Supporting information for

Fluorinated carbide-derived carbon: More hydrophilic, yet apparently more hydrophobic

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1) Interaction parameters of the developed force field

Table S1. LJ interaction parameters of the developed force field.

Molecule	Pair	$\varepsilon^1_{s\text{-}f}/k_B$ (K)	$\varepsilon^2_{s\text{-}f}/k_B$ (K)	$\sigma_{s\text{-}f}$ (Å)	$\varepsilon_{s\text{-}f}/k_B{}^*$ (K)
H_2O	C-O	39.49	45.09	3.311	53.43
	C-H	16.93	19.33	2.623	00.00
	F-O	51.29	51.29	3.113	- - -
	F-H	0.0	0.0	0.0	- - -
CO_2	C-C	55.73	63.63	3.053	32.36
	C-O	31.64	36.12	3.287	54.71
	F-C	75.68	75.68	2.814	- - -
	F-O	38.92	38.92	3.006	- - -

$\varepsilon^1_{s\text{-}f}$: Original ε parameter developed in this study.

$\varepsilon^2_{s\text{-}f}$: scaled ε parameters using scaling factor $\alpha = 1.1417$ for carbon (solid) – fluid pairs based on equation 5. These parameters are applied in our GCMC and MD simulations.

NB. Only potential well-depths of carbon(solid)-fluids are scaled using this factor, considering carbon atoms are the only one which contribute to curvature of the disordered structure.

$\varepsilon_{s\text{-}f}/k_B{}^*$: ε parameter of the virgin SiCDC as used in our previous studies[1-3].

2) Bonded and non-bonded interaction parameters used for geometry optimization of the F-SiCDC models

Table S2. Non-bonded[4] and bonded[5] interaction parameters used for geometry optimization of the F-SiCDC models.

	Bond strength ($kJ/mol.Å^2$)*	**Bond length (Å)**	**Bond angle strength ($kJ/mol.rad^2$)****	**Angle (degree)**
F-C	2532.41	1.336	---	---
F-C-C	---	---	419.81	118.32
	ε_{i-i}/k_B (K)		**σ_{i-i} (Å)**	
F-F	26.68		2.95	
F-C	29.76		3.225	

$*U_{two-body} = \frac{1}{2}K_r(r - r_0)^2$

$**U_{three-body} = \frac{1}{2}[\frac{K_\theta}{sin^2(\theta_0)}](\cos(\theta) - \cos(\theta_0))^2$

3) Partial charges of the fluorinated systems

Table S3. Partial charge distribution of fluorinated graphene sheet and fluorinated disordered carbon cluster compared with the pattern derived for F-SiCDC.2 and F-SiCDC.3 models

	F	1st near C to 1 F	1st near C to 2 F	1st near C to 1 or 2 F	2nd near C to 1 F	2nd near C to 2 F	2nd near C to 1 or 2 F
F-graphene	-0.1579	+0.2578	+0.5219	+0.3144	-0.09715	-0.15725	-0.11719
F-disordered cluster	-0.15411	+0.27498	---	---	-0.14882	---	---
Derived pattern	-0.154	+0.275	---	---	-0.116* -0.149**	---	---

* used for F-SiCDC.2

** used for F-SiCDC.3

4) Equilibration state of some unfinished GCMC simulations

As noted in the paper, some of the high-pressure data points in GCMC simulation of water in the fluorinated systems did not reach equilibrium even after very lengthy simulations. These include the last data point (data point 19) in adsorption isotherm of F-SiCDC.2 model, where $P/P_o = 1.0$, in addition to the last 6 data points (data points 14 to 19) corresponding to $P/P_o = 0.72$ to 1.0 in the adsorption isotherm of F-SiCDC.3 model. Nevertheless in most cases the simulations at these data points are close to equilibration. We emphasize that this slow equilibration does not affect our finding regarding the increasing trend of water adsorption in fluorinated systems, so that one can still safely conclude that fluorination does increase the level of water uptake. This is consistent with other evidence provided in our paper including analysis of free energy of binding of water in the systems studied and GCMC results of other data points, which are all fully equilibrated. Figures S1 to S3 illustrate equilibration state of data point 19 in F-SiCDC.2 model, as well as point 14 and 19 in the F-SiCDC.3 model. We note that in these figures the *X* axis represents the number of cycles in GCMC simulation rather than the number of MC steps. In RASPA simulation package[6], which is used in this study, a cycle consists of *N* MC steps, where *N* is the amount of molecules with a minimum of 20 steps. In other words, on average one Monte Carlo move is attempted (either successful or unsuccessful) on each molecule during each cycle, so that the number of MC steps is roughly equal to the number of cycles times the average number of molecules in the simulation.

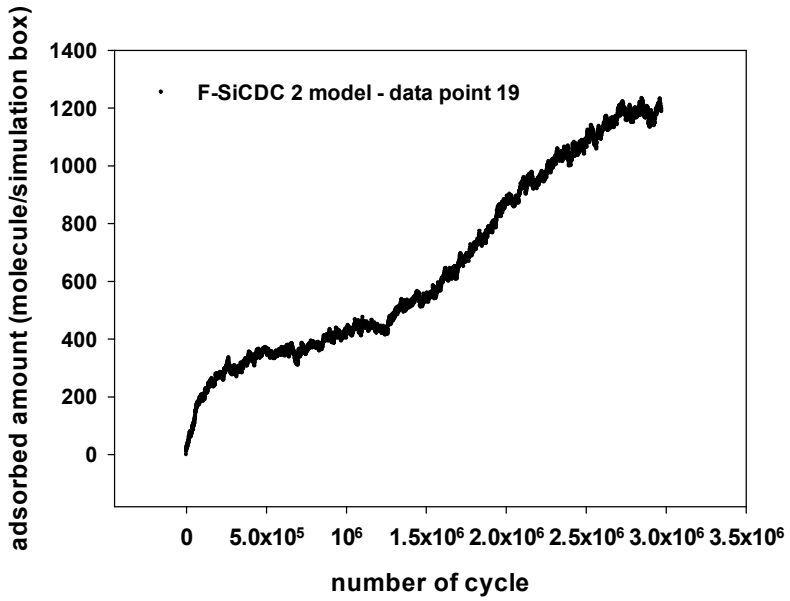


Figure S1. Equilibration state of GCMC simulation for data point 19 in adsorption isotherm of water in F-SiCDC.2 model

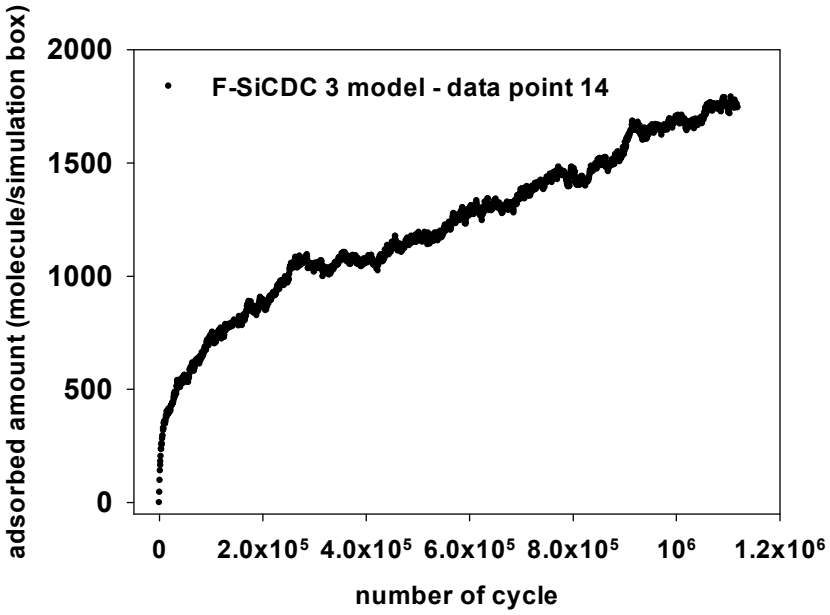


Figure S2. Equilibration state of GCMC simulation for data point 14 in adsorption isotherm of water in F-SiCDC.3 model

