

Supporting Information

“Li-Doped Metal Organic Frameworks for Reversible H₂ Storage at Ambient Temperature”

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The supporting material is organized as follows: Section 1 describes quantum mechanics calculation details and more results. Section 2 describes the force fields derived from *ab-initio* calculations and section 3 shows H₂ adsorption isotherms in gravimetric and volumetric units of Li-doped metal organic frameworks (MOFs) at 273 and 300 K.

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 the organics of MOFs. 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 H₂ on benzene, we used the triple zeta valence basis (TZV) [3] supplemented with polarization functions from the cc-pVTZ basis [4], which is denoted as TZVPP (the 1s electrons of the C and O atoms are not correlated, frozen-core approximation). The binding energy of H₂ with benzene was corrected for basis-set superposition error (BSSE) by the full counterpoise procedure. In addition, the appropriate auxiliary-TZVPP basis set was used for the RI-MP2 calculations [5].

In the case of H₂-MOF clusters, the geometries were optimized up to the RI-MP2/TZVPP level of theory with frozen cores in all cases. Then single point energies were calculated using RI-MP2 with the quadruple zeta QZVPP basis. Here we did not use BSSE corrections, since this has been shown not to be necessary for Zn-MOF cluster [6].

The QM calculated H-H bond length, 0.74 Å, is comparable to the experimental value of 0.75 Å for free H₂ molecule [7]. Moreover, the QM vibration frequency of H₂ is 4224 cm⁻¹, which is close to the experimental value of 4400 cm⁻¹ for free H₂ [7]. We calculate the H₂ binding energy with the Zn containing cluster to be -1.49 kcal/mol (Table S1), in good agreement with the result of -1.51 kcal/mol from Ref. [6].

Table S1. QM data (RI-MP2, energies in Hartree) and force field data (energies in kcal/mol) for binding of an H₂ molecule to the metal oxide cluster and to the benzene ring.

	Zn cluster- H ₂ ^a	Benzene- H ₂ ^b
H ₂	-1.166651	-1.164698
M ₄ O(CO ₂) ₆ H ₆	-8322.821264	-231.733624
M ₄ O(CO ₂) ₆ H ₆ -H ₂	-8323.990283	-232.899789
Binding energy	-1.49	-0.91
Force field	-1.48	-0.91

^aQZVPP basis set

^bTZVPP basis set

S.2 Fitting of the Force Field

We used QM calculations to determine interaction potential of H₂ with the metal sites and organic linkers of the MOF with different. Then we fitted these results to obtain Morse pair potentials (Eq. (1)) between each atom of H with the MOF

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

Here the parameters D is the well depth, r₀ is the equilibrium bond distance, and α determines the stiffness (force constant).

For the C-H cross term, we carried out RI-MP2/TZVPP calculations for the interaction between H₂ and C₆H₆ molecules as shown in Fig. S1.

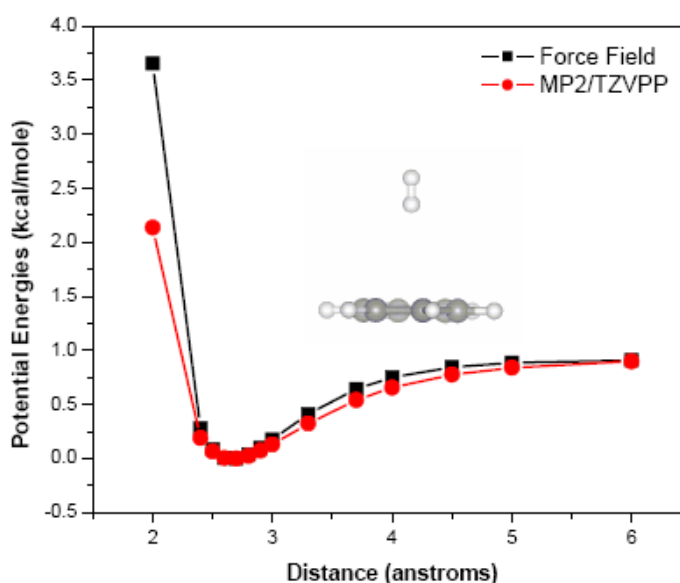


Figure S1. Comparison of the quantum calculations and fitted force fields for H₂ interacting with C₆H₆. In these calculations, the H₂ was oriented vertically to the C₆H₆ ring and the distance between the bond midpoint of H₂ and the center of the benzene were varied.

