A Covalent Organic Framework that Exceeds the DOE 2015
Volumetric Target for H₂ Uptake at 298 K

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Supporting Information

ABSTRACT: Physisorption in porous materials is a promising approach for meeting H₂ storage requirements for the transportation industry, because it is both fully reversible and fast at mild conditions. However, most current candidates lead to H₂ binding energies that are too weak (leading to volumetric capacity at 298 K of <10 g/L compared to the DOE 2015 Target of 40 g/L). Using accurate quantum mechanical (QM) methods, we studied the H₂ binding energy to 48 compounds based on various metalated analogues of five common linkers for covalent organic frameworks (COFs). Considering the first transition row metals (Sc though Cu) plus Pd and Pt, we find that the new COF-301-PdCl₂ reaches 60 g total H₂/L at 100 bar, which is 1.5 times the DOE 2015 target of 40 g/L and close to the ultimate (2050) target of 70 g/L. The best current materials, MOF-200 and MOF-177, are predicted to store 7.6 g/L (0.54 wt % excess) and 9.6 g/L (0.87 wt % excess), respectively, at 298 K and 100 bar compared with 60 g/L (4.2 wt % excess) for COF-301-PdCl₂.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

A current major obstacle to molecular hydrogen (H₂) as an alternative source of energy is the difficulty of storage at operational temperatures. The U.S. Department of Energy (DOE) has set the 2015 targets of 5.5 wt % and 40 g/L at 233–358 K and 3–100 bar (and ultimate 7.5 wt % and 70 g/L). Among the most promising routes to obtain this goal is physisorption because it is fully reversible and has fast kinetics at desired conditions. However, current materials have been limited to <10 kJ/mol, which decreases as the sorption sites get saturated. Thus, sorption sites that are able to accommodate more H₂ molecules and have a stronger affinity for H₂ are needed. We and others have found that this is necessary to keep a constant heat of adsorption (Qₐ) as the loading increases, so that the loading/unloading cycle is efficient, which is a requirement for materials to attain the DOE targets. There have been several theoretical studies trying to put stronger interactions between H₂ and the material host; however, they have proven to be experimentally challenging. Thus a more straightforward experimental method to create strong interaction sites is needed.

The interactions that H₂ can have with other atoms, molecules or solids, are dispersion (≈ 5 kJ/mol), electrostatics (charge – quadrupole ≈ 3.5 kJ/mol, charge – induced dipole ≈ 6.8 kJ/mol), and orbital interactions (≈ 20–160 kJ/mol). The nature and magnitude of these interactions can allow us to tune the interaction with H₂.

Orbital interactions require either a very high pressure of 490 GPA or d-orbitals of transitions metals (TMs) to appear. The use of the d-orbital of TM is the most obvious choice because of the constraint of using up to 100 bar of pressure. The orbital interactions have different magnitude depending on the TM and the ligands used, and ultimately affect the H–H bond. The more the H–H bond elongates, the higher the interaction and the less reversible the binding is.

We need all these different kinds of interaction in order to obtain strong sorption of H₂ in surfaces but without modifying the H–H bond length significantly in order to obtain reversibility. For example, combinations of charge-quadrupole, dispersion, as well as orbital interactions can give us ion–H₂ and ligands–H₂ interactions in the range of 0.4–35 kJ/mol by changing the charge on the ligand or the ligand itself. Thus ligands that bind to transition metals can have different interaction sites and by designing the counteranion, we can obtain different kinds of strong interactions with H₂.

Thus we expect that the exposed sites with TM in the porous structure can enable H₂ interaction higher than 10 kJ/mol at 298 K. We have been trying to create such sites in different porous materials without successfully cleaning completely the
Our trials have focused on using precious late TMs such as Pd. After a systematic study of the binding energy of H₂ interacting with 48 compounds (5 linkers and 11 different transition metals), we found that early TMs (Sc to Cu) can attain the same strength of interactions as precious late TMs (Pd and Pt). From all these cases (Figure 1a), we found that one candidate, COF-301-PdCl₂, overcomes the 2015 DOE H₂ volumetric standards due to their ideal pore for interacting with H₂ (Figure 1b). In this Letter we present its properties and explain why this framework reaches such a high performance.

To estimate the interactions between H₂ and the different linkers with TM, we used the M06 hybrid DFT functionals that contain corrections for dispersion interactions as implemented in the Jaguar code. Here we used the 6-31G** basis set for the light elements. For the TMs we used the Los Alamos LACVP**++ electronic core potential which includes relativistic corrections. The unrestricted open shell procedure for the self-consistent field calculations was used for all spin states. All geometries were optimized using the analytic Hessian to determine that the local minima have no negative curvatures (imaginary frequencies). The vibrational frequencies from the analytic Hessian were used to calculate the zero-point energy correction at 0 K.

