Electronic Supplementary Information

Effects of Substituent Groups on Methane Adsorption in Covalent Organic Frameworks

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I. Experimental covalent organic frameworks (all with space group: I-43D)[1]

COF-102

Lattice parameters: a=b=c=27.177Å; α=β=γ=90°

Atom	x	y	z
B1	0.83533	0.71325	0.26216
O1	0.82850	0.74693	0.30298
C1	0.90490	0.76629	0.22758
C2	0.87894	0.72231	0.22630
C3	0.93120	0.69419	0.16049
C4	0.95634	0.73930	0.15960
C5	0.89252	0.68630	0.19272
C6	0.94306	0.77459	0.19484
C7	1.00000	0.75000	0.12500
H1	0.89552	0.79460	0.25352
H2	0.94125	0.66415	0.13717
H3	0.87377	0.65150	0.19176
H4	0.96223	0.80911	0.19660

COF-103

Lattice parameters: a=b=c=28.248Å; α=β=γ=90°

Atom	x	y	z
B1	0.24102	0.17052	0.21731
O1	0.20173	0.17738	0.24979
C1	0.34070	0.07966	0.20001
C2	0.33591	0.05139	0.24007
C3	0.30021	0.06125	0.27253
C4	0.26989	0.09921	0.26533
C5	0.27496	0.12788	0.22549
C6	0.31062	0.11783	0.19290
Si1	0.37500	0.00000	0.25000
H1	0.36748	0.07242	0.17407
H2	0.29575	0.03949	0.30345
H3	0.24263	0.10607	0.29100
H4	0.31517	0.13920	0.16171

COF-105

Lattice parameters: a=b=c=44.886Å; α=β=γ=90°

Atom	x	y	z
B1	0.28905	0.10906	0.22877
O1	0.24923	0.26434	0.11672
O2	0.12931	0.20284	0.29149
Si1	0.37500	0.00000	0.25000
C1	0.22645	0.21781	0.18335
C2	0.20018	0.23477	0.19174
C3	0.23455	0.25261	0.14166
C4	0.20882	0.26778	0.14873
C5	0.19137	0.25958	0.17328
C6	0.24387	0.22787	0.15826
C7	0.35228	0.05035	0.21728
C8	0.34987	0.03288	0.24348
C9	0.32755	0.03978	0.26475
C10	0.30811	0.06410	0.26008
C11	0.31075	0.08180	0.23403
C12	0.33294	0.07478	0.21265
H1	0.17131	0.27270	0.17680
H2	0.26464	0.21763	0.15114

H3	0.36894	0.04522	0.20028
H4	0.33529	0.08803	0.19228
H5	0.32518	0.02632	0.28497
H6	0.29108	0.06904	0.27686

II. Substituted covalent organic frameworks (all with space group: I-43D)[a)]

II.1 COF-102-X

COF-102-Cl

Lattice parameters: a=b=c=27.354Å; α=β=γ=90°

Atom	x	y	Z
B1	0.46449	0.58466	0.01163
O1	0.42407	0.55226	0.00357
C1	0.51805	0.65215	0.97845
C2	0.47338	0.62660	0.97798
C3	0.44581	0.68133	0.91314
C4	0.49118	0.70696	0.91089
C5	0.43722	0.64182	0.94478
C6	0.52700	0.69092	0.94576
C7	0.50000	0.75000	0.87500
H1	0.54493	0.64229	0.00261
H2	0.41696	0.69152	0.89190
H3	0.40391	0.62457	0.94369
Cl1	0.58400	0.71482	0.95133

COF-102-Br

Lattice parameters: a=b=c=27.357Å; α=β=γ=90°

Atom	x	y	Z
B1	0.46459	0.58445	0.01135
O1	0.42421	0.55197	0.00342
C1	0.51756	0.65271	0.97880
C2	0.47339	0.62635	0.97761
C3	0.44624	0.68018	0.91183

C4	0.49106	0.70684	0.91062
C5	0.43770	0.64069	0.94352
C6	0.52645	0.69146	0.94616
C7	0.50000	0.75000	0.87500
H1	0.54424	0.64356	0.00342
H2	0.41771	0.68952	0.88982
H3	0.40478	0.62277	0.94179
Br1	0.58876	0.71812	0.95363

