FINAL TECHNICAL REPORT FOR THE US DEPARTMENT OF ENERGY

Project title: A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs for On-Board Vehicular Hydrogen Storage
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Executive Summary

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressure gas or very low temperature liquid. Because of the importance of hydrogen as a fuel, the DOE has set system targets for hydrogen storage of gravimetric (5.5 wt%) and volumetric (40 g/L) densities to be achieved by 2015. From our continuous efforts on hydrogen storage, it is believed that metalation of highly porous solids with high-valence metals is promising and provides a rational direction to realize high volumetric hydrogen density near room temperature.

This grant was focused on the study of high surface area covalent organic frameworks (COFs) with these specific objectives (1) to introduce potential metal binding sites through the COF synthesis and (2) to implement metalation experiments and evaluate their respective hydrogen adsorption properties. To maximize our efforts, simulation calculations were also performed (prior to experiments) for the prediction of binding enthalpy of hydrogen for molecular building units containing transition metals and promising COF structures to increase volumetric hydrogen uptake at room temperature.

In this effort, first molecular building units with optimal binding energy for hydrogen storage (20 kJ/mol) were designed by quantum mechanical (QM) methods. Employing these results, it was revealed that one of metalated COFs takes up 60 g/L (total) of H_2 at 100 bar and 298 K. To realize proposed COF structures, chemistry of COF synthesis has been developed; for instance, new air stable COFs were synthesized via hydrazone (COF-41 to 43) and imine condensation (COF-301, 320, 340, and 366) and some of them were tested the effect on metalation. Finally, a new triazine COF with high volumetric hydrogen uptake capacity was presented as a proposed future direction.

This report does not contain any proprietary, confidential,
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Objectives

- Predict binding enthalpy of H_2 for molecular building units containing transition metals
- Develop new Force Fields for H_2 adsorption
- Predict promising COF structures to maximize volumetric H_2 uptake at room temperature
- Introduce potential metal binding sites through the COF synthesis
- Implement metalation experiments and evaluate their respective H_2 adsorption properties

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

(C) Efficiency

(E) Charging/Discharging Rates

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of several fundamental studies on covalent organic frameworks (COFs). Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage targets:

- Volumetric density: 40 g/L
- Gravimetric density: 5.5 wt%

Accomplishments

- Calculated binding energy of H_2 for molecular building units with different first row transition metals
- Found building units containing metals with optimal binding energy for H_2 storage (20 kJ/mol)
- Synthesized new air stable COFs via hydrazone (COF-41 to 43) and imine condensation (COF-301, 320, 340, and 366)
- Develop structural determination technique using *ab initio* charge-flipping method
- Predicted H_2 isotherms and Q_{st} values of a series of imine COFs with and without metalation (at 298 K, up to 100 bar)
- Predicted that metalated COF-301 takes up 60 g/L (total) of H_2 at 100 bar and 298 K
- Performed metalation experiments of COFs using COF-301
- Proposed a new triazine COF (COF-102-Tri-$PdCl_2$) for high volumetric H_2 uptake (48 g/L of total H_2 uptake at 100 bar and 298 K)

Introduction

Conventional storage of large amounts of H_2 in its molecular form is difficult and expensive because it requires employing either extremely high pressure as a gas or very low temperature as a liquid [1]. In order to achieve practical compact fuel cell systems, the storage issues associated with the high volumetric and gravimetric density of H_2 must be addressed. Two basic approaches have emerged to achieve the targets for on-board H_2 storage systems set by the DOE: 5.5 wt % and 40 g/L by the year 2015. One is to chemisorb H_2 as metal hydrides or chemical hydrides [2, 3]. Although some metal hydrides are able to meet the DOE target for H_2 storage capacity, their high discharge temperature and poor cycle performance remain roadblocks to their successful implementation in real-world systems. The other approach is to physisorb H_2 in porous materials such as carbon-based materials, zeolites, polymers, and metal-organic frameworks (MOFs) [1, 4]. Several MOFs and porous carbon materials with high surface area meet the DOE targets at 77 K; however, significant room temperature uptake remains a challenge. One of the reasons for the diminished storage capacity at room temperature is the weak adsorbent-H_2 interaction due to the lack of strong binding sites.

To meet the DOE 2015 targets by physisorption, adsorbents must have a high surface area (> 3500 m^2/g) and a relatively high density (> 0.75 g/cm^3). We have already demonstrated how to design high surface area MOFs and covalent-organic frameworks (COFs) [5-7]; however, in many cases, these materials do not show steep H_2 uptake in the low pressure region indicative of the weak interaction with H_2 (small heat of adsorption, Q_{st}). It is generally believed that open metal sites can provide large binding energy sites for H_2 (i.e. large Q_{st}) [1]; however, when such open metal sites are occupied by H_2, observed Q_{st} value drops to 5 kJ/mol. This indicates that the realistic strategy is to introduce strong H_2 binding sites in the porous solids, where each binding site can capture multiple H_2 molecules, rather than to create H_2 binding sites with a significantly large Q_{st} value. It is fair to say that, as a general approach, metalation of COFs with high-valence metals is promising and provides a rational direction to realize high volumetric H_2 density near room temperature. Therefore, in this project, discovery of highly porous COF with high-valence metals for H_2 storage was endeavored.

Results

1. Binding enthalpy of H_2 for molecular building units containing transition metals

To synthesize metalated COFs, it is important to synthesize COFs with metal binding sites. Various types of metal binding sites are known, but only a few of them are feasible to incorporate into COF structures. Therefore, five types of ligands (**BBH**, **PIP**, **PIA**, **BPY**, and **BPYAM**, see Figure 1) are down-selected to study how the metalation improves the binding energy and how many H_2 molecules can be adsorbed on each metal site, since these potential metal binding sites cannot show strong interaction with H_2 molecules (typical ΔH^0_{bind} values are from -5 to -7 kJ/mol for the first four H_2).

Ligand containing the hydrazide binding group: The first linker we studied is the hydrazide containing linker (**BBH**, Figure 1). To determine which transition metal would have the best binding enthalpy to H_2, the interactions of such compounds using first row transition metals (TM; Sc to Cu) and Pd were estimated. The results are shown in Figure 2. For all these cases, Sc to Cu and Pd(II), the H_2 does not bind chemically to the TM. Strong interactions between the first H_2 with Cr(III), Mn(II) and Ni(II) indicates formation of η^2-H_2 interaction

complexes. The rest of the TMs exhibit a similar behavior. The range of ΔH^0_{bind} is from 11 to 14 kJ/mol for the 1st-4th interacting H_2 and no H_2 dissociation was observed.

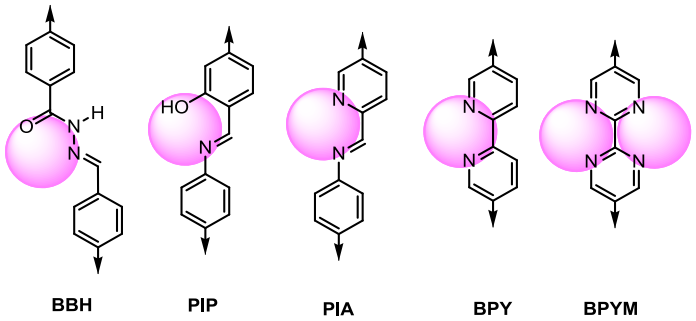

Figure 1. Structures of organic unit with potential metal binding sites can be used for COF synthesis. Potential metal binding sites are shown in pink circles.

