Electronic Supplementary Information

“H_2 sponge”: Pressure as a means for reversible high-capacity hydrogen storage in nanoporous Ca-intercalated covalent organic framework

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Part Ⅰ Results for van der Waals density functional (vdW-DF)

1. Interlayer interaction for COF-1 (AA stacking sequence)

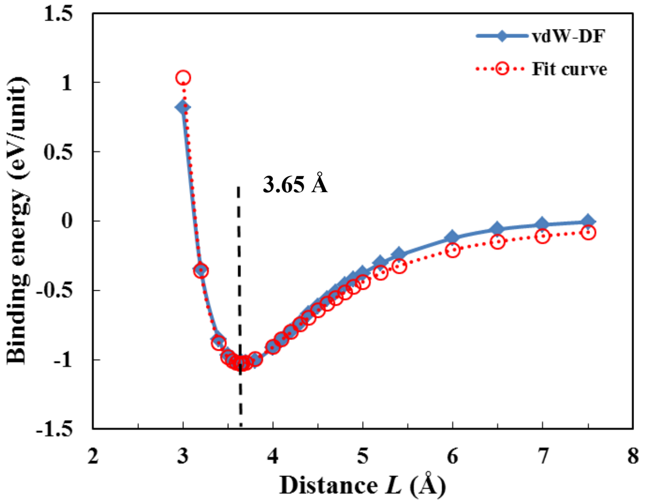

Figure S1: Interlayer binding energy (E_b) of COF-1 (AA stacking) as a function of interlayer distance L in the range of 2.0-7.5 Å. Black dotted line represents an equilibrium interlayer distance, ~ 3.65 Å.

The experimental layer separation of COF-1 (AB stacking) is 3.328 Å [1]. And for comparison, the equilibrium interlayer distance of graphite (AB stacking) is obtained by quantum Monte Carlo (QMC), ~3.354 Å [2].

The formula of the fit curve for COF-1 is given, as follow:

$$E_b = -696.32\times L^{-4.5}+118058.9183\times L^{-9}$$

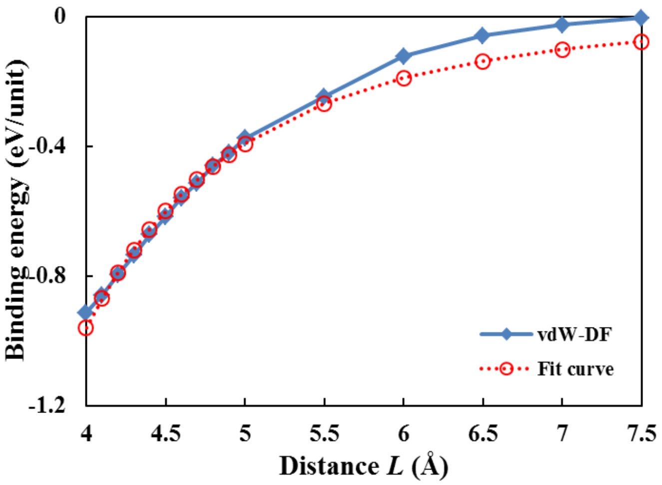

Figure S2: Interlayer binding energy of COF-1 (AA stacking) as a function of interlayer distance *L* in the range of 4.0-7.5 Å.

The formula of the new fit curve is $E_b = -247.86 \times L^{-4.0}$, which is very close to the result of graphite (AB stacking). By quantum Monte Carlo (QMC) calculations, at the same range the binding energy curve shows a $\sim L^{-4.2}$ behavior as a function of interlayer distance *L* [2].

2. Interlayer interaction for CaCOF-1

(1) The convergence test for K-point

K-point	total energy/cell (eV)
1×1×3	-335.8331008
1×1×5	-335.9223510
1×1×7	-335.9186698
1×1×9	-335.8937460

It is shown that 1×1×5 K-point sampling for vdW-DF calculations is indeed satisfactory.