For the interactions of H₂ with the metal site in MOF, we carried RI-MP2/QZVPP calculations for clusters such as Zn₄O(CO₂)₆H₆+H₂ in Table S1. And the optimized structures are indicated in Table S2.

To determine the interactions of H₂ with the Li bonded to an aromatic hydrocarbon we considered one H₂ bonded to a planar C₃₂ cluster (ten aromatic rings) doped with one Li atom on each side [8]. These calculations used the X3LYP flavor of DFT with the 6-311G(d,p) basis set. Such DFT calculations are expected to yield an accurate description of van der Waals and hydrogen bond interactions [9].

Finally the developed FFs from QM calculations in this work are summarized in Table S3.

Table S2. Coordinates (Å) of $\text{Zn}_4\text{O}(\text{CO}_2)_6\text{H}_6$ and $\text{Zn}_4\text{O}(\text{CO}_2)_6\text{H}_6\text{-H}_2$ optimized by RI-MP2/TZVPP.

Zn-MOF	x	y	z	Zn-MOF-H2	x	y	z
O	0.004	-0.002	0.006	O	0.008	0.003	0.000
Zn	0.976	1.119	-1.294	Zn	0.973	1.112	-1.316
Zn	1.296	-1.087	1.032	Zn	1.308	-1.066	1.027
Zn	-1.014	1.153	1.239	Zn	-1.003	1.165	1.233
Zn	-1.238	-1.197	-0.955	Zn	-1.240	-1.201	-0.942
O	1.196	-0.676	2.949	O	1.231	-0.629	2.942
O	3.135	-0.759	0.426	O	3.144	-0.740	0.412
O	0.933	-3.006	0.819	O	0.945	-2.988	0.843
O	-0.741	3.053	0.816	O	-0.769	3.061	0.769
O	-0.450	0.870	3.10	O	-0.431	0.899	3.093
O	-2.941	0.781	1.132	O	-2.928	0.781	1.153
O	-1.120	-0.932	-2.897	O	-1.141	-0.944	-2.887
O	-0.842	-3.084	-0.583	O	-0.829	-3.083	-0.559
O	-3.097	-0.863	-0.416	O	-3.095	-0.868	-0.388
O	0.409	0.720	-3.132	O	0.391	0.700	-3.149
O	2.913	0.802	-1.197	O	2.908	0.788	-1.242
O	0.667	3.028	-0.955	O	0.642	3.023	-1.000
C	0.049	-3.594	0.145	C	0.064	-3.585	0.172
C	-0.416	-0.127	-3.560	C	-0.444	-0.144	-3.563
C	-3.565	-0.049	0.421	C	-3.557	-0.051	0.450
C	-0.041	3.590	-0.080	C	-0.085	3.590	-0.144
C	3.569	0.020	-0.461	C	3.570	0.024	-0.493
C	0.439	0.115	3.570	C	0.469	0.158	3.563
H	0.054	-4.686	0.200	H	0.075	-4.677	0.232
H	-0.538	-0.169	-4.646	H	-0.582	-0.187	-4.647
H	-4.651	-0.063	0.547	H	-4.643	-0.067	0.584
H	-0.048	4.684	-0.102	H	-0.126	4.682	-0.200
H	4.652	0.019	-0.611	H	4.653	0.024	-0.648
H	0.570	0.149	4.655	H	0.609	0.203	4.646
				H	2.328	2.362	1.567
				H	2.554	1.757	1.9245

Table S3. van der Waals force field parameters developed from QM data in this work. Here H_ and H_A indicate hydrogen bonded with aromatic carbon rings such as C₆H₆ and hydrogen in a H₂ molecule.

