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# HyMARC Seedling: Fluorinated Covalent Organic Frameworks: A Novel Pathway to Enhance Hydrogen Sorption and Control Isothermic Heats of Adsorption

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Project Start Date: October 1, 2017  
Project End Date: November 30, 2019

## Overall Objectives

- Synthesize and characterize a series of partially fluorinated covalent organic frameworks (COFs) that are intended to exhibit improved long-range ordering and assist in tuning hydrogen binding enthalpy.
- Substitute metal-chelating moieties in the framework structure to enhance hydrogen binding enthalpy and demonstrate a pathway to values between 10 and 15 kJ/mol.
- Tune adsorption isotherms using a target mixture of binding sites, assisted by theoretical predictions.
- Produce a COF with at least 4 wt% of excess hydrogen capacity and 40 g/L total volumetric capacity. Isothermic heat of adsorption will be >10 kJ/mol for a non-metallated COF or >12 kJ/mol for a metallated COF.

## Fiscal Year (FY) 2018 Objectives

- Produce 100 mg of pure COF-0, COF-OH, COF-F50, and COF-F100.

- Synthesize 100 mg of COF series (1 and 2) with linker sites for metal chelation.
- Determine relative degrees of enhanced long-range ordering between H-bonding and fluorination strategies.
- Metallate COFs and determine influence of fluorine on enhanced binding of hydrogen at metal sites.
- Determine influence of strategic fluorination on hydrogen adsorption enthalpy through solvent and modified linker adaptations.

## Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan<sup>1</sup>:

- (A) Durability/Operability
- (D) Charging/Discharging Rates
- (O) Lack of Understanding of Hydrogen Physisorption and Chemisorption.

## Technical Targets

Technical targets are shown in Table 1.

The operating ambient temperature target is recast in terms of isothermic heats of adsorption for hydrogen for this project as >12 kJ/mol.

## FY 2018 Accomplishments

- Discovered that partial fluorination of COF structures can increase crystallinity and improve Brunauer-Emmet-Teller (BET) surface areas by nearly a factor of two compared with the non-fluorinated COFs.
- Measured an enhanced hydrogen gravimetric capacity for the partially fluorinated COF (~2.8 wt%) vs. the nonfluorinated COF (~1.9 wt%).

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<sup>1</sup> <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Measured an enhanced hydrogen isosteric heat of adsorption for the fluorinated COF (~7 kJ/mol at low coverage) compared with the partially fluorinated COF (~6 kJ/mol at low coverage).
- Performed metalation of COF structures and discovered high binding enthalpy sites for hydrogen that can be tuned through strategic fluorination (quantitative estimates are forthcoming).
- Performed COF densification and achieved pelleted COFs with densities of 0.5–0.8 g/cm<sup>3</sup>.

**Table 1. Progress Toward Meeting Technical Targets for Materials-Based Automotive Hydrogen Storage Systems**

Characteristic	Units	DOE 2025 Storage System Targets	Project Status (unoptimized) – Material Performance
Excess gravimetric capacity	wt% H <sub>2</sub>	≥5.5	2.8
Total volumetric	g/L H <sub>2</sub>	40	~20

## INTRODUCTION

Organic framework materials, as a unique subclass of carbon-based sorbents, have gained increasing attention for promising attributes toward gas storage. Calculations of the hydrogen capacity of optimized frameworks show potential to achieve greater than 60 g/L storage of hydrogen, placing metal-organic frameworks and COFs near the top of the class of porous materials. However, at the ensemble level, poor stacking creates a quasi-amorphous material with low structural integrity and low effective surface area. The chemical versatility of COFs allows for additional methods for producing long-range order that specifically target the inter-layer interactions in COFs but leave key pore-accessible linker sites open. These modifications (either during synthesis or post-synthetic) enable a host of strategies to improve crystalline order for better stability and higher surface area as well as to add metals with open coordination sites for enhanced hydrogen binding enthalpy.

## APPROACH

Synthesis of the COF structures was performed using a condensation reaction involving aldehyde and amine precursors (Figure 1). The different COFs 1–4 were functionalized through substitution of the precursors. Reaction conditions were optimized to produce a high yield and the highest crystalline material possible as a powder. Metals were introduced into the COF structures post-synthetically using metal salts and thermal treatments. Subsequent characterization included X-ray diffraction studies for crystallinity determination, BET surface area analysis, transmission electron microscopy, and thermogravimetric analysis for COF thermal stability. Hydrogen sorption studies involved diffuse-reflectance infrared spectroscopy, temperature-programmed desorption, and pressure-composition-temperature (PCT) analysis. The PCT technique provided gravimetric capacities and isosteric heats of adsorption, which are compared for different COF structures and metalation techniques. Computational modeling was also employed to predict and understand the locations of high binding enthalpy sites for hydrogen.