COF-102-I

Lattice parameters: a=b=c=27.386Å; α=β=γ=90°

Atom	x	y	z
B1	0.46548	0.58360	0.01053
O1	0.42514	0.55113	0.00260
C1	0.51740	0.65322	0.97948
C2	0.47424	0.62550	0.97686
C3	0.44794	0.67809	0.90993
C4	0.49165	0.70653	0.91040
C5	0.43950	0.63848	0.94140
C6	0.52629	0.69221	0.94715
C7	0.50000	0.75000	0.87500
H1	0.54331	0.64481	0.00509
H2	0.41993	0.68609	0.88686
H3	0.40735	0.61944	0.93853
I1	0.59415	0.72264	0.95851

COF-102-CF_3

Lattice parameters: a=b=c=27.492Å; α=β=γ=90°

Atom	x	y	z
B1	0.46632	0.58342	0.01090
O1	0.42599	0.55148	0.00230
C1	0.51710	0.65510	0.98333
C2	0.47598	0.62524	0.97767
C3	0.45297	0.67572	0.90904
C4	0.49497	0.70643	0.91174
C5	0.44383	0.63621	0.93981
C6	0.52822	0.69464	0.95145

C7	0.50000	0.75000	0.87500
H1	0.53948	0.64764	0.01236
H2	0.42627	0.68163	0.88413
H3	0.41291	0.61594	0.93454
C8	0.57402	0.72196	0.96551
F1	0.56295	0.75917	0.99666
F2	0.60027	0.74106	0.92803
F3	0.60842	0.69360	0.98789

COF-102-NH_2

Lattice parameters: a=b=c=27.352Å; α=β=γ=90°

Atom	x	y	z
B1	0.46415	0.58497	0.01173
O1	0.42377	0.55240	0.00389
C1	0.51708	0.65337	0.97932
C2	0.47297	0.62684	0.97789
C3	0.44600	0.68015	0.91145
C4	0.49079	0.70686	0.91058
C5	0.43746	0.64089	0.94343
C6	0.52612	0.69200	0.94648
C7	0.50000	0.75000	0.87500
H1	0.54329	0.64413	0.00438
H2	0.41777	0.68892	0.88884
H3	0.40472	0.62269	0.94165
N1	0.57054	0.71278	0.95118
H4	0.59275	0.70219	0.97669
H5	0.58065	0.73851	0.92913

COF-102-CN

Lattice parameters: a=b=c=27.388Å; α=β=γ=90°

Atom	x	y	z
B1	0.46572	0.58390	0.01094
O1	0.42524	0.55168	0.00266
C1	0.51936	0.65170	0.97832
C2	0.47477	0.62608	0.97765
C3	0.44695	0.68123	0.91344
C4	0.49218	0.70689	0.91112

C5	0.43859	0.64155	0.94474
C6	0.52826	0.69106	0.94593
C7	0.50000	0.75000	0.87500
H1	0.54570	0.64089	0.00284
H2	0.41789	0.69144	0.89260
H3	0.40537	0.62430	0.94372
C8	0.57155	0.71098	0.94996
N1	0.60987	0.72755	0.95375

COF-102-OCH_3

Lattice parameters: a=b=c=27.284Å; α=β=γ=90°

Atom	x	y	z
B1	0.46351	0.58569	0.01236
O1	0.42302	0.55310	0.00442
C1	0.51776	0.65224	0.97755
C2	0.47233	0.62770	0.97849
C3	0.44391	0.68336	0.91441
C4	0.49014	0.70733	0.91088
C5	0.43539	0.64400	0.94643
C6	0.52697	0.69092	0.94447
C7	0.50000	0.75000	0.87500
H1	0.54484	0.64152	0.00096
H2	0.41486	0.69460	0.89386
H3	0.40162	0.62754	0.94653
O2	0.57208	0.71282	0.94372
C8	0.61507	0.70495	0.97300
H4	0.64369	0.73016	0.96103
H5	0.60731	0.71207	0.01160
H6	0.62852	0.66754	0.96866

COF-102-CH_3

Lattice parameters: a=b=c=27.459Å; α=β=γ=90°

Atom	x	y	z
B1	0.46525	0.58414	0.01121
O1	0.42492	0.55187	0.00318
C1	0.51638	0.65505	0.98209
C2	0.47452	0.62586	0.97758