Term	D (kcal/mol)	r0 (Å)	α
C---H_A	0.10082	3.12022	12.00625
H_---H_A	0.00087	3.24722	12.00625
H_A---H_A ^a	0.01815	3.56980	10.70940
O---H_A	0.02515	3.32249	12.00187
Zn---H_A	0.12447	2.76130	13.41420
Li---H_A	2.15752	2.01844	7.12510

^a For H_A---H_A vdW term, the potential curves were fitted between two H₂ molecules using CCSD(T) with aug-cc-pVQZ basis set [9].

S.3 H₂ adsorption isotherms of Li-doped MOFs

To determine the performance of H₂ storage capacity designed in this project, we used grand canonical Monte Carlo (GCMC) [10]. In these calculations, the structure of the Li-MOF system is fixed at the value determined using our FF. Then used the new force field defined Table S3 to describe van der Waals interactions of H₂ in the MOF systems. To obtain an accurate measure of H₂ loading, we constructed 10,000,000 configurations to compute the average loading for each condition. The sorbent model used a three-dimensional structure (2×2×2 supercell) consisting of eight Zn₄O(CO₂)₆ linker units each of which is connected to 6 organic linkers.

In all simulations, periodic boundary conditions were applied in order to minimize undesirable surface effects. Generally, MOF structures can have both of cubic and hexagonal crystals. Experimentally, the hexagonal Zn-MOF177 has a larger surface area based on the higher N₂ uptake amount than cubic MOF12. However, the hexagonal structure leads to lower H₂ storage [11]. Thus, we have studied optimization the cubic MOF systems in this work.

Table S4 lists the crystal sizes and surface areas of the MOFs considered in this study. These crystal structures were minimized using the DREIDING force field [12]. The predicted structures for Zn-MOF-C6, C10 and C16 are in good agreement with experimental data [13].

Figure S2 shows the relationship between the Connolly surface area and the H₂ BET surface area for pure MOFs. The BET surface area is ~ 1/3 the Connolly area, but the relationship is ~ linear.

Using these optimized structures, we calculated H₂ adsorption isotherms at 77 and 100 K. For Zn-MOF-C6, our predicted H₂ adsorption isotherms are compared with experiment [14] in Fig. S3, where we find good agreement.

Figs. S4 and S5 show H₂ adsorption isotherms in gravimetric and volumetric units of Li-doped MOFs at 273 K and pressures <100 bar where the total and excess isotherm data at 273 and 300 K are indicated in detail in Tables S5-S9.

In addition, we plot the distribution of H₂ in the Li doped MOF-C30 at 243 K and 100 bar to meet the DOE target, seen in Fig. S6. The adsorbed H₂ are found mainly near Li atoms on aromatic carbon atoms.

Table S4. Lattice parameters (Å) and surface area (m²/g) of MOFs used in this simulation where we assumed that all structures have cubic lattice (F_{m-3m} space group).

	MOF6	MOF10	MOF16	MOF22	MOF30
Lattice parameter	26.025 (25.832) ^a	30.252 (30.092) ^a	34.374 (34.381) ^a	38.652	42.824
Connolly surface area ^b	3851 ^c (3834) ^d	3518 ^c (3378) ^d	3808 ^c (3528) ^d	4550 ^c (3940) ^d	4641 ^c (3938) ^d
H ₂ BET surface area ^e	1287 ^c (395) ^d	1494 ^c (693) ^d	1746 ^c (920) ^d	1955 ^c (1040) ^d	2046 ^c (1138) ^d

^a Experimental results [Ref. 13]

^b The Connolly surface area was calculated by the Cerius2 software.

^c For pure Zn-MOFs

^d For Li-doped Zn-MOFs. Here we assumed that lattice parameters of Li-doped MOFs were same to those of pure MOFs.

^e The H₂ BET surface area was calculated from our H₂ adsorption isotherms at 300 K for Li-doped MOFs and at 77 K for pure MOFs.

