DOE Hydrogen Program

A Joint Theory and Experimental Project in the High-Throughput Synthesis and Testing of Porous COF and ZIF Materials for On-Board Vehicular Hydrogen Storage

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Project ID
stp_31_britt

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Overview

Timeline

Project start date: 9/1/2008
Project end date: 1/31/2013
Percent complete: 5%

Barriers

Barriers addressed

- ❑ Improved gravimetric and volumetric density of hydrogen uptake
- ❑ Hydrogen capacity and fast kinetics at 77 K
- ❑ Improved hydrogen binding energy
- ❑ Synthetic scale up of COFs/ZIFs to cubic meters

Budget

- ❑ Total project funding
  - DOE share: $1.38 M
- ❑ Funding received in FY08: $75 K
- ❑ Funding for FY09: $400 K

Collaborating Partner

- ❑ BASF

Objectives

Room temperature H_2 storage in COFs and ZIFs to meet DOE 2010 Targets

- Synergistic work between Yaghi (UCLA) and Goddard (Caltech)
- High-throughput computational screening to identify new materials for favorable H_2 uptake
- High-throughput preparation/characterization of doped materials predicted for high uptake
- High-throughput screening to testing a diverse set of compositions and structures
- Develop chemistry and perform computational testing of Li/Na/K doping effects on H_2 uptake
- Predict and determine heat evolved upon reversible uptake and release

Milestones

Year 1

1. Develop new force fields for modeling adsorption properties of ZIFs and COFs. Test models using reported adsorption data for a range of known ZIFs and COFs.

2. Experimentally explore metal impregnation conditions in existing ZIFs and COFs, and characterize metal density in the frameworks. Compare with predictions from theory.

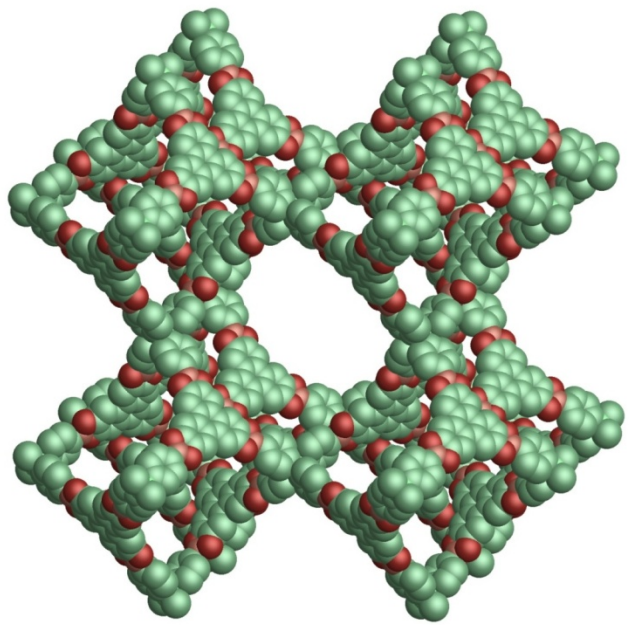
3. Investigate pressure and temperature dependence of H_2 uptake in impregnated existing ZIFs and COFs over the parameter range specified in DOE YR2010 guidelines (6 wt % and 45 g L^{-1} up to 100 bar, -30/50 °C). Compare with predictions from theory.

4. Discover new ZIF and COF materials utilizing high-throughput methods and explore hydrogen uptake properties of ZIFs and COFs in the same parameter range.

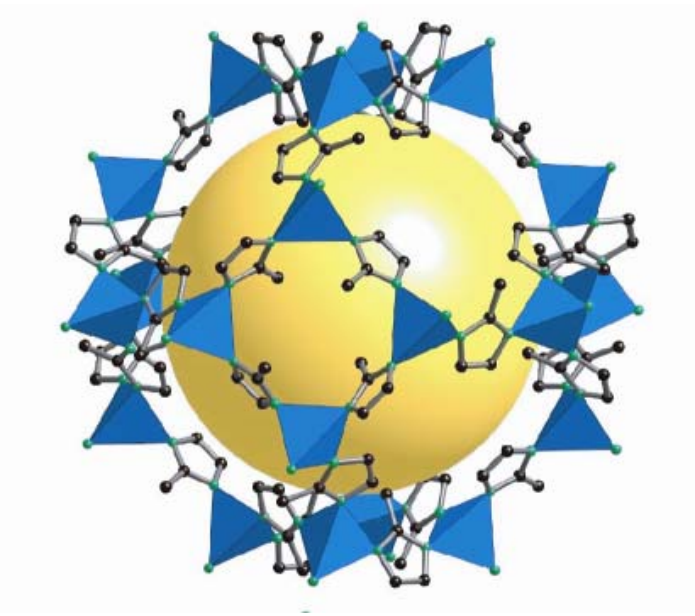
Description of new materials

Covalent Organic and Zeolitic Imidazolate Frameworks (COFs and ZIFs)

- COFs are lightweight materials
- ZIFs are highly stable materials
- COFs and ZIFs are suitable towards light metal impregnation