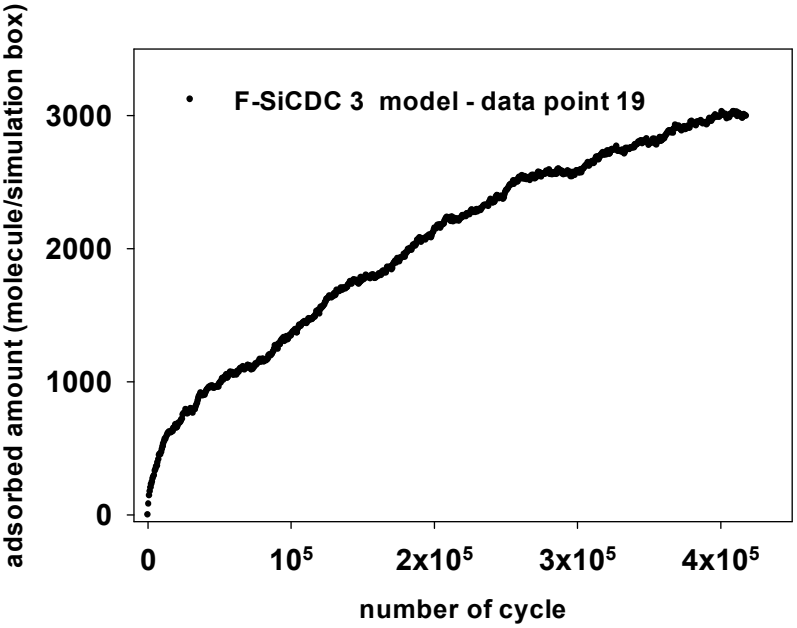
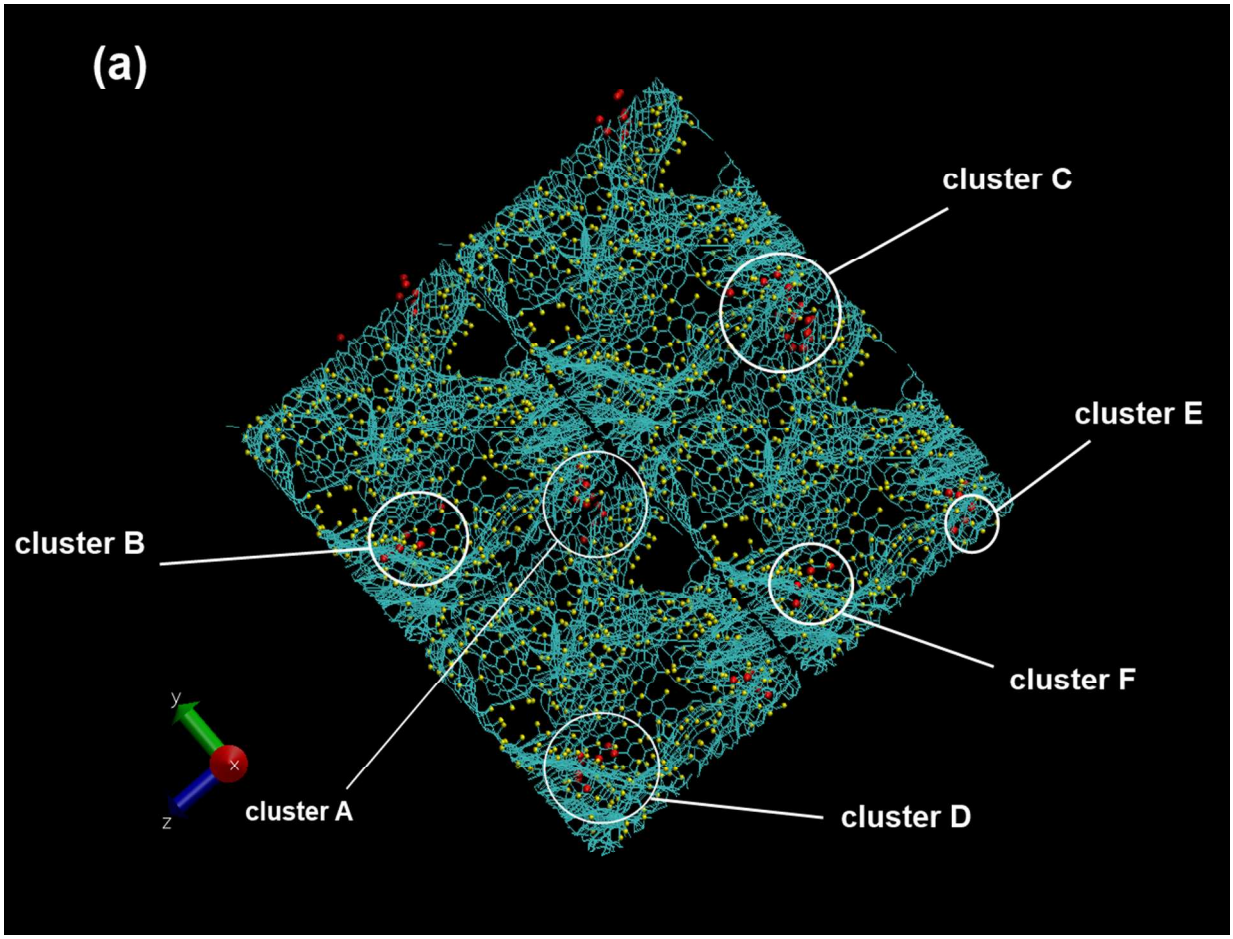
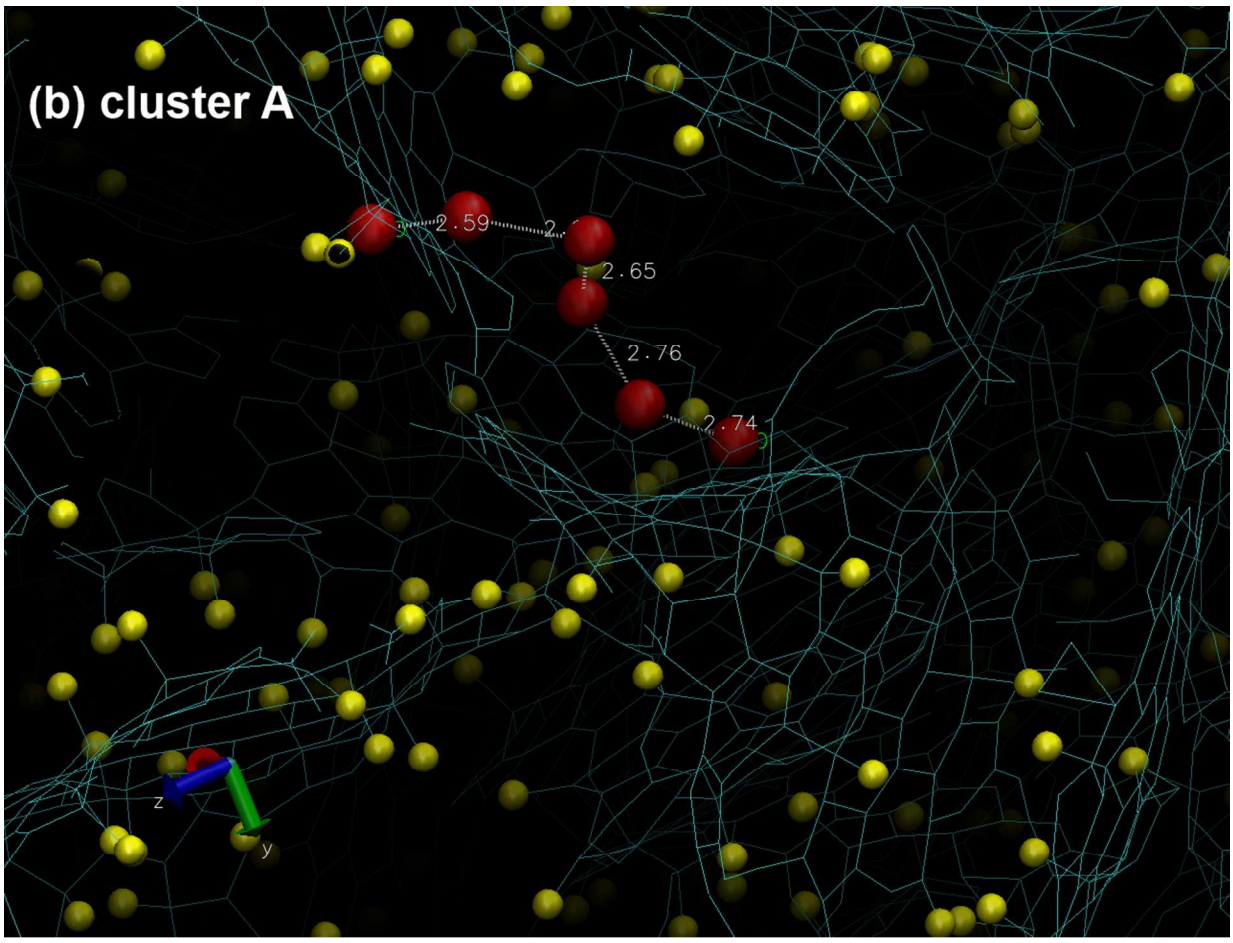