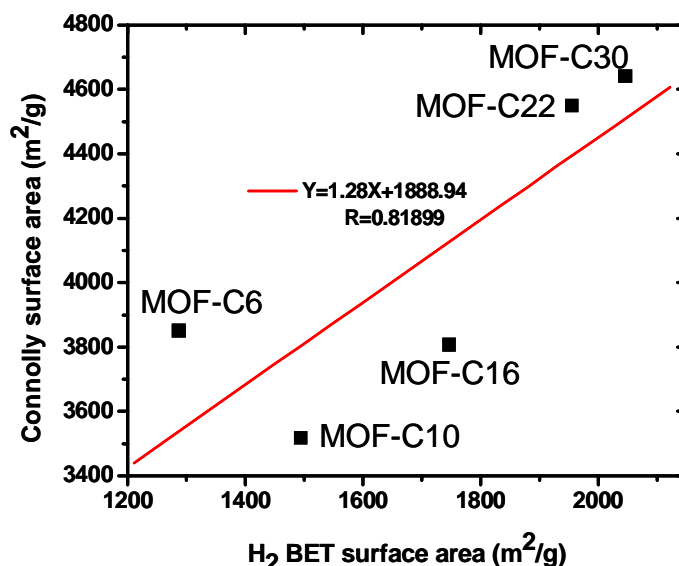


Figure S2. Comparison of the Connolly surface area and H₂ BET surface area for pure MOFs.

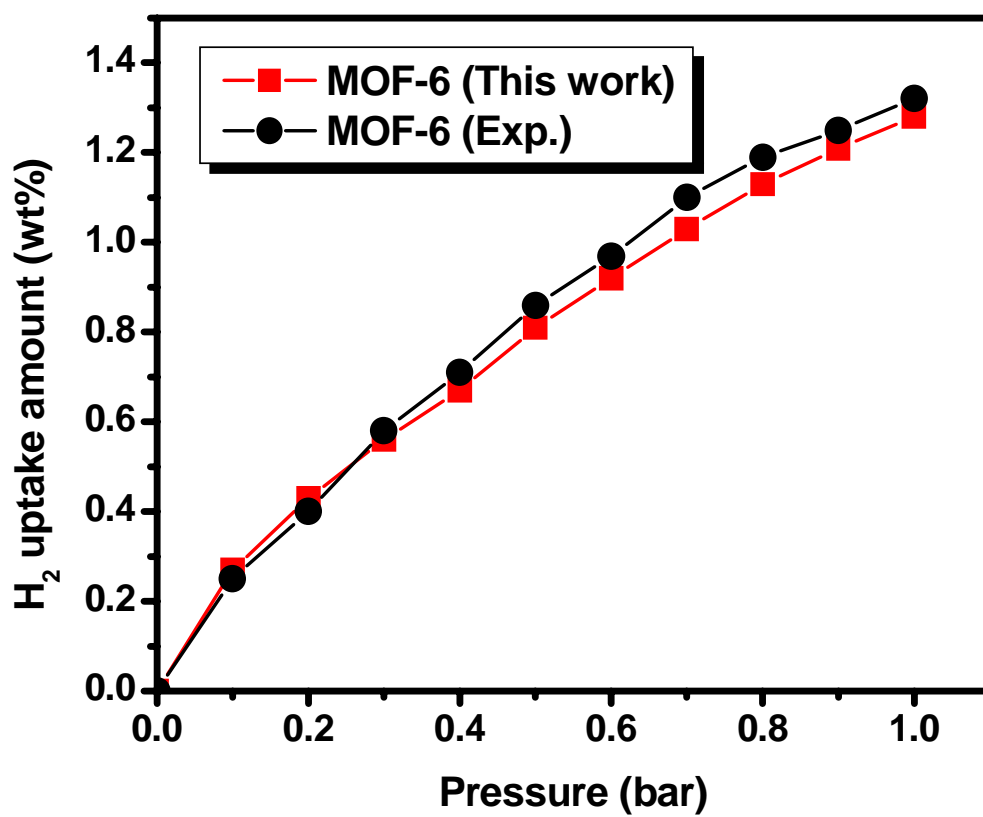


Figure S3. Comparison of predicted and experimental [14] data on H₂ adsorption of Zn-MOF-C6 at 77 K.

