

## Supporting Information (14 pages)

### Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials

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## S.1 Quantum mechanics calculation of van der Waals interaction parameters

DFT methods are well known to lead to poor descriptions of the London dispersion attractive terms dominating weakly bound van der Waals molecules. Hence, DFT is not useful for predicting exact interaction energies between dihydrogen and covalent organic frameworks (COFs) where the building blocks are linked by strong covalent bonds such as C-C, C-O, B-O, and Si-C. Therefore, we optimized all coupled clusters using the second-order Møller-Plesset (MP2) calculations with the approximate resolution of the identity (RI-MP2) [1,2]. These calculations were carried out with the TURBOMOLE program [2].

For H<sub>2</sub> on boroxine (B<sub>3</sub>O<sub>3</sub>H<sub>3</sub>) and silane (SiH<sub>4</sub>), we used the quadruple zeta valence basis (QZV) [3] supplemented with polarization functions from the cc-pVTZ basis [4], which is denoted as QZVPP. The binding energy of H<sub>2</sub> with the boroxine and silane was corrected for basis-set superposition error (BSSE) by the full counterpoise procedure. In addition, the appropriate auxiliary-QZVPP basis set was used for the RI-MP2 calculations [5].

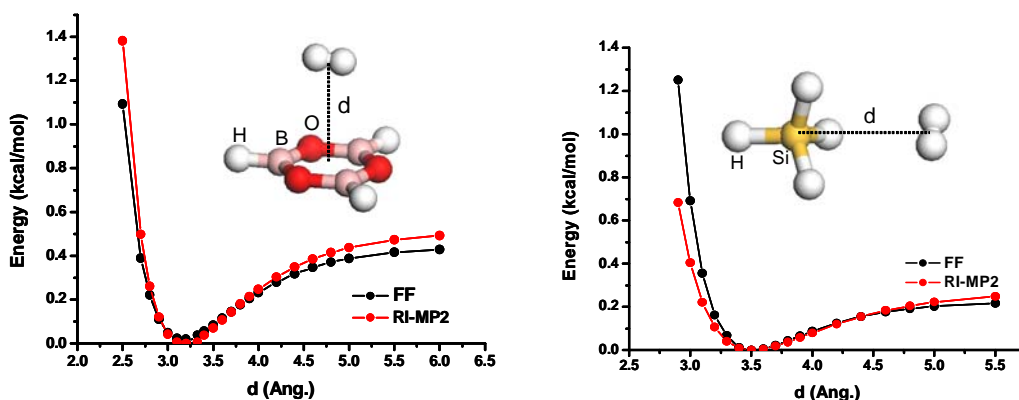
## S.2 Fitting of the Force Field (FF)

We used QM calculations to determine interaction potential of H<sub>2</sub> with organic linkers of the COF. Then we fitted these results to obtain Morse pair potentials (Eq. (1)) between each atom of H with the COF

$$U_{ij}(r_{ij}) = D \left\{ \exp\left[\alpha\left(1 - \frac{r_{ij}}{r_o}\right)\right] - 2 \cdot \exp\left[\frac{\alpha}{2}\left(1 - \frac{r_{ij}}{r_o}\right)\right] \right\} \quad (1)$$

Here the parameter D is the well depth, r<sub>0</sub> is the equilibrium bond distance, and α determines the stiffness (force constant).

For the B-H and Si-H cross terms, we carried out RI-MP2/QZVPP calculations for the interaction between H<sub>2</sub> and boroxine molecule and between H<sub>2</sub> and silane as shown in Fig. S1. Other terms such as C-H were already developed and published in Ref. 6 and 7. Moreover all FFs used in this work from QM calculations are summarized in Table S1.



**Figure S1.** Comparison of the quantum calculations and fitted force fields for H<sub>2</sub> interacting with boroxine (B<sub>3</sub>O<sub>3</sub>H<sub>3</sub>) (left) and silane (SiH<sub>4</sub>). In these calculations, the H<sub>2</sub> was oriented parallel to the B<sub>3</sub>O<sub>3</sub>H<sub>3</sub> ring and the distance between the bond midpoint of H<sub>2</sub> and the center of the boroxine and silane were varied.

**Table S1.** van der Waals force field parameters developed from QM data in this work. Here H<sub>-</sub> and H<sub>A</sub> indicate hydrogen bonded with aromatic carbon rings such as C<sub>6</sub>H<sub>6</sub> and hydrogen in a H<sub>2</sub> molecule.