C3	0.45072	0.67626	0.90853
C4	0.49320	0.70630	0.91079
C5	0.44174	0.63713	0.94005
C6	0.52678	0.69374	0.94948
C7	0.50000	0.75000	0.87500
H1	0.54013	0.64735	0.00984
H2	0.42392	0.68252	0.88378
H3	0.41062	0.61670	0.93565
C8	0.57425	0.71801	0.96019
H4	0.57020	0.74148	0.99201
H5	0.58794	0.73978	0.93041
H6	0.60272	0.69124	0.96760

II.2 COF-103-X

COF-103-Cl

Lattice parameters: a=b=c=27.785Å; α=β=γ=90°

Atom	x	y	z
B1	0.46499	0.58305	0.01092
O1	0.42527	0.55087	0.00332
C1	0.44617	0.67687	0.91230
C2	0.49020	0.70321	0.91237
C3	0.52516	0.68925	0.94721
C4	0.51668	0.65086	0.97921
C5	0.47339	0.62434	0.97759
C6	0.43820	0.63790	0.94362
Si1	0.50000	0.75000	0.87500
H1	0.41831	0.68560	0.88978
H2	0.40607	0.61968	0.94167
H3	0.54284	0.64216	0.00378
Cl1	0.57976	0.71586	0.95348

COF-103-Br

Lattice parameters: a=b=c=27.787Å; α=β=γ=90°

Atom	x	y	z
B1	0.46534	0.58266	0.01049
O1	0.42564	0.55044	0.00295
C1	0.44676	0.67595	0.91130
C2	0.49029	0.70306	0.91215
C3	0.52493	0.68952	0.94745
C4	0.51655	0.65106	0.97932
C5	0.47367	0.62395	0.97715
C6	0.43884	0.63693	0.94258
Si1	0.50000	0.75000	0.87500
H1	0.41920	0.68413	0.88824
H2	0.40703	0.61823	0.94016
H3	0.54256	0.64288	0.00417
Br1	0.58460	0.71914	0.95544

COF-103-I

Lattice parameters: a=b=c=27.819Å; α=β=γ=90°

Atom	x	y	z
B1	0.46664	0.58147	0.00936
O1	0.42697	0.54931	0.00177
C1	0.44889	0.67412	0.90968
C2	0.49136	0.70272	0.91202
C3	0.52530	0.68998	0.94839
C4	0.51691	0.65113	0.97975
C5	0.47498	0.62286	0.97623
C6	0.44106	0.63487	0.94057
Si1	0.50000	0.75000	0.87500
H1	0.42187	0.68134	0.88579
H2	0.40996	0.61527	0.93706
H3	0.54219	0.64345	0.00543
I1	0.59016	0.72360	0.96062

COF-103-CF_3

Lattice parameters: a=b=c=27.930Å; α=β=γ=90°

Atom	x	y	z
B1	0.46599	0.58305	0.01157
O1	0.42624	0.55158	0.00310
C1	0.45324	0.67326	0.91027
C2	0.49470	0.70308	0.91401
C3	0.52733	0.69238	0.95322
C4	0.51616	0.65361	0.98464
C5	0.47561	0.62417	0.97874
C6	0.44415	0.63463	0.94100
Si1	0.50000	0.75000	0.87500
H1	0.42728	0.67893	0.88497
H2	0.41380	0.61449	0.93573
H3	0.53815	0.64650	0.01338
C7	0.57216	0.71981	0.96712
F1	0.56051	0.75630	0.99758
F2	0.59498	0.74026	0.92908
F3	0.60703	0.69205	0.98762

COF-103-NH_2

Lattice parameters: a=b=c=27.782Å; α=β=γ=90°

Atom	x	y	z
B1	0.46565	0.58250	0.01022
O1	0.42594	0.55024	0.00272
C1	0.44760	0.67518	0.91025
C2	0.49057	0.70308	0.91219
C3	0.52487	0.69047	0.94829
C4	0.51636	0.65177	0.97999
C5	0.47400	0.62389	0.97692
C6	0.43974	0.63618	0.94153
Si1	0.50000	0.75000	0.87500
H1	0.42068	0.68251	0.88623
H2	0.40843	0.61679	0.93850
H3	0.54161	0.64367	0.00562
N1	0.56717	0.71342	0.95472
H4	0.58880	0.70326	0.98027
H5	0.57666	0.74026	0.93457