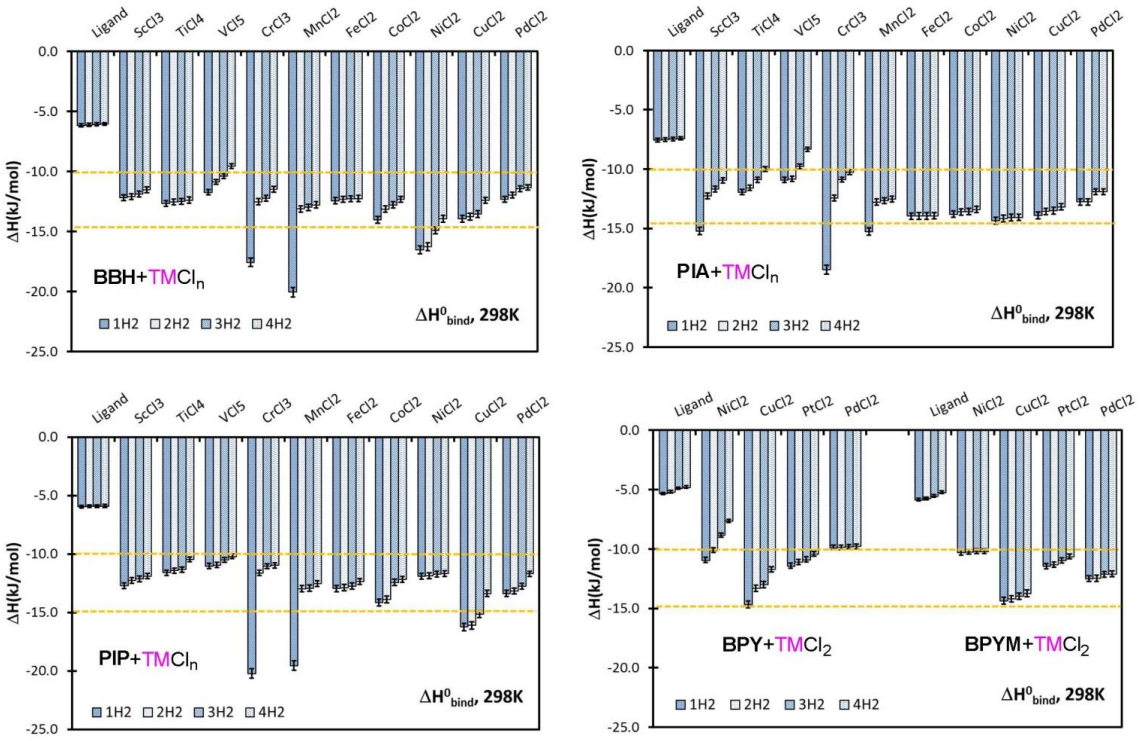

Figure 2. Incremental binding enthalpies ΔH^0_{bind} at 298 K obtained for **BBH**, **PIP**, **PIA**, **BPY**, and **BPYM** ligands interacting with up to four H_2. A variety of TMs, Sc to Cu and $PdCl_2$ in various oxidation states, were considered. The error bars indicate the differences found for various configurations with the same number of H_2.

Ligand containing the imine binding group: Before the estimation of binding enthalpies, the equilibrium between **PIP** and the un-protonated ligand was studied through the calculation of

the pK_a. The pK_a value was equals to 8.7 in water, indicating that the **PIP** ligand at normal neutral conditions does not dissociates considerably to create the conjugated base and H^+. Data for the imine binding group (**PIP**) with different TMs are shown in Figure 2. In this case, almost all the compounds (i.e. **PIP**+TM(n)Cl_n) do not bind chemically to H_2 and have an ΔH^0_{bind} that ranges from -10 to -15 kJ/mol for the 1st-4th interacting H_2. Also, the H-H bond was not perturbed significantly. However, the case of Cr(III), Mn(II), and Cu(II) these metal ions interact strongly with the first H_2 (stronger than -15 kJ/mol).

Ligand containing the iminopyridine binding group: Since it is known that iminopyridine moiety can bind $PdCl_2$ [8], the interaction between H_2 and **PIA** with and without metal ions was studied (Figure 2). As in the other cases, it is observed that TMs that interacts strongly (< -15 kJ/mol) with the 1st H_2 through a η^2-H_2 interaction; Sc(III), Cr(III), Mn(II). The other TMs have interactions in the ideal ΔH^0_{bind} range of 10-15 kJ/mol.

Ligand containing the bipyridine group: MOFs with 2,2'-bipyridine unit (**BPY**) are also reported [9], the H_2 binding enthalpy was calculated (Figure 2). For this linker, except for the Ni(II) case, all of the other TMs have a constant ΔH^0_{bind} over the first four H_2, which is desirable for a host in real applications. Also the interactions are slightly larger than 10 kJ/mol, showing the utility of metalation as a way to improve the interactions with H_2. The compound that offers the stronger interaction with H_2 was **BPY**-Cu(II)Cl_2.

Ligand containing two bipyrimidine group: The linker 2,2'-bipyrimidine (**BPYM**) was also examined to see the interaction of TMs with H_2. Unexpectedly, the additive effect on ΔH^0_{bind} given that two TMs are close to each other was only found for the case of $PdCl_2$. The compound that offers the stronger interaction with H_2 was **BPYM**-Cu(II)Cl_2.

2. Synthesis and characterization of crystalline porous COFs

As demonstrated in the previous section, metal impregnation is one of the most promising strategies to improve the adsorption enthalpy of COFs. However, before the metal impregnation experiments, it is necessary to prepare stable COFs, and it is preferable to introduce metal binding sites in the framework through the condensation reaction. To this end, new COFs having hydrazone and imine moieties have been designed and prepared. In addition, we applied new techniques to the structural analysis of COFs, which can be useful in determining the structure from low resolution powder X-ray diffraction (PXRD) data.

Synthesis of crystalline hydrazone COFs: New COFs constructed from the dehydration of aromatic carbohydrazides and aldehydes to form carbohydrazones were synthesized. This functional group shows interesting features such as the presence of both of amides and imines, resulting in materials with high thermal and chemical stability as well as dynamic reversibility forming libraries of polymers that exchange monomers in solution. Moreover, hydrazones possess both carbonyls and nitrogen atoms that can be available for metal coordination/impregnation. An additional advantage for the synthesis of hydrazide-based materials is the easy synthesis of the hydrazide building blocks, which are prepared from the condensation of hydrazine and a carboxylic acid ester in refluxing alcohols with high yields.

Originally a new COF, termed COF-41, was crystallized by reacting terephthalohydrazide (**1**, Figure 3) with 1,3,5-tris(4-formyl-phenyl)-benzene (**2**) through solvothermal conditions. The formation of the hydrazone linkages was determined by solid state FT-IR and ^{13}C NMR spectra. The crystallinity of COF-41 was also confirmed by PXRD from which the diffraction peaks were

indexed into a primitive hexagonal unit cell (a = 43.52 Å, c = 3.62 Å). However, obtained BET surface area (110 m^2/g) is much lower than expected value, so that ethoxy functionality was introduced to the starting material to improve the solubility of starting material.

COF-42 and COF-43 (Figure 4) were synthesized by suspending 2,5-diethoxyterephthalohydrazide (**3**) and 1,3,5-triformylbenzene (**4**) and 1,3,5-tris(4-formylphenyl)benzene (**2**), respectively, in a flame-sealed Pyrex tube in a mixture of mesitylene, dioxane and acetic acid at 120 °C. These materials were immersed in tetrahydrofuran to remove occluded guests for 3 days, and the solvent was subsequently removed by heating at 85 °C under dynamic vacuum.

