SUPPORTING INFORMATION

Investigation of Metal-organic Frameworks and Fluorocarbon Refrigerants Promising for Adsorption Cooling Systems

Dipankar Singha, Debansh Mohapatra, and Malay Kumar Rana*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER), Berhampur, Berhampur 760010, Odisha, India

*Corresponding author Email: mrana@iiserbpr.ac.in

Table S1: The Lennard-Jones parameters of the C_2F_4 molecule from the Universal Force Field (UFF).

Atoms	Potential	ε/k_B (K)	σ (Å)
C1	Lennard-Jones	47.8562	3.47299
C2	Lennard-Jones	47.8562	3.47299
F1	Lennard-Jones	36.4834	3.0932
F2	Lennard-Jones	36.4834	3.0932
F3	Lennard-Jones	36.4834	3.0932
F4	Lennard-Jones	36.4834	3.0932

Table S2: The Lennard-Jones parameters of the C_2F_6 molecule obtained from the TraPPE force field.

Atoms	Potential	ε/k_B (K)	σ (Å)
CF3	Lennard-Jones	87.0	4.360
CF3	Lennard-Jones	87.0	4.360

Table S2: The Lennard-Jones parameters of the N_2 molecule taken from UFF.

Atoms	Potential	ε/k_B (K)	σ (Å)
N_n2	Lennard-Jones	38.298	3.306
N_com	none		

Table S3: The Lennard-Jones parameters of the MOF atoms taken from UFF.

Atoms	Potential	ε/k_B (K)	σ (Å)
O	Lennard-Jones	48.1581	3.03315
N	Lennard-Jones	38.9492	3.26256
C	Lennard-Jones	47.8562	3.47299
B	Lennard-Jones	47.8058	3.58141
P	Lennard-Jones	161.03	3.69723
S	Lennard-Jones	173.107	3.59032
Cl	Lennard-Jones	142.562	3.51932
Br	Lennard-Jones	186.191	3.51905

H	Lennard-Jones	7.64893	2.84642
Zn	Lennard-Jones	62.3992	2.46155
Be	Lennard-Jones	42.7736	2.44552
Cr	Lennard-Jones	7.54829	2.69319
Fe	Lennard-Jones	6.54185	2.5943
Mn	Lennard-Jones	6.54185	2.63795
Cu	Lennard-Jones	2.5161	3.11369
Co	Lennard-Jones	7.04507	2.55866
Ga	Lennard-Jones	208.836	3.90481
Ti	Lennard-Jones	8.55473	2.8286
Sc	Lennard-Jones	9.56117	2.93551
V	Lennard-Jones	8.05151	2.80099
Ni	Lennard-Jones	7.54829	2.52481
Zr	Lennard-Jones	34.7221	2.78317
Mg	Lennard-Jones	55.8574	2.69141
Ne	Lennard-Jones	21.1352	2.88918
Ag	Lennard-Jones	18.1159	2.80455
In	Lennard-Jones	301.428	3.97608
Cd	Lennard-Jones	114.734	2.53728
Sb	Lennard-Jones	225.946	3.93777
Te	Lennard-Jones	200.281	3.98232
Al	Lennard-Jones	155.998	3.91105
Si	Lennard-Jones	155.998	3.80414
He	Lennard-Jones	10.9	2.64
CH4_sp3	Lennard-Jones	158.5	3.72
CH3_sp3	Lennard-Jones	108.0	3.76
CH2_sp3	Lennard-Jones	56.0	3.96
CH_sp3	Lennard-Jones	17.0	4.67
C_sp3	Lennard-Jones	0.8	6.38
H_com	Lennard-Jones	36.7	2.958
H_h2	none		
O_co2	Lennard-Jones	85.671	3.017
C_co2	Lennard-Jones	29.933	2.745
C_benz	Lennard-Jones	30.70	3.60
H_benz	Lennard-Jones	25.45	2.36
N_n2	Lennard-Jones	38.298	3.306
N_com	none		
Ow	Lennard-Jones	89.633	3.097
N_dmf	Lennard-Jones	80.0	3.2
Co_dmf	Lennard-Jones	50.0	3.7
Cm_dmf	Lennard-Jones	80.0	3.8
O_dmf	Lennard-Jones	100.0	2.96
H_dmf	Lennard-Jones	8.0	2.2
Ar	Lennard-Jones	124.070	3.380
Kr	Lennard-Jones	166.4	3.636
Xe	Lennard-Jones	221.0	4.1