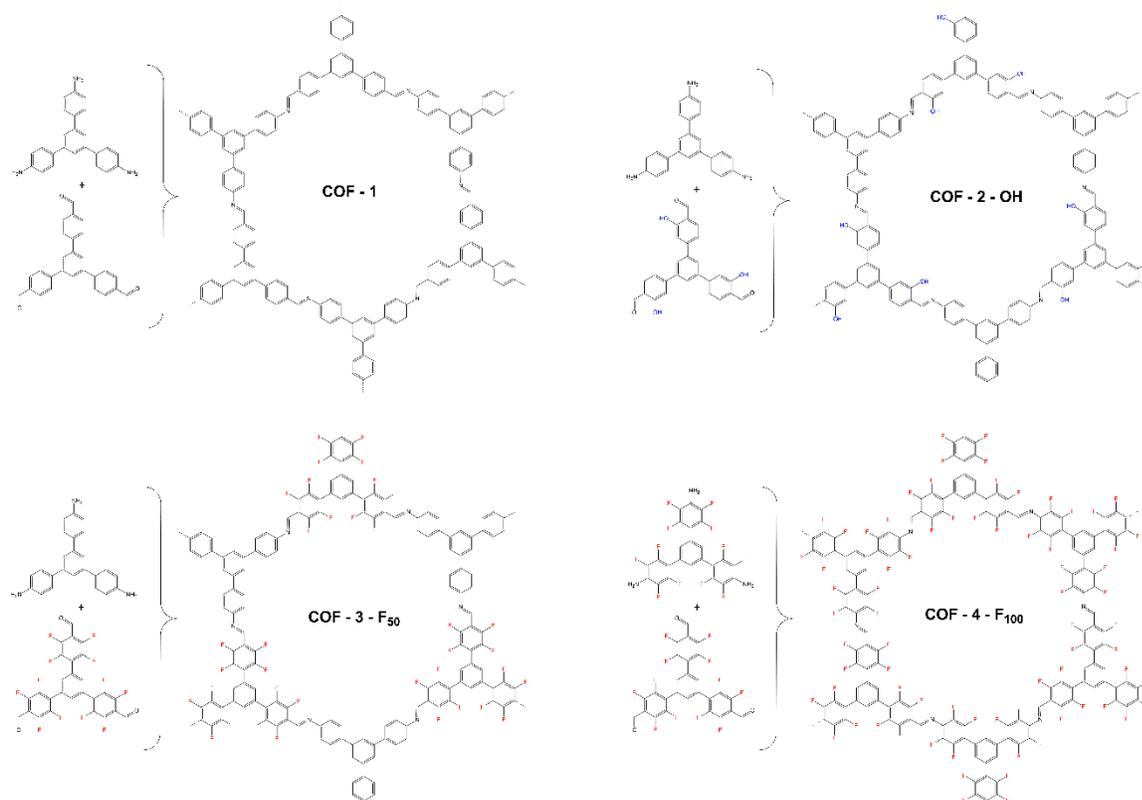
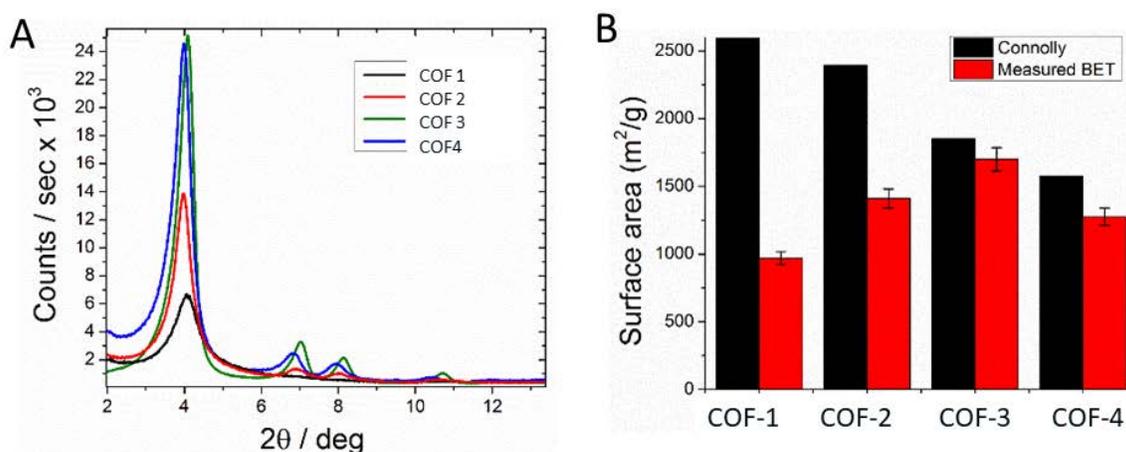