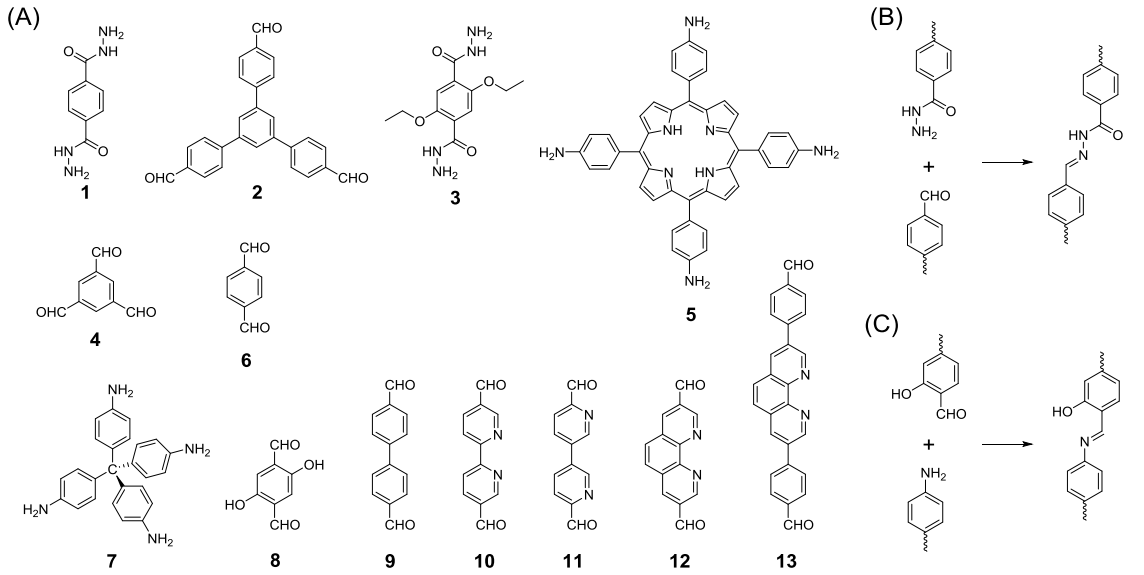

Figure 3. (A) Molecular structures of building units for COF synthesis. Reaction scheme of hydrazone (B) and imine COF (C) formation.

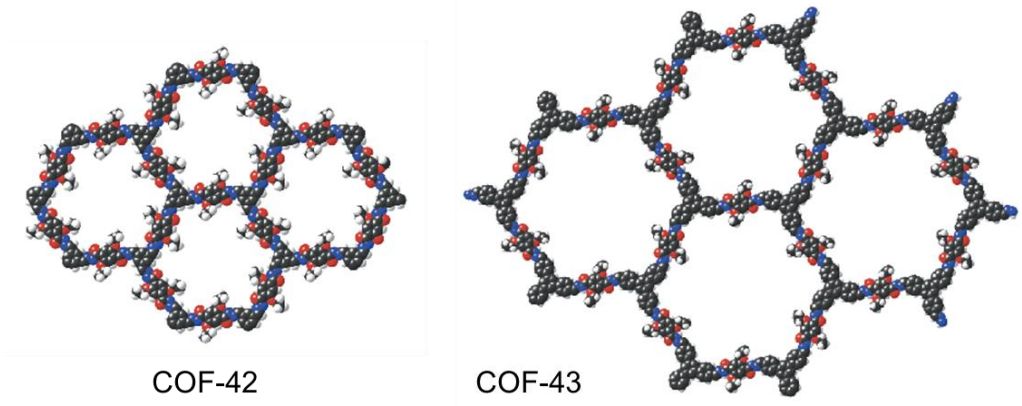

Figure 4. Space-filling models of COF-42 and COF-43 in **bnn** topology. Atom colors: C, black; H, white; O, red; N, blue.

PXRD measurements were performed on samples of COF-42 and COF-43 to determine their crystallinity. The experimental PXRD patterns of both COFs were indexed based on a primitive

hexagonal lattice. Next, the raw data was compared to models of possible crystal structures that can be obtained from linking the trigonal and the linear building blocks. It is anticipated that 2-dimensional trigonal layers will be formed given that the hydrazone moiety is approximately coplanar with respect to the aromatic rings due to resonance effects and internal hydrogen bonding. These layers can pack in eclipsed **bnn** (*P*6/*mmm*), or staggered modes, **gra** (*P*6$_3$/*mmc*). However, at this resolution, the framework topologies, for both COFs, as either **bnn** or **gra** could not be assigned.

N_2 and H_2 uptake by COF-42 and 43: Gas adsorption isotherms were measured on fully activated samples in order to ensure the architectural stability and porosity of each COF. The Ar isotherm of COF-42 measured at 87 K showed a sharp uptake below P/P_0 = 0.05 with a step at P/P_0 = 0.05-0.20. This profile is best described as a Type IV isotherm, which is characteristic of mesoporous materials. The BET surface area of COF-42 was calculated to be 710 m^2/g. The 87 K Ar adsorption isotherm of COF-43 also possesses a type IV shape indicating that it is a mesoporous material. The BET surface area of COF-43 was calculated to be 620 m^2/g. Notably, the surface area and pore volume values obtained for COF-42 and COF-43 are comparable to those of other 2D COFs with hexagonal pore systems [4]. A non-local density functional theory (NLDFT) model was fitted to the isotherms of COF-42 and COF-43 yielding average pore sizes of 23 and 38 Å, respectively. These values are in good agreement with the expected pore size observed in the crystal simulations based on a **bnn** topology. More importantly, this is large enough to accommodate metal ions (and possibly their counter anions) in the pore.

The H_2 isotherms for these COFs are illustrated in Figure 5A. The H_2 uptake for COF-42 and 43 at 1 bar and 77 K is 0.60 and 0.51 wt%, respectively. Although COF-42 has a smaller BET surface area, the H_2 uptake for COF-42 under the present experimental conditions was larger than that of COF-43. We attribute these results to the smaller pore diameter of COF-42. Furthermore, this theory is supported by the isosteric heats of adsorption (Q_{st}) data for these COFs (Figure 5B). The initial Q_{st} values for both COFs are almost the same (6.6 kJ/mol), because of the similarity in the surface environment of COFs. Once a majority of strong binding sites are occupied by H_2, the adsorption potential in the pore should be more important (i.e. larger pore material has smaller adsorption potential). Consequently, it is likely that the values for COF-43 quickly dropped with an increase in the H_2 loading.

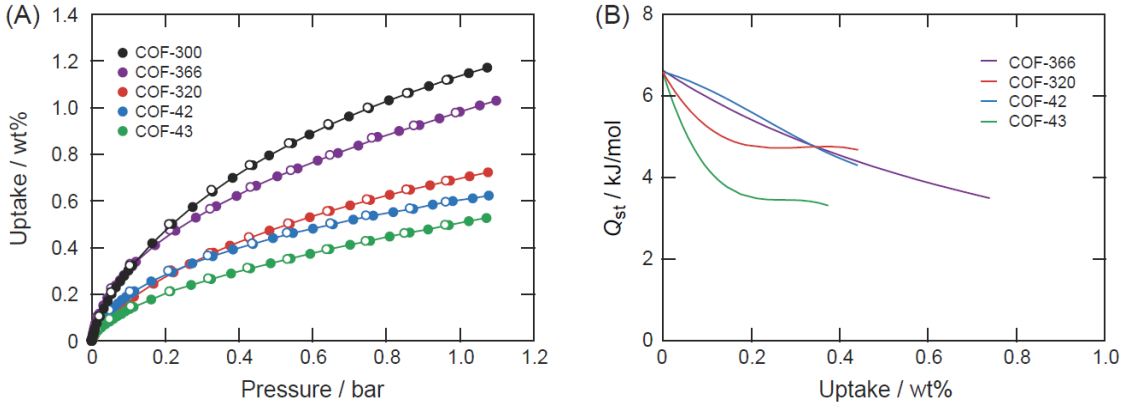

Figure 5. (A) Low-pressure excess H_2 uptake at 77 K. (B) Coverage dependencies of the Q_{st} for H_2 in COFs.