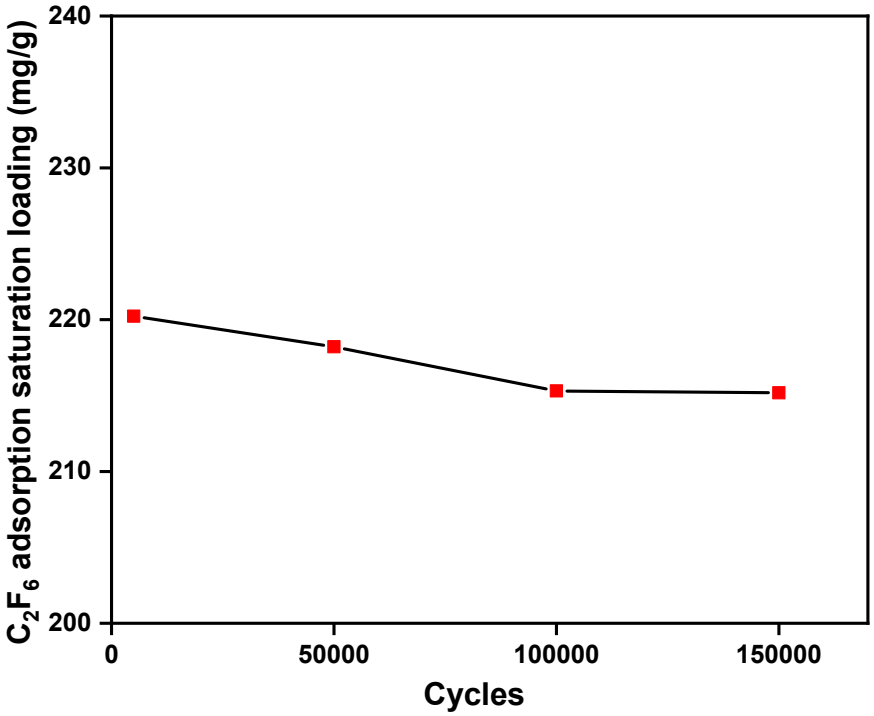

Figure S1: Convergence test of C_2F_6 adsorption data (uptake) on unit cell of MOF-5 for the Grand Canonical Monte Carlo (GCMC) simulation cycles performed.

Table S4: Computed pore diameter, surface area, and accessible volume of selected MOFs. D_i = included sphere, D_f = the largest free sphere, D_{if} = the largest free sphere.

Sl. No.	MOF	Pore diameter			Surface area (m^2/g)	Accessible volume (cm^3/g)
		D_i	D_f	D_{if}		
1	IRMOF-1	15.09	14.83	7.97	3770.17	0.92
2	F-MOF-6	6.48	6.39	4.67	1789.94	0.15
3	MOF-177	17.38	12.35	11.17	4885.52	2.01
4	MOF-200	17.97	17.07	15.8	4556.99	2.89
5	MOF-205	22.81	22.79	8.54	4207.14	1.57
6	MOF-210	28.01	27.6	12.18	5440.24	3.06
7	MOF-801	7.65	7.65	3.33	1472.67	0.09
8	MOF-1011	5.08	4.29	2.78	1073.4	0.04
9	MOP-1	10.98	10.98	6.22	2692.82	0.35
10	Co-MOF-74	1.58	1.34	0.83	0	0
11	Mn-MOF-74	3.15	3.14	1.3	0	0
12	Zn-MOF-74	2.63	2.18	1.07	0	0
13	Ni-MOF-74	2.91	2.88	1.27	0	0
14	F-MOF-1	3.04	3.02	1.77	0	0
15	CD-MOF	16.15	16.15	6.68	1536.75	0.23