Term	D (kcal/mol)	r <sub>0</sub> (Å)	α
C---H <sub>A</sub>	0.10082	3.12022	12.00625
H <sub>-</sub> ---H <sub>A</sub>	0.00087	3.24722	12.00625
H <sub>A</sub> ---H <sub>A</sub> <sup>a</sup>	0.01815	3.56980	10.70940
O---H <sub>A</sub>	0.02515	3.32249	12.00187
B---H <sub>A</sub>	0.04825	3.49300	10.56518
Si---H <sub>A</sub>	0.11014	3.53350	14.16509

<sup>a</sup> For H<sub>A</sub>---H<sub>A</sub> vdW term, the potential curves were fitted between two H<sub>2</sub> molecules using CCSD(T) with aug-cc-pVQZ basis set [8].

### S.3 Simulation of H<sub>2</sub> adsorption isotherms for COFs

To determine the performance of H<sub>2</sub> storage capacity designed in this work, we used grand canonical Monte Carlo (GCMC). During these calculations, the structure of the COF system is fixed at the value determined using our FF. Then used the new force field defined Table S1 to describe van der Waals interactions of H<sub>2</sub> in the COF systems. To obtain an accurate measure of H<sub>2</sub> loading, we constructed 10,000,000 configurations to compute the average loading for each condition. For the simulation, we used experimental COF structures [9,10]. The sorbent model is an infinite three-dimensional periodic super cell, 2×2×3 for COF-1, 2×2×6 for COF-5, and 2×2×2 for COF-102, 103, 105, and 108 of each unit cell to eliminate boundary effects. Here both supercells for two-dimensional COFs, COF-1 and COF-5 have six layers.

Also through the GCMC simulation, we investigated H<sub>2</sub> adsorption sites in COFs at 77 K. Figure S2 shows snapshots of structures of COF-108 with adsorbed H<sub>2</sub> at two pressures, 0.1 and 80 bar. At 0.1 bar, one can find that the most favored adsorption site of H<sub>2</sub> is on benzene rings in the organic linkers. In addition at 80 bar, most H<sub>2</sub> is adsorbed on the benzene rings as well as some H<sub>2</sub> can occupy near boron-oxygen networks. For other COFs, the similar behavior is observed. From this fact the most important adsorption site in COFs is the benzene ring.

#### S.4 Sample preparation and high-pressure H<sub>2</sub> isotherm for COF-5

*Sample preparation.* Crystalline sample of the as-synthesized COF-5 was obtained using already published procedure [9]. Briefly, 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) and 1,4-benzenediboronic acid (BDBA) were purchased from TCI and Aldrich, respectively. Mesitylene (98%, Fluka) and anhydrous 1,2-dioxane (99.8%, Aldrich) were used for the condensation reactions. Typically, the reaction mixture (i.e. boronic acid and HHTP in mesitylene/dioxane (1:1, v/v)) was heated at 100 °C for 72 h to afford powder precipitates. The resulting powder was filtered off and was washed with dry acetone (3 ×). The powder was then activated with acetone (2 ×) for 2 days then dried at 85 °C/10<sup>-5</sup> torr for 12 h to afford COF-5. The identity was confirmed using elemental microanalysis, thermal gravimetric analysis, FT-IR spectroscopy, and powder X-ray diffraction.

*Gravimetric high-pressure gas adsorption measurements.* Gravimetric gas sorption isotherms were measured by use of GHP-300 (Gravimetric High Pressure analyzer) from the VTI Corporation [11]. A Rubotherm magnetic suspension balance MC-5 was used to measure the change in mass of samples suspended within a tube (22 mm i.d.) constructed from Inconel 625 under a chosen atmosphere. Prior to admittance of the analyte gas, the entire chamber and manifold were evacuated at room temperature, and the weight of Al sample bucket (12 mm i.d. × 21 mm length) was measured. After loading COF samples (200-400 mg) the system was purged at room temperature with helium, and the sample was outgassed, using a turbomolecular drag pump (Pfeiffer, TSH 071 E), until a constant mass was attained. Ultra-high purity grade He and H<sub>2</sub> (99.999% purity) were used throughout the adsorption experiments. When H<sub>2</sub> gas was used, water and other condensable impurities were removed with a liquid nitrogen trap. Pressure was measured with a MKS Baratron transducer 120AA (0 to 1000 Torr) and an electronic Bourdon gauge-type transducer (Mensor, up to 1500 psi). The adsorbate was added incrementally, and data points were recorded when no further change in mass was observed. The temperature in the Inconel tube was also monitored with a platinum resistance thermometer.