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(2) Difference between GGA and vdW-DF for interlayer interaction in CaCOF-1

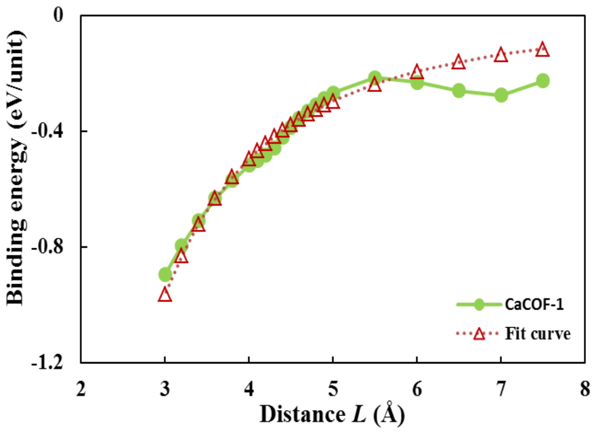

Figure S3: Interlayer binding energy of CaCOF-1 as a function of interlayer distance *L*. E_{b} (CaCOF-1) is obtained: E_b (CaCOF-1) = $E_{vdW\text{-}DF} - E_{GGA}$.

Many studies show that the GGA results for interlayer binding energy of graphite is ~0 at the distance *L* in the range of 3.4-8.0 Å [3, 4], and our calculation results of the interlayer binding energy of COF-1 by GGA also give the same trends, so E_{b} (CaCOF-1) could be approximately defined as the interaction between two layers for CaCOF-1 by vdW-DF. The formula of the fit curve is $E_b = -12.20 \times L^{-2.3}$. This places it in the same class of power law as layered metals $D^{-5/2}$ but in a different class to layered insulator's D^{-4} power laws [4].

Part Ⅱ Interaction between H_2 and Ca atoms in CaCOF-1

1. Charge density of CaCOF-1 before and after H_2 adsorption

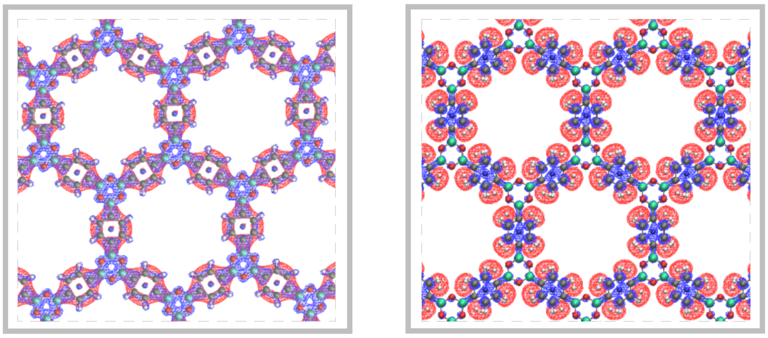
(a) (b)

Figure S4: (a) Charge density difference in CaCOF-1 upon Ca adsorption. (b) Charge density difference in CaCOF-1 upon H_2 adsorption. Red and blue clouds correspond to electron depletion and accumulation regions upon Ca binding (a) and H_2 binding (b), respectively.

The charge density difference of clean CaCOF-1 at *L* = 4.4 Å and H_2-CaCOF-1 at *L* = 4.9 Å is provided. It could be found hydrogen prefers to be adsorbed at 45° or

135° orientations with respect to the lattice vector in fully optimized geometry, thanks to the charge redistribution of Ca atom in the system.

2. Positive charge on Ca in clean and H_2 adsorbed CaCOF-1 with layer separation

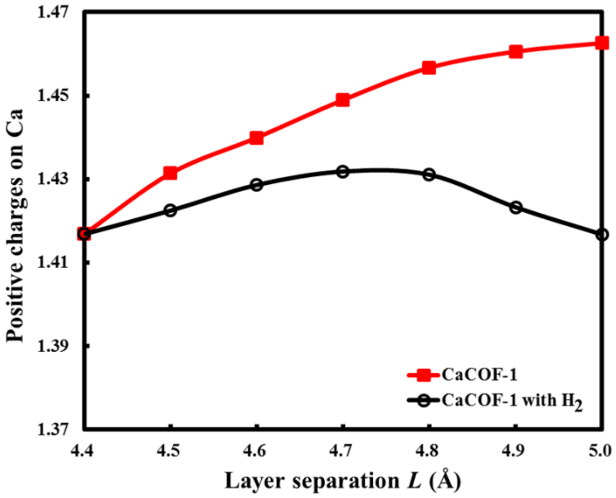

Figure S5 Positive charges on Ca atoms in clean and hydrogen adsorbed CaCOF-1 as a function of layer separation.