16	IRMOF-5	19.81	19.81	11.82	3313.48	1.06
17	IRMOF-74	23.43	23.43	22.77	3292.09	1.14
18	IRMOF-76	25.06	25.05	12.95	5514.54	2.51
19	IRMOF-77	11.59	11.59	6.85	1768.68	0.25
20	LIC-1	5.32	5.32	1.61	0	0
21	CPL-2	18.37	18.35	18.15	4544.58	1.92
22	HKUST-1	8.62	8.57	2.91	1787.92	0.14
23	MIL-47	7.54	7.54	7	2295.36	0.26
24	MIL-53	2.12	2.11	1.17	0	0
25	MIL-88	5.66	5.63	2.34	0	0
26	MIL-101	16.94	16.94	12.83	3095.31	0.64
27	UiO-66	8.73	8.73	3.84	1257.77	0.09
28	UiO-67	11.64	11.64	3.48	1929.42	0.21
29	UiO-68	17.84	17.84	5.56	4086.41	0.74
30	ZIF-1	2.69	2.68	1.56	0	0
31	ZIF-2	3.16	1.88	1.39	0	0
32	ZIF-4	4.55	4.42	2.57	1359.06	0.05
33	ZIF-5	3.87	3.86	2.15	0	0
34	ZIF-7	5.18	4.58	2.42	825.73	0.04
35	ZIF-8	11.39	11.39	3.44	2024.67	0.28
36	ZIF-23	2.24	2.23	1.43	0	0
37	ZIF-67	11.37	11.37	3.29	2017.22	0.27
38	ZIF-70	15.28	15.28	13.37	2116.97	0.36
39	ZIF-202	1.86	1.6	1.06	0	0
40	Cd-MOF-2	2.45	2.39	1.12	0	0
41	CN-HTB'	27.43	27.42	17.55	5129.36	3.37
42	CPM-7	10.5	10.5	3.97	1919.12	0.14
43	Cu2(pzd)2	2.77	0	0	0	0
44	DUT-49	24.85	24.85	13.11	4840.96	2.25
45	F-MOF-11	2.78	2.78	1.75	0	0
46	IRMOF-3	14.93	14.93	6.64	3102.13	0.63
47	IRMOF-16	16.21	16.21	8.58	5345.55	0.76
48	IRMOF-18	14.24	14.24	5.62	2700.48	0.49
49	IRMOF-74-II	16.4	16.4	15.8	2394.32	0.72
50	IRMOF-74-III	17.92	17.92	17.51	2791.94	0.86
51	Meso-MOF-1	25.46	25.46	15.65	1369.63	2.86
52	MIL-53-Fe-Cl	6.15	6.15	5.9	771.56	0.07
53	MOF-48	2.43	2.43	2	0	0
54	MOF-73	2.56	2.56	1.41	0	0
55	MOF-112	6.56	6.56	5.02	1450.76	0.1
56	MOF-180	15.41	14.77	13.34	4642.05	2.25
57	MOF-399	37.83	37.83	24.25	6069.4	6.56
58	MOF-525	4.49	4.15	1.95	3.83	0

