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, $\sim$ 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), $\sim$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 $\approx L^{-4.2}$ behavior as a function of interlayer distance $L$ [2].

2. **Interlayer interaction for CaCOF-1**

   (1) The convergence test for K-point

<table>
<thead>
<tr>
<th>K-point</th>
<th>total energy/cell (eV)</th>
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<tr>
<td>1×1×5</td>
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<td>1×1×9</td>
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</tbody>
</table>

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

   (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) = $E_{\text{vdW-DF}} - E_{\text{GGA}}$.

Many studies show that the GGA results for interlayer binding energy of graphite is $\sim$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

![Figure S4](image-url)

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 H₂ 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 H₂ adsorption the charge variation of Ca ion in CaCOF-1 is flattened as the interlayer distance changes.

3. Distance between Ca and adsorbed H₂ on its variation with interlayer distance

Figure S6: Average distance between Ca and adsorbed H₂ molecules on CaCOF-1 (d(Ca-nH₂)) as a function of interlayer distance L. With the distance L increasing, d(Ca-nH₂) 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-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\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2}-CaCOF-1 at 0, 100, 500, 1000, and 2000 fs, respectively.]

In the process of H\textsubscript{2} release, the external pressure is given to CaCOF-1 in which four H\textsubscript{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