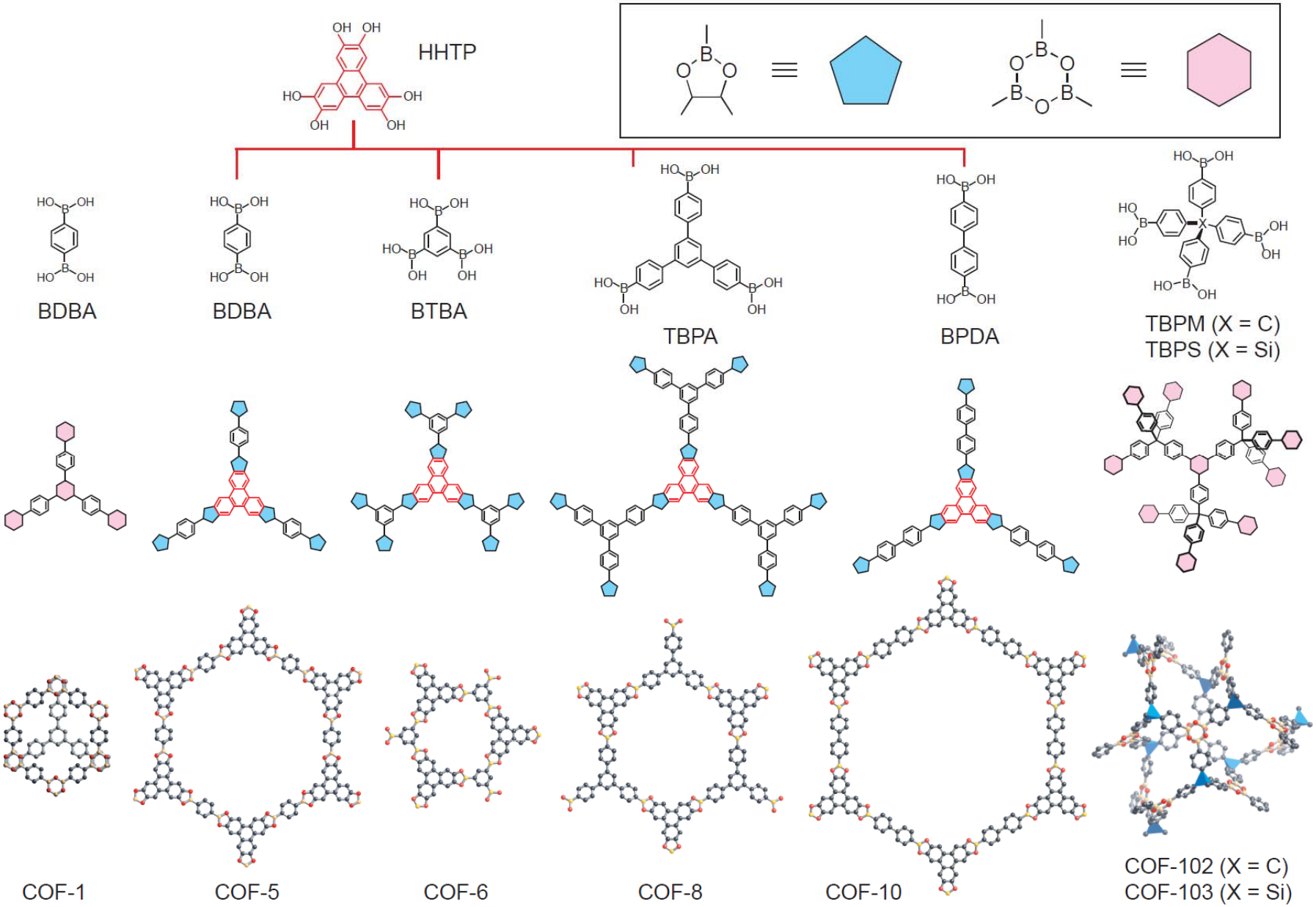


COF-108

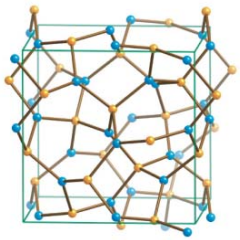


ZIF-8

Covalent Organic Frameworks (COFs)



Low density crystalline 3D COFs



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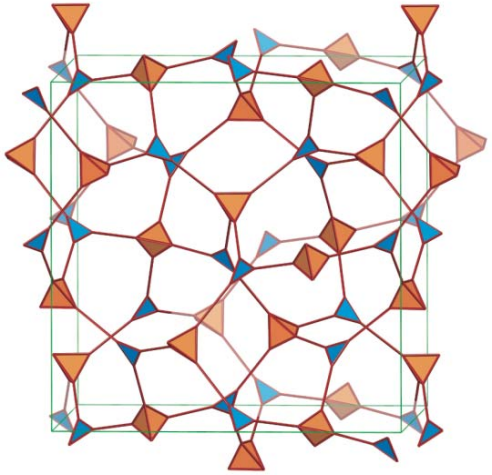