Using the optimized structures obtained from QM, we develop the force field (FF) for the grand canonical Monte Carlo (GCMC) calculations. As described previously, the organic part of the FF is based on second-order Møller–Plesset (MP2) perturbation theory, but we have added N(sp²) term to the previous parameters (Figure 2). For the Pd and Cl parameters (H₁₂–Cl₁₂ and H₁₂–P₁₂), the level of QM was M06-DFT, which was developed to provide accurate van der Waals binding. We show the comparison between the FF and the QM/M06 for the estimation of binding energies in Table 1. The FF energies are within the 1 kJ/mol range of the QM results.

We used the first-principles-based FF described above in GCMC ensemble simulations. Here for each temperature and pressure, we constructed 3 000 000 configurations to compute the average loading for which the observed convergence was obtained. Every GCMC step allows four possible events: translation, rotation, creation, and annihilation, each at equal probability. We used the GCMC as implemented in Cerius2.

In the design of the new COF we used only the dia-c5 topology (I₄/a space group), which has been found experimentally for imine based linkers such as COF-300. To construct COF-301, we used 4,4′,4″,4‴-methanetetrayltertraniline (MTA) and 2, 5-dihydroxyterephthalaldehyde (HTA), which is metalated to give COF-301-PdCl₂ (Figure 1b). The coordinates are reported in the Supporting Information.

The current strategy for putting TM in COF-301 would involve postmetalation with PdCl₂. In order to determine whether this is feasible, we calculate the energetics of this
By metalating COF-301, we reduced the surface area from 3700 to 1080 m² g⁻¹ and pore volume from 1.08 to 0.42 cm³ g⁻¹ (Table 2); however, the metalation still reaches high uptake due to the high interaction between the TM site and H₂.

This combination of an ideal pore aperture and strong affinity toward the surface of the porous material is responsible for the drastic improvement in the uptake for COF-301-PdCl₂, which increases by more than 8 times its volumetric H₂ uptake compared to the unmetalated framework, reaching 60 total g H₂/L (and 4.2 wt % excess) at 100 bar. This makes COF-301-PdCl₂ a promising material for H₂ storage, indeed the best materials, MOF-200 and MOF-177, are predicted to reach 7.6 g/L (0.54 wt % excess) and 9.6 g/L (0.87 wt % excess), respectively, while COF-103 is calculated to reach 7.7 g/L (0.55 wt % excess). This difference in performance arises because these unmetalated materials, however, have a predicted Qst of less than 5 kJ/mol (MOF-177; 4.9, MOF-200; 3.5 and COF-103; 4.4 kJ/mol).³⁵

We calculate the pore sizes (Pₚₑₑ) of the COF-300 (synthesized), COF-301, and COF-301-PdCl₂ within the layers giving 10.6, 9.0, and 6.5 Å, respectively. However, the space between neighboring framework layers (Dₚₑₑ), is 8.9, 10.4, and 9.9 Å (Table 2). This provides the space where most of H₂ are hosted (Figure 3).

We calculate that Qₑₑ ranges from 24.5 kJ/mol at 1 bar to 23.0 kJ/mol at 100 bar, which is ≈90% larger than from QM on the isolated metalated linker (≈12.5 kJ/mol, Table 2). This is because the small distance between metalated sites in COF-301-PdCl₂ is ideal to allow H₂ to interact with all the PdCl₂ from neighboring layers, giving a cooperative effect. This cooperative effect is observed when the distance between metalated sites is less than 10 Å. For example, the highest Qₑₑ observed for a hydrogen adsorption porous material, M’MOF-1, has curve pores of 5.6 × 12 Å and narrower reaching Qₑₑ of 12.3 kJ/mol at zero surface coverage, which drops to 9.5 kJ/mol with higher uptake.²³

Table 1. Comparison of Binding Energies Obtained from M06-DFT and FF for the PdCl₂ Metalated Linkers Interacting with Different Number of H₂.

