Supporting Information

A Covalent Organic Framework that Exceeds the DOE 2015 Volumetric Target for H_2 Uptake at 298 K

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1 FF parameters

These FF parameters for non-bonded interactions between H_2 and COFs use the functional form the Morse potential,

$$\boldsymbol{U}_{ij}^{Morse}(r_{ij}) = D\left\{e^{\alpha(1-\frac{r_{ij}}{r_0})} - 2e^{-\frac{\alpha}{2}(1-\frac{r_{ij}}{r_0})}\right\} \quad (1)$$

the parameter D is the well depth, r_0 is the equilibrium bond distance, and α determines the stiffness (force constant). The parameters used are shown in Table 1. The H_{H2}-$N(sp^2)_{COF}$ is based on MP2 for ligand 1,3,5-triazine. The H_{H2}-Cl_{PdCl2} and H_{H2}-Pd_{PdCl2} are based on DFT/M06. The rest of the terms have been reported previously.[1, 2]

Table 1: The nonbonded FF parameters used for this study. The Morse function form (eq 1) is used. D is the well depth, r_0 is the equilibrium bond distance, and α determines the force constant.

Term	D/kJ mol^{-1}	r_0/Å	α
H_{H2}-H_{H2}	7.60x10^{-2}	3.57	10.7
H_{H2}-H_{COF}	3.63x10^{-3}	3.25	12
H_{H2}-O_{COF}	1.05x10^{-1}	3.32	12
H_{H2}-$C(sp^3)_{COF}$	2.19x10^{-1}	3.02	14.9
H_{H2}-$C(sp^2)_{COF}$	4.22x10^{-1}	3.12	12
H_{H2}-$N(sp^2)_{COF}$	1.23x10^{-1}	3.25	10.1
H_{H2}-Cl_{PdCl2}	6.58x10^{-1}	3.46	13.9
H_{H2}-Pd_{PdCl2}	3.92	3.39	5.85

2 Sorption results

From our GCMC calculations the total H_2 adsorbed amount (N_{total}) can be obtained. From this quantity, the excess amount can be calculated as shown in Table 2 and 3.

On the other hand, in sorption experiments the excess amount is obtained but the absolute amount can only be estimated. The absolute adsorbed amount can be estimated from experimental data by using,

$$N_{\text{total}} = N_{\text{excess}} + V_{\text{p}} \times \rho_{\text{bulk}} \quad (2)$$

where N_{excess} is the excess mass, V_{p} is the pore volume, N_{total} is the total adsorbed amount of H_2 and ρ_{bulk} is the bulk density of H_2. This approach for N_{excess} is also called surface excess. Thus this N_{excess} obtained from our calculations can be compared to the experimental results.

In this work we report the wt% as

$$\text{wt\%} = N_{\text{H}_2}/(N_{\text{H}_2} + \text{mass}_{\text{framework}}) * 100 \quad (3)$$

Table 2: Total H_2 uptake

Pres	COF301			COF-301-PdCl2			COF300		
Bar	Tot. H_2	Tot. wt%	Tot. g L^{-1}	Tot. H_2	Tot. wt%	Tot. g L^{-1}	Tot. H_2	Tot. wt%	Tot. g L^{-1}
0	0.0	0.00	0.00	0.0	0.00	0.00	0.0	0.00	0.00
1	0.7	0.03	0.17	120.6	2.20	28.74	0.8	0.03	0.18
2	1.2	0.05	0.27	143.7	2.61	34.25	1.2	0.05	0.28
3	1.5	0.06	0.36	156.4	2.84	37.26	1.6	0.07	0.37
4	1.9	0.07	0.44	166.2	3.01	39.60	1.9	0.08	0.46
5	2.2	0.09	0.52	172.4	3.12	41.07	2.4	0.11	0.57
10	4.0	0.16	0.96	192.6	3.47	45.90	4.2	0.18	1.01
20	7.7	0.30	1.83	211.7	3.80	50.46	8.1	0.35	1.93
30	11.1	0.43	2.64	222.3	3.98	52.96	11.8	0.51	2.82
40	14.5	0.57	3.45	229.6	4.11	54.70	15.4	0.67	3.66
50	17.5	0.68	4.17	235.3	4.21	56.07	18.7	0.81	4.45
60	20.6	0.80	4.91	239.6	4.28	57.09	21.8	0.94	5.20
70	23.4	0.91	5.58	243.8	4.35	58.08	24.8	1.07	5.91
80	26.1	1.02	6.22	247.6	4.42	59.01	27.6	1.19	6.58
90	28.5	1.11	6.80	249.5	4.45	59.46	30.5	1.32	7.27
100	30.9	1.20	7.36	251.9	4.49	60.02	33.0	1.42	7.87

