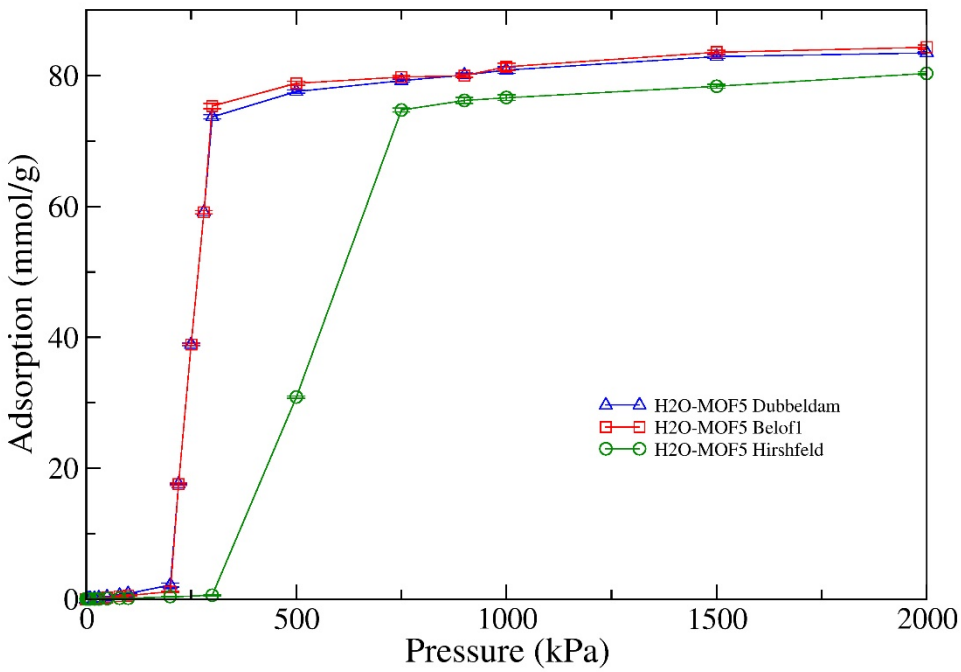

Figure S10 – Plot showing adsorption isotherms of H_2Oin IRMOF-1 at 298K with corresponding error bars. For the vast majority of simulations, the error bars are of the same size as, or smaller than, the symbols used, and are therefore not shown in the main paper to avoid crowding the plots.

Table S5 – Energy decomposition and amount adsorbed for adsorption of CO_2 in IRMOF-1 at 298K and 750 kPa using various charge sets and including the neutral framework.

Charge set	E_{LJ}	E_q	N_{ads}
No charge	-9.5055	0.0000	9.1702
Manz (DDEC)	-9.6230	-0.5679	12.0191
Campana (REPEAT)	-9.6770	-0.3896	11.2140
Manz (Hirshfeld)	-9.5591	-0.0404	10.7978
Manz (ISA)	-9.6097	-0.5535	11.7359
Sagara (CHELPG)	-9.7897	-0.3454	11.6510
Yang (CHELPG)	-9.7975	-0.4993	12.1300
Yazayidin 1 (CHELPG)	-9.8368	-0.4465	11.8160
Babarao (RESP)	-9.7855	-0.5951	13.0149
Dubbeldam (CHELPG)	-9.7157	-1.9726	16.3071
Fischer (MSK)	-9.5864	-3.1268	19.7159
Wilmer 1 (Eqeq)	-9.4035	-2.2139	17.4632
Xu (CBAC)	-9.4658	-1.0419	14.0952