Synthesis of porphyrin containing COFs: In the pursuit for the preparation of a material in which different metals can be inserted, we are exploring the synthesis of COFs containing porphyrin rings. Porphyrin is a well-defined molecule and much effort has been devoted to study the nature of metal substituted porphyrins. Therefore, we implemented the imine condensation of tetra(4-aminophenyl)porphyrin (**5**) with terephthaldehyde (**6**) to obtain a new porphyrin COF (termed COF-366, Figure 6) whose condensation manor is the same as COF-300 [10]. COF-366 was prepared by the following procedure: tetra(4-aminophenyl) porphyrin and terephthalaldehyde in a solvent mixture of ethanol/mesitylene/acetic acid were placed in a Pyrex tube. The tube was sealed at 77 K and under vacuum, and heated at 120 °C for 3 days. The obtained purple powder was washed with absolute ethanol and immersed in anhydrous THF for 24 h. The solvent was removed under vacuum at room temperature, resulting in a porous material (yield: 79% based on the porphyrin).

The PXRD pattern of COF-366 demonstrates its crystalline nature (Figure 6A). A strong diffraction peak appears at a low angle, characteristic of the expected large unit-cell parameters, 2θ = 3.5°, along with some other peaks with lower diffraction intensities. To elucidate the atomistic connectivity, we constructed crystal models using *Materials Studio* software package. When the PXRD for the model was calculated and compared with the experimental ones, excellent agreement with the fully eclipsed model was observed. A full profile pattern matching Pawley refinement was subsequently carried out to determine the unit cell parameters for COF-366, giving good agreement factors. Therefore, it is highly likely that the materials as being composed of square layers, stacking along the 001 direction with interlayer distances between the centroids of the stacked porphyrin units of 5.64 Å. Hollow channels are produced, running along the c axis, with a diameter of 20.2 Å.

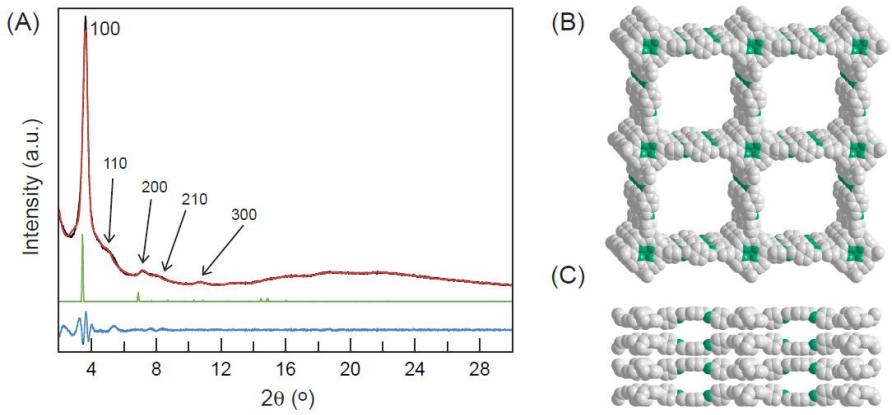

Figure 6. (A) PXRD study of COF-366 with the observed pattern in black, the refined profile in red, and the difference plot in blue (observed minus refined profiles). The calculated PXRD pattern from the proposed models is shown in green. Structural representation of COFs based on powder diffraction and modeling projected along the *c*-axis (B) and the *b*-axis (C). C, N, B, and O are represented in turn as gray, green, yellow and red spheres. H atoms are omitted.

This solvent exchanged sample was activated on a supercritical CO_2 dryer to obtain porous crystalline solids. To investigate the details of the pore characteristics, an Ar isotherm

measurement was performed at 87 K. The Ar isotherm shows significant uptake in the low-pressure region (P/P0 < 0.1), which is indicative of the porous character. The BET surface area and pore volume for COF-366 was calculated to be 735 m^2/g and 0.32 cm^3/g. The porous structures of COF-366 were further corroborated by fitting NLDFT models to isotherms to determine pore size distribution that is centered (17.6 Å) close to pore diameter obtained from the crystal structure (20.2 Å). Low-pressure H_2 uptake capacity for COF-366 was also evaluated (Figure 5A). The H_2 uptake at 1 bar and 77 K is 1.0 wt%. Based on the 77 and 87 K isotherms, the Q_{st} was estimated (Figure 5B). The calculated Q_{st} at the zero coverage (6.6 kJ/mol) is better than other COFs (COF-1, 5, 10, 102, 103) except COF-6 (7.0 kJ/mol).

Pore structure from low resolution PXRD data: One of the difficulties in the COF projects is precise structure determination. Since COFs are synthesized by a condensation reaction of organic materials, it is possible to predict the connectivity of these building units. However unlike MOFs, COFs are comprised of light elements; therefore, obtained PXRD patterns may not provide enough diffraction lines and resolutions to resolve the structure. Indeed, there was this problem when we prepared COF-300 [10]. Recently, an *ab initio* charge-flipping method was developed [11, 12]. In this method, the unit cell parameters are required (i.e. *hkl* indices with intensity) while no information related to the connectivity and space group is necessary. Since it can be possible to determine the atomistic connectivity based on the PXRD data, we applied this technique to solve the COF structure.

Originally, structural determination of as-synthesized COF-300 was implemented, because the degree of interpenetration is not clear. However, due to the disordered solvent molecules, meaningful result could not be obtained so that activated COF-300 was used. Figure 7 demonstrates the PXRD pattern of COF-300. Using obtained *hkl* information (including intensity of each diffraction), an electron density map was generated on *Superflip* [12]. Figure 7 (inset) demonstrates the electron density map for COF-300 along the *c*-axis. As expected, a square channel was observed and the dimension of the pore is almost identical to the space filling model of COF-300.

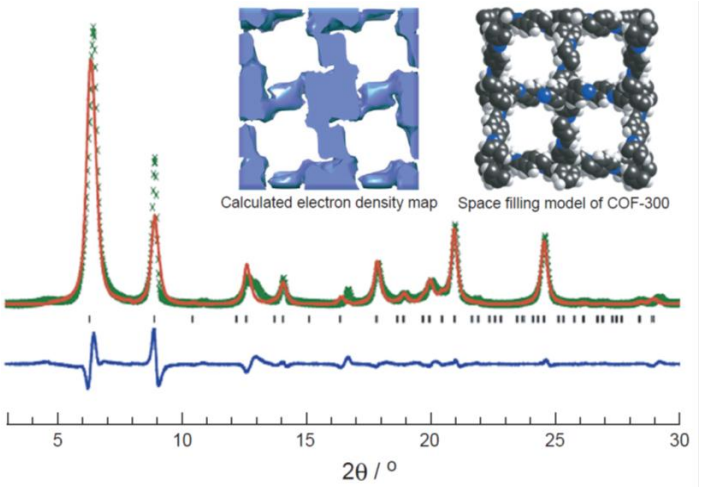

Figure 7. Powder X-ray diffraction pattern of COF-300 (red), refined profile (green), and the deviation (blue). (Inset) Calculated electron density map (left) and space filling model (right) of COF-300.