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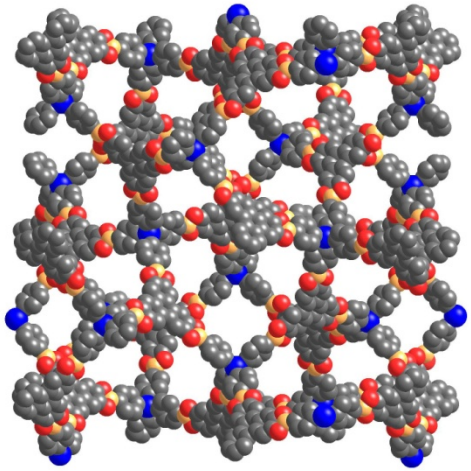
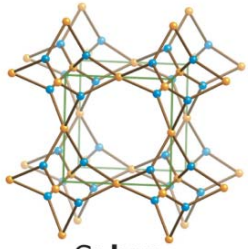
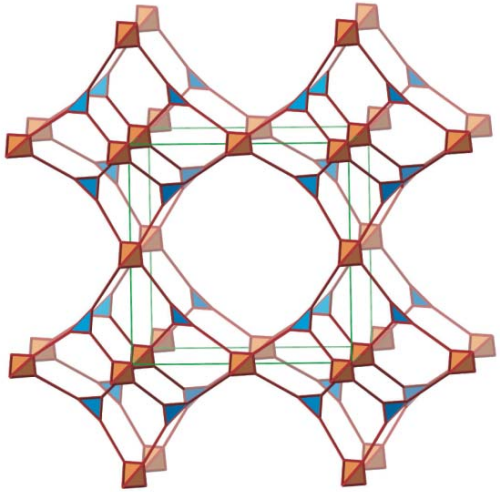


COF-105
(d = 0.18 g cm^{-3})



G: **bor**



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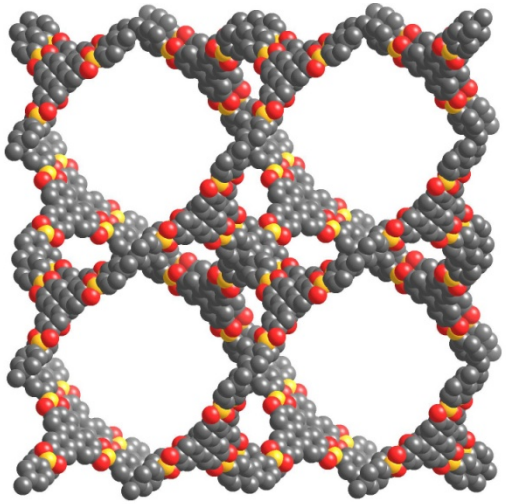


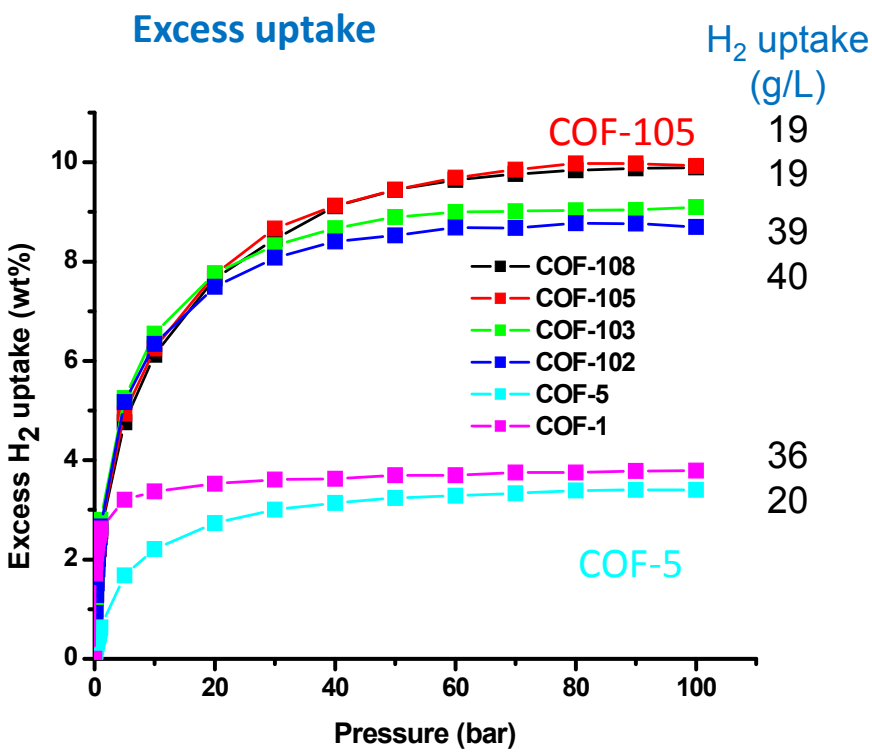
COF-108
(d = 0.17 g cm^{-3})