59	MOF-604	2.87	2.85	2.17	0	0
60	n.a.	11.95	11.95	6.57	3067.45	0.57
61	NOTT-119	21.39	20.91	11.87	5001.82	1.68
62	NU-100	28.66	28.66	11.54	5617.28	2.4
63	PCMOF-5	2.22	2.21	1.29	0	0
64	PCN-6'	22.94	22.94	14.87	5012.71	2.47
65	PCN-14	6.82	6.82	5.02	3285.6	0.31
66	PCN-20	17.06	17.06	9.83	4266.07	1.14
67	PCN-61	18.72	18.72	5.21	4167.76	0.8
68	PCN-66	25.74	18.82	12.09	4288.77	0.98
70	PCN-68	23.24	15.12	8.24	4655.73	1.27
71	PCN-69	21.69	20.7	11.87	4621.68	1.49
72	PCN-610	25.74	18.82	12.09	5653.93	2.28
73	POST-1	11.77	11.77	8.71	1444.94	0.25
74	rho-ZMOF	13.65	13.65	1.07	0	0
75	SIFSIX-3-Zn	4.12	4.12	3.34	485.64	0.02
76	UiO-66-Br	7.89	7.88	2.83	594.63	0.05
77	UiO-66-NH2	7.9	7.9	3.41	1066.83	0.08
78	UiO-66-NO2	11.93	11.93	7.29	2141.98	0.49
79	UTSA-200	2.93	2.93	2.49	348.37	0
80	UTSA-280	3.81	3.81	3	545.82	0.01
81	UTSA-300	3.99	3.97	1.74	0	0
82	NU-108	66.49	66.49	64.86	6876.81	12.58
83	NU-109	30.85	30.85	12.94	5625.56	3.21
84	NU-111	4.87	4.87	4.03	1236.09	0.07
85	MOF-508	3.39	3.89	2.53	953.82	0.02
86	MOF-1000	13.55	13.55	8.94	4109.47	0.88
87	MOF-1140	11.74	111.74	8.03	2185.04	0.36
88	CMOF-1	9.21	9.21	7.07	8047.73	1.65
89	CAUMOF-11	3.18	3.18	1.83	0	0
90	UMCM-1	23.9	0	0	4122.98	1.49
91	UMCM-151	14.44	14.44	10.21	4806.44	1.21
92	UMCM-152	13.86	13.86	5.24	4284.03	0.75
93	IRMOF-9	7.64	7.63	0	2793.05	0.28
94	SNU-50	11.31	11.31	3.5	3047.13	0.35
95	MIL-53-OH	6.68	6.68	6.47	1447.54	0.14
96	MIL-88-NH2	11.93	11.93	10.69	10075.1	3.33
97	bio-MOF-100	8.83	8.83	5.03	1751.68	0.22
98	bio-MOF-	1.65	0	0	0	0

	29					
99	bio-MOF-13	2.71	0	0	0	0
100	bio-MOF-200	3.34	6.63	4.57	0	0.45

Table S5: N_2 adsorption enthalpy and saturation loading data on shortlisted 50 MOFs.

Sl. No.	MOF	N_2 adsorption enthalpy (kJ/mol)	N_2 saturation loading (mg/g)
1	CN-HTB'	-6.05	0
2	CD-MOF	-13.76	6.21
3	CPL-2	-7.96	0.34
4	CPM-7	-16.04	8.48
5	DUT-49	-7.52	8.85
6	F-MOF-6	-14.69	8.01
7	PCN-14	-11.55	11.61
8	HKUST-1	-13.66	9.03
9	IRMOF-5	-8.54	5.3
10	IRMOF-74	-5.39	2.62
11	IRMOF-76	-7.7	10.05
12	LIC-1	-15.04	2.28
13	MIL-47	-9.96	3.74
14	MIL-101	-7.09	2.34
15	MOF-5	-7.94	5.65
16	MOF-177	-7.27	6.95
17	MOF-200	-6.27	9.26
18	MOF-205	-8.73	10
19	MOF-210	-6.01	8.46
20	NOTT-119	-8.69	9.85
21	NU-108	-8.57	7.3
22	UiO-67	-18.74	0.28
23	UiO-68	-2.48	16.24
24	ZIF-8	-11.68	5.64
25	ZIF-67	-11.52	5.62
26	ZIF-70	-16.22	10.82
27	IRMOF-1	-8.04	5.6
28	IRMOF-3	-9.06	5.58
29	IRMOF-16	-5.86	2.08
30	IRMOF-18	-11.17	9.3
31	IRMOF-74-II	-7.53	3.35
32	IRMOF-74-III	-7.01	2.87
33	IRMOF-77	-2.49	1.17
34	Meso-MOF-1	-6.25	8.35
35	MIL-53-Fe-Cl	-17.71	11.84
36	MIL-88	-12.56	2

