

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

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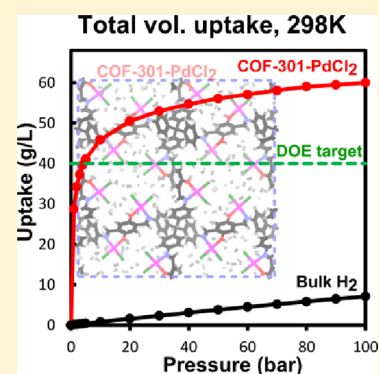
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S Supporting Information

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 through 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).^{1–3} 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.^{4,5} 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 (Q_{st}) as the loading increases, so that the loading/unloading cycle is efficient, which is a requirement for materials to attain the DOE targets.^{5,6} 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.^{7–10} 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/mol⁶), electrostatics (charge – quadrupole ≈ 3.5 kJ/mol,¹¹ charge – induced dipole ≈ 6.8 kJ/mol¹¹), and orbital interactions (≈ 20 –160 kJ/mol^{12–14}). 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 GPA¹⁵ or d-orbitals of transition metals (TMs) to appear.^{12–14} 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.¹¹ 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

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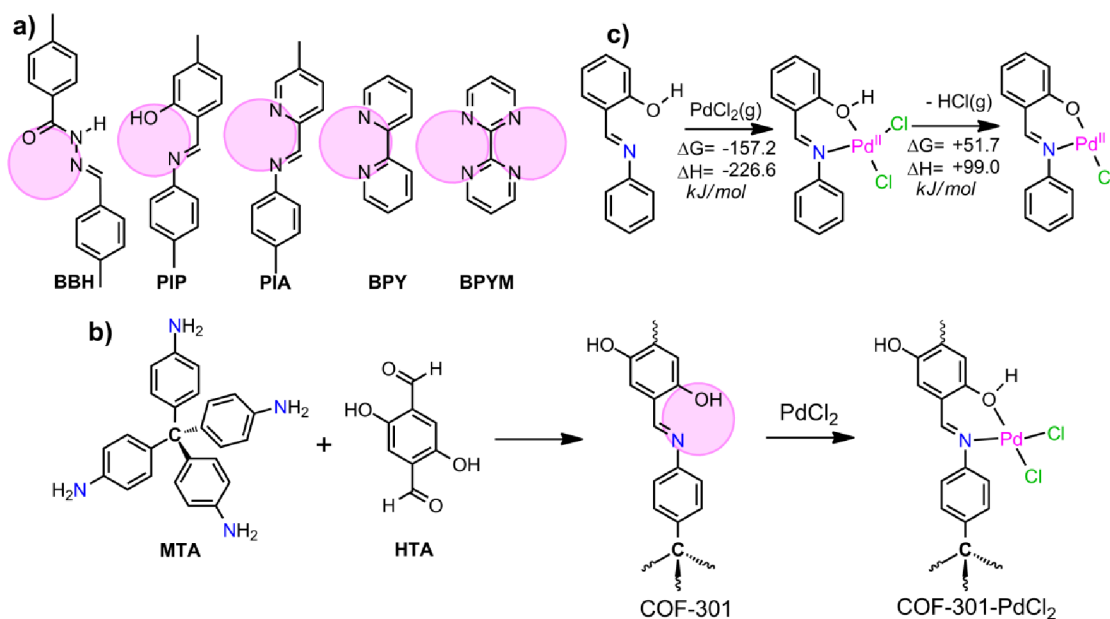


Figure 1. (a) Connectivity developed in linkers used for COFs and MOFs where metalation sites are present. The pink circle indicates the sites where a transition metal can be placed. (b) We show the building blocks (MTA and HTA) for the construction of new COF-301 through imine formation, which contains binding sites to host transition metals (pink circle). This framework is metalated with PdCl_2 to give COF-301- PdCl_2 . (c) Our calculations show that the metalation with PdCl_2 is favorable for this ligand, and the liberation of HCl is unfavorable.

pores.^{16,17} Our trials have focused on using precious late TMs such as Pd. After a systematic study of the binding energy of H_2 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).¹⁸ From all these cases (Figure 1a), we found that one candidate, COF-301- PdCl_2 , overcomes the 2015 DOE H_2 volumetric standards due to their ideal pore for interacting with H_2 (Figure 1b). In this Letter we present its properties and explain why this framework reaches such a high performance.