To obtain the excess adsorption isotherm, all data points were corrected for buoyancy and the thermal gradient that arises between the balance (313 K) and the sample bucket. Buoyancy and

thermal-gradient effects exhibited by the bucket and the components associated with the magnetic-suspension balance were corrected on the basis of the change in mass of the empty bucket within the analyte gas at experimental temperature. The weight loss due to the buoyancy of the adsorbent was determined by multiplying the volume of COF framework skeleton (i.e. backbone density,  $d_{bb}$ ) times the density of  $H_2$  (i.e. corrected mass for buoyancy is  $V_{bb} \times \rho_{bulk}$ ). The volume of COF framework skeleton was determined from the helium (< 15 bar) buoyancy curve at 298 K using the same gravimetric system [11].

**Table S2.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-1 at 77 K.

<b>COF-1</b>					
Pressure (bar)	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
	Total	Excess	Total	Excess	
0.1	1.72	1.72	15.89	15.88	8.81
0.2	1.94	1.94	17.98	17.98	8.52
0.3	2.11	2.11	19.59	19.59	8.29
0.4	2.23	2.23	20.75	20.74	8.13
0.5	2.34	2.33	21.74	21.74	8.04
0.6	2.42	2.42	22.53	22.53	7.98
0.7	2.49	2.49	23.23	23.23	7.90
0.8	2.53	2.53	23.65	23.64	7.85
0.9	2.59	2.59	24.19	24.18	7.80
1	2.62	2.62	24.49	24.49	7.76
5	3.21	3.20	30.12	30.09	7.40
10	3.38	3.37	31.77	31.73	7.29
20	3.54	3.53	33.34	33.26	7.23
30	3.62	3.61	34.14	34.04	7.16
40	3.64	3.63	34.35	34.22	7.15
50	3.71	3.69	35.02	34.87	7.12
60	3.72	3.70	35.09	34.92	7.09
70	3.77	3.75	35.62	35.43	7.07
80	3.77	3.75	35.64	35.44	7.06
90	3.81	3.78	35.97	35.75	7.05
100	3.82	3.79	36.08	35.84	7.03

**Table S3.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-5 at 77 K.

<b>COF-5</b>					
	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
Pressure (bar)	Total	Excess	Total	Excess	
0.1	0.08	0.08	0.48	0.45	4.60
0.2	0.16	0.15	0.93	0.88	4.59
0.3	0.24	0.23	1.42	1.35	4.63
0.4	0.30	0.29	1.77	1.69	4.62
0.5	0.37	0.35	2.15	2.06	4.61
0.6	0.44	0.43	2.59	2.49	4.58
0.7	0.49	0.47	2.87	2.75	4.57
0.8	0.53	0.51	3.09	2.96	4.54
0.9	0.61	0.58	3.55	3.41	4.56
1	0.66	0.63	3.85	3.69	4.56
5	1.81	1.68	10.71	9.93	4.34
10	2.46	2.21	14.67	13.13	4.15
20	3.23	2.73	19.42	16.32	3.90
30	3.73	3.00	22.54	17.98	3.73
40	4.12	3.14	24.96	18.86	3.59
50	4.43	3.24	26.96	19.47	3.50
60	4.68	3.28	28.56	19.73	3.41
70	4.92	3.33	30.10	20.03	3.35
80	5.16	3.39	31.61	20.39	3.30
90	5.35	3.40	32.83	20.46	3.27
100	5.50	3.40	33.81	20.49	3.23



**Table S4.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-102 at 77 K.

<b>COF-102</b>					
Pressure (bar)	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
	Total	Excess	Total	Excess	
0.1	0.52	0.51	2.18	2.15	5.68
0.2	0.93	0.92	3.96	3.90	5.64
0.3	1.30	1.28	5.55	5.47	5.64
0.4	1.54	1.52	6.60	6.50	5.59
0.5	1.84	1.81	7.88	7.76	5.58
0.6	2.04	2.01	8.76	8.63	5.56
0.7	2.26	2.23	9.71	9.57	5.55
0.8	2.40	2.37	10.36	10.20	5.49
0.9	2.58	2.55	11.16	10.99	5.47
1	2.71	2.67	11.70	11.53	5.46
5	5.30	5.17	23.54	22.93	5.00
10	6.59	6.34	29.66	28.49	4.72
20	7.96	7.49	36.38	34.07	4.52
30	8.76	8.08	40.37	36.95	4.44
40	9.28	8.40	43.01	38.59	4.38
50	9.60	8.53	44.65	39.20	4.32
60	9.93	8.69	46.37	40.01	4.26
70	10.10	8.68	47.28	39.98	4.28
80	10.34	8.77	48.56	40.43	4.25
90	10.51	8.77	49.39	40.43	4.23
100	10.60	8.70	49.89	40.06	4.22