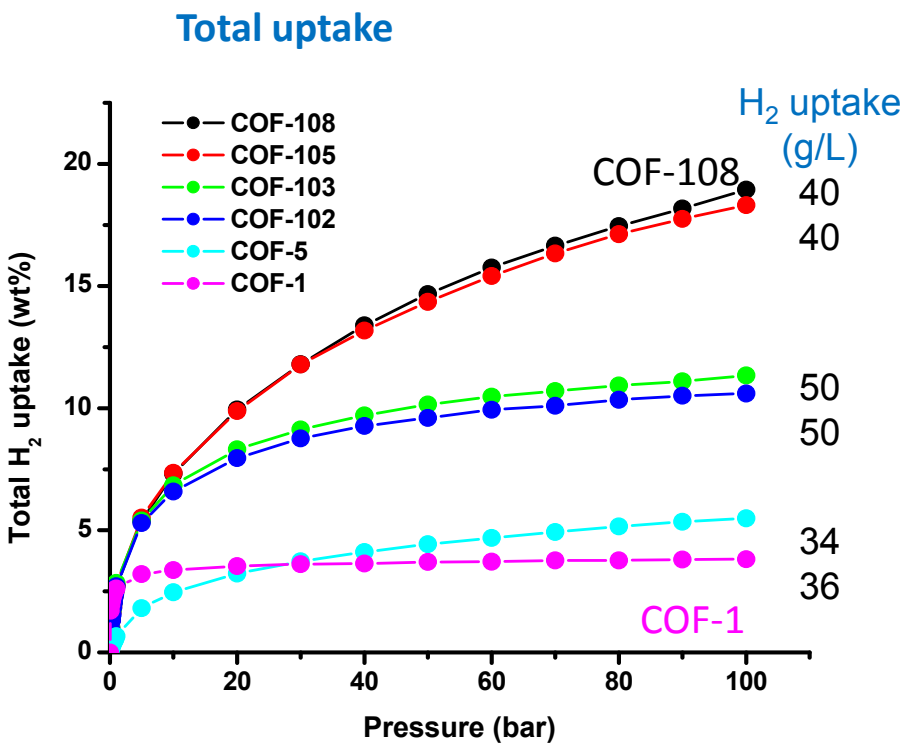
Science 2007

Gravimetric excess and total H_2 uptake of COFs at 77 K

COF-105 will have the highest uptake (excess 10% and total 20%)