To estimate the interactions between H_2 and the different linkers with TM, we used the M06¹⁹ hybrid DFT functionals that contain corrections for dispersion interactions as implemented in the Jaguar code.²⁰ 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.²¹ 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,⁵ but we have added $\text{N}(\text{sp}^2)$ term to the previous parameters (Figure 2). For the Pd and Cl parameters ($\text{H}_{\text{H}_2}-\text{Cl}_{\text{PdCl}_2}$ and $\text{H}_{\text{H}_2}-\text{Pd}_{\text{PdCl}_2}$), 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

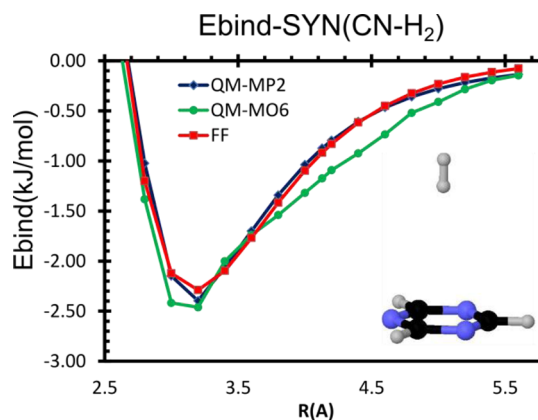


Figure 2. QM calculations executed for the 1,3,5-triazine interacting with H_2 with MP2 and M06. Our calculations showed that the MP2 gives a better estimation of the binding curve shape than M06. However M06 gives a similar estimation than MP2 for the bottom of the curve. We also show the FF results based on MP2.

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 ($I4_1/a$ space group), which has been found experimentally for imine based linkers such as COF-300.²² To construct COF-301, we used 4,4',4'',4'''-methanetetrayl-tetraaniline (MTA) and 2, 5-dihydroxyterephthalaldehyde (HTA), which is metalated to give COF-301- PdCl_2 (Figure 1b). The coordinates are reported in the Supporting Information.

The current strategy for putting TM in COF-301 would involve postmetalation with PdCl_2 . In order to determine whether this is feasible, we calculate the energetics of this

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

| linker-PdCl ₂ | no. of H ₂ | $E_{\text{bind-QM}}$ (kJ/mol) | $E_{\text{bind-FF}}$ (kJ/mol) | energy rms (kJ/mol) | coordinates rms (Å) |
|--------------------------|-----------------------|-------------------------------|-------------------------------|---------------------|---------------------|
| BBH-PdCl ₂ | 1, 2 | -12.3, -12.0 | -12.1, -11.6 | 0.495 | 0.314 |
| | 3, 4 | -11.4, -11.3 | -11.3, -11.2 | | |
| PIP-PdCl ₂ | 1, 2 | -13.4, -13.2 | -13.1, -12.9 | 0.439 | 0.370 |
| | 3, 4 | -12.7, -11.7 | -12.6, -11.5 | | |
| PIA-PdCl ₂ | 1, 2 | -12.8, -12.8 | -12.6, -12.6 | 0.333 | 0.223 |
| | 3, 4 | -11.9, -11.9 | -11.8, -11.7 | | |
| BPY-PdCl ₂ | 1, 2 | -9.89, -9.86 | -10.1, -10.1 | 0.344 | 0.151 |
| | 3, 4 | -9.81, -9.78 | -9.90, -9.86 | | |
| BPYM-PdCl ₂ | 1, 2 | -12.5, -12.5 | -12.8, -12.6 | 0.385 | 0.223 |
| | 3, 4 | -12.1, -12.1 | -12.3, -12.2 | | |