COF-103-CN

Lattice parameters: a=b=c=27.853Å; α=β=γ=90°

Atom	x	y	z
B1	0.46698	0.58176	0.00985
O1	0.42718	0.54994	0.00182
C1	0.44892	0.67606	0.91210
C2	0.49229	0.70313	0.91298
C3	0.52716	0.68963	0.94854
C4	0.51852	0.65043	0.97982
C5	0.47573	0.62337	0.97711
C6	0.44108	0.63682	0.94280
Si1	0.50000	0.75000	0.87500
H1	0.42122	0.68440	0.88946
H2	0.40934	0.61823	0.94021
H3	0.54371	0.64093	0.00518
C7	0.56846	0.71166	0.95460
N1	0.60470	0.73074	0.95958

COF-103-OCH_3

Lattice parameters: a=b=c=27.726Å; α=β=γ=90°

Atom	x	y	z
B1	0.46410	0.58376	0.01129
O1	0.42438	0.55129	0.00401
C1	0.44497	0.67676	0.91139
C2	0.48891	0.70332	0.91196
C3	0.52411	0.69042	0.94688
C4	0.51548	0.65206	0.97923
C5	0.47232	0.62503	0.97761
C6	0.43718	0.63803	0.94316
Si1	0.50000	0.75000	0.87500
H1	0.41753	0.68506	0.88816
H2	0.40525	0.61938	0.94121
H3	0.54129	0.64355	0.00408
O2	0.56663	0.71539	0.94816
C7	0.60746	0.71136	0.97981
H4	0.63446	0.73808	0.96938
H5	0.59684	0.71836	0.01714
H6	0.62370	0.67554	0.97721

COF-103-CH_3

Lattice parameters: a=b=c=27.867Å; α=β=γ=90°

Atom	x	y	z
B1	0.46971	0.57899	0.00701
O1	0.42996	0.54709	0.99910
C1	0.45174	0.67338	0.90955
C2	0.49353	0.70274	0.91286
C3	0.52724	0.69099	0.95031
C4	0.51891	0.65035	0.97986
C5	0.47795	0.62107	0.97478
C6	0.44438	0.63329	0.93912
Si1	0.50000	0.75000	0.87500
H1	0.42488	0.68046	0.88557
H2	0.41386	0.61313	0.93472
H3	0.54296	0.64183	0.00636
C7	0.57081	0.71983	0.96275
H4	0.55990	0.75185	0.98250
H5	0.59105	0.73074	0.93124
H6	0.59613	0.70044	0.98560

II.3 COF-105-X

COF-105-Cl

Lattice parameters: a=b=c=43.855Å; α=β=γ=90°

Atom	x	y	z
B1	0.47794	0.64475	0.96150
O1	0.49777	0.63596	0.98626
O2	0.45213	0.62437	0.96016
Si1	0.50000	0.75000	0.87500
C1	0.47488	0.56898	0.03414
C2	0.44815	0.56067	0.01690
C3	0.48370	0.61159	0.99869
C4	0.45709	0.60461	0.98318
C5	0.43935	0.57969	0.99185
C6	0.49274	0.59430	0.02380
C7	0.46573	0.70417	0.89929
C8	0.49386	0.72045	0.89881

C9	0.51632	0.71133	0.92048
C10	0.51099	0.68710	0.94090
C11	0.48330	0.67078	0.94033
C12	0.46068	0.67959	0.91927
H1	0.42021	0.57654	0.97919
H2	0.51261	0.60108	0.03359
H3	0.44792	0.70996	0.88533
H4	0.44017	0.66827	0.91851
H5	0.52771	0.68133	0.95624
Cl1	0.55120	0.72771	0.92380

COF-105-Br

Lattice parameters: a=b=c=43.861Å; α=β=γ=90°

Atom	x	y	z
B1	0.47810	0.64446	0.96117
O1	0.49786	0.63579	0.98603
O2	0.45240	0.62396	0.95974
Si1	0.50000	0.75000	0.87500
C1	0.47512	0.56872	0.03385
C2	0.44842	0.56036	0.01660
C3	0.48386	0.61136	0.99842
C4	0.45734	0.60425	0.98282
C5	0.43966	0.57930	0.99148
C6	0.49290	0.59411	0.02355
C7	0.46607	0.70356	0.89862
C8	0.49390	0.72035	0.89866
C9	0.51613	0.71150	0.92065
C10	0.51086	0.68722	0.94097
C11	0.48342	0.67051	0.94001
C12	0.46104	0.67894	0.91855
H1	0.42058	0.57606	0.97874
H2	0.51270	0.60100	0.03339
H3	0.44844	0.70900	0.88430
H4	0.44073	0.66730	0.91746
H5	0.52748	0.68177	0.95650
Br1	0.55426	0.72977	0.92504