Goddard's calculations

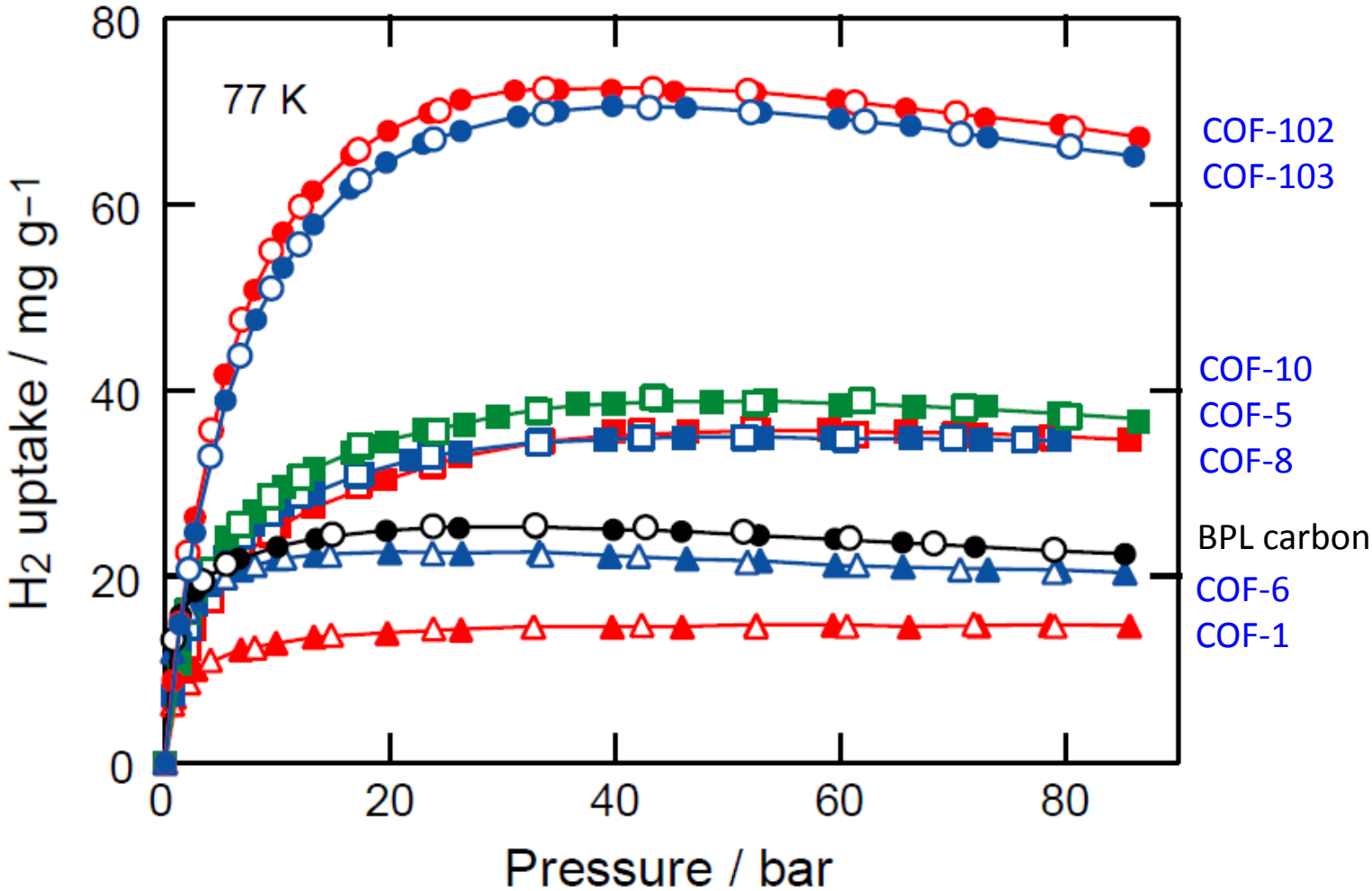




S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard:
J. Am. Chem. Soc., **2008**, *130*, 11580–11581.

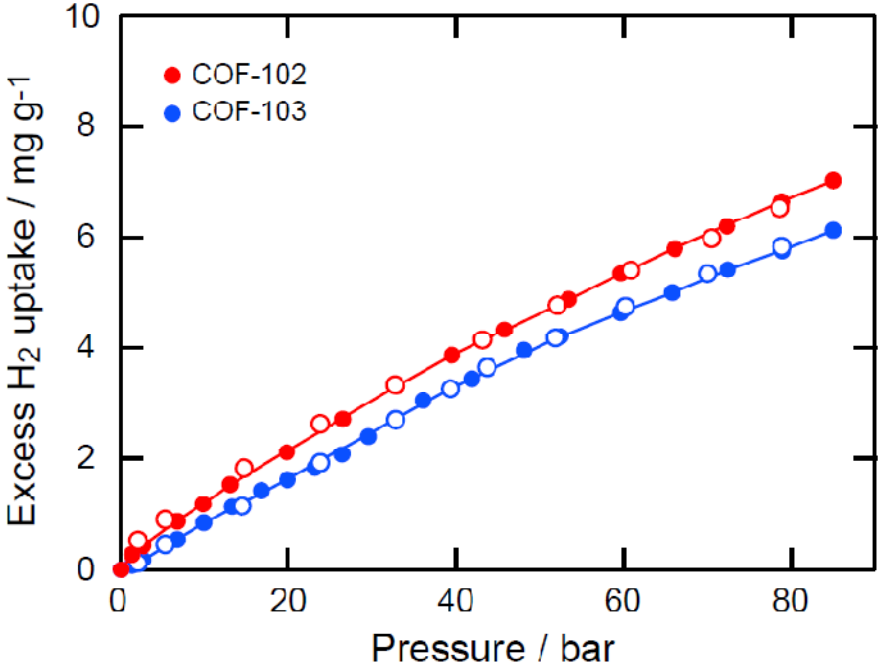
Accomplishments: High-pressure H_2 isotherms of COFs at 77 K

Surface excess mass

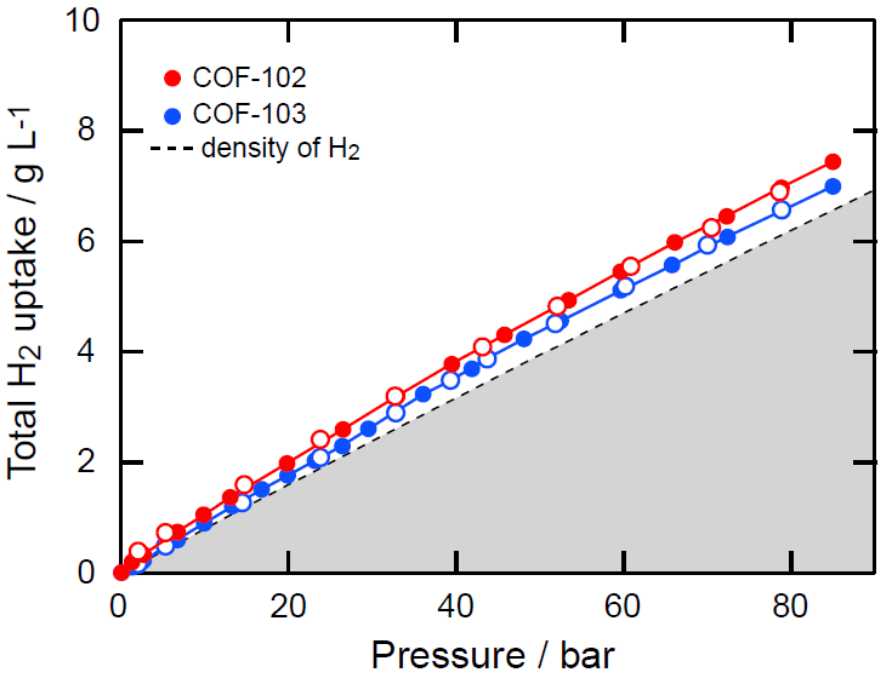


H_2 uptake in 3D COFs is almost same as that in MOF-177.