3. Preparation of imine COF and its metalation reaction.

Synthesis of COF-301 for metalation: It is demonstrated that the condensation of the tetrahedral building block tetra-(4-anilyl)methane (**7**) with the linear linking unit terephthaldehyde (**6**) produces a material with an extended 3-D framework structure (COF-300) [10]. COF-300 is an interpenetrated diamond net and has a 1D channel with a diameter of 7.8 Å. However, due to the lack of potential metal binding sites, it is not easy to metalate this material. To create metal binding sites in the COF frameworks, we believe salicylidene-aminophenyl and iminopyridine moieties are good candidates. Therefore, a new imine COF (terms COF-301) was synthesized.

The synthesis of COF-301 was carried out by solvothermolysis of a suspension of **7** and 2,5-dihydroxyterephthalaldehyde (**8**) in a mixture of 1,4-dioxane and aqueous acetic acid (Figure 8). The material is insoluble in water and common organic solvents such as hexanes, methanol, acetone, tetrahydrofuran (THF), and *N*,*N*-dimethylformamide (DMF). Therefore, it seems the resultant crystalline material is an extended structure. The formation of imine linkages in COF-301 was confirmed by FT-IR spectra. The crystallinity of COF-301 was confirmed by powder X-ray diffraction analysis. Although its atomistic connectivity is not determined yet, it is presumed that the connectivity (topology) of COF-301 is a diamond net due to the similarity of PXRD pattern. However, no information is available with regard to the degree of interpenetration.

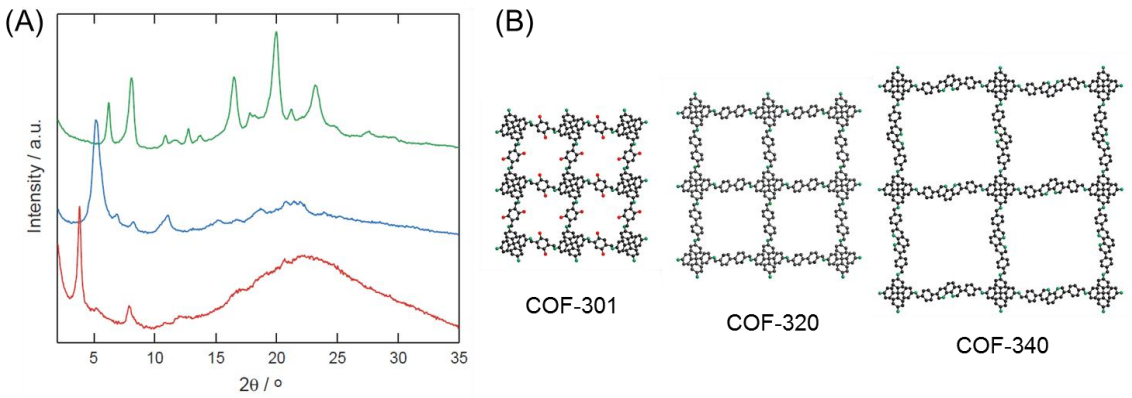

Figure 7. (A) PXRD patterns for COF-301 (green), COF-320 (blue), and COF-340 (red). (B) Modeled structure of COF-301, 320, and 340 based on the PXRD pattern.

The permanent porosity of COF-301 was demonstrated by measuring the N_2 adsorption at 77 K. The isotherm shows a sharp uptake below $P/P_0 < 0.10$. The application of the BET model results in a surface area of 1040 m^2/g. The N_2 isotherm was fit with NLDFT models from which the pore size distribution was calculated, resulting in a value of 10.5 Å, which is close to the values observed in the proposed structure (ca. 9.5 Å).

Prediction of H_2 uptake capacity by COF-301-$PdCl_2$: Prior to the metalation reaction, the total H_2 isotherms of pristine and COF-301-Pd (using $PdCl_2$ as the source) with different metal loadings were predicted. As shown in Figure 8, metalated material shows steep H_2 uptake below 10 bar even at room temperature, which is in sharp contrast to the pristine COF-301. The excess H_2 uptakes at 100 bar are calculated to be 4.2, 2.3, 2.1 wt% for 100%, 50%, and 25% Pd loading COF-301. These values are much greater than pristine COF-301 (0.4 wt%) under the same

conditions, so it is presumed that the interaction between Pd and H_2 is strong enough to improve the H_2 uptake capacity. Total volumetric uptakes in metalated COF-301 are also high. As shown in Figure 8B, the predicted total uptake reaches 60 g/L at 100 bar and 298 K. These high uptake should be related to the binding energy of H_2; the average Q_{st} values for 100%, 50%, and 25% Pd loading COF-301 are 23.6, 17.8, and 14.0 kJ/mol, respectively, while only 6.0 kJ/mol for pristine COF-301. Although the metalated compound would have a smaller pore volume and a larger bulk density, the simulated isotherms encourage us to implement the metalation. Therefore, metalation of COF-301 with metal salts was implemented, and obtained materials are termed COF-301-M; M = Pd(II) and Pt(II).

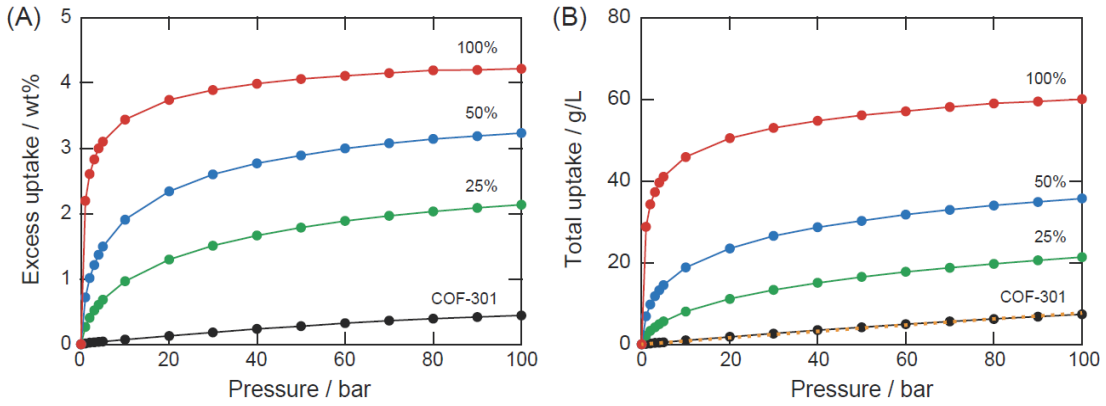

Figure 8. Predicted (A) excess gravimetric and (B) total volumetric H_2 isotherms of pristine COF-301 and COF-301-$PdCl_2$ with different metal loadings (100%, 50%, and 25%). Orange broken line indicates the bulk density of H_2 at 298 K.

The metalation of COF-301: The metalation of COF-301 was carried out by a reflux reaction of a suspension of COF-301 and metal source ($PdCl_2$ or $PtCl_2$) in acetonitrile. The resulting yellow solid was filtered off, washed with ethanol and diethyl ether and then dried under vacuum. After the metalation, the peak position of PXRD for metalated COF-301 is almost identical to that of COF-301. Therefore, it is likely that the crystallinity of these metalated materials is retained, although the intensity of the pattern decreased. However, there is no clear evidence to confirm whether the metal ion was bound to the framework. The metal coordination environment can be revealed by the NMR spectra with ^{15}N enriched material.

Before the H_2 tests, N_2 isotherms of a series of materials were recorded. After the metalation, the BET surface areas of the samples were much smaller than that of the pristine material (60 m^2/g for COF-301-Pd, 20 m^2/g for COF-301-Pt). Although the metalated samples have larger density than original COF-301, this should not be the only reason for the significant surface area drop. Possible explanation of this drop is (i) the presence of leaving groups (perhaps two Cl^-) bound to the metal ion and/or unreacted metal salts (i.e. MCl_2), (ii) pore openings of the metalated samples could be partly blocked, which would reduce the accessible pore space, and/or (iii) crystallinity of the materials was partially lost. To mitigate the surface area drop, optimization of metalation and sample activation procedures can be useful. However, considering

that the pore diameter of metalated COF-301 is very small, expansion of the pore should be more effective.