COF-105-I

Lattice parameters: a=b=c=43.893Å; α=β=γ=90°

Atom	x	y	z
B1	0.47908	0.64348	0.96030
O1	0.49862	0.63499	0.98536
O2	0.45366	0.62268	0.95855
Si1	0.50000	0.75000	0.87500
C1	0.47618	0.56764	0.03280
C2	0.44956	0.55922	0.01548
C3	0.48478	0.61040	0.99754
C4	0.45852	0.60306	0.98168
C5	0.44096	0.57801	0.99022
C6	0.49378	0.59321	0.02269
C7	0.46749	0.70219	0.89742
C8	0.49459	0.72009	0.89855
C9	0.51634	0.71184	0.92133
C10	0.51110	0.68726	0.94129
C11	0.48434	0.66966	0.93932
C12	0.46256	0.67737	0.91707
H1	0.42209	0.57461	0.97727
H2	0.51339	0.60031	0.03270
H3	0.45023	0.70693	0.88249
H4	0.44274	0.66504	0.91518
H5	0.52723	0.68219	0.95742
I1	0.55771	0.73283	0.92854

COF-105-CF_3

Lattice parameters: a=b=c=43.986Å; α=β=γ=90°

Atom	x	y	z
B1	0.47857	0.64565	0.96332
O1	0.49704	0.63761	0.98922
O2	0.45335	0.62479	0.96087
Si1	0.50000	0.75000	0.75000
C1	0.47353	0.57042	0.03606
C2	0.44719	0.5622	0.01832
C3	0.48286	0.61318	0.00114
C4	0.45728	0.60561	0.98446
C5	0.43945	0.58074	0.99268

C6	0.49108	0.59619	0.02660
C7	0.47077	0.70120	0.89776
C8	0.49699	0.72029	0.89990
C9	0.51784	0.71382	0.92475
C10	0.51068	0.68976	0.94534
C11	0.48487	0.67118	0.94193
C12	0.46494	0.67713	0.91780
H1	0.42113	0.57723	0.97908
H2	0.51018	0.60361	0.03724
H3	0.45437	0.70441	0.88153
H4	0.44573	0.66418	0.91478
H5	0.52465	0.68555	0.96369
C13	0.54671	0.73084	0.93290
F1	0.54030	0.75330	0.95339
F2	0.56052	0.74463	0.90882
F3	0.56923	0.71242	0.94408

COF-105-NH_2

Lattice parameters: a=b=c=43.851Å; α=β=γ=90°

Atom	x	y	z
B1	0.47831	0.64421	0.96080
O1	0.49790	0.63574	0.98588
O2	0.45281	0.62344	0.95916
Si1	0.50000	0.75000	0.87500
C1	0.47541	0.56843	0.03352
C2	0.44875	0.55999	0.01622
C3	0.48402	0.61117	0.99816
C4	0.45770	0.60383	0.98235
C5	0.44010	0.57879	0.99095
C6	0.49304	0.59399	0.02335
C7	0.46671	0.70277	0.89759
C8	0.49406	0.72030	0.89861
C9	0.51593	0.71221	0.92133
C10	0.51058	0.68774	0.94148
C11	0.48361	0.67033	0.93968
C12	0.46172	0.67812	0.91748
H1	0.57882	0.92462	0.97805
H2	0.48731	0.89893	0.03333
H3	0.55044	0.79251	0.88249
H4	0.55819	0.83414	0.91580