Accomplishments: High-pressure H_2 isotherms of COFs at 298 K



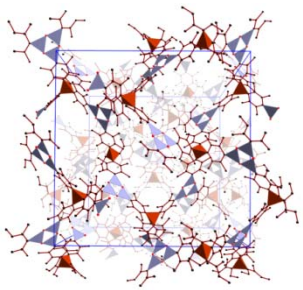
Gravimetric excess H_2 uptake



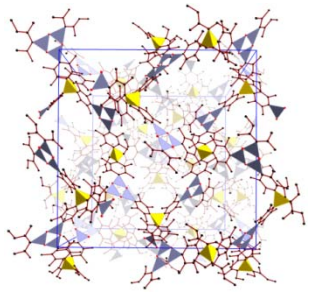
Volumetric total H_2 uptake

Better volumetric H_2 density compared to compressed H_2

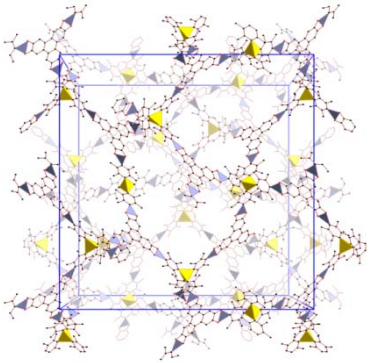
Accomplishments: Modeling study of new 3D COFs