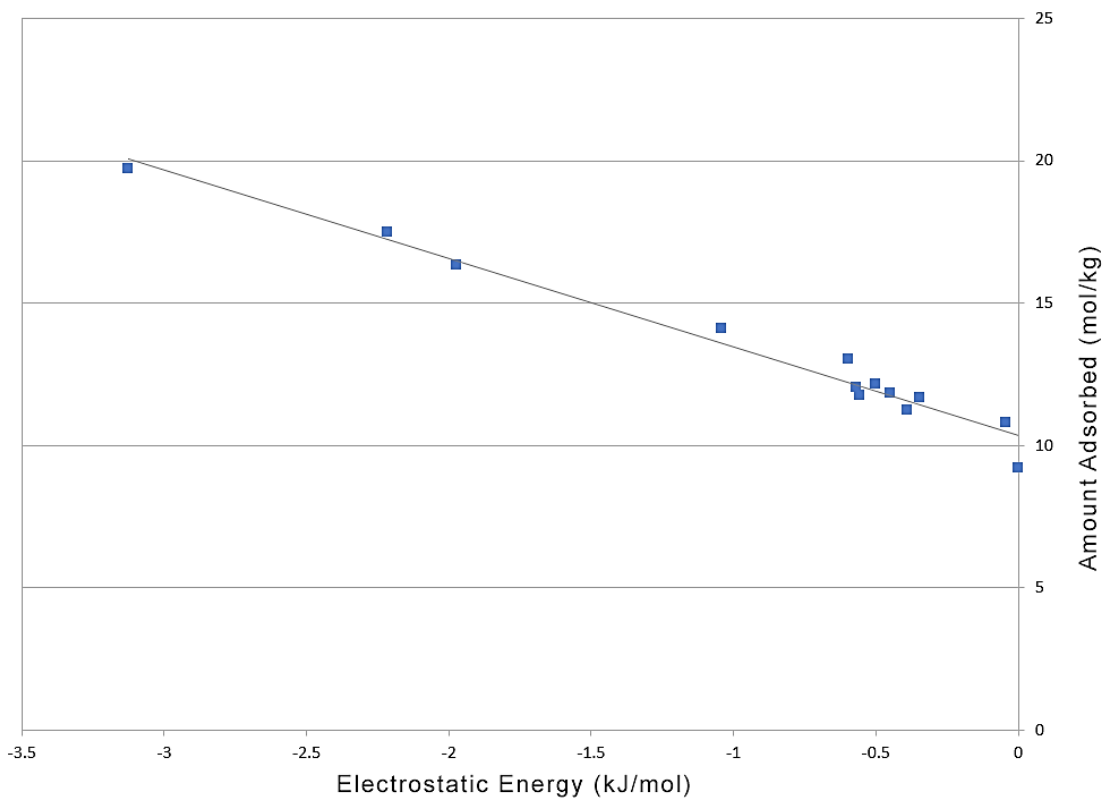

Figure S11 – Plot showing a linear increase of amount adsorbed as a function of electrostatic energy contribution for CO_2 in IRMOF-1 at 298K and 750 kPa.

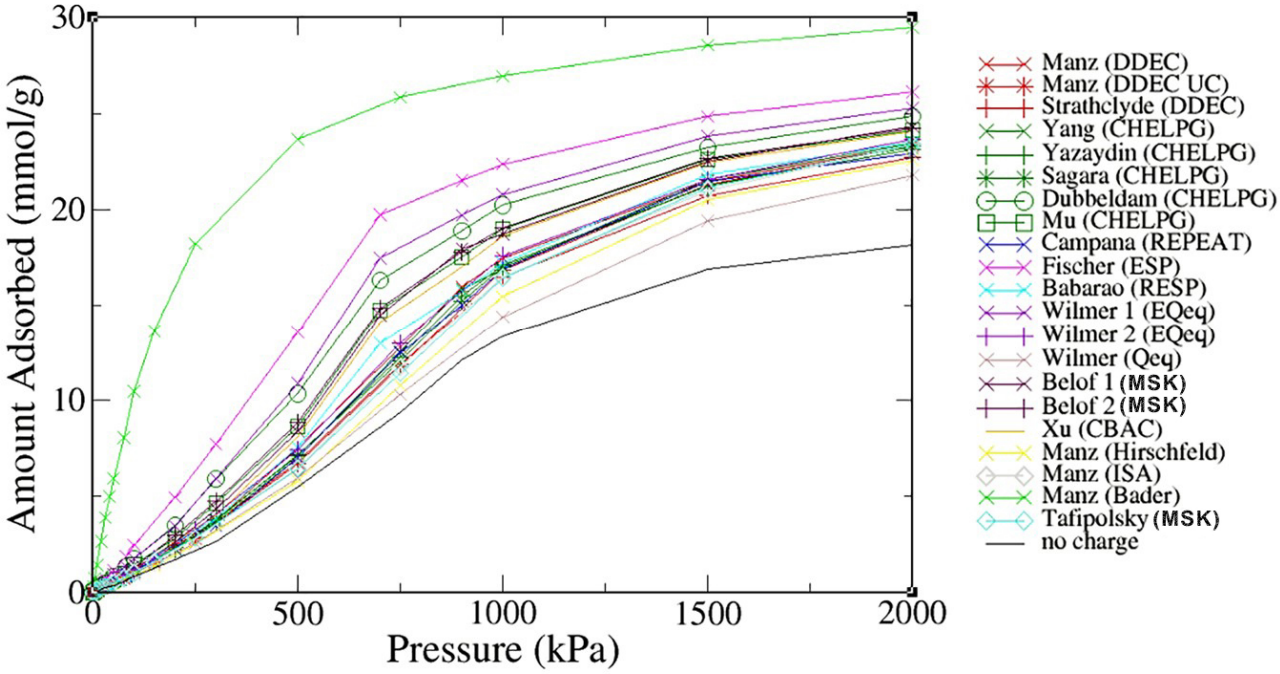

Figure S12 – Plot of all point charge set isotherms for CO_2 at 298K in IRMOF-1.