37	MOF-180	-6.18	7.57
38	MOF-399	-4.86	13.01
39	MOF-525	-9.81	4.09
40	MOF-801	-16.63	7.11
41	MOF-1011	-17.3	2.67
42	MOF-1140	-10.6	4.1
43	n.a	-8.41	4.71
44	UiO-66	-16.24	7.12
45	ZIF-4	-18.77	6.44
46	ZIF-7	-22.50	23.86
47	MOF-112	-16.18	5.75
48	NU-100	-7.95	9.51
49	PCN-610	-7.35	9.10
50	PCN-61	-9.85	8.91

Table S6: C_2F_4 adsorption enthalpy and saturation loading data on shortlisted 50 MOFs:

Sl. No.	MOF	C_2F_4 adsorption enthalpy (kJ/mol)	C_2F_4 saturation loading (mg/g)
1	CN-HTB'	-17.97	371.94
2	CD-MOF	-25.89	323.3
3	CPL-2	-18.86	14.73
4	CPM-7	-34.12	293.16
5	DUT-49	-21.5	613
6	F-MOF-6	-45.87	344.89
7	PCN-14	-37.12	1072.73
8	HKUST-1	-39.2	750.81
9	IRMOF-5	-20.07	318.09
10	IRMOF-74	-14.4	46.22
11	IRMOF-76	-20.92	566.24
12	LIC-1	-32.13	145.43
13	MIL-47	-30.28	280.86
14	MIL-101	-15.41	68.80
15	MOF-5	-26.69	788.96
16	MOF-177	-23.79	816.59
17	MOF-200	-17.9	387.4
18	MOF-205	-25.65	1200.55
19	MOF-210	-12.37	305
20	NOTT-119	-19.48	686.87
21	NU-108	-35.09	1288.59
22	UiO-67	-39.21	175.25
23	UiO-68	-42.35	447.73
24	ZIF-8	-39.35	427.92
25	ZIF-67	-38.02	418.54
26	ZIF-70	-24.67	379.77
27	IRMOF-1	-26.68	775.48

28	IRMOF-3	-27.49	690.44
29	IRMOF-16	-13.34	21.65
30	IRMOF-18	-38.58	786.91
31	IRMOF-74-II	-18.38	127.47
32	IRMOF-74-III	-17.43	79.97
33	IRMOF-77	-2.49	4.04
34	Meso-MOF-1	-20.02	455.26
35	MIL-53-Fe-Cl	-47.66	179.81
36	MIL-88	-30.92	113.74
37	MOF-180	-16.42	253.02
38	MOF-399	-14.84	307.44
39	MOF-525	-22.70	266.94
40	MOF-801	-41.84	260.42
41	MOF-1011	-30.15	60.97
42	MOF-1140	-26.39	381.62
43	n.a	-30.31	667.14
44	UiO-66	-43.81	174.44
45	ZIF-4	-43.04	201.78 (up to10000 Pa)
46	ZIF-7	-39.65	204.19
47	MOF-112	-38.165	254.88
48	NU-100	-18.59	429.38
49	PCN-610	-17.79	432.84
50	PCN-61	-28.47	1039.98e

Table S7: C_2F_6 adsorption enthalpy and saturation loading data on shortlisted 50 MOFs:

SI. No.	**MOF**	**C_2F_6 adsorption enthalpy (kJ/mol)**	**C_2F_6 saturation loading (mg/g)**
1	CN-HTB'	-12.91	120.16
2	CD-MOF	-20.42	154.69
3	CPL-2	-15.27	6.44
4	CPM-7	-25.89	160.17
5	DUT-49	-17	251.73
6	F-MOF-6	-32.38	183.96
7	PCN-14	-29.77	269.68
8	HKUST-1	-28.07	372.71
9	IRMOF-5	-16.41	139.45
10	IRMOF-74	-11.2	14.15
11	IRMOF-76	-15.56	246.06
12	LIC-1	-30.54	46.22
13	MIL-47	-19.04	89.3
14	MIL-101	-10.02	31.48
15	MOF-5	-18.52	220.24
16	MOF-177	-15.74	192.85
17	MOF-200	-12.97	147.57
18	MOF-205	-18.52	362.37