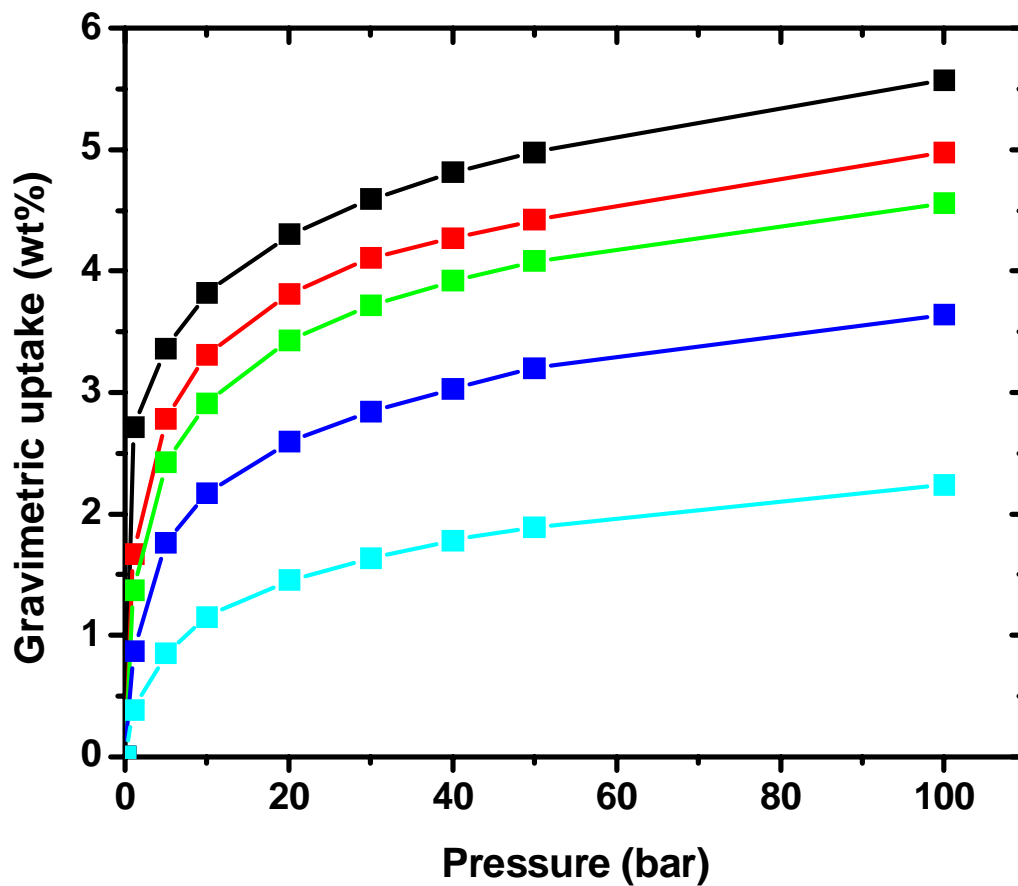


Figure S4. Predicted excess gravimetric H₂ uptake of Li-doped MOFs at 273 K. Here cyan, blue, green, red, and black indicate Li-MOF-C6, C10, C16, C22, and C30, respectively.