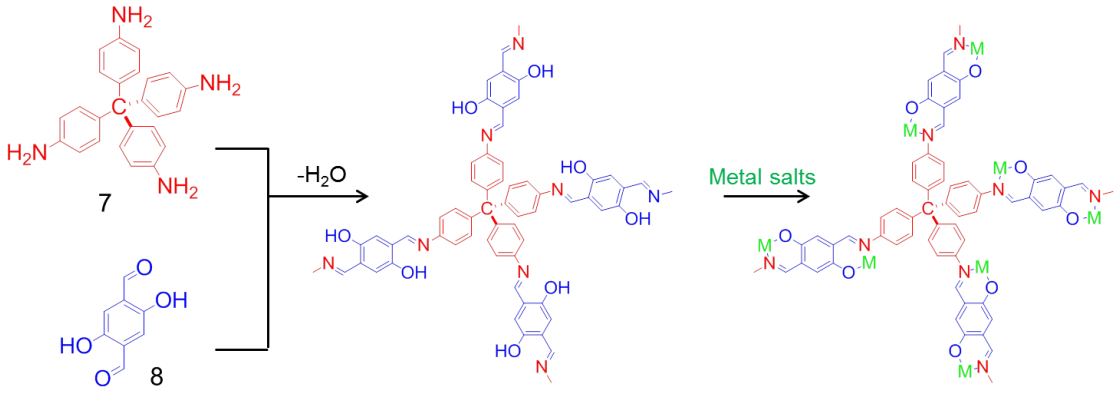

Figure 9. Schematic representation for the synthesis of COF-301 and metalation.

4. Design and preparation of expanded version of COF-300.

Prediction of H_2 uptake in imine COFs. It is reasonable that larger pore COFs are easier to metalate than smaller pore COFs; however, it is necessary to find out the optimal pore diameter. Therefore, expanded versions of imine COFs (COF-320 (**7** + **9**), COF-322 (**7** + **10**), COF-330 (**7** + **11**), COF-333 (**7** + **12**), and COF-340 (**7** + **13**)) were modeled. In the design of the new imine-COFs we only considered the **dia-c5** topology, since a similar structure is observed in COF-300. The geometric surface area and pore volume of these COFs are listed in Table 1. COF-320, 322, 333, and 340 have very similar surface areas, which are greater than 7000 m^2/g, while COF-300 and COF-330 show lower values.

Table 1. Summary of predicted porosity data, H_2 uptake, and adsorption enthalpy for imine-COFs (dia-c5 net) at 298 K and 100 bar. Surface area (S_A), pore volume (V_p), isosteric heat of adsorption (Q_{st}) obtained from GCMC and binding enthalpy of the linker to H_2 (ΔH^0_{bind}) from quantum mechanical (QM) methods.

Material	S_A (m^2/g)	V_p (cm^3/g)	Q_{st} (kJ/mol)	ΔH^0_{bind} (kJ/mol)	Excess H_2 uptake (wt%)	Total H_2 uptake (g/L)
COF-300	3820	1.25	5.8	5.9	0.55	7.9
COF-301	3700	1.08	6.0	5.9	0.44	7.4
COF-320	7850	2.57	4.4	5.0	0.72	8.0
COF-322	7300	2.47	4.4	5.0	0.71	8.0
COF-330	5990	2.12	4.7	5.0	0.75	8.3
COF-333	7710	2.57	4.3	5.0	0.68	7.9
COF-340	7300	4.68	3.6	5.0	0.68	7.6
COF-301-$PdCl_2$	1080	0.42	23	13	4.20	60
COF-322-$PdCl_2$	5550	1.62	8.8	9.8	2.20	17
COF-330-$PdCl_2$	3900	1.40	9.4	9.8	2.20	12
COF-333-$PdCl_2$	2990	1.14	14	12	2.40	16
COF-340-$PdCl_2$	6620	3.32	6.6	9.8	1.77	9.4

Next, high-pressure H_2 isotherms by these imine-COFs were calculated to compare the H_2 uptake by COF-300 (Figure 10). It was found that the uptakes for the other COFs at room temperature are very similar to each other. The maximum excess H_2 uptakes for these COFs in gravimetric units are ranging from 0.68 wt% for COF-333 to 0.75 wt% for COF-330 (Table 1), where these uptakes are greater than that for COF-300. This implies that higher surface area is not enough to store large amount of H_2 at ambient temperature. Indeed, the total volumetric H_2 uptakes in imine-COFs are below 10 g/L, even though these COFs have large pore volume.

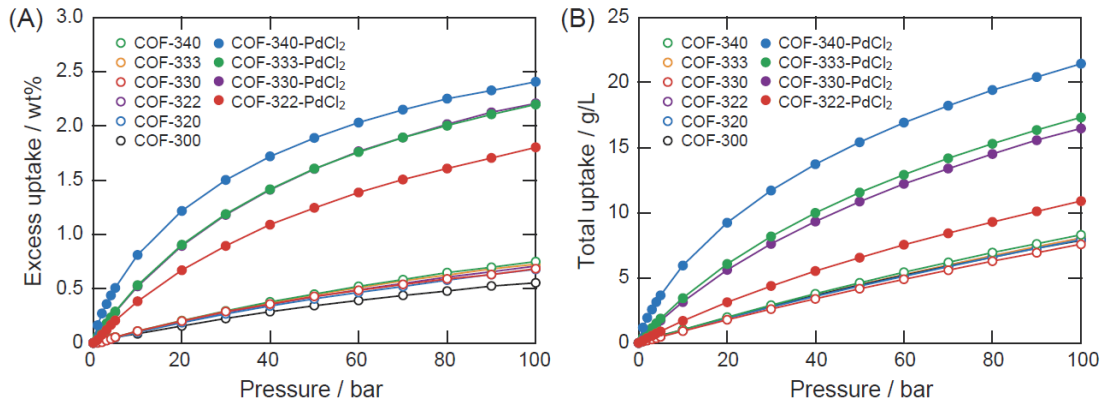

Figure 10. Predicted (A) excess gravimetric and (B) total volumetric H_2 isotherms of pristine imine COFs and their metalated version.

The Q_{st} values for pristine imine-COFs were also estimated. Since all the COFs contain C, H, and N and have an imine bond, it is expected that the interaction between framework and H_2 is also similar. The degree of this interaction should be derived from the Q_{st}. Obtained initial Q_{st} values for all pristine COFs are summarized in Table 1. The values of Q_{st} are ranging from 4.3 and 5.8 kJ mol^{-1}, leading to the fact that these COFs have essentially similar binding energy of H_2. COF-300 showed the highest Q_{st}, but the gravimetric uptake is the lowest among these COFs. The potential energy surface for the pore overlaps and makes the H_2 interacts strongly with framework. Although, it is well known that the small pore provides a limited amount of H_2 uptake.

To evaluate the effects of metalation, imine-COFs (COF-322, 330, 333, and 340) with $PdCl_2$ units are modeled using pristine COFs (i.e. post-metalation of the framework). Similar to the case of COF-301, no obvious structural change was observed after the structure minimization of metalated COFs with $PdCl_2$. The porosity data of metalated materials are also shown in Table 1. Although the calculated surface areas of these materials are smaller than original COFs, these values are still larger than 3000 m^2/g.