Figure 1. Structures of synthesized non-metallated COFs and the condensation reaction precursors

## RESULTS

The first series of COFs synthesized to test the notion of fluorination on crystallinity and surface area is shown in Figure 1. COF-1 contains standard functionalization, COF-2 contains hydroxyl functionalization, COF-3 has roughly 50% fluorination, and COF-4 is 100% fluorinated. The respective powder X-ray diffraction patterns and BET surface areas can be found in Figure 2. The partially fluorinated COF-3 was clearly superior in terms of crystallinity and in terms of BET surface area, which reached about 95% of the predicted (Connolly) surface area. An alternating stacking motif was shown by calculations to be the most likely COF crystallization configuration; this takes advantage of perfluorophenyl and phenyl interactions that other COFs do not possess.



**Figure 2. Powder X-ray diffraction (A) and BET surface area measurements (B) for the series of non-metallated COFs**

Hydrogen sorption measurements were undertaken for all COFs, but in particular a comprehensive comparison was made between COF-1 and COF-3. The PCT sorption curves are shown in Figure 3, which reveal stronger hydrogen sorption for COF-3 than for COF-1 at 77 K. The capacity was collected at several temperatures to determine the isosteric heat of adsorption. The overall values were determined to be about 5.5 kJ/mol and about 5.0 kJ/mol for COF-3 and COF-1 respectively. However, at low coverages, the value turned up significantly for COF-3 toward 7 kJ/mol. The binding enthalpy for some preferred hydrogen sorption sites may be causing this upturn, and diffuse-reflectance infrared measurements are now being performed to confirm the result. Calculations predict a value of about 10 kJ/mol for hydrogen binding enthalpy for preferred sites in COF-3.

Metallation of COF-2 and two other related series of partially fluorinated COFs (COF-9 and COF-10) was undertaken (Figure 4). Copper salts were intercalated into the structures, and bound copper was identified using various X-ray spectroscopies as well as electron dispersive spectroscopy. Temperature-programmed desorption experiments have revealed larger binding enthalpies in the range of 9–12 kJ/mol, as well as a very strong binding site in thermally treated copper COFs, which likely have been reduced to Cu(I). Fluorination appears to affect the binding enthalpy of hydrogen in a logical fashion. Completing measurements on this series of COFs and determining an isosteric heat of adsorption is a near-term goal.

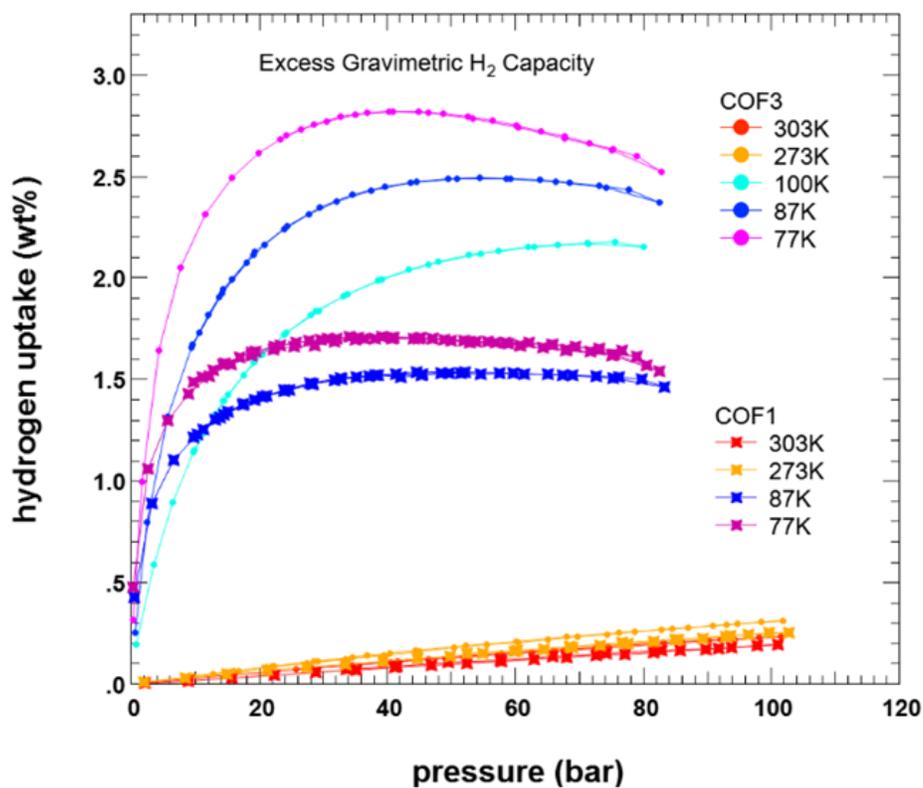


Figure 3. Hydrogen uptake vs. pressure curves measured with PCT for COF-1 and COF-3 at various temperatures

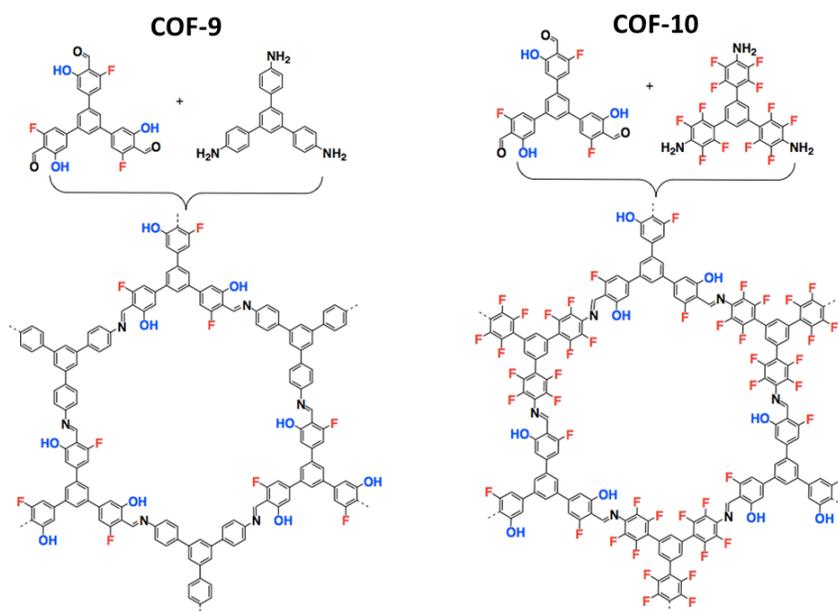


Figure 4. Structures of partially fluorinated COFs with metal binding sites between the nitrogen from the imide group and the oxygen of the hydroxyl group

## CONCLUSIONS AND UPCOMING ACTIVITIES

We conclude that partially fluorinated COFs have better thermal stability, crystallinity, and gas sorption properties compared with nonfluorinated COFs. COFs with sites for binding of metal species show larger hydrogen binding enthalpies compared with non-metallated COFs, and we can tune the binding energy using fluorination. With the remaining funding for about one month of work, we will finalize the isosteric heat values using PCT for metallated COFs with differing degrees of fluorination. We will also optimize gravimetric and volumetric capacities using crystallization techniques and powder densification.

## FY 2018 PUBLICATIONS/PRESENTATIONS

1. Wade A. Braunecker, Katherine E. Hurst, Zbyslaw R. Owczarczyk, Keith Ray, Madison Martinez, Noemi Leick, Amy Keuhlen, Alan Sellinger, Justin C. Johnson, “Phenyl/Perfluorophenyl Stacking Interactions Enhance Structural Order in Two-Dimensional Covalent Organic Frameworks,” *Crystal Growth and Design* 18 (2018): 4160.
2. HyMARC Kickoff Meeting, Livermore, CA, September 29, 2017.
3. Fall ACS Meeting, Boston, MA, August 20, 2018.