H5	0.47338	0.81755	0.95765
N1	0.45717	0.77336	0.92520
H6	0.44338	0.77983	0.94131
H7	0.45115	0.75641	0.91236

COF-105-CN

Lattice parameters: a=b=c=43.915Å; α=β=γ=90°

Atom	x	y	z
B1	0.48004	0.64346	0.96063
O1	0.49962	0.63458	0.98552
O2	0.45444	0.62290	0.95884
Si1	0.50000	0.75000	0.87500
C1	0.47670	0.56719	0.03259
C2	0.45009	0.55901	0.01519
C3	0.48562	0.61003	0.99757
C4	0.45926	0.60303	0.98176
C5	0.44155	0.57804	0.99012
C6	0.49452	0.59262	0.02258
C7	0.46785	0.70314	0.89892
C8	0.49539	0.72028	0.89915
C9	0.51777	0.71172	0.92144
C10	0.51254	0.68686	0.94134
C11	0.48536	0.66982	0.93987
C12	0.46308	0.67827	0.91846
H1	0.42261	0.57488	0.97724
H2	0.51423	0.59943	0.03258
H3	0.45012	0.70845	0.88476
H4	0.44294	0.66642	0.91714
H5	0.52866	0.68075	0.95728
C13	0.54400	0.72570	0.92498
N1	0.56701	0.73782	0.92787

COF-105-OCH_3

Lattice parameters: a=b=c=43.790Å; α=β=γ=90°

Atom	x	y	z
B1	0.47699	0.64525	0.96154
O1	0.49683	0.63670	0.98646

O2	0.45123	0.62472	0.96027
Si1	0.50000	0.75000	0.87500
C1	0.47419	0.56967	0.03464
C2	0.44742	0.56121	0.01743
C3	0.48283	0.61227	0.99899
C4	0.45624	0.60508	0.98346
C5	0.43856	0.58010	0.99225
C6	0.49195	0.59509	0.02422
C7	0.46483	0.70412	0.89852
C8	0.49290	0.72053	0.89849
C9	0.51540	0.71207	0.92029
C10	0.50992	0.68784	0.94085
C11	0.48231	0.67123	0.94016
C12	0.45982	0.67968	0.91873
H1	0.41943	0.57679	0.97958
H2	0.51178	0.60202	0.03403
H3	0.44733	0.70963	0.88406
H4	0.43944	0.66808	0.91785
H5	0.52636	0.68216	0.95640
O3	0.54251	0.72756	0.92072
C13	0.56869	0.72453	0.94029
H6	0.58592	0.74126	0.93352
H7	0.56249	0.72887	0.96409
H8	0.57867	0.70173	0.93832

COF-105-CH_3

Lattice parameters: a=b=c=43.923Å; α=β=γ=90°

Atom	x	y	z
B1	0.48198	0.64100	0.95802
O1	0.50147	0.63240	0.98307
O2	0.45698	0.61977	0.95570
Si1	0.50000	0.75000	0.87500
C1	0.47965	0.56418	0.02944
C2	0.45313	0.55578	0.01201
C3	0.48799	0.60737	0.99471
C4	0.46198	0.59988	0.97856
C5	0.44466	0.57456	0.98672
C6	0.49705	0.58999	0.01967
C7	0.46957	0.70125	0.89696
C8	0.49604	0.71992	0.89891

C9	0.51759	0.71258	0.92262
C10	0.51263	0.68660	0.94119
C11	0.48676	0.66794	0.93789
C12	0.46518	0.67566	0.91558
H1	0.42602	0.57102	0.97353
H2	0.51649	0.59721	0.02987
H3	0.45239	0.70574	0.88190
H4	0.44589	0.66268	0.91293
H5	0.52799	0.68110	0.95790
C13	0.54511	0.73104	0.93054
H6	0.53809	0.75133	0.94306
H7	0.55802	0.73798	0.91060
H8	0.56120	0.71886	0.94512

[a)]The geometry optimizations were performed with DREIDING force field[2] and conjugate gradient algorithm. During the whole process of optimization, all of them are treated as P1 space group with all atoms and full cell flexibility. After the optimization, all the frameworks still hold ctn topology with I-43D space group. By using the above method, we also optimize the basic COF-102, COF-103, and COF-105. Their optimized structures possess ctn topology and the cell lengths are 27.262 Å (COF-102), 27.759 Å (COF-103), and 43.821 Å (COF-105) respectively, comparable with their experimental data, i.e. 27.1771 Å (COF-102), 28.2477 Å (COF-103), and 44.8860 Å (COF-105) respectively.