Our Bader charge analysis (using PAW PBE) shows that there are 1.42 electrons transferred from Ca to COF-1 during CaCOF-1 formation, and more electrons of Ca atoms are depleted with layer separation increasing. Moreover, after H_2 adsorption the charge variation of Ca ion in CaCOF-1 is flattened as the interlayer distance changes.

3. Distance between Ca and adsorbed H_2 on its variation with interlayer distance

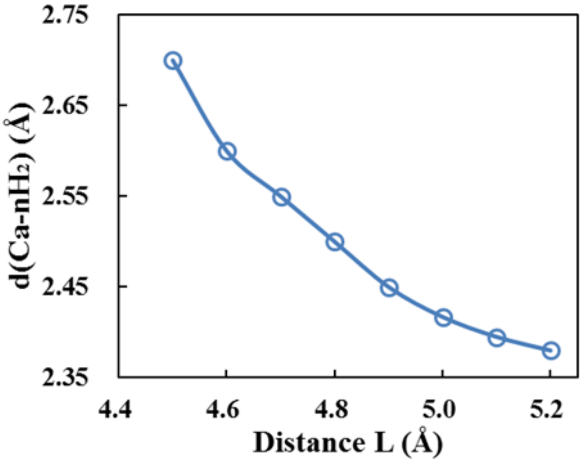

Figure S6: Average distance between Ca and adsorbed H_2 molecules on CaCOF-1 (d(Ca-nH_2)) as a function of interlayer distance *L*. With the distance *L* increasing, d(Ca-nH_2) is getting small that shows a stronger interaction.

Part Ⅲ Process of hydrogen release

1. Pressure for CaCOF-1 by two methods

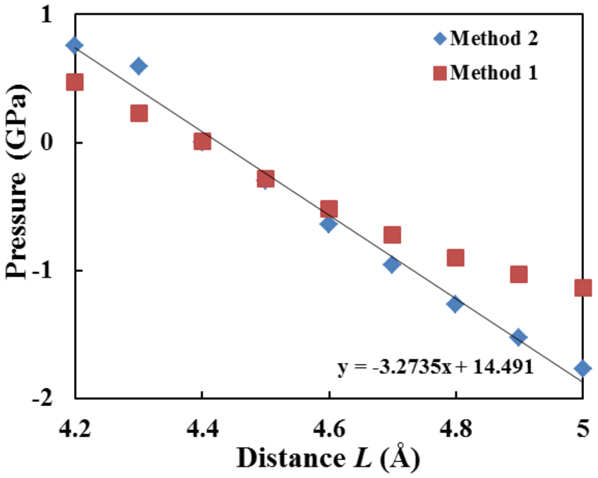

Figure S7: Pressure as a function of interlayer distance *L*. The method *1* is to get the pressure directly by VASP and method *2* [5] means to obtain the pressure by formula, namely, $P(V) = -dE(V)/dV$.