<table>
<thead>
<tr>
<th>linker</th>
<th>no. of H₂</th>
<th>Ebind/QM (kJ/mol)</th>
<th>Ebind/FF (kJ/mol)</th>
<th>energy rms (kJ/mol)</th>
<th>coordinates rms (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BBH</td>
<td>1, 2</td>
<td>−12.3, −12.0</td>
<td>−12.1, −11.6</td>
<td>0.495</td>
<td>0.314</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>3, 4</td>
<td>−11.4, −11.3</td>
<td>−11.2, −11.2</td>
<td>0.439</td>
<td>0.370</td>
</tr>
<tr>
<td>PIP</td>
<td>1, 2</td>
<td>−13.4, −13.2</td>
<td>−13.1, −12.9</td>
<td>0.333</td>
<td>0.223</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>3, 4</td>
<td>−12.7, −11.7</td>
<td>−12.6, −11.5</td>
<td>0.344</td>
<td>0.151</td>
</tr>
<tr>
<td>PIA</td>
<td>1, 2</td>
<td>−12.8, −12.8</td>
<td>−12.6, −12.6</td>
<td>0.385</td>
<td>0.223</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>3, 4</td>
<td>−11.9, −11.9</td>
<td>−11.8, −11.7</td>
<td>0.385</td>
<td>0.223</td>
</tr>
<tr>
<td>BPY</td>
<td>1, 2</td>
<td>−9.89, −9.86</td>
<td>−10.1, −10.1</td>
<td>0.385</td>
<td>0.223</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>3, 4</td>
<td>−9.81, −9.78</td>
<td>−9.90, −9.86</td>
<td>0.385</td>
<td>0.223</td>
</tr>
<tr>
<td>BPPM-</td>
<td>1, 2</td>
<td>−12.5, −12.5</td>
<td>−12.8, −12.6</td>
<td>0.385</td>
<td>0.223</td>
</tr>
<tr>
<td>PdCl₂</td>
<td>3, 4</td>
<td>−12.1, −12.1</td>
<td>−12.3, −12.2</td>
<td>0.385</td>
<td>0.223</td>
</tr>
</tbody>
</table>

"Linkers: (E)-N’-benzylidenebenezhydrizade (BBH), (E)-2- ((phenylimino)methyl)phenol (PIP), (E)-N’-(pyridin-2-ylmethylene)-aniline (PIA), 2,2’-bipyridine (BPY) and 2,2’-bipirimidine (BPPM)."

Figure 3. The GCMC supercell (2 × 2 × 2 primitive cells). For (a) COF-301 and (b) COF-301-PdCl₂ each supercell contains 8 MTA as nodes and 16 HTA linkers with 32 possible metalation sites. In panel b, all these sites are occupied by PdCl₂. Shown also are the equilibrium H₂ molecules at 100 bar: (a) 15 for COF-301 and (b) 126 for COF-301-PdCl₂. Color code: C, black; H, gray; O, red; N, blue; Pd, pink; and Cl, green.
We made several attempts to metalate COF-301 for which we carried out by reflux reaction of a suspension of COF-301 and metal source (PdCl₂ or PtCl₂) in acetonitrile. The resulting yellow solid was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. However, we believe that the COF was not well metalated. For example, the Brunauer–Emmett–Teller (BET) area of metalated sample was quite low, and the thermogravimetric analysis (TGA) data did not show the presence of significant amounts of metal residue. It may be that most of metal was bound to the COF surface or near the surface. We suspect that the metals may not have diffused throughout the interior of the material. This is not surprising because solvation of these metal sources may lead to diameters too large for the pore diameter of COF-301. In summary, we propose that COF-301-PdCl₂ reaches 60 g total H₂/L and 4.2 wt % excess uptake at 100 bar, which is 1.5 times the DOE 2015 target of 40 g/L and close to the ultimate (2050) target of 70 g/L. The best current materials, MOF-200 and MOF-177, are predicted to store 7.6 g/L (0.54 wt % excess) and 9.6 g/L (0.87 wt % excess), respectively at 298 K and 100 bar, which is 1.5 times the DOE 2015 target.

## Table 2. H₂ Uptake Obtained from Our Simulations for Pure and Metalated Imine-COFs at 298 K and 100 bar

<table>
<thead>
<tr>
<th>COF</th>
<th>S_a (m² g⁻¹)</th>
<th>V_p (cm³ g⁻¹)</th>
<th>P_max (Å)</th>
<th>D_inter (Å)</th>
<th>Q_s (kJ/mol)</th>
<th>H₂ excess uptake (wt%)</th>
<th>H₂ total uptake (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-300</td>
<td>3820</td>
<td>1.25</td>
<td>10.6</td>
<td>8.9</td>
<td>5.8</td>
<td>0.55</td>
<td>7.9</td>
</tr>
<tr>
<td>COF-301</td>
<td>5760</td>
<td>1.08</td>
<td>9.3</td>
<td>10.4</td>
<td>6.0</td>
<td>0.44</td>
<td>7.4</td>
</tr>
<tr>
<td>COF-301-PdCl₂</td>
<td>1083</td>
<td>0.42</td>
<td>6.3</td>
<td>9.9</td>
<td>23</td>
<td>4.2</td>
<td>60</td>
</tr>
</tbody>
</table>

*Surface area (S_a), pore volume (V_p), pore size (P_max), distance between neighboring framework layers (D_inter), and weighted average isosteric heat of adsorption (Q_s) are also presented.

## ACKNOWLEDGMENTS

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