H_2 uptake capacity is drastically enhanced by the metalation (Figure 10). Metalated version of COF-322, 330 and COF-333 take up 3.1, 2.9, and 3.5 times larger amount of H_2 compared to their original COFs at 100 bar and 298 K, respectively, which demonstrates the importance of the metalation. The estimated excess (total) gravimetric H_2 uptakes are estimated to be 2.2 (3.2), 2.2 (3.1), and 2.4 (3.2) wt% in metaltated COF-322, 330 and COF-333, respectively. In the case of COF-340, the effect of metalation is smaller than others. This is perhaps due to the low metal density per volume. With that being said, predicted excess H_2 uptake reaches 1.77 wt% at 100 bar and 298 K.

The total volumetric uptake for these compounds was also estimated (Table 1). It should be noted that both frameworks show much greater H_2 uptake; COF-330 has 1.6 times higher uptake at 100 bar than bulk density of H_2 (7.6 g L^{-1}), while COF-322 has 2.2 times higher uptake. This clearly proves the advantage of metalation of the frameworks, although these values should still be improved more.

The initial Q_{st} values for these compounds were also calculated. The Q_{st} for metalated COF-333 (19 kJ mol^{-1} and 12.4 kJ mol^{-1} in average between 1-100 bar) is higher than other expanded imine-COFs shown in this report, while this value is similar to metalated COF-301. Unlike other expanded imine-COFs, COF-333 has two metal binding sites per edge of the diamond net, leading to the fact that the average pore diameter should be smaller than COF-322, 330, and 340. Since these materials have the same metal sites, the high Q_{st} value can be related to the average pore diameter (i.e. more overlap of attractive potential) rather than high metal density in the framework.

Preparation of expanded version of imine-COFs. To expand the COF framework, followed by metalation experiments, it is intuitively found that linker **12** is a good candidate. However, in view of organic synthesis, it is not easy to add aldehyde groups to the 3 and 8 positions. It could be possible to synthesize linker **10** according to a literature procedure, but our final decision was to synthesize linker **11** due to the greater density of potential metal binding sites compared to **10**. In addition, the preparation of an expanded version of phenanthroline linker (**13**) was synthesized.

The synthesis of COFs was carried out by solvothermal synthesis of a suspension of linker **7** and ditopic linker (**9**, **11**, or **13**) in a mixture of organic solvents. For a comparison of the porosity, a new COF (COF-320) using linker **9** was also synthesized. Synthetic conditions of these COFs were similar to COF-300 [10], but these conditions are not optimized yet. Typically, a mixture of 1,4-dioxane and aqueous acetic acid with starting materials were heated at 120 °C. All resulting materials are insoluble in water and common organic solvents such as: hexanes, methanol, acetone, tetrahydrofuran, and DMF. Therefore, the resultants are an extended structure.

The crystallinity of COF-320 and 340 was confirmed by PXRD analysis (Figure 7A). Although its atomistic connectivity (including the degree of interpenetration) is not yet determined due to the limited numbers of diffraction lines, it is important to note that the position of the first peak is located at lower angle when extended linkers were employed. This clearly demonstrates the successful pore expansion. Assuming that the connectivity (topology) of these COFs is in a diamond net, it is possible to build modeled structures (Figure 7B). The simulated PXRD patterns are similar to those of experimental data, so that the full refinement of these COF will be performed in the future. With regard to COF-333, the solid material did not diffract well, although there are a few weak diffraction lines observed. Further modification of the synthetic condition is necessary to obtain crystalline solids.

The permanent porosity of COF-320 was demonstrated by measuring N_2 adsorption at 77 K. The application of the BET model results in a surface area of 1620 m^2/g, which is higher than COF-300 and 301. However, low-pressure H_2 uptake at 77 K by COF-320 was not exceptional (Figure 5A). The uptake at 1 bar and 77 K was 0.6 wt%, which is even smaller than COF-300 (1.1 wt%). It is likely that the activation conditions of COF-320 are not fully optimized yet. In the case of COF-340, N_2 isotherms using activated samples were also recorded. Unexpectedly N_2 uptake was very low (BET surface area = 35 m^2/g), although the PXRD pattern indicates that the crystallinity still remains after the sample activation. Since the pore diameter of COF-340 is even

greater than COF-320, this may be due to the presence of oligomers (i.e. fragments of COFs) in the pore. Another possibility can be the degree of catenation is very high, although it is unlikely this is the primary reason of low surface area.

The role of interpenetration. Linker **13** is the longest among the ditopic linkers used this work. Therefore, the degree of catenation can be much larger than COF-300 (**dia-c5**). Here different models for COF-340 based on the diamond topology with different degrees of catenation (terms COF-340-c11, c9, c7, c5, and c3 for 11, 9, 7, 5, and 3-fold catenation, respectively) were prepared and their H_2 uptake capacity was studied. Each structure (pristine and metalated version) was minimized with the same symmetry followed by GCMC on the minimized structure. The surface area, pore volume, and predicted H_2 uptakes in COF-340s are demonstrated in Figure 11 and Table 2.

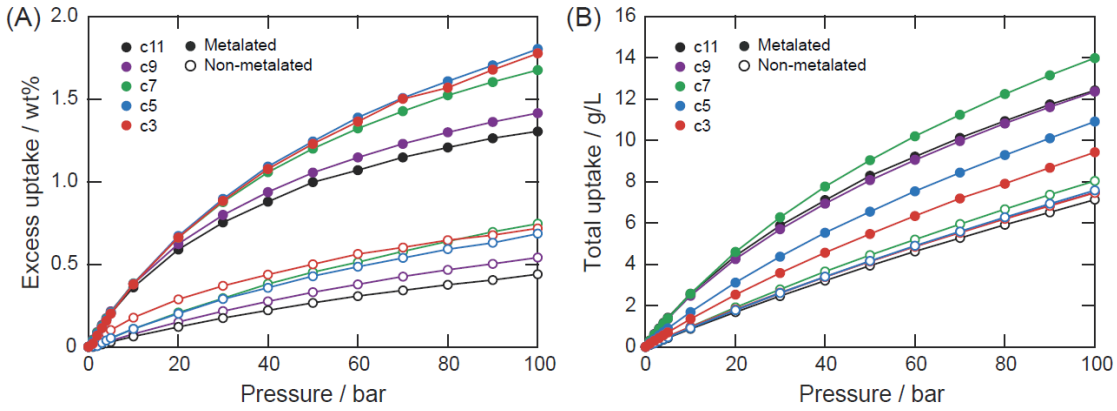

Figure 11. Predicted (A) excess gravimetric and (B) total volumetric H_2 isotherms of pristine COF-340 and COF-340-$PdCl_2$ with different degree of catenation (c3, c5, c7, c9, and c11).

Table 2. Summary of predicted porosity data, H_2 uptake, and adsorption enthalpy for COF-340 with different catenation degree at 298 K and 100 bar. Surface area (S_A), pore volume (V_p), isosteric heat of adsorption (Q_{st}) obtained from GCMC and binding enthalpy of the linker to H_2 (ΔH^0_{bind}) from QM methods.