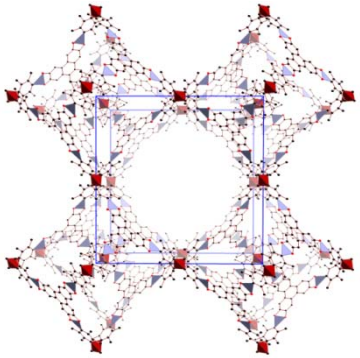
COF-192



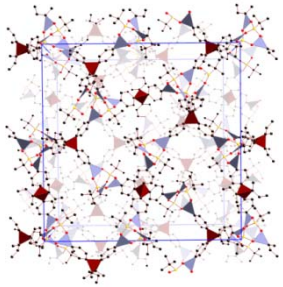
COF-193



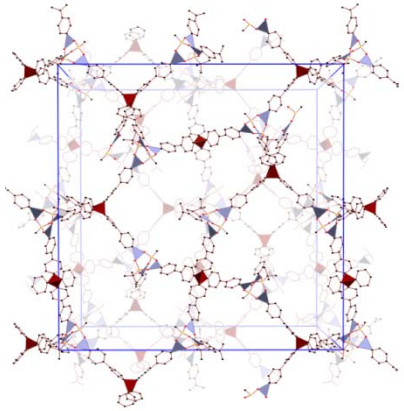
COF-195



COF-198



COF-202

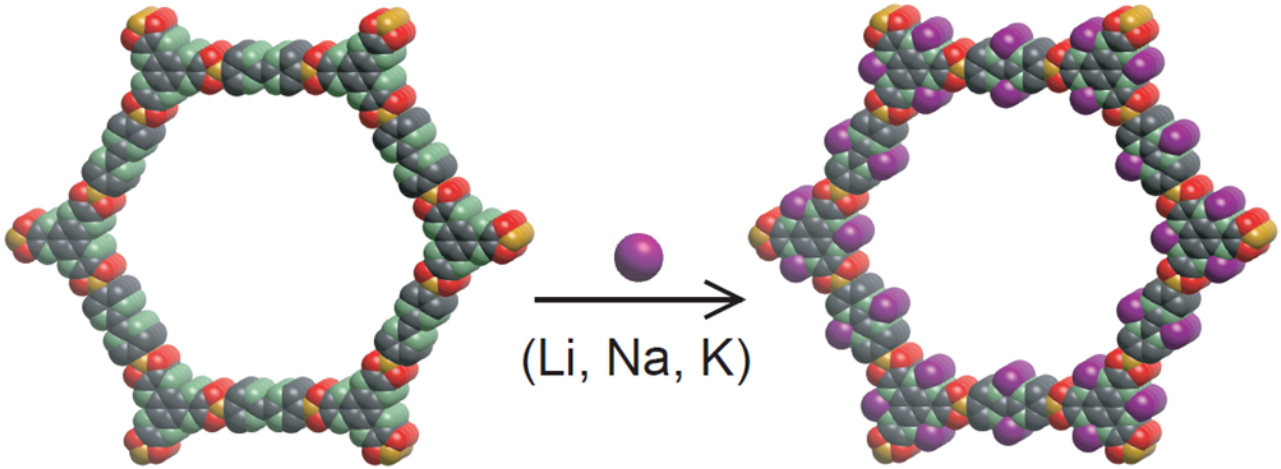


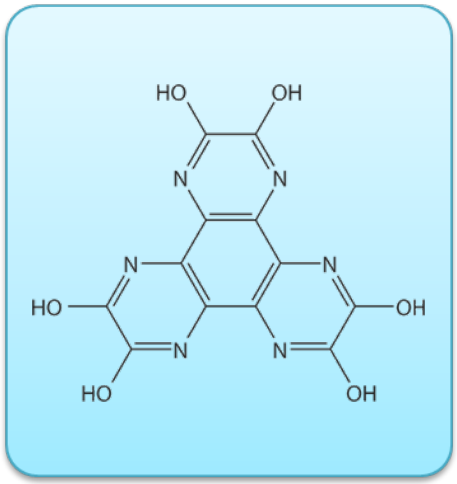
COF-212

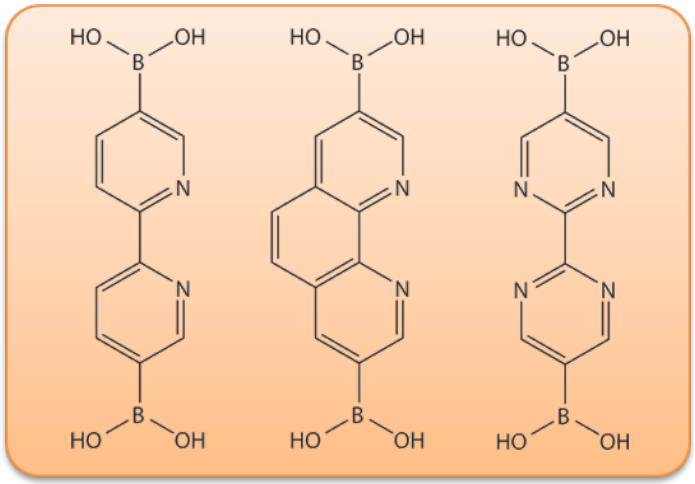
Material	BET area / $m^2\ g^{-1}$	Pore volume / $cm^3\ g^{-1}$	Density / $g\ cm^{-3}$
COF-192	3157	1.04	0.627
COF-193	3297	1.16	0.574
COF-195	5531	3.71	0.233
COF-198	5400	3.99	0.218
COF-202	4150	4.05	0.537
COF-212	6711	4.11	0.217

H_2 uptake in COFs will be simulated using GCMC simulation with *ab-initio* based FFs.

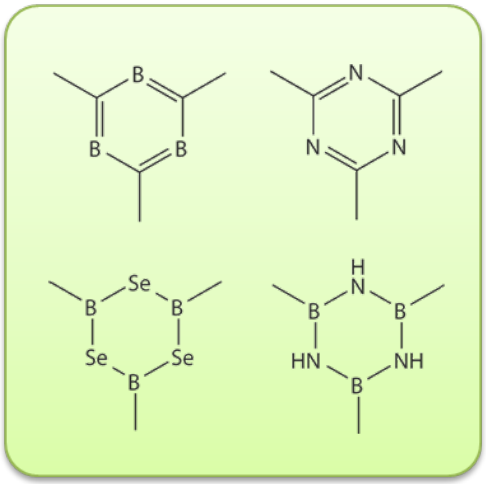
Approach 1: Post-synthesis modification of COFs
(e.g. Impregnation of COFs with metals)





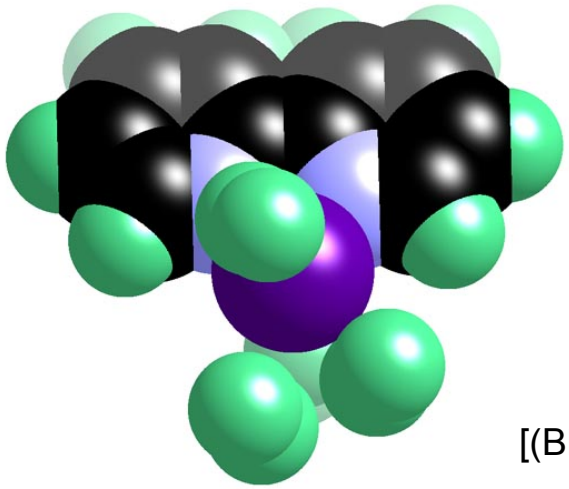


N-containing building units



Various connectivity

Theoretical prediction of binding energy



$[(BPy)V^{2+}](H_2)_4$

Model system:
$[(BPyDC)M(CO)_4]^{2-}$

- M^{n+} = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn (n = 0, 1 and 2)
- Preliminary DFT calculations

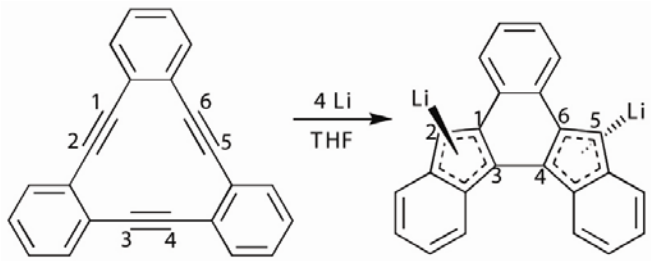
n = 0: Mn has stronger binding energy to BPyDC than its cohesive energy.
n = 1: Mn^+, Co^+, Ni^+, Cu^+, and Zn^+ have stronger binding energy to the ligand.
n = 2: All metals are favorable for formation of $(BPyDC)M^{2+}$ complexes.
Metal impregnated materials would be experimentally accessible