References

1. H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortes, A. P. Cote, R. E. Taylor, M. O'Keeffe and O. M. Yaghi, *Science*, 2007, 316, 268-272.
2. S. L. Mayo, B. D. Olafson and W. A. Goddard, *J. Phys. Chem.*, 1990, 94, 8897-8909.

III. Complete figures for excess methane uptake and methane delivery of COF-102-Xs and COF-103-Xs.

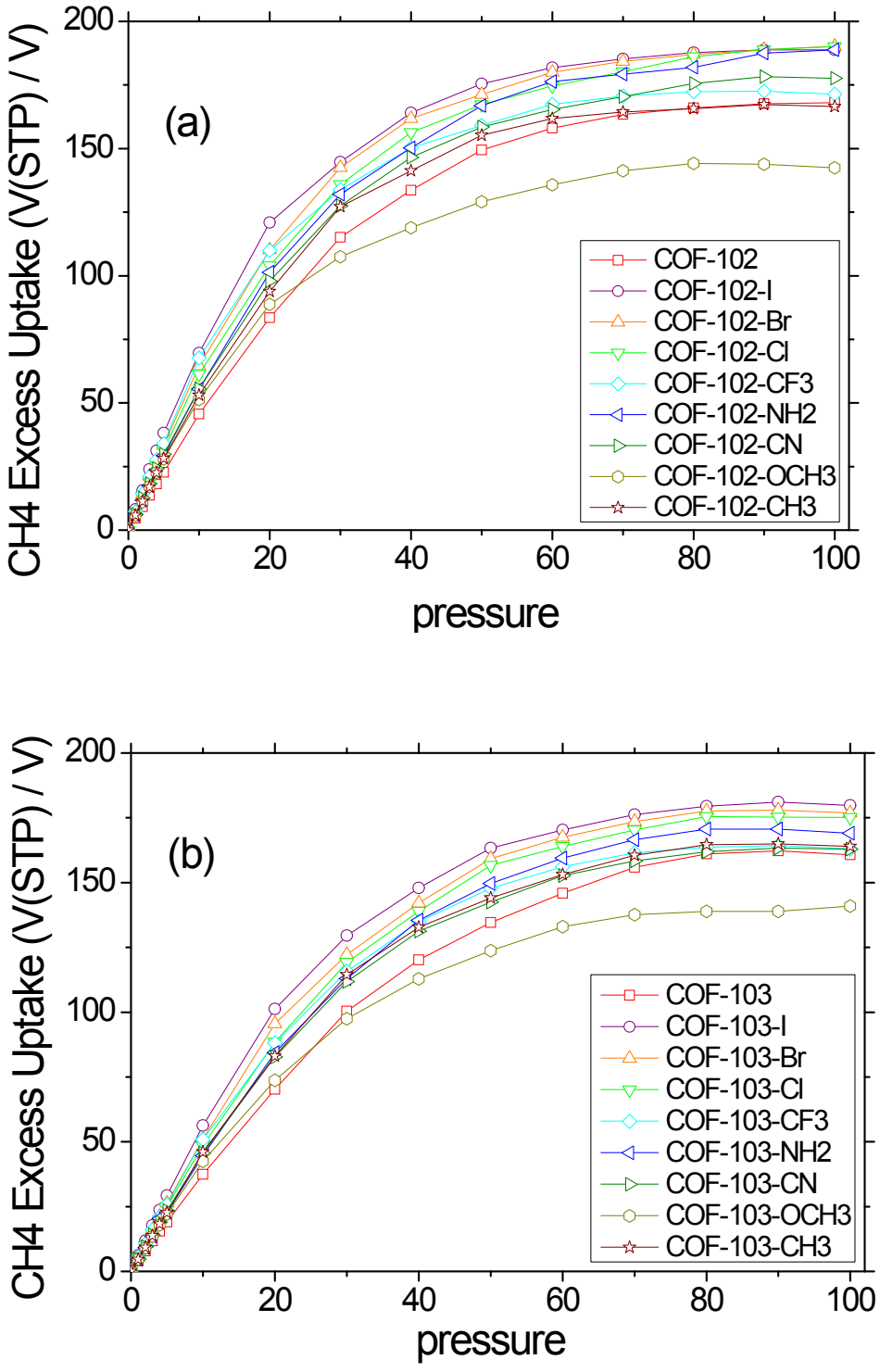

Figure S1. Complete isotherms of excess volumetric methane uptake at 298 K from 0 to 100 bar. (a) is for COF-102-Xs and (b) is for COF-103-Xs.