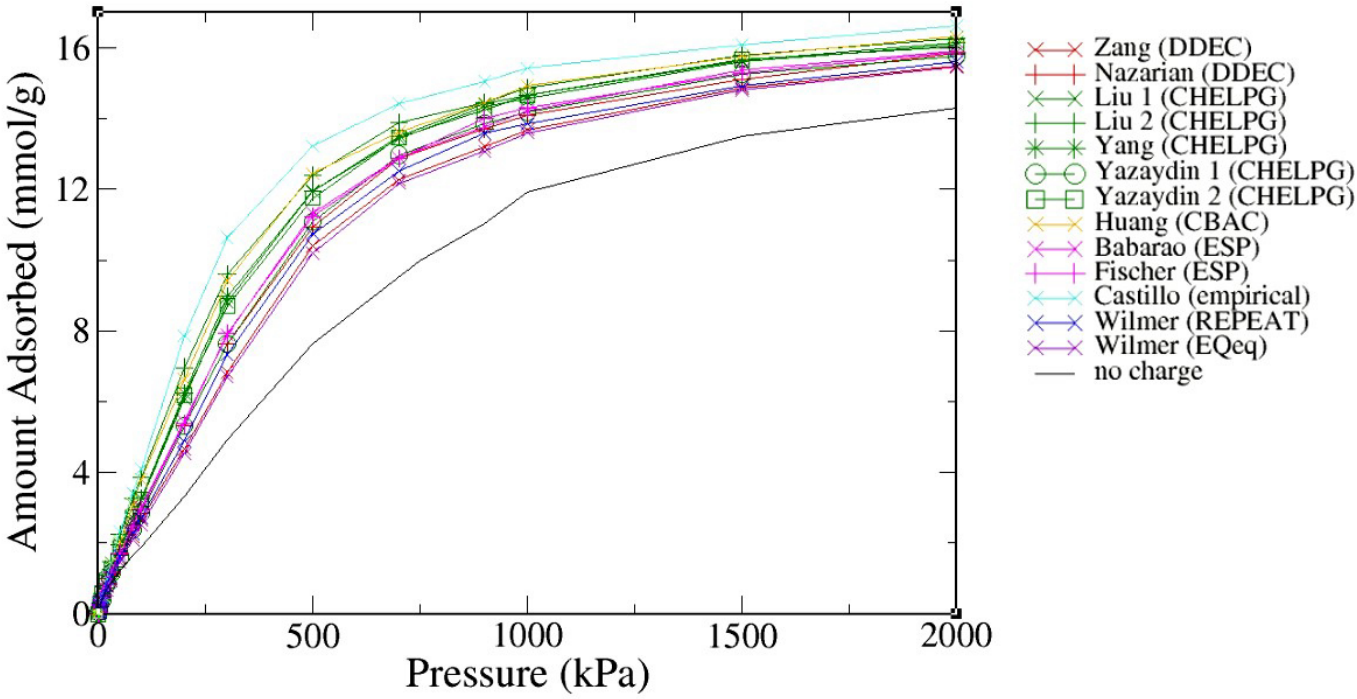

Figure S13 – Plot of all point charge set isotherms for CO_2 at 298Kin CuBTC.

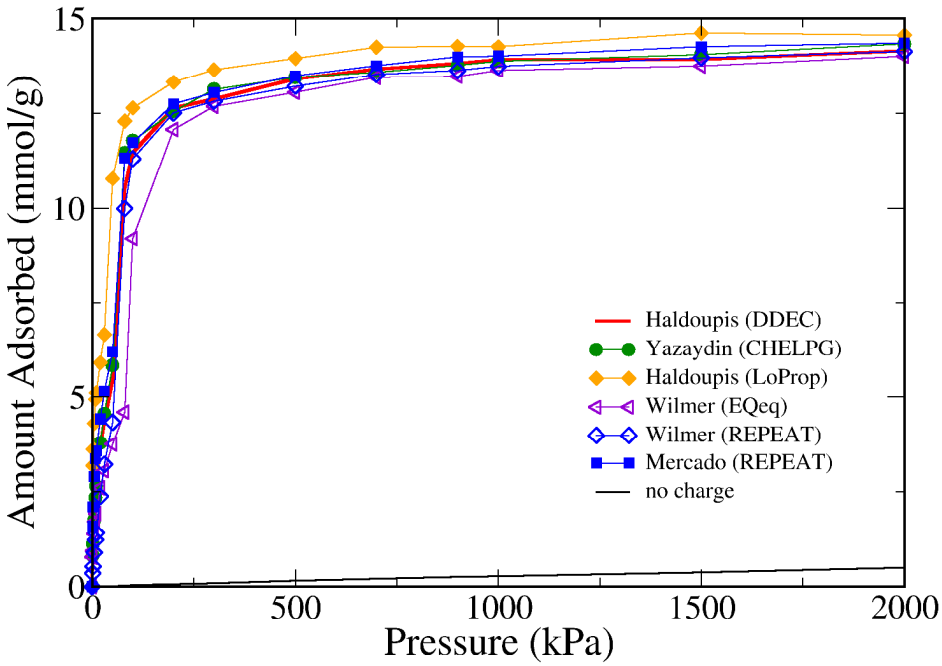

Figure S14 – Full pressure range plot of adsorption isotherms of water in Co-MOF-74 at 298K using different point charge sets for the framework atoms.

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