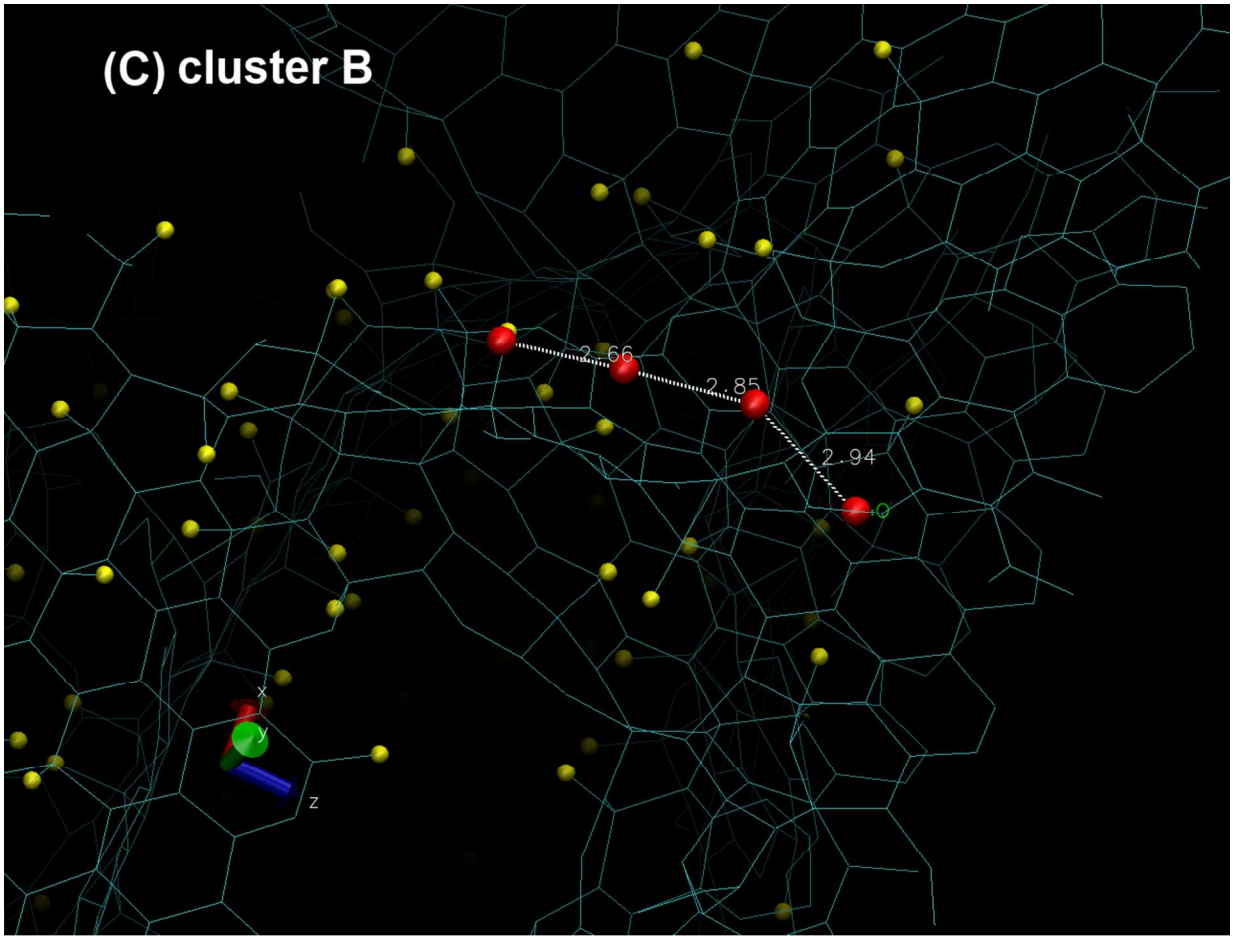
Figure S3. Equilibration state of GCMC simulation for data point 19 in adsorption isotherm of water in F-SiCDC.3 model