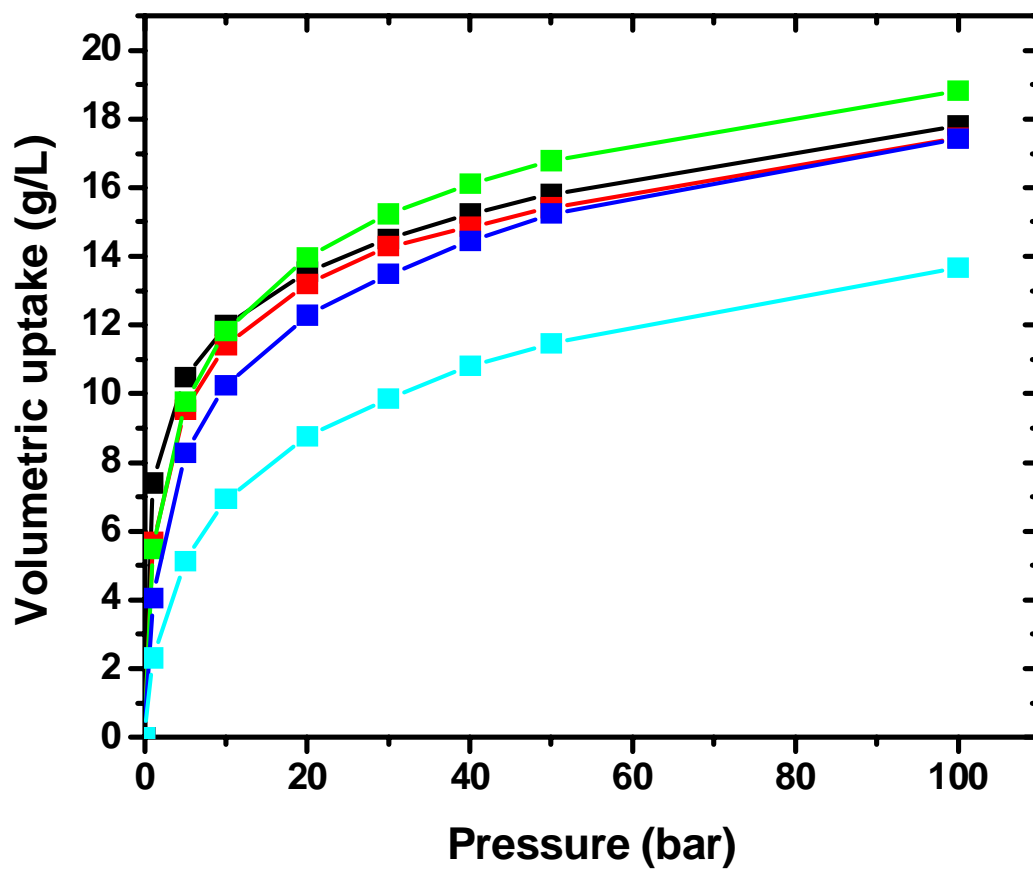


Figure S5. Predicted excess volumetric H₂ uptake of Li-doped MOFs at 273 K. Here cyan, blue, green, red, and black indicate Li-MOF-C6, C10, C16, C22, and C30, respectively.

Table S5. Simulated H₂ adsorption data for Li-MOF-C6 at 273 and 300 K.

Li-MOF-C6				
	273 K		300 K	
Pressure (bar)	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a
1	1.58	1.51	1.09	1.04
5	3.64	3.37	2.67	2.41
10	5.02	4.55	3.79	3.36
20	6.51	5.76	5.37	4.65
30	7.47	6.49	6.33	5.41
40	8.27	7.11	7.10	6.00
50	8.88	7.54	7.76	6.49
100	11.12	9.01	10.04	8.03

^a f.u. = Zn₄OL_x formula unit

Table S6. Simulated H₂ adsorption data for Li-MOF-C10 at 273 and 300 K.

Li-MOF-C10				
	273 K		300 K	
Pressure (bar)	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a
1	4.26	4.17	2.64	2.55
5	8.91	8.55	6.66	6.32
10	11.18	10.58	8.97	8.40
20	13.65	12.69	11.61	10.71
30	15.16	13.93	13.19	12.03
40	16.41	14.93	14.40	13.01
50	17.48	15.76	15.38	13.77
100	20.86	18.00	19.03	16.35

^a f.u. = Zn₄OL_x formula unit

Table S7. Simulated H₂ adsorption data for Li-MOF-C16 at 273 and 300 K.