Table 3: Excess Uptake

Pres	COF301			COF-301-PdCl2			COF300		
Bar	Exc. H_2	Exc. wt%	Exc. g L^{-1}	Exc. H_2	Exc. wt%	Exc. g L^{-1}	Exc. H_2	Exc. wt%	Exc. g L^{-1}
0	0.0	0.00	0.00	0.0	0.00	0.00	0.0	0.00	0.00
1	0.4	0.02	0.09	120.3	2.20	28.67	0.4	0.02	0.10
2	0.6	0.02	0.14	143.3	2.61	34.14	0.6	0.03	0.15
3	0.8	0.03	0.18	155.8	2.83	37.12	0.8	0.04	0.19
4	0.9	0.04	0.22	165.4	3.00	39.42	1.0	0.04	0.23
5	1.0	0.04	0.25	171.4	3.10	40.85	1.2	0.05	0.29
10	1.8	0.07	0.43	190.8	3.44	45.47	1.9	0.08	0.46
20	3.3	0.13	0.79	208.2	3.74	49.61	3.6	0.16	0.86
30	4.7	0.18	1.11	217.0	3.89	51.70	5.2	0.23	1.24
40	6.0	0.24	1.43	222.6	3.99	53.05	6.6	0.29	1.57
50	7.1	0.28	1.68	226.8	4.06	54.03	7.9	0.34	1.88
60	8.2	0.32	1.96	229.4	4.11	54.67	9.0	0.39	2.15
70	9.2	0.36	2.19	232.1	4.15	55.31	10.1	0.44	2.40
80	10.0	0.39	2.39	234.5	4.19	55.87	11.0	0.48	2.62
90	10.7	0.42	2.55	234.9	4.20	55.97	12.0	0.52	2.87
100	11.3	0.44	2.70	235.8	4.22	56.20	12.8	0.55	3.04

Table 4: Qst

Pres	COF301		COF-301-PdCl2		COF300	
Bar	kcal/mol	kJ/mol	kcal/mol	kJ/mol	kcal/mol	kJ/mol
1	1.43	6.00	5.85	24.48	1.39	5.82
2	1.43	6.00	5.81	24.32	1.39	5.81
3	1.44	6.02	5.79	24.23	1.39	5.84
4	1.43	6.00	5.77	24.16	1.39	5.82
5	1.42	5.95	5.76	24.08	1.31	5.49
10	1.45	6.08	5.71	23.89	1.40	5.84
20	1.43	5.99	5.66	23.66	1.39	5.81
30	1.43	5.97	5.62	23.50	1.40	5.84
40	1.43	5.99	5.59	23.38	1.40	5.84
50	1.43	5.96	5.57	23.30	1.39	5.83
60	1.43	5.99	5.56	23.25	1.39	5.83
70	1.44	6.01	5.54	23.19	1.39	5.81
80	1.43	5.99	5.53	23.13	1.39	5.81
90	1.42	5.95	5.52	23.08	1.39	5.83
100	1.42	5.94	5.50	23.03	1.38	5.79

3 Coordinates of the optimized linkers

In this section we report the coordinates of the minimized structures of H_2 interaction with the metalated linkers:

1. (E)-N'-benzylidenebenzohydrazide (**BBH**),
2. (E)-2-((phenylimino)methyl)phenol (**PIP**),
3. (E)-N-(pyridin-2-ylmethylene)aniline (**PIA**),
4. 2,2'-bipirydine (**BPY**) and
5. 2,2'-bipirimidine (**BPYM**)

These structures were used to parametrize the Force Field. We present only the structure with 4 interacting H_2, the other structures can be derived.

3.1 BBH-PdCl2-4H2

C	2.19260	2.79400	0.05770
C	1.43930	2.33960	1.14920
C	0.05420	2.41460	1.11840
C	-0.58420	2.91570	-0.01520
C	0.15910	3.33810	-1.11610
C	1.54400	3.28290	-1.08380
C	3.63430	2.70630	0.14290
H	1.94900	1.95010	2.03000
H	-0.52850	2.08170	1.97330
H	-1.66990	2.97100	-0.04290
H	-0.34140	3.72690	-1.99890
N	4.46010	3.45430	-0.50360
C	6.67620	3.68050	-1.28750
N	5.79640	3.11510	-0.40950
H	4.04200	1.92820	0.80460
H	6.03240	2.24630	0.06170
O	6.31830	4.57820	-2.06260
C	10.68280	2.24220	-1.37530
C	10.13800	2.90800	-2.47110
C	8.83270	3.37910	-2.42110
C	8.06100	3.17050	-1.27430
C	8.61480	2.51390	-0.16930
C	9.92420	2.05260	-0.22230
H	11.70660	1.87840	-1.41500
H	10.73400	3.06420	-3.36630
H	8.39190	3.91110	-3.26020
H	8.05100	2.39910	0.75500
H	10.35730	1.55530	0.64160
H	2.12850	3.61680	-1.93860
Pd	4.38030	5.36540	-1.48430
Cl	2.51320	6.22640	-0.45230
Cl	4.64620	7.33650	-2.59670
H	6.56900	6.34140	0.90020
H	6.05620	6.52420	0.39100
H	3.97760	4.46220	-4.08900
H	3.83470	3.83150	-4.45880
H	1.32040	5.72640	-3.82820
H	1.60870	5.99530	-3.19590
H	4.28380	4.75020	2.45930
H	3.93900	5.11900	1.91050