19	MOF-210	-12.89	117.79
20	NOTT-119	-15.81	240.36
21	NU-108	-21.64	432.38
22	UiO-67	-30.9	257.7
23	UiO-68	-2.5	48.75 (up to 5000 Pa)
24	ZIF-8	-30.76	218.71
25	ZIF-67	-29	198.78
26	ZIF-70	-21.17	207.45
27	IRMOF-1	-18.68	223.80
28	IRMOF-3	-21.72	297.65
29	IRMOF-16	-8.96	9.2
30	IRMOF-18	-31.61	411.13
31	IRMOF-74-II	-13.83	51.56
32	IRMOF-74-III	-14.13	39.27
33	IRMOF-77	-12.21	122.62
34	Meso-MOF-1	-15.06	162.73
35	MIL-53-Fe-Cl	-35.11	108.29
36	MIL-88	-24.73	48.77
37	MOF-180	-12.33	98.48
38	MOF-399	-10.61	114.07
39	MOF-525	positive value	130.5
40	MOF-801	-36.52	124.73
41	MOF-1011	-34.29	20.94
42	MOF-1140	-21.18	139.91
43	n.a	-21.26	241.95
44	UiO-66	-29.63	91.32
45	ZIF-4	-34.9	91.87
46	ZIF-7	-33.25	139.18
47	MOF-112	-28.43	114.09
48	NU-100	-12.56	181.32
49	PCN-610	-14.78	181.29
50	PCN-61	-21.05	324.62

Table S8: C_2F_4 and C_2F_6 adsorption enthalpies from UFF-based GCMC simulations.

SI. No.	MOF	C_2F_4 adsorption enthalpy (kJ/mol)	C_2F_6 adsorption enthalpy (kJ/mol)
1	MIL-47	-30.27	-27.34
2	DUT-49	-21.5	-19.66
3	IRMOF-5	-20.07	-16.41
4	ZIF-7	-39.65	-40.07
5	F-MOF-6	-45.87	-43.79

DFT Calculations:

The binding of MOFs (MIL-53-Fe and MIL-53-Fe-Cl) with C_2F_4 refrigerant is investigated within the framework of periodic density functional theory (DFT)[1] using the SIESTA package[2]. We first optimized the MOF crystal structures by fully relaxing their lattice parameters. The fully relaxed MOFs were subjected to C_2F_4 adsorption, computing binding strength and observing characteristic changes due to refrigerant binding. The generalized gradient approximation parameterized by the Perdew-Burke-Ernzerhof functional (GGA-PBE)[3] was used for all calculations to consider exchange and correlation energies. The DFT-D2[4] method was employed to treat van der Waals interactions. The non-relativistic Troullier-Martins pseudopotentials for all molecules were taken from the FHI pseudopotential database[5]. We took the mesh cutoff of 350 Ry for the Fourier expansion of the electron density in a 1 × 1 × 1 unit cell. The binding energies were determined using the formula $\Delta E = \Delta E_{\mathrm{MOF + refrigerant}} - \Delta E_{\mathrm{MOF}} - \Delta E_{\mathrm{refrigerant}}$ for C_2F_4 refrigerant, where E represents the system's overall energy. E_{MOF}, $E_{\mathrm{refrigerant}}$, and $E_{\mathrm{MOF + refrigerant}}$ are the energy of the bare MOF without the guest molecule, refrigerant molecule in the gas phase, and MOF with an adsorbed refrigerant molecule, respectively.

References:

1 Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **140**, A1133-A1138, doi:10.1103/PhysRev.140.A1133 (1965).

2 Soler, J. M. *et al.* The SIESTA method for ab initio order- N materials simulation. *J. Phys.: Condens. Matter* **14**, 2745-2779, doi:10.1088/0953-8984/14/11/302 (2002).

3 Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **77**, 3865-3868, doi:10.1103/PhysRevLett.77.3865 (1996).

4 Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *Journal of Computational Chemistry* **27**, 1787-1799, doi:10.1002/jcc.20495 (2006).

5 SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms).