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Fluorinated Covalent Organic Frameworks: A Novel Pathway to Enhance Hydrogen Sorption and Control Isosteric Heats of Adsorption

P.I. : Justin Johnson
National Renewable Energy Laboratory
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DOE Hydrogen and Fuel Cells Program
2018 Annual Merit Review and Peer Evaluation Meeting

Project ID # ST142

Overview

Timeline and Budget

- Project start date: 10/01/17
- Project end date: 11/30/18
- Total project budget: $277.8K
  - Total recipient share: $27.8K
  - Total federal share: $250K
  - Total DOE funds spent*: $116K

* As of 3/31/18

Barriers

- **A. System Weight and Volume**
- **D. Durability/Operability**
- **O. Lack of Understanding of Hydrogen Physisorption and Chemisorption**

Partners

- Funded: Colorado School of Mines
- Collaborations: Lawrence Livermore Laboratory (HyMARC), Lawrence Berkeley Laboratory (HySCORE), Stanford Linear Accelerator

Relevance

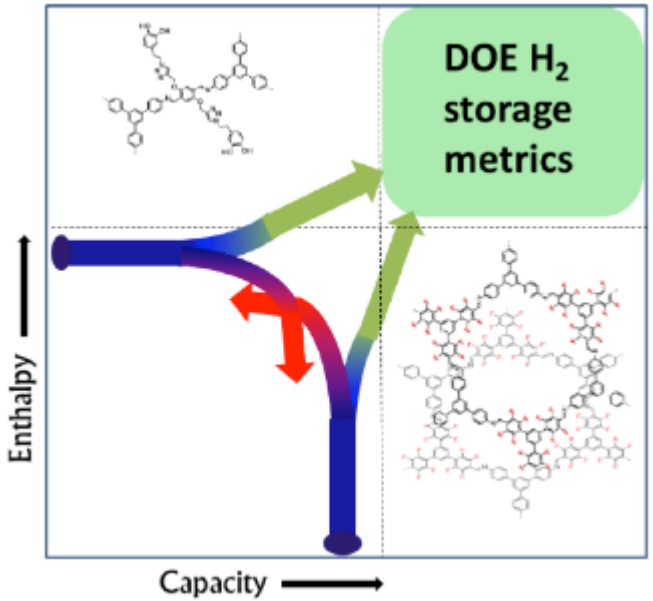
Objectives

- To facilitate ambient storage of a large amount of hydrogen in a lightweight material, we will develop a series of partially fluorinated covalent organic frameworks (COFs) that can show high surface area and tunable H_2 binding enthalpy;
- To substitute metal-chelating moieties in the framework structure to enhance H_2 binding enthalpy and demonstrate a pathway to values between 10-15 kJ/mol;
- To tune adsorption isotherms using a target mixture of binding sites, for meeting systems targets for capacity at operating temperature/pressure

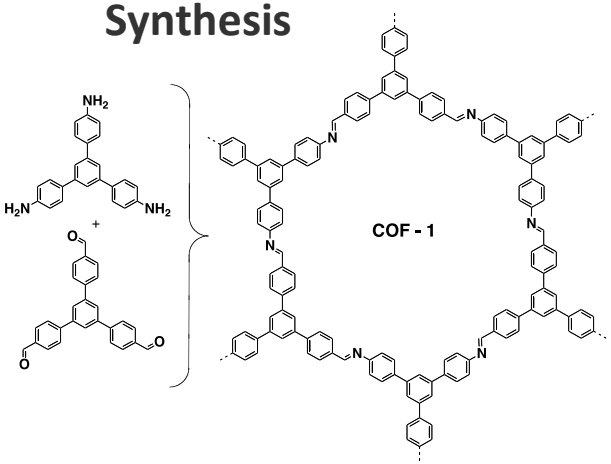
Challenge	NREL impact
A. System Weight and Volume	Materials developed are highly compressible but permanently porous; COFs composed of light elements
D. Durability/Operability	Fluorinated COFs show high thermal and chemical stability
O. Lack of Understanding of Hydrogen Physisorption and Chemisorption	Measurements are designed to elucidate the effect of fluorination on H_2 interactions with binding sites

Approach: Design, Synthesis, and Characterization of Fluorinated COFs

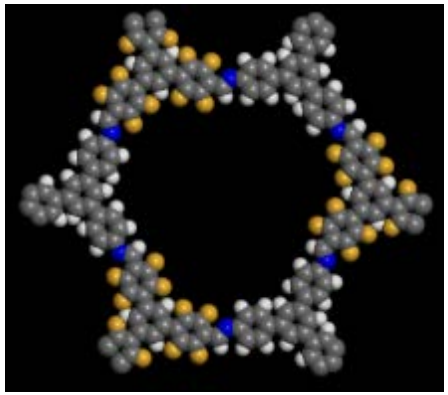
- Design functionalized COFs to meet capacity and enthalpy metrics



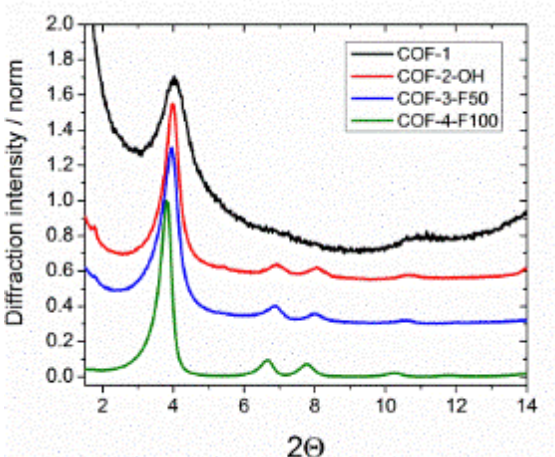
Synthesis



Modelling



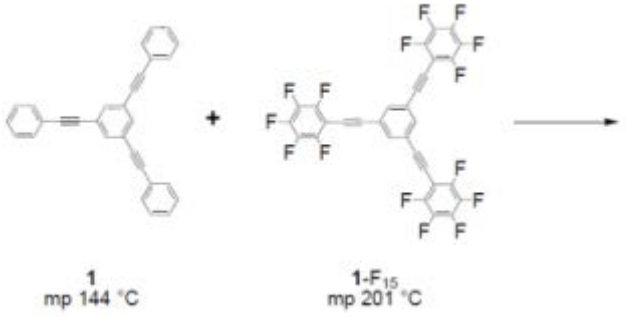
Characterization



Testing/Validation

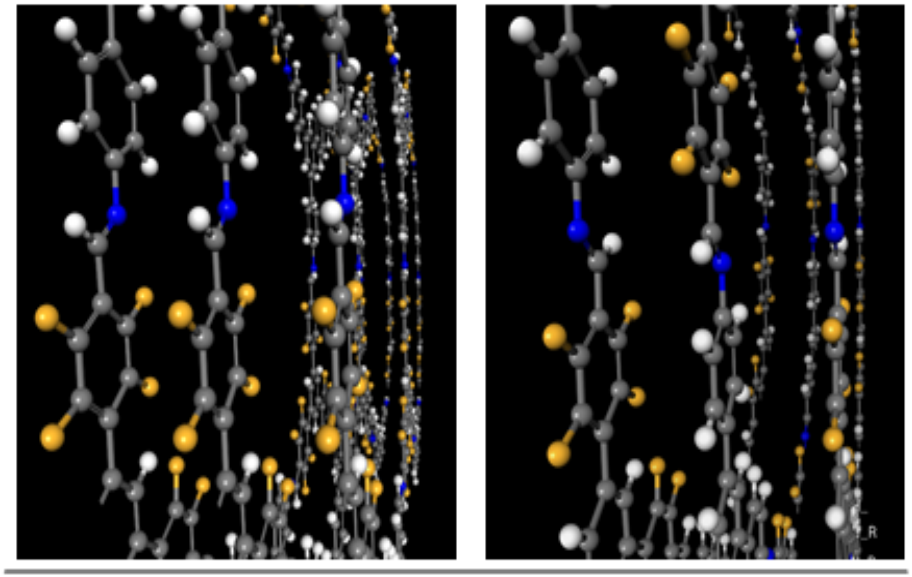
Approach: Partial Fluorination for Improved Crystallinity

- Crystal packing in small organic molecules is driven by perfluoropheny/phenyl interactions



Angew. Chem. Int. Ed. **2000**, *39*, 2323.

- Can we apply this concept to covalent organic frameworks to improve ordering?



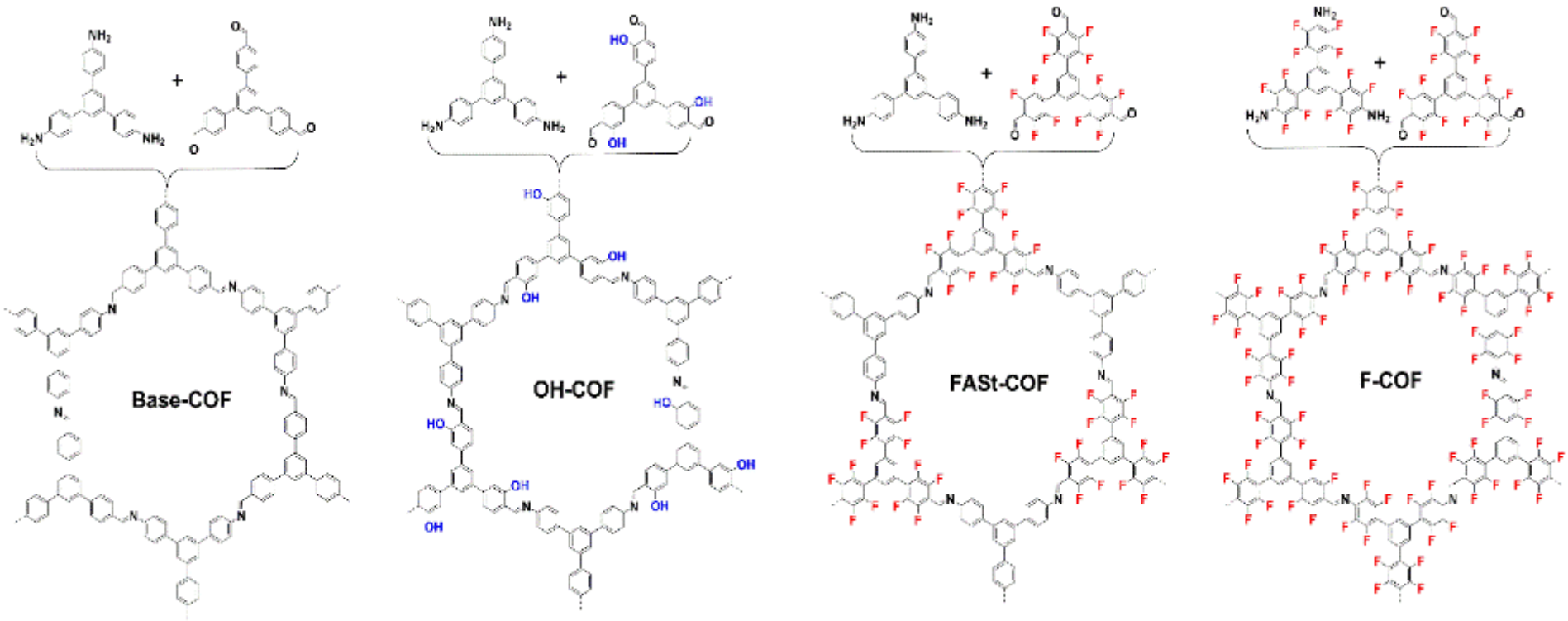
- Improved order should enhance surface area, stability, and may lead to sites for strong H_2 binding

Approach: Milestone Summary

Milestones for Phase I		
Date	Milestone Description (Go/No-Go Decision Criteria)	Completion (as of 4/15/18)
11/30/17	Produce 100 mg of first COF series	100%
01/31/18	Determine relative degrees of enhanced long-range ordering between H-bonding and fluorination strategies	100%
06/30/18	Determine influence of strategic fluorination on H_2 adsorption enthalpy through solvent and modified linker adaptations	75%
06/30/18	Synthesize 100 mg of COF series (1 and 2) with linker sites for metal chelation	30%
09/30/18	Determine influence of fluorine on enhanced binding of H_2 at metal sites	10%
11/30/18	Produce a COF with at least 4% excess gravimetric capacity and at least 40 g H_2/L total volumetric capacity at 77K and 100 bar. COF will have isosteric heat of adsorption ≥ 10 kJ/mol for a non-metalated COF or ≥ 12 kJ/mol for a COF with intercalated metals	--

Accomplishments and Progress

Synthesized COF series for testing H-bonding vs. fluorination

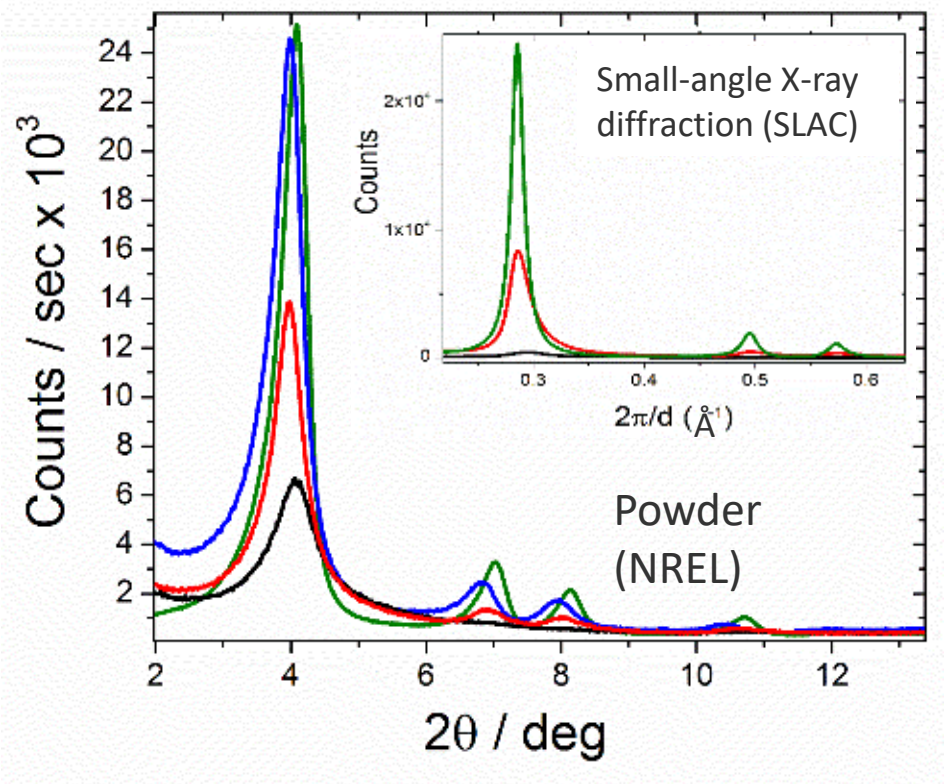


- Reactions involve amine + aldehyde condensation to form imine bonds
- Lewis acid/base chemistry is influenced by fluorines
- In most cases high yields can be achieved for scale-up toward gram amounts

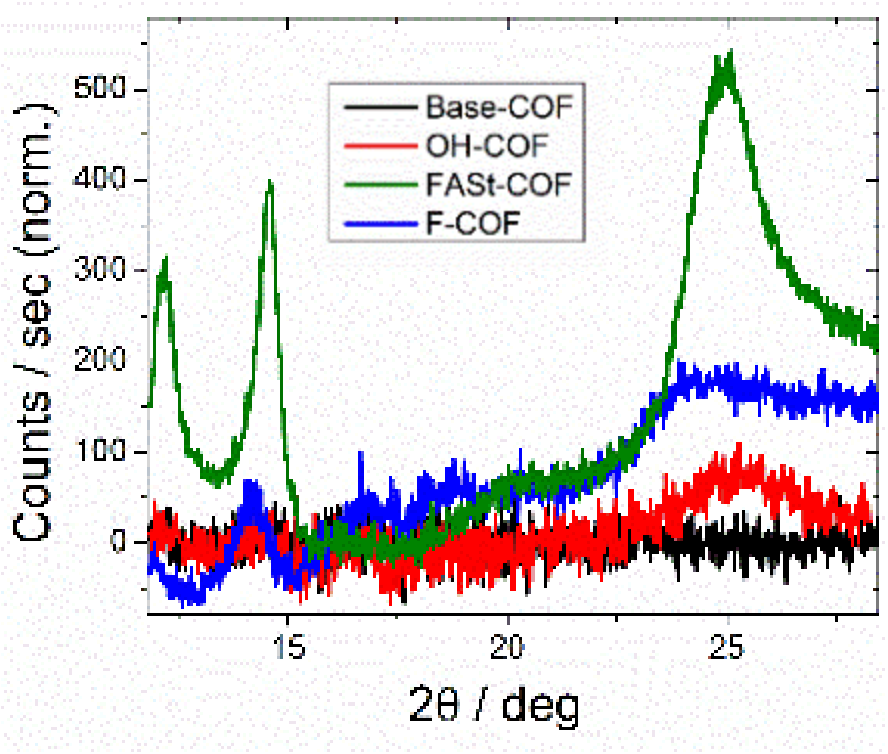
Accomplishments and Progress

- **X-ray diffraction (XRD) shows improved ordering for FASt-COF**

  - FASt-COF peaks are narrowest

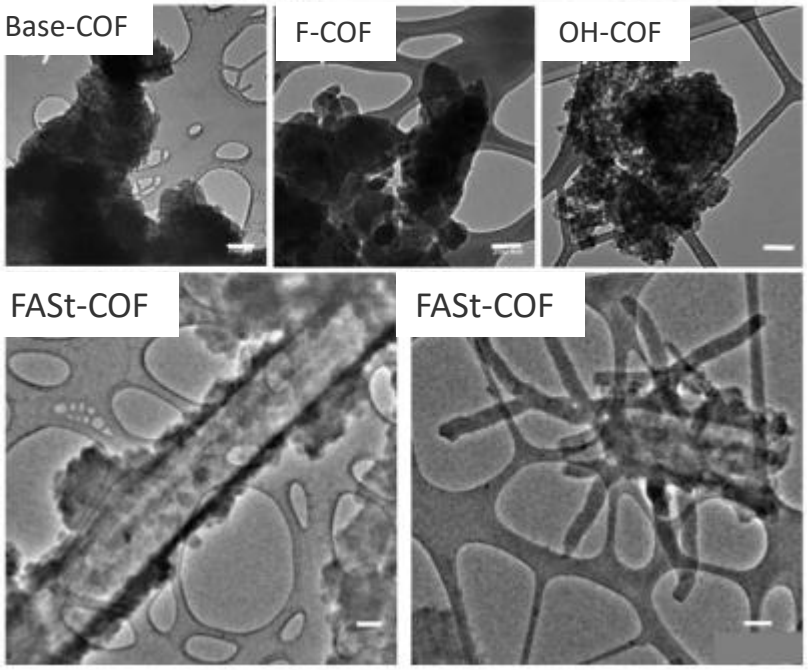


  - Interlayer diffraction peak is most pronounced



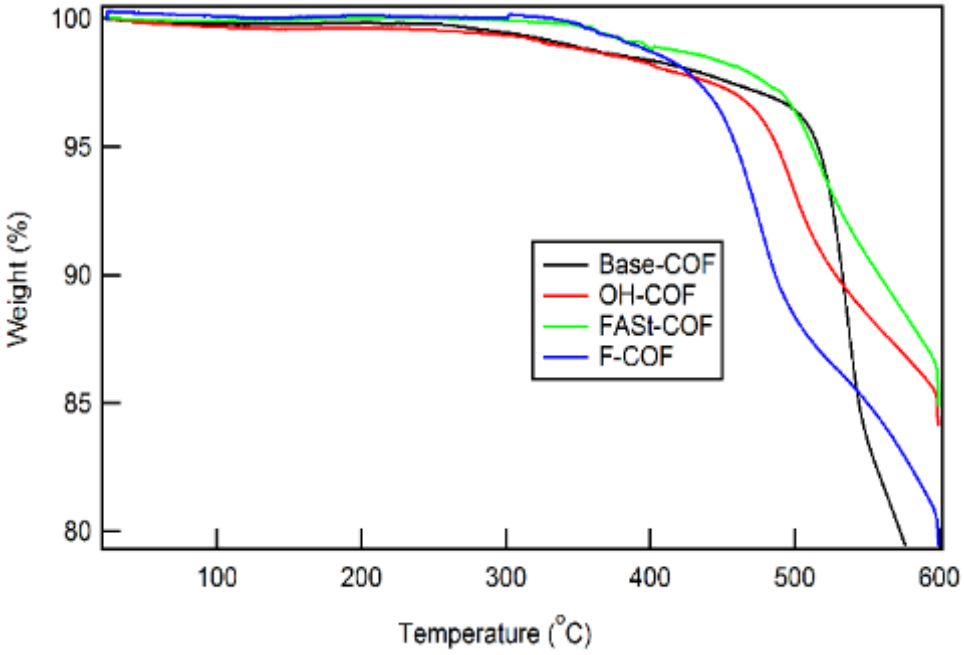
Accomplishments and Progress

- Transmission electron microscopy (TEM) images show directed crystallization on a micron scale for FASt-COF only



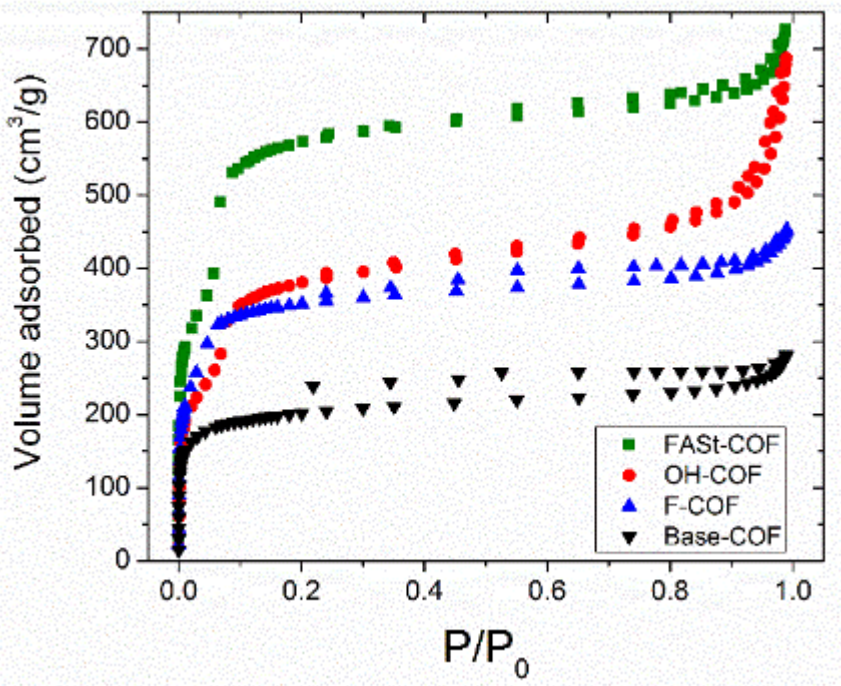
Scale bar – 200 nm

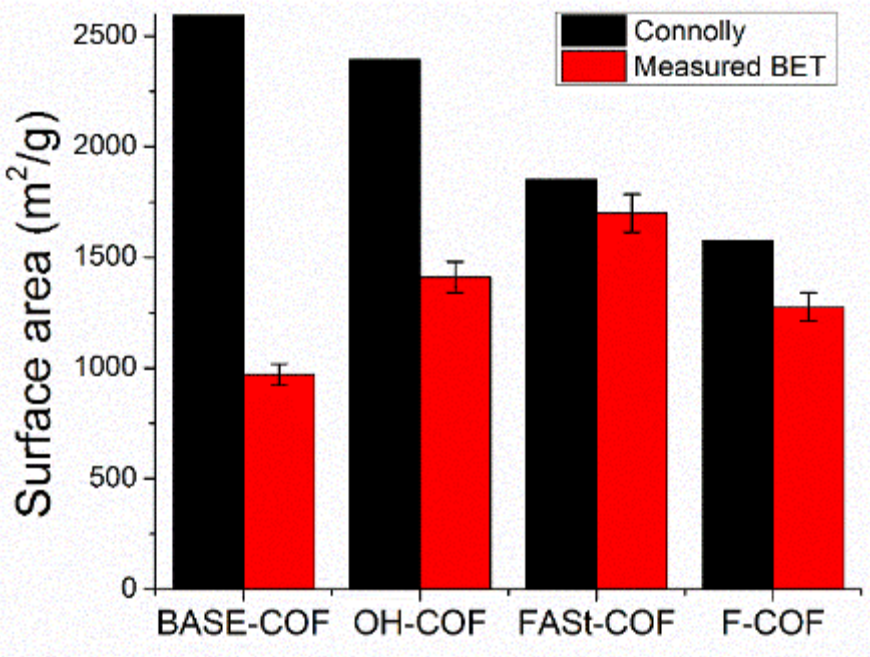
- Thermogravimetric analysis (TGA) shows good thermal stability for all COFs up to 300°C



Accomplishments and Progress

- **Brunauer-Emmett-Teller (BET) surface area is maximized with FASt-COF**



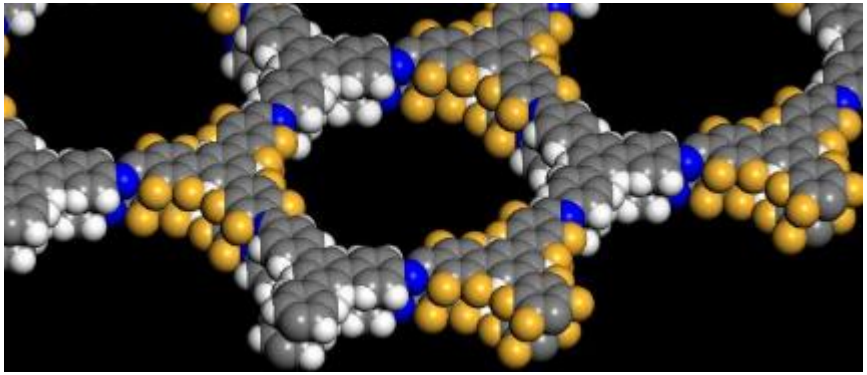


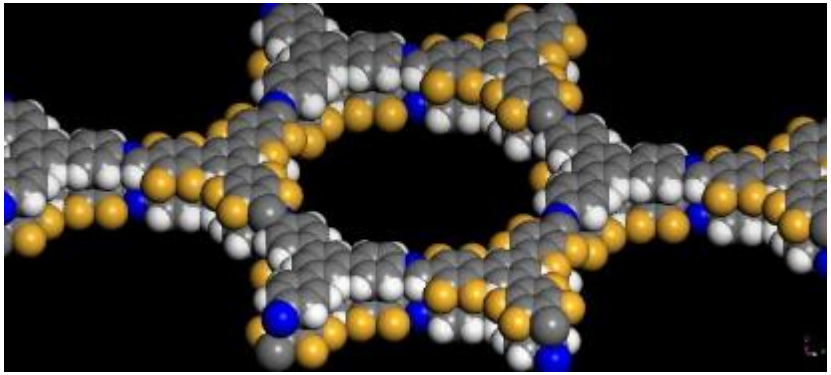
- Higher crystallinity leads to larger surface area for N_2 sorption

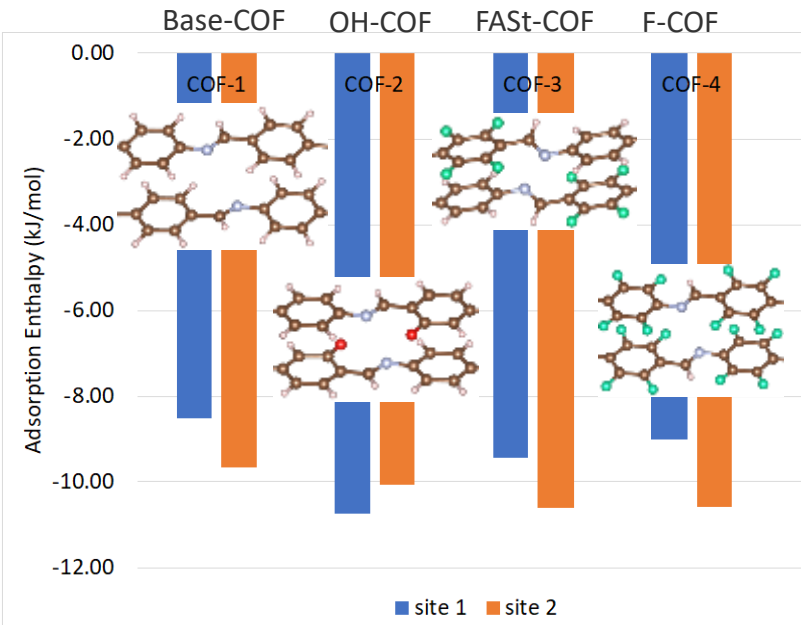
Accomplishments and Progress

- Calculations confirm higher crystal energy for alternating FASt-COF structure

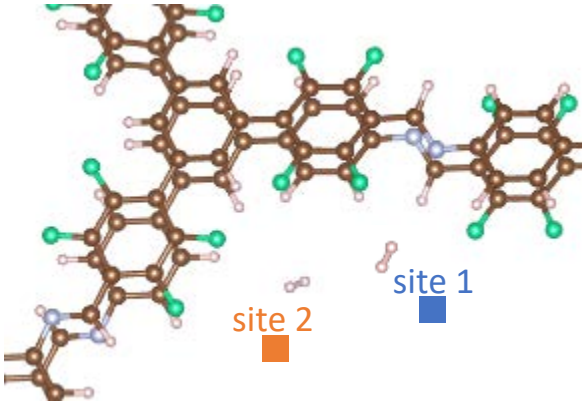
28.2 kJ/(mol) higher cohesive energy for alternating structure







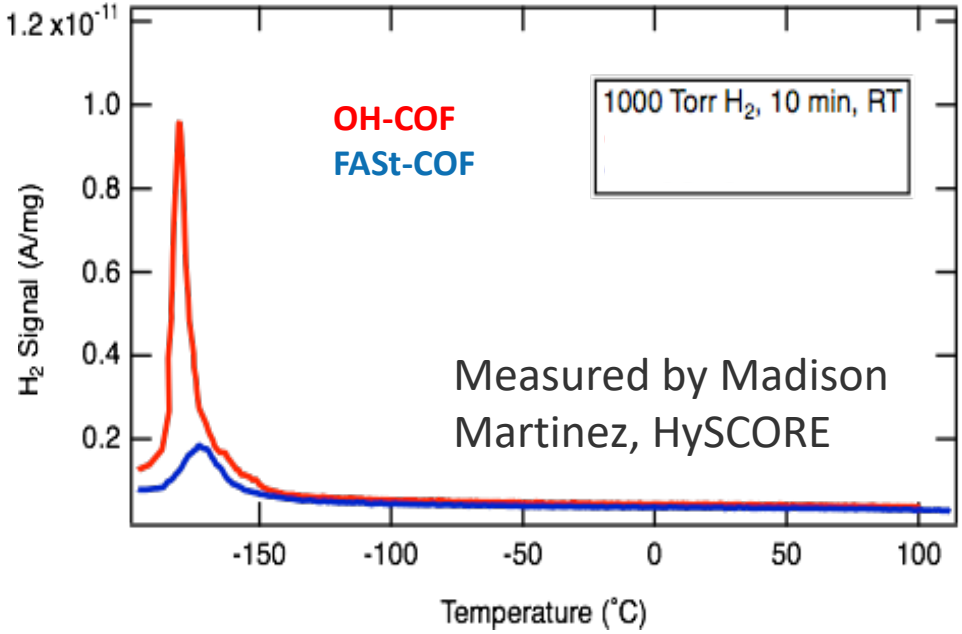
- H_2 adsorption enthalpies are calculated to be highest for fluorinated COFs

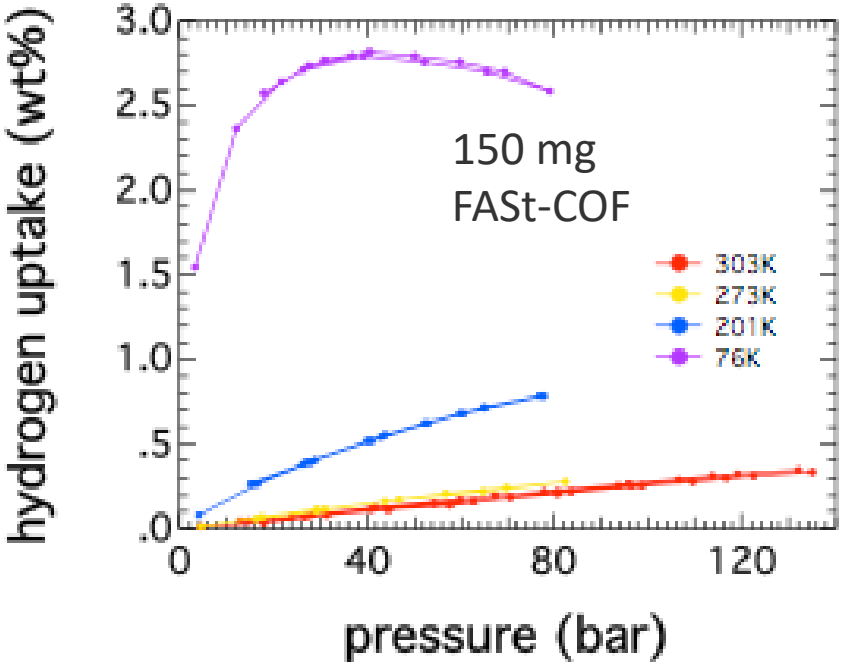


Keith Ray, LLNL, HyMARC

Accomplishments and Progress

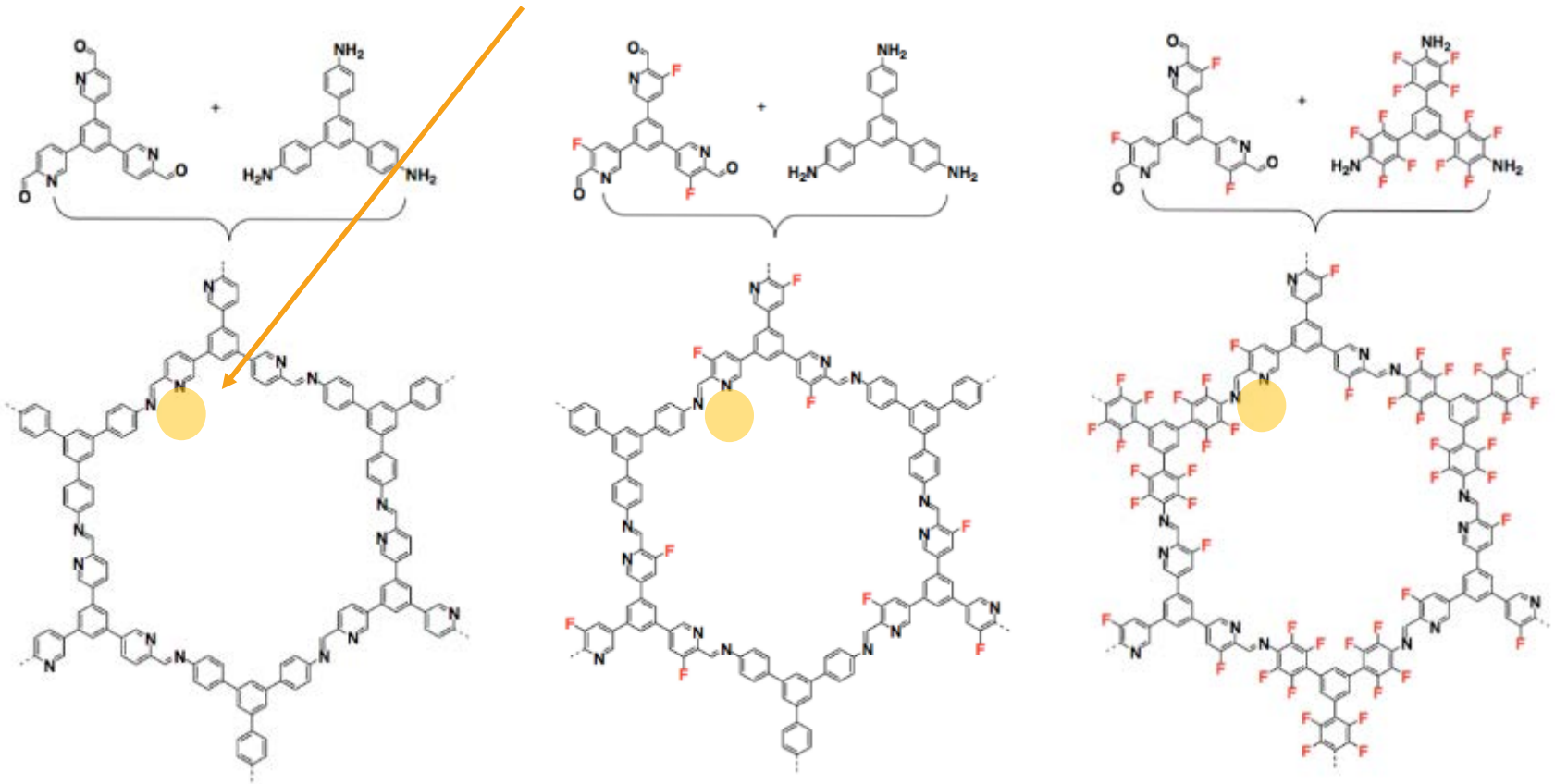
- Temperature programmed desorption (TPD) shows weak H_2 physisorption peak for FASt-COF compared with non-fluorinated COF
- Pressure-composition-temperature (PCT) data shows moderate uptake at 77K, low uptake at room temperature
- 2.8 wt% excess capacity





Accomplishments and Progress

- COF series synthesized with different fluorination strategy and aniline-imide "bay" for metalation



- Preliminary results show Cu binding occurs, possibly between COF layers

Collaboration and Coordination

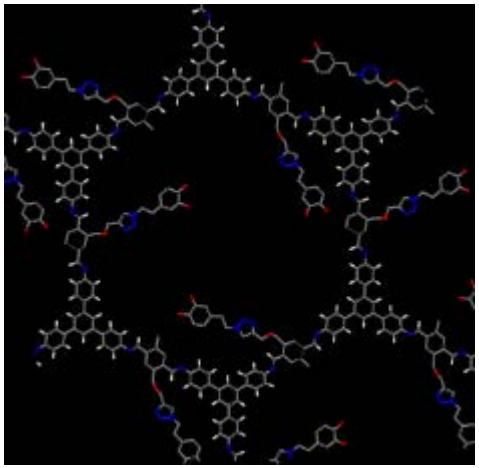
- **Colorado School of Mines**
  - University cost-share and subcontract partner
  - Graduate student with Prof. Alan Sellinger
  - Synthesis of COF precursors and chemical/porosity analysis of COFs
- **Stanford Linear Accelerator**
  - DOE National Lab collaborator on x-ray studies (Michael Toney)
  - In-situ SAXS/WAXS measurements up to 100 bar of gas and 200°C.
  - XPS for metal coordination
- **Lawrence Livermore National Laboratory (LLNL)**
  - National Laboratory within DOE HyMARC core team
  - DFT calculations on fluorinated COFs (Brandon Wood and Dr. Keith Ray), for crystal stability and H_2 binding enthalpies
- **LBNL (DRIFTS)**
  - Part of HySCORE team (Jeff Long group)
  - Planned for future: Diffuse reflectance infrared spectroscopy for monitoring H_2 binding in COFs at low temperatures

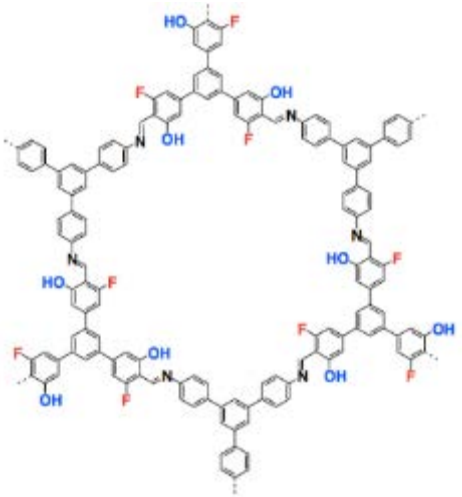
Remaining Challenges and Barriers

- Optimize metal intercalation for strong and stable binding to proposed sites
- Demonstrate open coordination sites for H_2 binding
- Understand the influence of fluorination on the strength of H_2 binding at metal sites
- Demonstrate improved capacity with fluorinated COFs
- Demonstrate improved binding enthalpy with fluorinated COFs
- Improve sample density for higher volumetric capacity

Proposed Future Work

- **Modify linkers on non-metallated COFs to produce differing binding sites for H_2 adsorption**
  - Milestone 3.1: Determine influence of strategic fluorination on H_2 adsorption enthalpy through modified linker adaptations
  - Catechol sites to be added post-synthetically using “click” chemistry
  - OH and imide sites with proximal fluorines for tuning adsorption enthalpy





Any proposed future work is subject to change based on funding levels.

Proposed Future Work

- **Initiate metalation procedures for fluorinated COFs**
  - Milestone 2.2: Determine influence of fluorine on enhanced binding of H_2 at metal site
  - Solvent-based methods with metal salts and dialkyl-salts
  - Gas-phase methods using atomic layer deposition precursors
  - XPS for metal incorporation and binding
  - Calculate best binding site geometries and potential for multiple H_2 binding

- **Decision point**: Continue with metalated or non-metalated COFs series based upon testing of best candidate materials
- **Go/No-go milestone**: Produce a COF with at least 4 w% of excess H_2 capacity based and 40 g/L total volumetric capacity at 77K and 100 bar. Isosteric heat of adsorption will be > 10 kJ/mol for a non-metallated COF *or* >12 kJ/mol for a metallated COF.

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- We have discussed materials development and applications with NREL's Technology Transfer office as new COFs are being synthesized
- Submitted ROI on fluorinated COFs but did not pursue a patent application due to publications on similar materials development from other labs at the same time

Summary

- Synthetic procedures for novel fluorinated COFs have been developed
  - A total of eight COFs have been made at the > 100 mg level
- COF crystallinity and surface area can be tuned with strategic fluorination
  - Notable directed crystal growth and surface areas exceeding 1700 m^2/g have been found for particular COFs
- Hydrogen sorption characteristics were calculated to be favorable for fluorinated COFs
  - Enthalpies of > 10 kJ/mol were computed for fluorinated COFs
- Capacity for H_2 sorption and enthalpy were measured
  - At present, values are lower than expected but procedures for preparing samples are not yet optimized
  - COFs with metal binding sites have been synthesized and metalation procedures have been initiated

Thank You

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Publication Number

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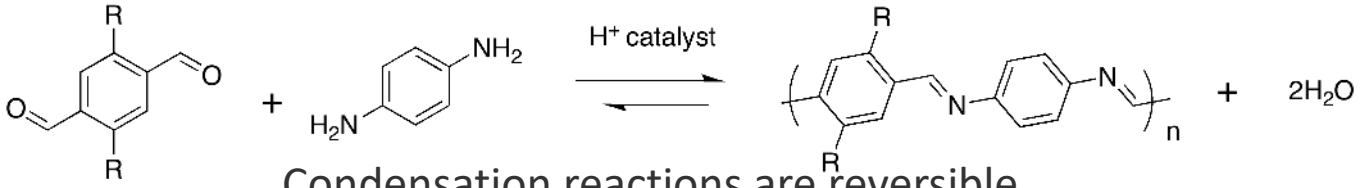
Technical Back-Up Slides

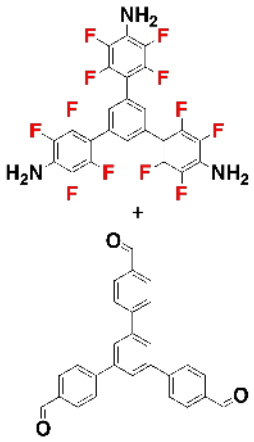
Technical Back-Up Slides

Conditions Must Be Optimized for Each COF

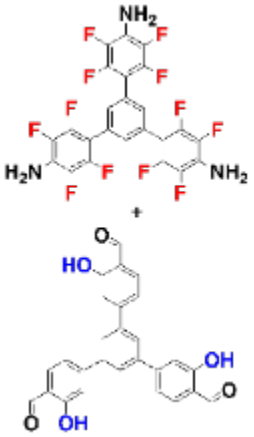


Condensation reactions are reversible

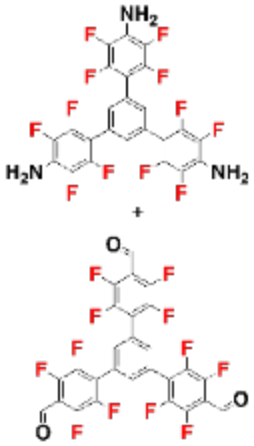
Typical "Optimal" COF conditions employ moisture/alcohol to promote reversibility → 1.9 *o*-DCB : 0.1 *n*-Butanol : 0.1 6M Acetic Acid



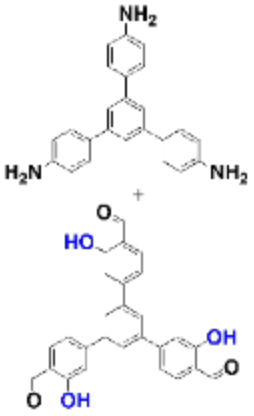
No Rxn



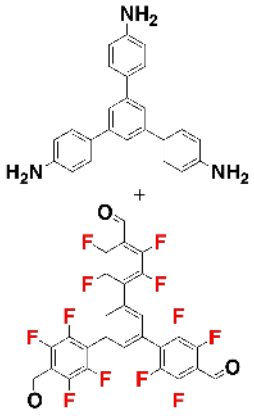
Very Slow Rxn



Slow Rxn



"Normal" Rxn



Very Fast Rxn

Technical Back-Up Slides

- Cleaning with supercritical CO_2 is sometimes necessary to remove residual solvent even with aggressive degassing procedures
- Residual solvent or contaminants can cause deviations from expected gas sorption behavior