3.2 PIP-PdCl2-4H2

H	4.35960	-3.98960	-0.45190
H	4.37880	-3.44130	0.05140
H	1.28130	1.64390	2.50310
H	1.60760	0.97340	2.50590
C	1.53580	2.18200	-0.73000
C	1.13900	3.51930	-0.58740
C	-0.12780	3.85690	-0.13410
C	-1.04100	2.84640	0.15600
C	-0.69240	1.51130	-0.01850
C	0.58290	1.18500	-0.45580
C	2.91760	1.94370	-1.13770
H	1.86190	4.30140	-0.81480
H	-0.40240	4.90000	-0.00760
H	-2.03710	3.09490	0.51230
H	-1.40560	0.71630	0.19000
N	3.64340	0.92210	-0.84860
C	7.62410	0.70960	-2.16150
C	7.15330	1.88800	-1.59020
C	5.83670	1.97390	-1.14840
C	4.99520	0.86980	-1.28400
C	5.47060	-0.32470	-1.82470
C	6.78120	-0.39510	-2.27530
H	8.65480	0.64380	-2.50090
H	7.81690	2.74080	-1.47060
H	5.47620	2.87500	-0.65590
H	4.80760	-1.18610	-1.87810
H	7.15140	-1.32290	-2.70380
H	3.37590	2.75030	-1.72470
O	0.92770	-0.12500	-0.67770
Pd	2.81370	-0.59420	0.30670
Cl	1.54880	-2.13530	1.48620
Cl	4.73600	-0.94290	1.49510
H	0.35790	-0.75090	-0.18270
H	2.14170	-2.62110	-2.32790
H	2.28450	-2.67300	-1.59920
H	3.93360	2.77810	1.75950
H	4.14630	2.06380	1.76990

3.3 PIA-PdCl2-4H2

H	2.35870	-3.08760	-0.21630
H	2.37070	-3.26660	0.50660
H	0.24810	2.72270	-3.62520
H	0.36440	1.98760	-3.62120
H	3.05990	1.59300	-4.45320
H	2.99460	0.90090	-4.18470
C	1.50360	2.38760	-0.66210
C	0.97400	3.59500	-0.21930
C	-0.40360	3.69850	-0.05250
C	-1.20140	2.59480	-0.32570
C	-0.60470	1.41600	-0.76900
N	0.71360	1.32190	-0.93080
C	2.92890	2.17530	-0.85020
H	1.63590	4.43290	-0.01590
H	-0.84660	4.63040	0.28810
H	-2.27960	2.63460	-0.20560
H	-1.16950	0.51850	-1.02230
N	3.35220	1.03650	-1.27810
C	7.46570	0.38020	-1.72300
C	6.90090	1.55220	-2.22040
C	5.53630	1.77860	-2.08570
C	4.73870	0.82020	-1.45450
C	5.29340	-0.37160	-0.98360
C	6.66130	-0.57630	-1.10630
H	8.53280	0.20350	-1.83200
H	7.52140	2.28670	-2.72750
H	5.07800	2.67120	-2.50810
H	4.64810	-1.11810	-0.52820
H	7.09890	-1.49790	-0.73160
H	3.62670	2.97580	-0.58270
Pd	1.76770	-0.28690	-1.75420
Cl	3.05540	-1.90690	-2.76530
Cl	-0.14880	-1.49530	-2.18640
H	2.27930	-0.54840	1.05180
H	2.53650	-0.31460	1.71050

3.4 BPY-PdCl2-4H2

H	1.26470	-0.14210	4.60810
H	1.36130	0.40400	5.10900
H	1.74110	0.90770	-1.22600
H	1.56770	0.30240	-0.82450
H	-1.06450	1.55660	4.32270
H	-1.31100	2.23330	4.51880
C	0.66130	2.36300	1.47450
C	1.37710	3.53300	1.23170
C	2.76360	3.51340	1.32670
C	3.40510	2.32920	1.66780
C	2.63680	1.19290	1.88920
H	3.33520	4.41840	1.13580
H	4.48600	2.27320	1.75580
H	3.06560	0.22060	2.13690
N	1.30560	1.21640	1.78850
Pd	0.06740	-0.45710	1.91850
N	-1.33740	1.05310	1.63920
C	-0.80910	2.27710	1.41540
C	-2.66070	0.87630	1.64590
C	-1.63630	3.37140	1.17550
C	-3.53790	1.93090	1.42440
H	-2.98970	-0.14850	1.82450
C	-3.01510	3.19490	1.18080
H	-4.60900	1.75260	1.44080
H	-3.67290	4.04130	0.99850
H	0.86080	4.45130	0.96750
H	-1.21230	4.35480	0.99460
Cl	1.80690	-1.95780	2.17270
Cl	-1.49370	-2.15860	1.94520
H	-1.53500	0.74570	-1.40080
H	-1.35520	0.15000	-0.98820