**Table S5.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-103 at 77 K.

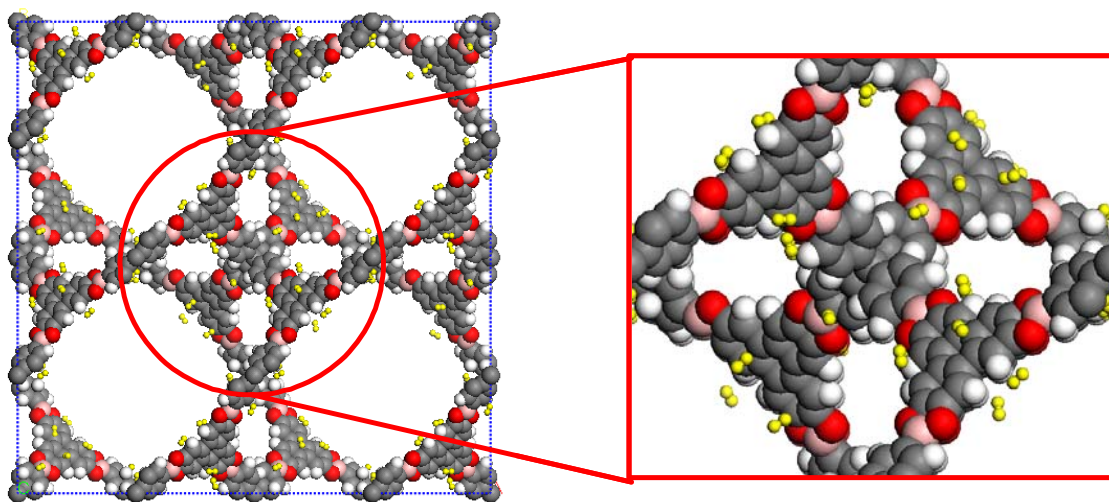
<b>COF-103</b>					
	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
Pressure (bar)	Total	Excess	Total	Excess	
0.1	0.59	0.58	2.31	2.28	5.78
0.2	1.00	0.99	3.95	3.88	5.74
0.3	1.41	1.39	5.56	5.48	5.74
0.4	1.72	1.69	6.80	6.70	5.69
0.5	1.98	1.95	7.85	7.74	5.68
0.6	2.14	2.11	8.52	8.39	5.64
0.7	2.38	2.34	9.47	9.33	5.64
0.8	2.56	2.52	10.22	10.07	5.60
0.9	2.65	2.61	10.59	10.42	5.55
1	2.84	2.80	11.37	11.19	5.57
5	5.40	5.25	22.19	21.54	4.97
10	6.84	6.55	28.55	27.26	4.70
20	8.32	7.77	35.27	32.74	4.45
30	9.13	8.33	39.07	35.32	4.35
40	9.71	8.67	41.79	36.92	4.28
50	10.15	8.90	43.95	37.98	4.22
60	10.48	9.02	45.50	38.44	4.19
70	10.70	9.03	46.61	38.53	4.18
80	10.93	9.04	47.70	38.60	4.15
90	11.10	9.10	48.52	38.65	4.10
100	11.34	8.70	49.72	38.91	4.10