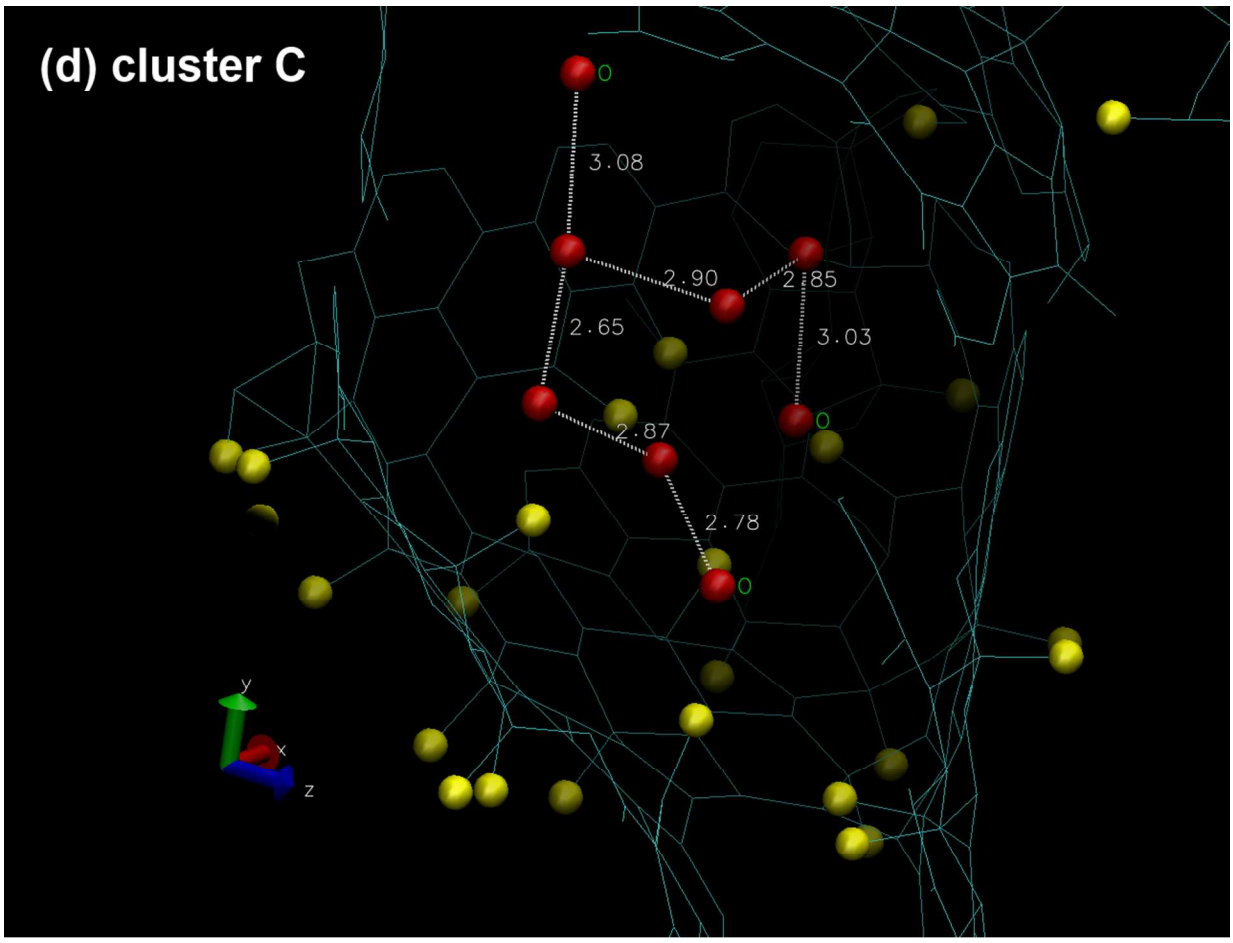
5) Water clusters in F-SiCDC3 model

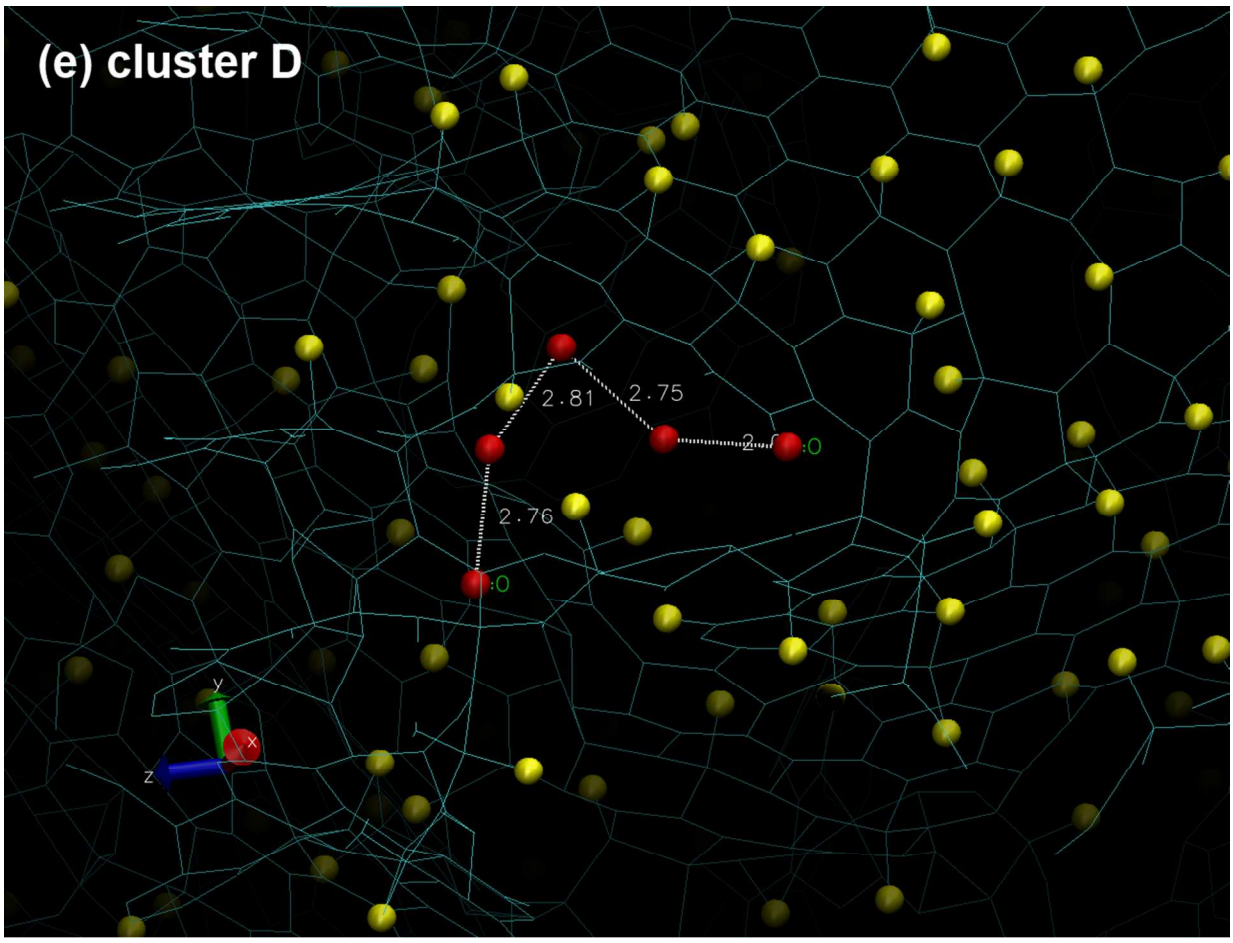
The following figures illustrate the formation of water clusters in F-SiCDC.3 model at the lowest pressure (P/P_o = 0.05). Here, oxygen – oxygen distances are given but hydrogen atoms are not illustrated for better visibility of other atoms.