Li-MOF-C16				
	273 K		300 K	
Pressure (bar)	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a
1	8.52	8.32	5.99	5.80
5	15.51	14.81	12.14	11.49
10	19.01	17.91	15.83	14.79
20	22.95	21.21	19.71	18.08
30	25.45	23.10	22.56	20.35
40	27.40	24.41	24.35	21.56
50	29.07	25.45	26.40	23.05
100	35.21	28.55	32.43	26.24

^a f.u. = Zn₄OL_x formula unit

Table S8. Simulated H₂ adsorption data for Li-MOF-C22 at 273 and 300 K.

Li-MOF-C22				
	273 K		300 K	
Pressure (bar)	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a
1	12.52	12.23	9.29	9.02
5	21.46	20.52	17.16	16.28
10	26.09	24.62	21.61	20.23
20	30.89	28.44	26.63	24.34
30	34.31	30.82	30.81	27.57
40	36.53	32.03	32.35	28.19
50	38.75	33.23	35.55	30.47
100	47.92	37.62	44.10	34.50

^a f.u. = Zn₄OL_x formula unit

Table S9. Simulated H₂ adsorption data for Li-MOF-C30 at 273 and 300 K.

Li-MOF-C30				
	273 K		300 K	
Pressure (bar)	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a	Total H ₂ per f.u. ^a	Excess H ₂ per f.u. ^a
1	22.04	21.66	18.21	17.85
5	31.91	30.73	27.38	26.27
10	37.02	35.12	32.56	30.78
20	43.12	39.77	38.89	35.80
30	47.46	42.54	42.83	38.35
40	51.09	44.71	46.76	40.92
50	54.21	46.35	49.50	42.29
100	66.87	52.20	61.18	47.68

^a f.u. = Zn₄OL_x formula unit

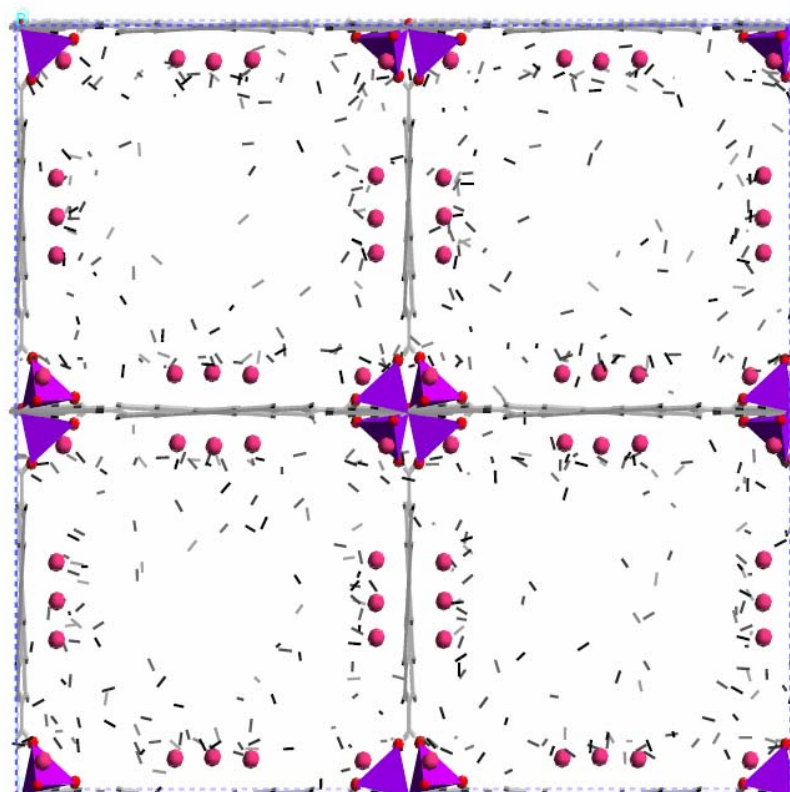


Figure S6. The distribution of adsorbed H₂ in Li-doped MOF-C30 at 243 K and 100 bar where black, grey, pink, red, and violet colors indicate hydrogen, carbon, lithium, oxygen, and zinc atoms, respectively. This leads to 6% wt H₂, meeting the DOE goals for 2010

S.4. References:

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