**Table S6.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-105 at 77 K.

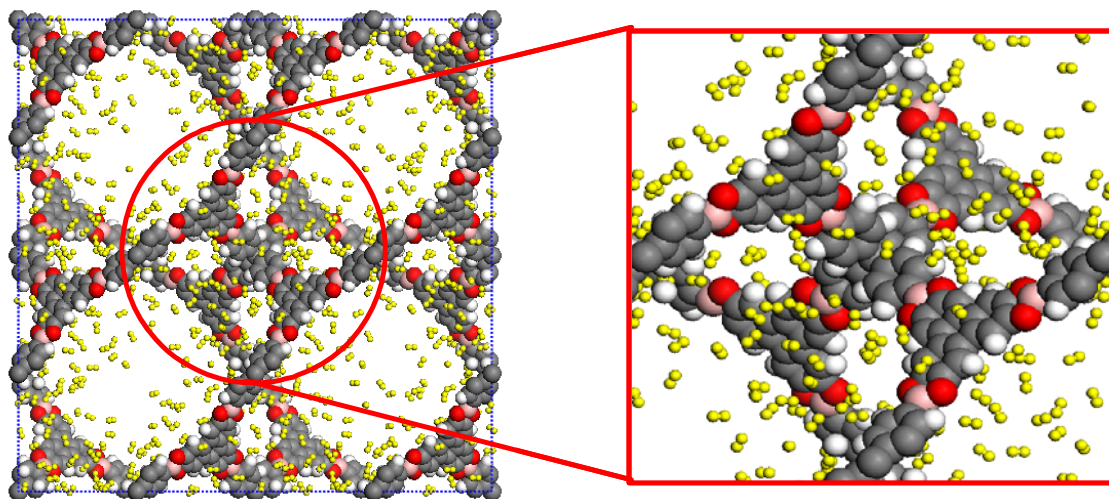
<b>COF-105</b>					
Pressure (bar)	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
	Total	Excess	Total	Excess	
0.1	0.60	0.58	1.07	1.03	5.64
0.2	1.02	0.98	1.81	1.75	5.56
0.3	1.36	1.31	2.42	2.35	5.51
0.4	1.65	1.60	2.95	2.86	5.48
0.5	1.86	1.80	3.35	3.23	5.42
0.6	2.08	2.00	3.74	3.60	5.38
0.7	2.29	2.21	4.14	3.98	5.35
0.8	2.47	2.37	4.46	4.28	5.31
0.9	2.60	2.49	4.71	4.50	5.27
1	2.76	2.64	5.00	4.77	5.23
5	5.51	4.94	10.29	9.16	4.42
10	7.36	6.25	14.00	11.75	3.99
20	9.88	7.75	19.33	14.81	3.49
30	11.79	8.66	23.56	16.72	3.26
40	13.18	9.12	26.76	17.70	3.07
50	14.35	9.45	29.53	18.40	2.95
60	15.41	9.69	32.13	18.91	2.85
70	16.33	9.85	34.42	19.26	2.80
80	17.13	9.98	36.44	19.54	2.75
90	17.75	9.97	38.04	19.53	2.72
100	18.31	9.93	39.51	19.43	2.69

**Table S7.** Simulated H<sub>2</sub> adsorption amount and isosteric heat of adsorption ( $Q_{st}$ ) for pure COF-108 at 77 K.

<b>COF-108</b>					
Pressure (bar)	Gravimetric unit (wt%)		Volumetric unit (g/L)		$Q_{st}$ (kJ/mol)
	Total	Excess	Total	Excess	
0.1	0.93	0.90	1.60	1.54	7.39
0.2	1.30	1.25	2.25	2.16	6.92
0.3	1.58	1.51	2.73	2.61	6.63
0.4	1.83	1.75	3.17	3.03	6.39
0.5	2.00	1.91	3.48	3.31	6.27
0.6	2.14	2.03	3.72	3.54	6.14
0.7	2.32	2.20	4.05	3.84	5.99
0.8	2.46	2.33	4.29	4.06	5.92
0.9	2.58	2.46	4.52	4.27	5.86
1	2.72	2.57	4.76	4.49	5.78
5	5.38	4.76	9.70	8.53	4.59
10	7.32	6.12	13.46	11.12	4.07
20	9.95	7.66	18.84	14.15	3.56
30	11.80	8.45	22.81	15.74	3.29
40	13.40	9.12	26.37	17.10	3.12
50	14.68	9.45	29.33	17.79	2.99
60	15.75	9.64	31.88	18.20	2.90
70	16.65	9.76	34.06	18.44	2.82
80	17.46	9.84	36.07	18.61	2.77
90	18.17	9.88	37.85	18.69	2.73
100	18.95	10.01	39.86	18.98	2.73



(a)



(b)

**Figure S2.** GCMC snapshots of the structures of COF-108 with adsorbed H<sub>2</sub> at two pressures, (a) 0.1 bar and (b) 80 bar. The atoms are colored as follows: gray = C, red = O, pink = B, white and yellow = H where the adsorbed H<sub>2</sub> is shown as yellow atoms.

## S.5 References

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