3.5 BPYM-PdCl2-4H2

H	1.15490	0.11370	-1.33550
H	1.29250	0.72840	-1.73320
C	0.74910	2.23580	1.71290
N	1.37720	3.40830	1.81200
C	2.71190	3.41940	1.71710
C	3.41100	2.23460	1.51740
C	2.68850	1.05200	1.41310
H	3.17750	4.40310	1.79100
H	4.49250	2.23440	1.43620
H	3.13470	0.07130	1.24140
N	1.35400	1.06340	1.51790
Pd	-0.01320	-0.53500	1.36160
N	-1.34310	1.06600	1.69590
C	-0.71540	2.23800	1.80300
C	-2.68080	1.06050	1.74100
N	-1.32310	3.41500	1.95930
C	-3.38260	2.25020	1.89650
H	-3.14690	0.07920	1.64140
C	-2.66070	3.43330	2.00320
H	-4.46670	2.25560	1.92960
H	-3.11050	4.42020	2.11890
Pd	0.03620	5.02630	1.96870
Cl	1.63190	-2.08550	0.98370
Cl	-1.69580	-2.08250	1.22010
Cl	1.70700	6.59220	1.86540
Cl	-1.62260	6.60240	2.11760
H	-1.10120	2.07130	-1.04460
H	-1.08440	2.81410	-0.98800
H	1.43770	3.99420	-0.96280
H	1.56320	3.31020	-1.22950
H	-0.54460	5.94900	-0.75710
H	-0.54230	5.66320	-1.44490

4 Coordinates of optimized pristine COF-301 and COF-301-PdCl2

4.1 COF-301

Name
COF-301

Space group symmetry
I 41/a
a = b = 27.53
c = 10.45 A
alpha = betha = gamma = 90.000

Label	El	x	y	z
C1	C	0.45326	0.48541	1.96585
C2	C	0.49351	0.46054	1.91556
C3	C	0.48411	0.42061	1.82425
C4	C	0.54093	0.47527	1.95068
N5	N	0.51904	0.40095	1.75894
C6	C	0.51289	0.36443	1.66271
C7	C	0.55090	0.33213	1.64018
C8	C	0.54701	0.29678	1.54503
C9	C	0.50517	0.29351	1.46727
C10	C	0.46659	0.32603	1.49226
C11	C	0.47077	0.36152	1.58738
H12	H	0.41702	0.47463	1.93754
H13	H	0.44697	0.40828	1.81173
O14	O	0.58195	0.45014	1.90688
H15	H	0.58331	0.33376	1.69891
H16	H	0.57703	0.27171	1.53263
H17	H	0.43267	0.32381	1.44040
H18	H	0.44143	0.38715	1.60101
H19	H	0.21676	0.63623	0.32001
C20	C	0.50000	0.25000	1.37500

4.2 COF-301-PdCl2

Name
COF-301-PdCl2

Space group symmetry
I 41/a
a = b = 26.20
c = 9.87 A
alpha = betha = gamma = 90.000

Label	El	x	y	z
C1	C	0.48267	0.45890	2.07729
C2	C	0.51313	0.44953	1.96330
C3	C	0.51728	0.39630	1.91421
C4	C	0.53111	0.49140	1.88572
N5	N	0.54976	0.38470	1.81992
C6	C	0.53725	0.35210	1.70763
C7	C	0.57524	0.33915	1.61414
C8	C	0.56389	0.30923	1.50050
C9	C	0.51322	0.29397	1.47318
C10	C	0.47478	0.31114	1.56179
C11	C	0.48648	0.33914	1.67741
H12	H	0.46904	0.42699	2.13650
H13	H	0.48690	0.37002	1.94114
O14	O	0.56206	0.48411	1.77190
H15	H	0.61425	0.35105	1.63054
H16	H	0.59530	0.29607	1.43852
H17	H	0.43543	0.30036	1.54545
H18	H	0.45494	0.35093	1.74088
H19	H	0.26568	0.66878	0.50747
Pd20	Pd	0.17993	0.63968	0.44386
Cl21	Cl	0.11559	0.58201	0.39124
Cl22	Cl	0.23486	0.57177	0.46145
C23	C	0.50000	0.25000	1.37500

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