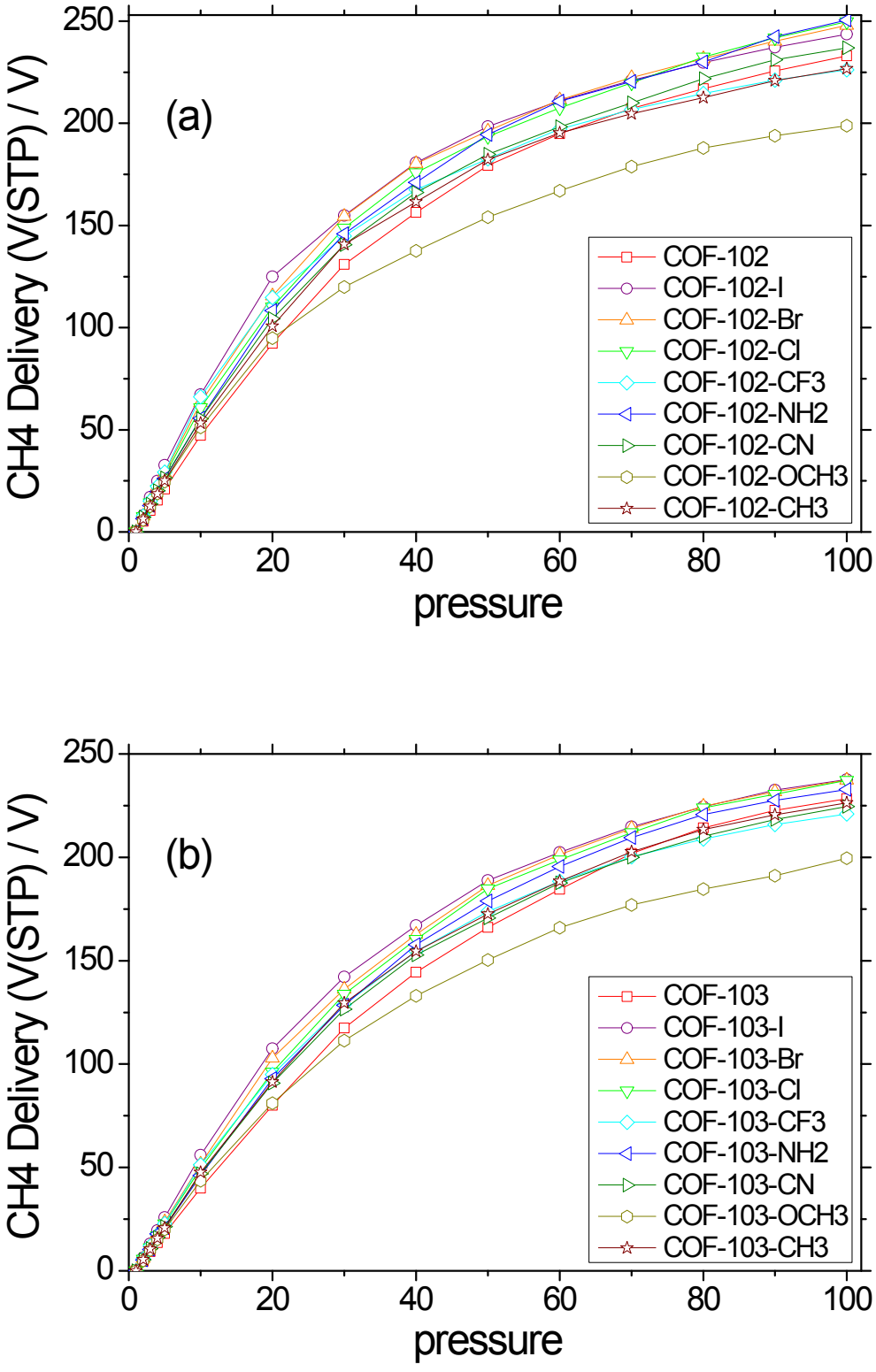

Figure S2. Complete isotherms of methane delivery at 298 K from 1 to 100 bar. (a) is for COF-102-Xs and (b) is for COF-103-Xs.