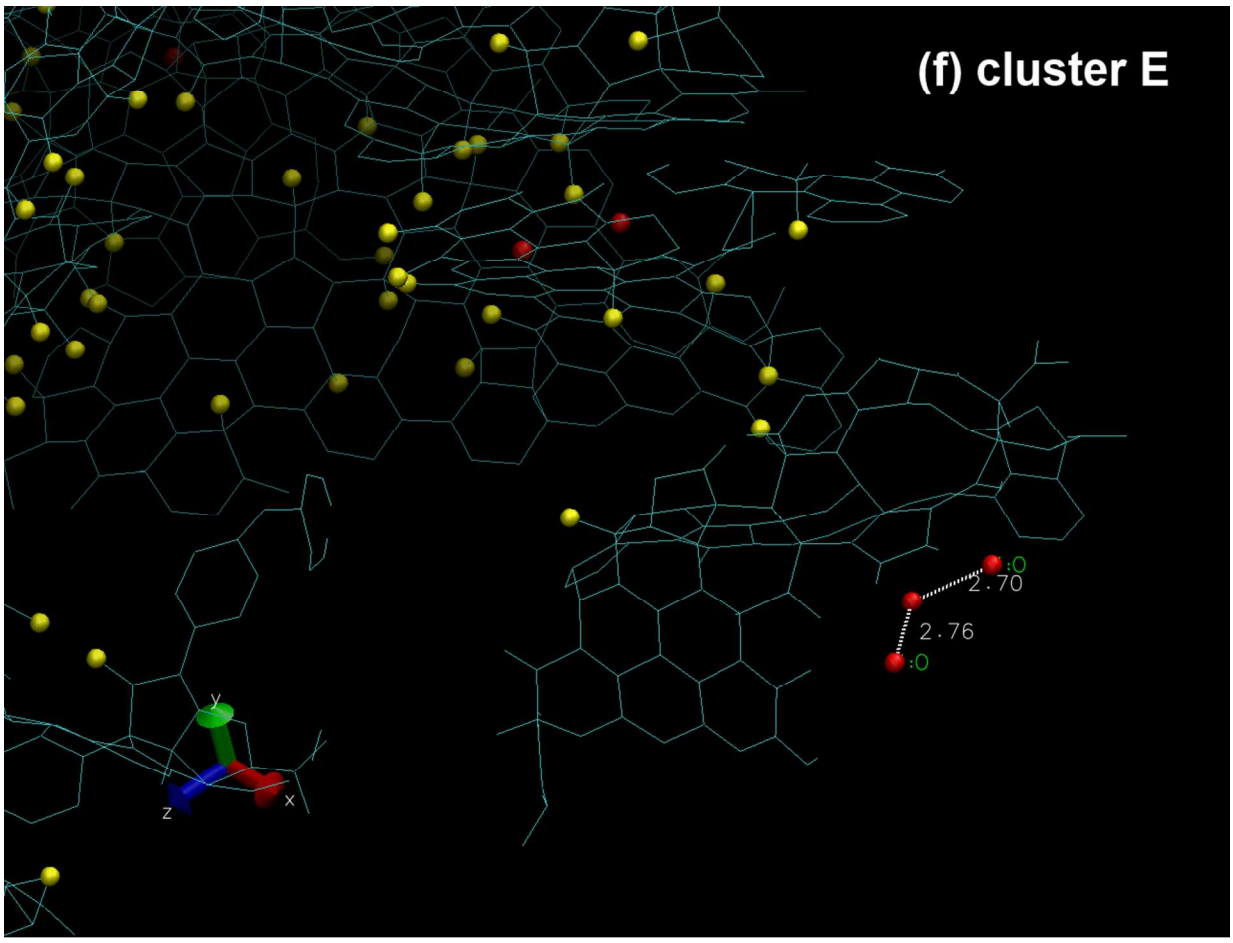



(b) cluster A
2.59
2.65
2.76
2.74
z
y


(C) cluster B
2.66
2.85
2.94
x
y
z


(d) cluster C
O
3.08
2.90
2.85
2.65
3.03
2.87
O
2.78
O
y
x
z


(e) cluster D
2.81
2.75
2.76
:O
:O
y
x
z


(f) cluster E
:O
2.70
2.76
:O
y
z
x

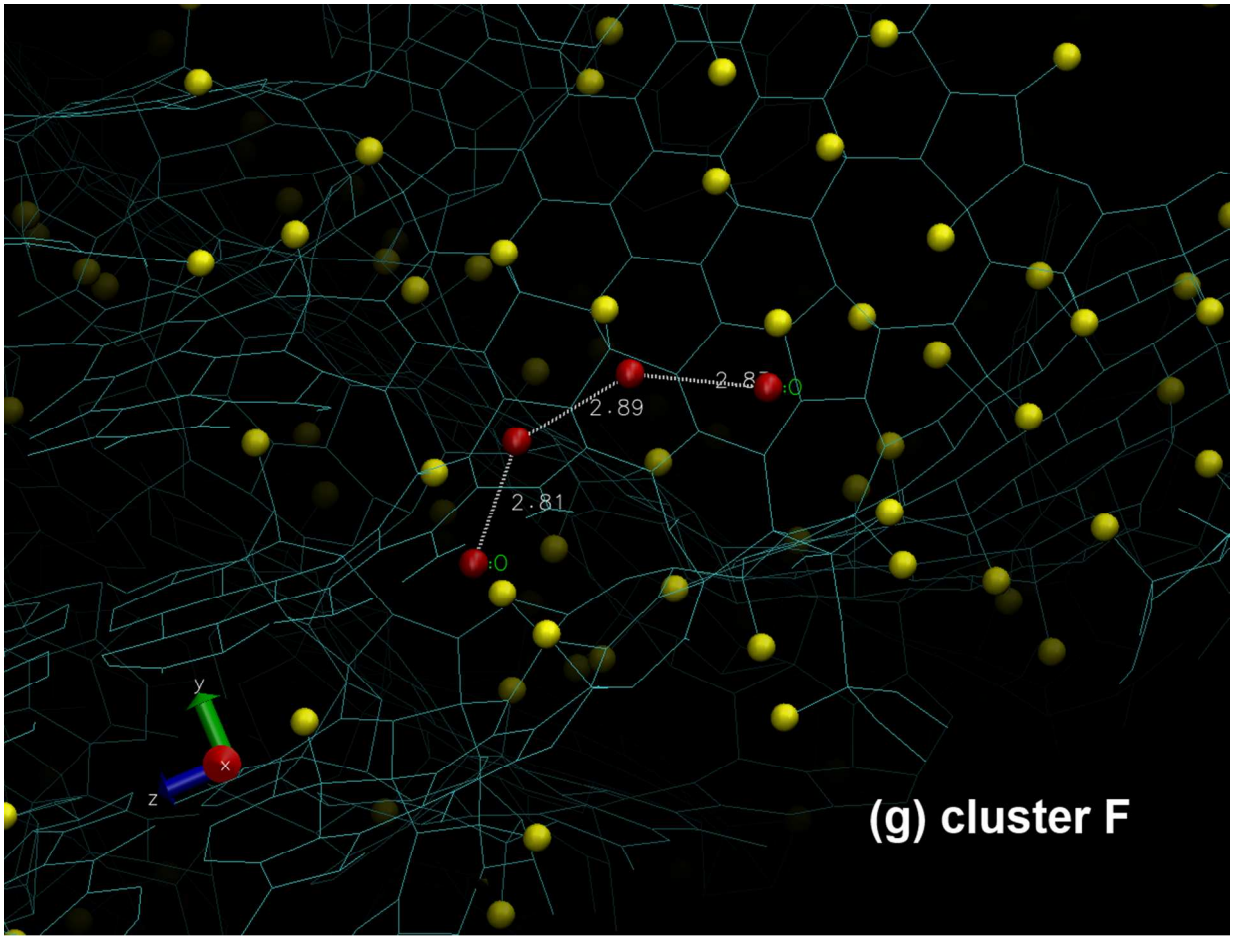


Figure S4. Formation of water clusters in F-SiCDC.3 model at P/P_o = 0.05

6) Contributions of heat of adsorption for CO_2 in virgin and fluorinated systems

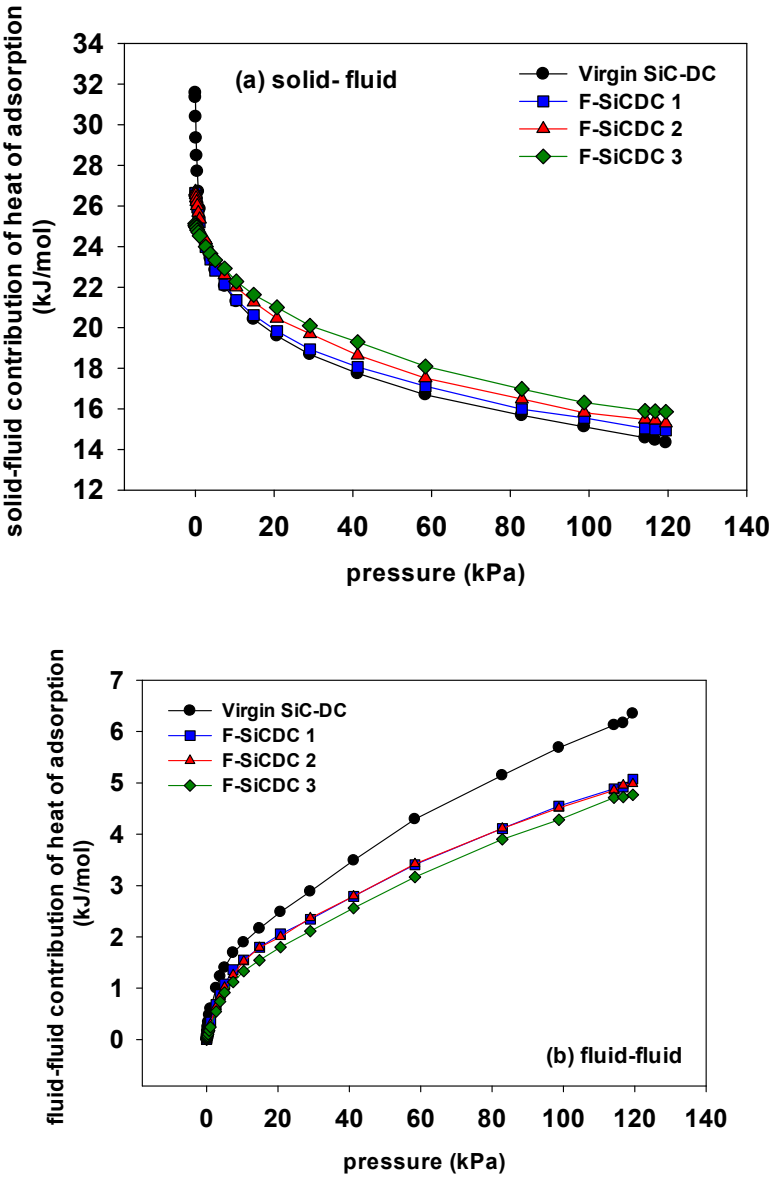


Figure S5. (a) Solid-fluid and (b) fluid-fluid contributions to heat of adsorption for CO_2

7) Adsorption energy of CO_2 in virgin and F-SiCDC.1 model

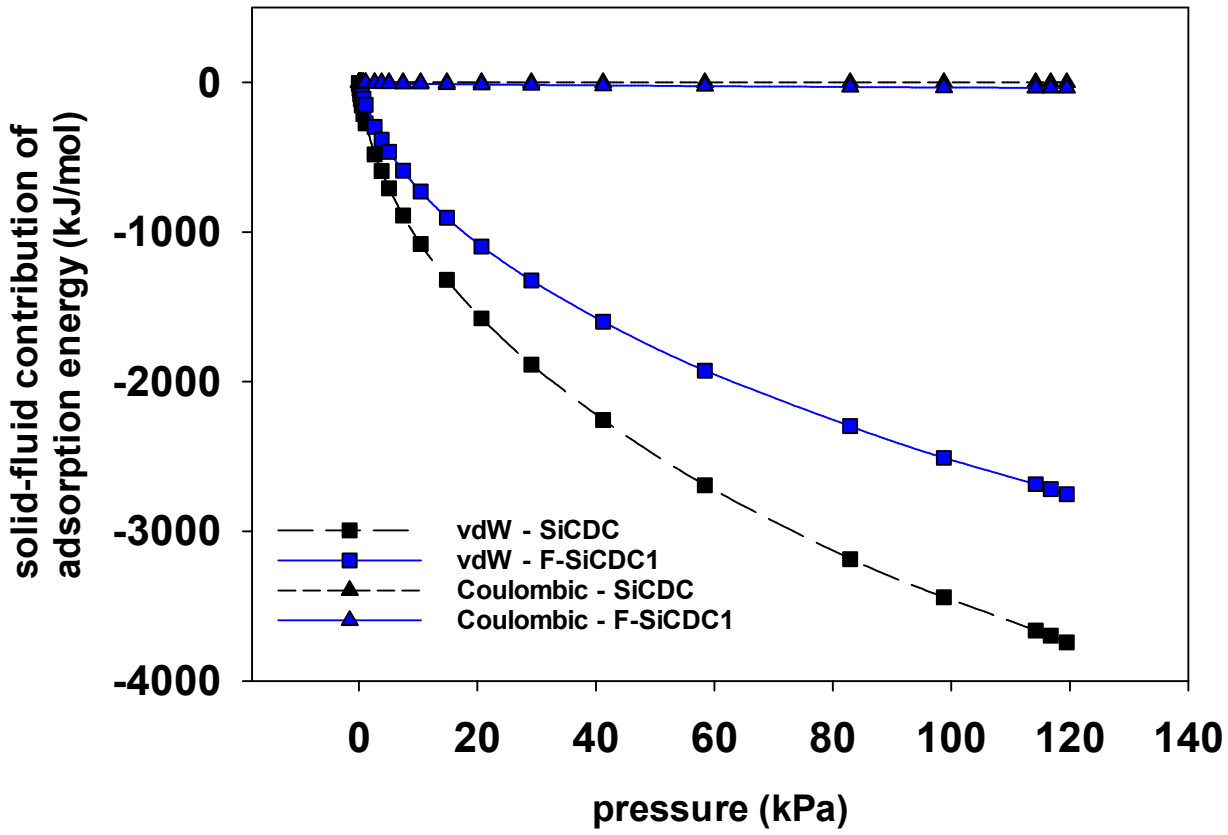


Figure S6. Solid-fluid interactions of CO_2 in virgin and F-SiCDC.1 models.

8) MSD of water and CO_2 in F-SiCDC models

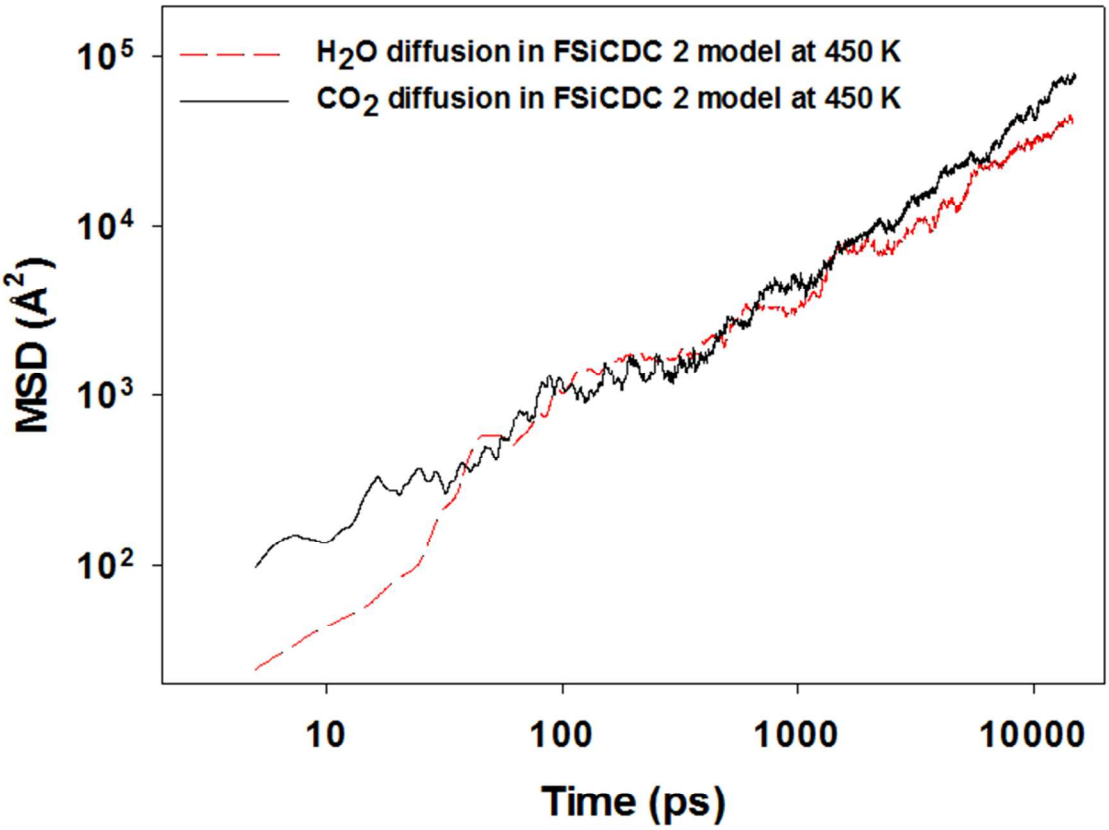


Figure S7. MSD of water and CO_2 in F-SiCDC.2 model at 450 K.

9) Optimized structure of the fluorinated graphene:

As explained in the paper, structure of the fluorinated graphene was optimized using the dispersion-corrected DFT method of Grimme (DFT-D2) implemented in VASP. After optimization, the system achieved energy level of -53.2831 Hartrees with lattice constants equal to $\begin{bmatrix} 22.21 & 0 & 0 \\ 0 & 21.56 & 0 \\ 0 & 0 & 20.00 \end{bmatrix}$. The final configuration along with the corresponding atomic charges calculated from DDEC method are given in Table S4.

Table S4. Atomic configurations of the fluorinated graphene

Index	Atom	X (Å)	Y (Å)	Z (Å)	Charge (e)
1	C	-0.032760	21.418696	10.074040	0.002875
2	C	20.942342	0.576299	10.049360	-0.000078
3	C	20.939677	2.010168	10.055860	0.004699
4	C	22.168356	2.728871	10.068380	-0.006943
5	C	2.429596	21.417769	10.145860	0.000384
6	C	1.196875	0.573970	10.103600	0.000528
7	C	1.195897	2.012755	10.084140	0.002842
8	C	2.422200	2.726284	10.090520	-0.002266
9	C	4.895128	21.418114	10.207600	-0.007597
10	C	3.662518	0.575630	10.175420	0.007304
11	C	3.662851	2.008228	10.153180	-0.006852
12	C	4.897105	2.715029	10.126540	0.040442
13	C	7.366035	21.421455	10.189500	-0.002936
14	C	6.127850	0.570650	10.174260	0.013445
15	C	6.128428	1.997038	10.094100	-0.031302
16	C	7.363726	2.693491	9.957660	0.073382
17	C	9.839074	21.428527	10.141680	-0.001878
18	C	8.599779	0.569443	10.129940	0.011642
19	C	8.597424	1.991713	10.007040	-0.035324
20	C	9.830368	2.692283	9.911440	0.073507
21	C	12.310514	21.432214	10.104880	-0.004810
22	C	11.075016	0.575178	10.091680	0.010446
23	C	11.070419	1.998267	10.013460	-0.029726
24	C	12.299187	2.712528	10.034860	0.038084
25	C	14.783331	21.428786	10.060020	0.004419
26	C	13.543880	0.586475	10.076840	0.004496
27	C	13.539838	2.009931	10.064160	-0.004249
28	C	14.781044	2.726887	10.031140	-0.006331
29	C	17.248019	21.423590	10.030960	-0.002499
30	C	16.013899	0.579339	10.037180	0.001202

31	C	16.011544	2.014265	10.030260	0.002224
32	C	17.246665	2.725572	10.041540	-0.006700
33	C	19.713707	21.420313	10.031400	-0.001370
34	C	18.482451	0.576881	10.027600	0.001705
35	C	18.479919	2.009327	10.037980	0.006809
36	C	19.707688	2.728159	10.053500	-0.004608
37	C	22.159916	4.159700	10.071760	0.016646
38	C	20.928661	4.882240	10.071040	-0.010069
39	C	20.922642	6.318136	10.074720	0.007566
40	C	22.148345	7.038499	10.052220	-0.003904
41	C	2.412739	4.160994	10.073580	0.028317
42	C	1.178996	4.876398	10.077200	-0.025199
43	C	1.168979	6.308736	10.058120	0.033193
44	C	2.394815	7.025197	10.116720	-0.073724
45	C	4.899748	4.153922	10.034720	-0.088605
46	C	3.644883	4.879589	10.147220	-0.067117
47	C	3.556332	6.262059	10.371860	0.239023
48	C	7.360150	4.108495	9.711120	-0.201648
49	C	6.099044	4.764976	9.678420	0.272528
50	C	9.831878	4.104507	9.664140	-0.198461
51	C	8.593649	4.764588	9.543700	0.307674
52	C	12.292302	4.146204	9.952300	-0.084672
53	C	11.092096	4.759111	9.605740	0.270098
54	C	14.785774	4.153577	10.061040	0.039697
55	C	13.542592	4.866825	10.129360	-0.084549
56	C	14.795658	6.984707	10.395040	-0.189431
57	C	17.248641	4.153081	10.079700	0.014288
58	C	16.017030	4.864777	10.117940	-0.029504
59	C	16.024782	6.288729	10.207840	0.063743
60	C	17.233361	7.033066	10.179280	-0.032557
61	C	19.703912	4.163538	10.069700	0.005971
62	C	18.472368	4.881292	10.090820	-0.007006
63	C	18.467793	6.315441	10.122680	0.019687
64	C	19.691497	7.038585	10.107800	-0.007320
65	C	22.143081	8.471700	10.063240	0.012180
66	C	20.910271	9.193788	10.092520	-0.000739
67	C	20.910582	10.630050	10.074240	-0.002314
68	C	22.145080	11.350262	9.980340	0.009776
69	C	2.385487	8.456112	9.925860	-0.033054
70	C	1.163449	9.190705	9.974640	0.001546
71	C	1.162205	10.624725	9.876960	0.005152
72	C	2.378869	11.352655	9.658120	-0.010711
73	C	3.516265	9.178653	9.494500	0.147783

74	C	3.513977	10.549286	9.334960	0.149889
75	C	14.804742	8.391324	10.436380	0.269789
76	C	14.699955	11.406879	10.135140	0.537075
77	C	17.213039	8.468552	10.214380	0.035073
78	C	15.964859	9.192494	10.290980	-0.061629
79	C	15.986403	10.637143	10.219360	-0.134741
80	C	17.195804	11.351836	10.170400	0.043348
81	C	19.681525	8.474330	10.122760	0.000937
82	C	18.442962	9.195512	10.164720	0.003044
83	C	18.445183	10.630805	10.158480	0.009275
84	C	19.679170	11.349766	10.109260	0.000692
85	C	22.148434	12.783032	9.963260	0.007294
86	C	20.919066	13.505895	10.022720	0.004701
87	C	20.937545	14.948346	10.016980	-0.014574
88	C	-0.028651	15.663771	10.014220	0.011579
89	C	2.365232	12.781803	9.754920	-0.137336
90	C	1.178529	13.500398	9.905420	0.038291
91	C	1.198674	14.955396	9.990220	-0.027290
92	C	2.432217	15.681192	10.075880	0.023129
93	C	3.664406	13.522820	9.777880	0.498262
94	C	3.677909	14.994872	10.133360	-0.079870
95	C	4.877782	15.689643	10.341960	-0.088830
96	C	6.180577	14.964537	10.634960	0.530474
97	C	7.429223	15.781036	10.685820	-0.258403
98	C	8.633249	15.131951	10.878960	0.329926
99	C	9.880518	15.794985	10.764200	-0.193799
100	C	11.129631	15.147495	10.852140	0.278900
101	C	12.320664	15.737291	10.413840	-0.080450
102	C	14.785819	12.891673	10.015860	-0.244301
103	C	13.607045	13.624519	9.966920	0.291280
104	C	13.552209	15.012185	10.205300	-0.076469
105	C	14.790105	15.712411	10.164900	0.037890
106	C	17.229252	12.809982	10.130060	-0.044627
107	C	16.017852	13.561477	10.103040	0.074891
108	C	16.020228	14.992393	10.104020	-0.022248
109	C	17.254283	15.694925	10.077200	0.011794
110	C	19.692230	12.791117	10.078240	-0.010060
111	C	18.457354	13.514951	10.093820	0.018345
112	C	18.475677	14.958608	10.063260	-0.003255
113	C	19.713374	15.669140	10.033920	0.005808
114	C	-0.029028	17.107795	10.043720	0.004897
115	C	20.946740	17.826627	10.032900	0.002929
116	C	20.946962	19.262976	10.040660	0.000045

117	C	-0.032005	19.982067	10.070520	0.002678
118	C	2.432417	17.114608	10.141000	0.009551
119	C	1.197030	17.828870	10.093880	-0.000022
120	C	1.198363	19.266706	10.105920	-0.001829
121	C	2.429952	19.983447	10.153820	0.001609
122	C	4.897327	17.118899	10.341620	0.025893
123	C	3.664739	17.830551	10.227360	0.006648
124	C	3.664383	19.268344	10.213500	0.000152
125	C	4.893640	19.986249	10.243320	0.004883
126	C	7.391444	17.179137	10.493800	0.076626
127	C	6.134646	17.854547	10.385340	-0.024828
128	C	6.132559	19.274748	10.296460	0.007392
129	C	7.368723	19.997439	10.259900	-0.003827
130	C	9.858197	17.192375	10.476680	0.073249
131	C	8.618413	17.888828	10.415540	-0.024878
132	C	8.609818	19.305083	10.283740	0.007306
133	C	9.843872	20.009728	10.215160	-0.000802
134	C	12.314779	17.163938	10.267720	0.038112
135	C	11.089608	17.883675	10.318820	-0.033242
136	C	11.083590	19.303983	10.216440	0.011826
137	C	12.315156	20.005718	10.139100	-0.003715
138	C	14.789062	17.145892	10.149980	0.000524
139	C	13.552387	17.863538	10.155360	-0.000408
140	C	13.549566	19.288460	10.116260	0.001598
141	C	14.785797	19.998884	10.075120	0.001975
142	C	17.253772	17.127307	10.068020	-0.008603
143	C	16.020762	17.847821	10.093620	0.001913
144	C	16.018230	19.282466	10.064980	-0.002568
145	C	17.250196	19.991920	10.039660	0.003983
146	C	19.715128	17.111417	10.026880	-0.005811
147	C	18.487560	17.835014	10.038180	0.007335
148	C	18.485894	19.271341	10.033020	0.001875
149	C	19.715195	19.982692	10.029140	0.000605
150	C	13.603958	6.211048	10.481300	0.279170
151	F	8.639868	13.804997	11.101440	-0.127224
152	F	11.171275	13.933861	11.435680	-0.127063
153	F	12.468405	12.977287	9.652520	-0.124044
154	F	13.950723	10.901016	9.066600	-0.229629
155	F	13.943838	11.204452	11.310300	-0.236566
156	F	13.596807	8.952790	10.582300	-0.108356
157	F	11.112440	6.029146	9.150980	-0.129365
158	F	8.595581	6.098677	9.349060	-0.131342
159	F	6.073036	6.031539	9.215960	-0.124690

160	F	4.599402	6.889778	10.959560	-0.130137
161	F	4.629897	8.528338	9.098060	-0.118006
162	F	4.634872	11.054179	8.791380	-0.104872
163	F	4.484599	12.800086	10.630920	-0.199097
164	F	4.202532	13.485370	8.473880	-0.231703
165	F	6.041520	14.350271	11.889960	-0.230643
166	F	6.431483	13.972087	9.697380	-0.203762
167	F	12.496257	6.794871	10.979900	-0.128786

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