^aLinkers: (*E*)-*N*'-benzylidenebenzohydrazide (BBH), (*E*)-2-((phenylimino)methyl)phenol (PIP), (*E*)-*N*-(pyridin-2-ylmethylene)-aniline (PIA), 2,2'-bipyridine (BPY) and 2,2'-bipirimidine (BPYM) are compared. Root mean square (rms) deviation for all coordinates and energies for the QM vs. FF are also reported. All systems lead to a singlet spin state and to a square planar Pd.

process in the gas phase (Figure 1c). Our results predict that the postmetalation of the linker used in COF-301 is exothermic with $\Delta H = -227$ kJ/mol and $\Delta G = -157$ kJ/mol. Once this metalation has occurred, a possible decomposition involves liberation of HCl; however, from our QM calculation we predict this to be endothermic ($\Delta H = +52$ kJ/mol and $\Delta G = +99$ kJ/mol). PdCl₂ melts at 680 °C, which may complicate the synthesis.

From these linkers, COF-301 and COF-301-PdCl₂ are constructed into a periodic structure and H₂ molecules are added by GCMC to construct the isotherm. At 100 bar, the pristine COF-301 reaches 15 H₂ per unit cell, while the COF-301-PdCl₂ reaches 126 H₂ per unit cell (Figure 3). This is 3.9 H₂ per PdCl₂ site in COF-301-PdCl₂, where we have assumed that all the 32 possible sites are metalated. This is an increase of more than 8 times the H₂ content inside the pores versus the nonmetalated framework. The sorption isotherm of these frameworks at 298 K up to 100 bar were also calculated (Figure 4).

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 first material that at 100 bar and 298 K exceeds the 2015 DOE volumetric target of 40 g/L, coming close to the ultimate target of 70 g/L. The mass density at room temperature 4.2 excess wt % does not meet the 2015 DOE target of 5.5 wt %; however, this performance is almost 5 times the value of the best previous performers. These 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 7.70 g/L (0.55 wt % excess). This difference in performance arises because these unmetalated materials, however, have a predicted Q_{st} of less than 5 kJ/mol (MOF-177; 4.9, MOF-200; 3.5 and COF-103; 4.4 kJ/mol).⁵

We calculate the pore sizes (P_{size}) 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 (D_{layers}), 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 Q_{st} ranges from 24.5 kJ/mol at 1 bar to 23.0 kJ/mol at 100 bar, which is $\approx 90\%$ 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 Q_{st} observed for a hydrogen adsorption porous material, M'MOF-1, has curve pores of 5.6×12 Å and narrower reaching Q_{st} of 12.3 kJ/mol at zero surface coverage, which drops to 9.5 kJ/mol with higher uptake.²³