2. MD simulation for $12H_2$-CaCOF-1

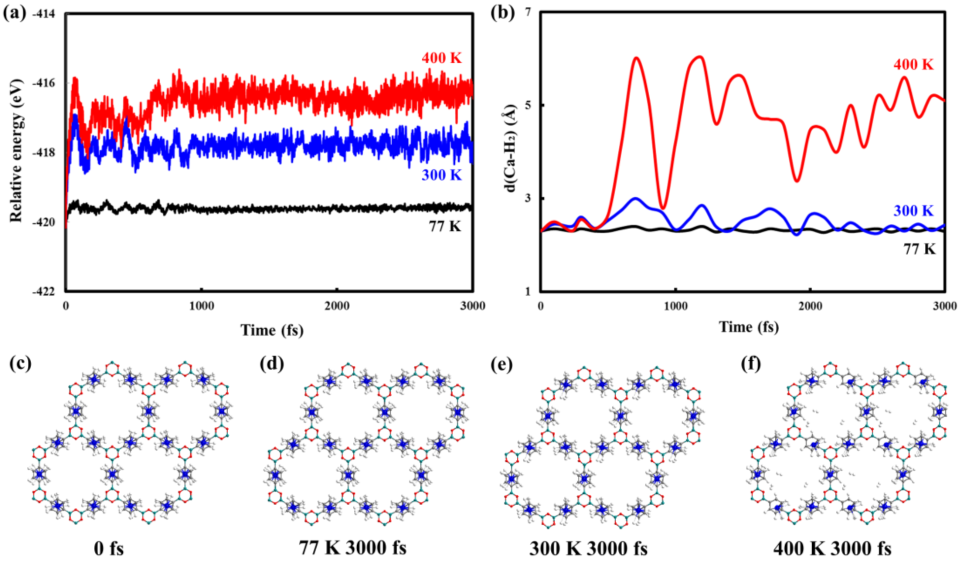

Figure S8: Molecular dynamics for hydrogen storage in CaCOF-1 at 4.8 Å at three different temperatures (77, 300 and 400 K). (a) Relative energy of $12H_2$ on CaCOF-1 in unit cell as a function of time. (b) Distance between Ca and one of adsorbed H_2 molecules on CaCOF-1 ($d(Ca\text{-}H_2)$) as a function of time. (c)-(f) Top view of H_2-CaCOF-1 at 0 fs and 3000 fs at 77, 300, 400 K, respectively.

It is shown that the most stable structure with four H_2 adsorbed on each Ca atom in CaCOF-1 at L = 4.8 Å keeps its optimized geometry at 77 and 300 K, and the system will release three out of twelve H_2 molecules when the temperature is increased to 400 K.

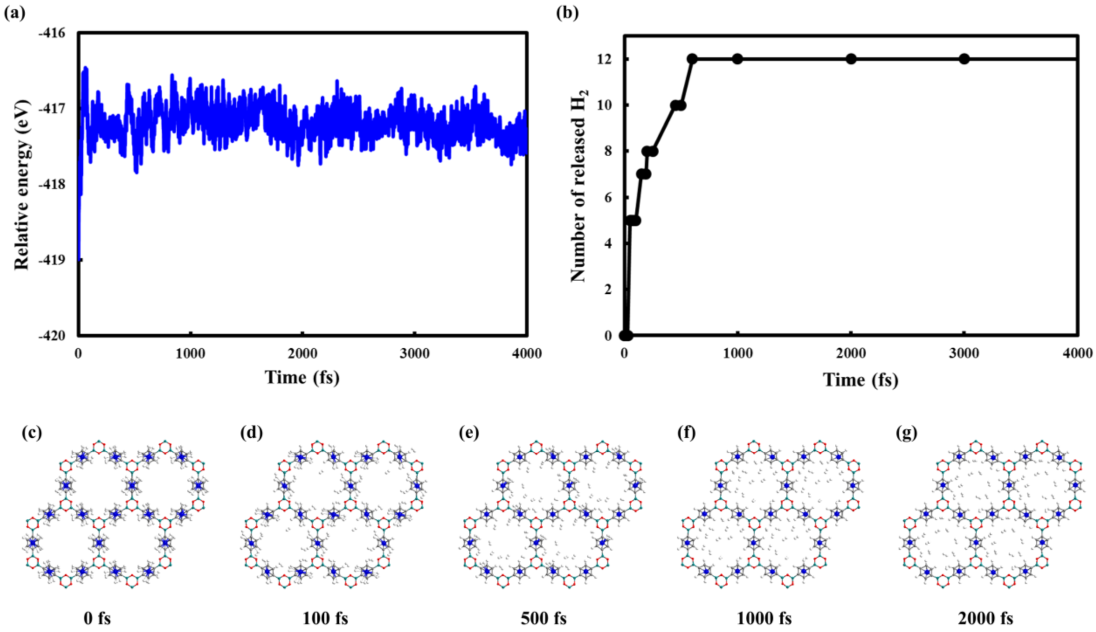

Figure S9: Molecular dynamics for hydrogen release process in CaCOF-1 at 4.3 Å at room temperature (300 K). (a) Relative energy of $12H_2$ on CaCOF-1 in unit cell as a function of time; (b) Number of released hydrogen in unit cell as a function of time; (c)-(g) Top view of H_2-CaCOF-1 at 0, 100, 500, 1000, and 2000 fs, respectively.

In the process of H_2 release, the external pressure is given to CaCOF-1 in which four H_2 are adsorbed on each Ca atom at 0 fs at 300K. The hydrogen molecules are desorbed gradually and all hydrogen can be released at room temperature at 4.3 Å after 600 fs.

Reference

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