Material	S_A (m^2/g)	V_p (cm^3/g)	Q_{st} (kJ/mol)	ΔH^0_{bind} (kJ/mol)	Excess H_2 uptake (wt%)	Total H_2 uptake (g/L)
COF-340-c11	3200	1.84	4.5	5.0	0.44	7.1
COF-340-c9	3630	2.16	4.5	5.0	0.54	7.5
COF-340-c7	6260	2.71	4.4	5.0	0.75	8.0
COF-340-c5	7300	4.68	3.6	5.0	0.68	7.6
COF-340-c3	8070	7.45	3.6	5.0	0.72	7.5
COF-340-$PdCl_2$-c11	2480	1.32	9.8	9.8	1.30	12.4
COF-340-$PdCl_2$-c9	2780	1.55	9.5	9.8	1.41	12.3
COF-340-$PdCl_2$-c7	3390	1.42	8.6	9.8	1.67	14.0
COF-340-$PdCl_2$-c5	6620	3.32	6.6	9.8	1.80	10.9
COF-340-$PdCl_2$-c3	6630	5.72	5.5	9.8	1.77	9.4

There is a rough trend that excess gravimetric uptakes in pristine COF-340 drop with an increase in the degree of catenation due to the decrement of the porosity. The exception is COF-340-c7, which reaches the highest uptake at 100 bar and 298 K. For the metalated systems with $PdCl_2$, although COF-340-$PdCl_2$-c5 showed the highest excess uptake (1.8 wt%), there is a similar trend; COF-340-$PdCl_2$-c11 has the lowest uptake (1.3 wt%) at 100 bar followed by c9, c7, and c3. In contrast to this, the total volumetric uptake does not show a simple tendency with the degree of interpenetration. However, considering that the c7 structure gives the best uptake for the pristine and $PdCl_2$ metalated COF-340 (8.0 and 14.0 g/L at 100 bar and 298 K, respectively), it seems that there is a magic catenation number to maximize the total volumetric uptake.

On the other hand, the heat of adsorption correlates positively with the degree of catenation, i.e. more catenation leads to higher Q_{st}. Although a series of COF-340 materials has a similar 1D channel along the *c*-axis, the distance between neighboring nets are different. Therefore, higher degree of catenation should be preferable to utilize larger effective energy of adsorption.

5. H_2 uptake in metalated triazine-COF

As demonstrated in the previous section, predicted volumetric H_2 uptake capacity in metalated COF-340 is not exceptional, although it is possible to find out the optimal catenation number. One of the reasons for this is the longer organic linker **13**. The key to increase the volumetric H_2 uptake is high density of metal binding sites. In this section, a new metalated COF having 2,4,6-tri(pyrimidin-2-yl)-1,3,5-triazine moieties (**TPT**, Figure 12A), which are inspired in the **BPY** and **BPYAM**, are modeled. The central triazine unit should be formed by a self-condensation reaction of linker **14**, where the connectivity is similar to COF-102 [7]. The modeled frameworks (terms COF-102-Tri) were minimized with molecular dynamics without symmetry constrains (Figure 12B).

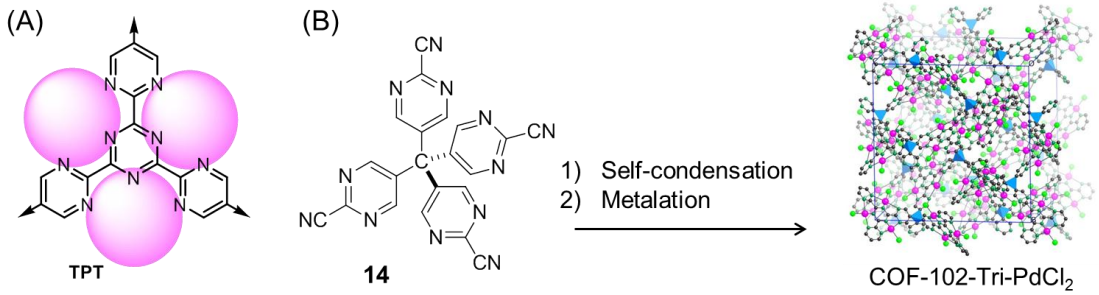

Figure 12. (A) Structure of **TPT** organic unit. (B) Schematic representation of metalated COF-102-Tri formation reaction.

The H_2 uptake by COF-102-Tri was calculated for 1 to 100 bar at 298 K (Figure 13). The excess gravimetric uptake in COF-102-Tri (0.43 wt%) is almost the same as other COFs demonstrated here, which is equivalent to the excess volumetric uptake of 7.4 g/L. As expected, metalation shows drastic improvement of the H_2 uptake capacity. Total volumetric uptake of COF-102-Tri-$PdCl_2$ is estimated to be 48 g/L (4.3 wt% of total gravimetric uptake). This enhancement should be due to the strong interaction of the framework with H_2 and the small pore (6-8 Å) that can minimize dead space. This is close to the postulate range of the ideal pore size for H_2 storage [1]. Thus this COF is still able to approach the DOE volumetric target of 40 g/L.

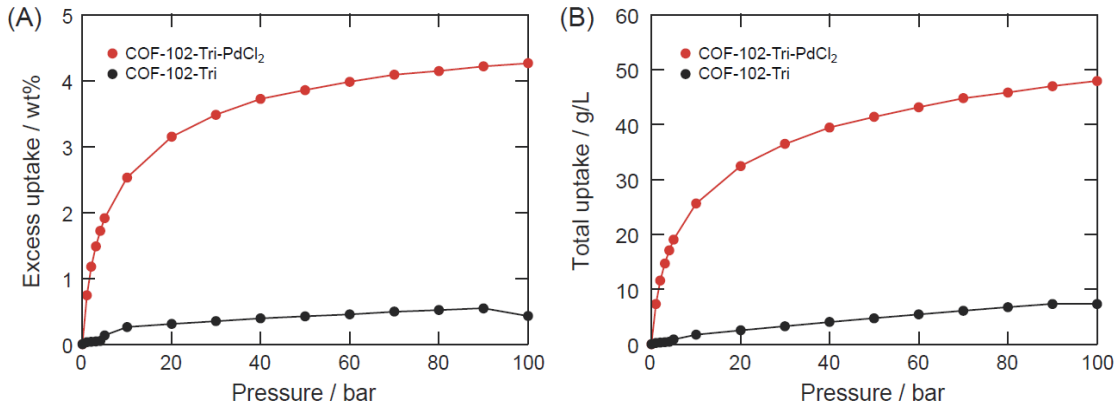

Figure 13. Predicted (A) excess gravimetric and (B) total volumetric H_2 isotherms of pristine COF-102-Tri and COF-102-Tri-$PdCl_2$.

Concluding Remarks

The aim of this project is to develop the next generation of COFs. Although it is believed that the H_2 adsorption behavior of porous solids would be improved by the addition of strong binding sites, it is not clear how the metalation of COFs enhances the interaction with H_2, how many H2 molecules can be adsorbed on a single metal site, and which metal should be used. To address these fundamental questions, simple QM calculations were performed. The calculation of ΔH^0_{bind} indicates that first row TMs (Sc to Cu) gives similar and sometimes superior van der Waals interactions with (up to 4th) H_2 than precious TMs (Pd and Pt). More importantly, it is revealed that ΔH^0_{bind} for the linker is a first approximation of the Q_{st} of the periodic structure. The finding indicates that it is possible to predict promising structures by introducing the H_2 binding sites into known framework structures. For the synthetic part, much effort was devoted to design and synthesize new COFs with chemically stable chemical bonds, such as hydrazine and imine COFs. By employing various organic linkers with different lengths, it is demonstrated that pore expansion of COFs is a good way to tune average the pore diameter and porosity. In conjunction with theoretical prediction, metalation experiments were also implemented. Due to the significant surface area drop of metalated materials, it is difficult to conclude if metalation enhances the binding energy, leading to the higher volumetric H_2 uptake. Some challenges still remain in meeting the DOE *system* targets (5.5 wt% and 40 g/L) for H_2 adsorption; however, it is believed that the concept of the isoreticular metalation of porous COFs is one of the best strategies to pursue practical storage targets.

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