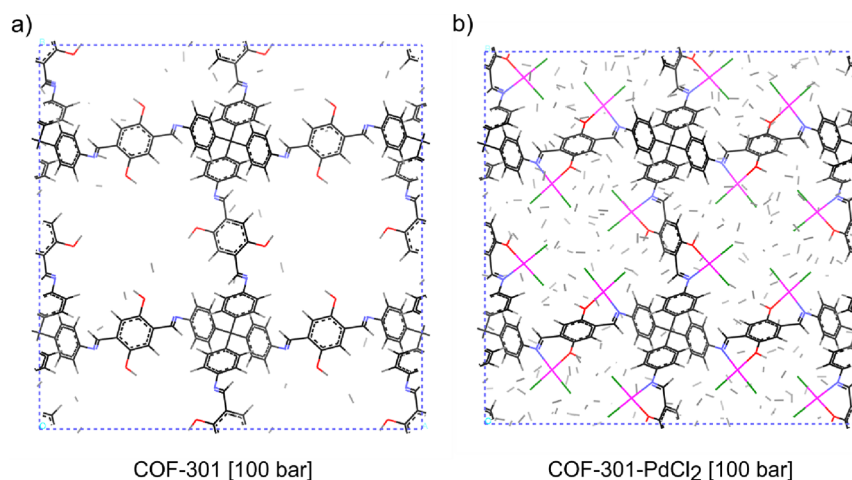


Figure 3. The GCMC supercell ($2 \times 2 \times 2$ primitive cells). For (a) COF-301 and (b) COF-301-PdCl₂, each supercell contains 8 MTA as nodes and 16 HTA linkers with 32 possible metalation sites. In panel b, all these sites are occupied by PdCl₂. Shown also are the equilibrium H₂ molecules at 100 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.

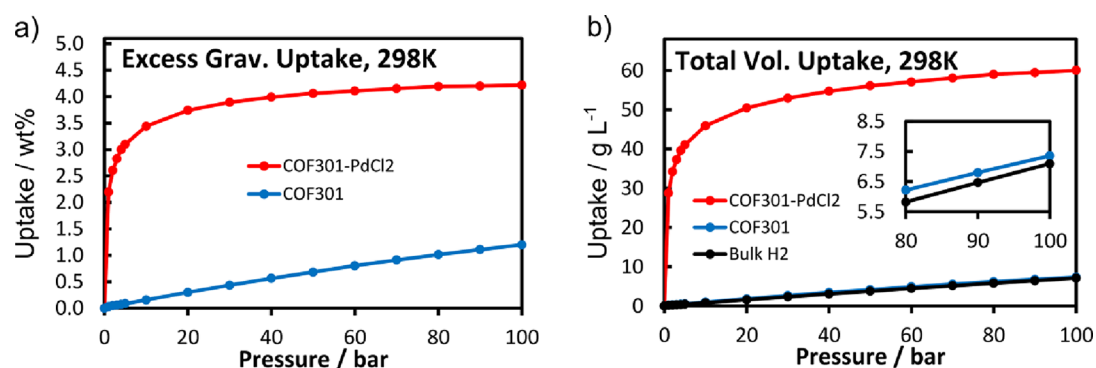


Figure 4. (a) Excess gravimetric and (b) total volumetric uptake H_2 isotherms obtained at 298 K for COF-301 and COF-301-PdCl₂.

Table 2. H_2 Uptake Obtained from Our Simulations for Pure and Metalated Imine-COFs at 298 K and 100 bar^a

| @298 K, 100 bar | S_A (m ² g ⁻¹) | V_p (cm ³ g ⁻¹) | P_{size} (Å) | D_{layers} (Å) | Q_{st} (kJ/mol) | H_2 excess uptake (wt%) | H_2 total uptake (g L ⁻¹) |
|---------------------------|---|--|----------------|------------------|-------------------|---------------------------|---|
| COF-300 | 3820 | 1.25 | 10.6 | 8.9 | 5.8 | 0.55 | 7.9 |
| COF-301 | 3700 | 1.08 | 9.3 | 10.4 | 6.0 | 0.44 | 7.4 |
| COF-301-PdCl ₂ | 1083 | 0.42 | 6.3 | 9.9 | 23 | 4.2 | 60 |

^aSurface area (S_A), pore volume (V_p), pore size (P_{size}), distance between neighboring framework layers (D_{layers}), and weighted average isosteric heat of adsorption (Q_{st}) are also presented.

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 H_2 /L and 4.2 wt % excess 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.

■ ASSOCIATED CONTENT

📄 Supporting Information

Geometry coordinates for optimized linkers COF-301 and COF-301-PdCl₂ are reported. The numerical H_2 uptake is also included. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The project was planned by J.L.M.-C. and W.A.G.; the calculations were carried out by J.M.L.C. The manuscript was

written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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