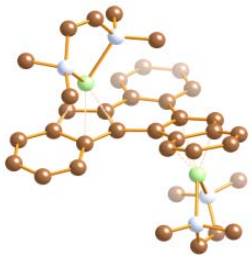
Interaction between H_2 molecules and the $(BPyDC)M^{2+}$
$(BPyDC)M^{2+}(H_2)_4$ average H_2 binding energies per one H_2 molecule:

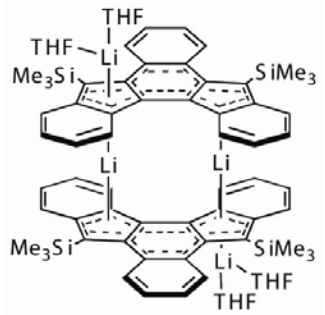
-24.6 kJ mol^{-1} for Zn^{2+} to -62.2 kJ mol^{-1} for V^{2+}

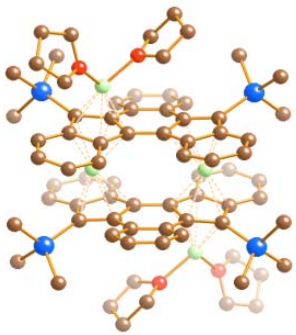
➔ These are ideal values for H_2 storage at room temperature.

Approach 2: Impregnation/intercalation of COFs with metals

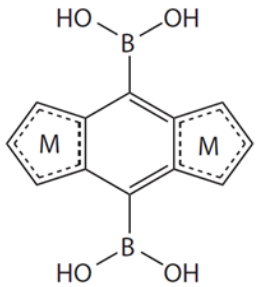


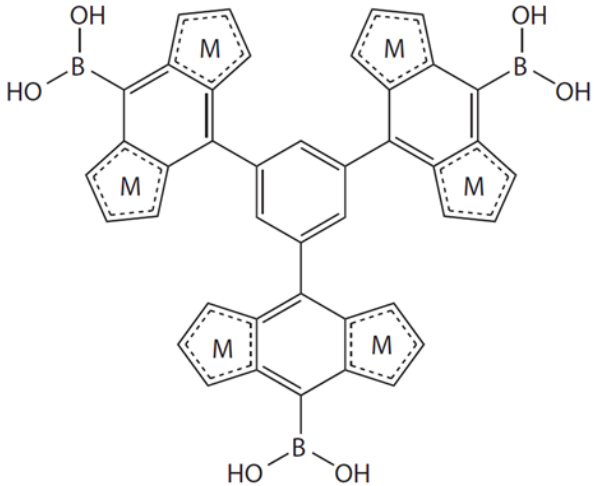






Youngs et al., *Organometallics*, **1991**, *10*, 2089; Zhang et al., *J. Org. Chem.*, **2005**, *70*, 10198; Malaba et al., *Organometallics*, **1993**, *12*, 1266.

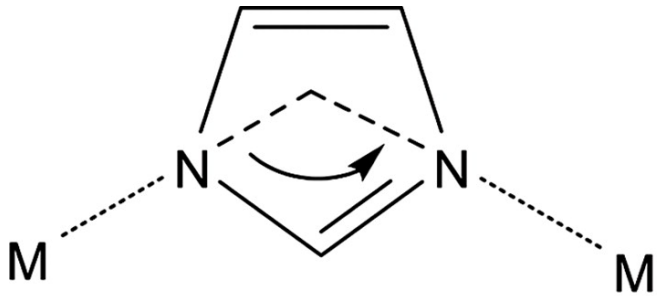




η^5-Cp-Li system seems versatile and stabile rather than η^6-benzene-Li system.

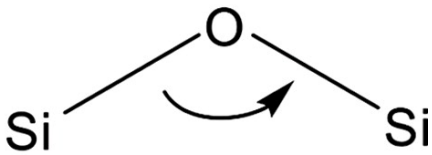
- Build model structures (e.g. known 2D and 3D COF structures)
- Estimate H_2 uptake behavior at room temperature
- Discover experimental materials

Zeolitic Imidazolate Frameworks (ZIFs)



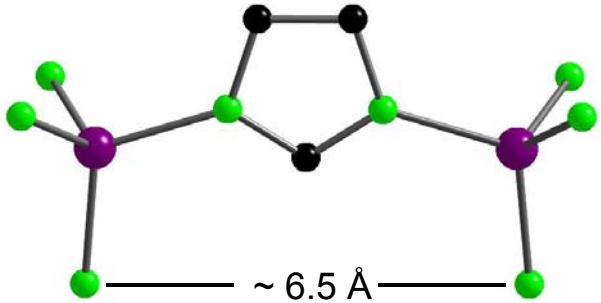
145 º
M - IM - M

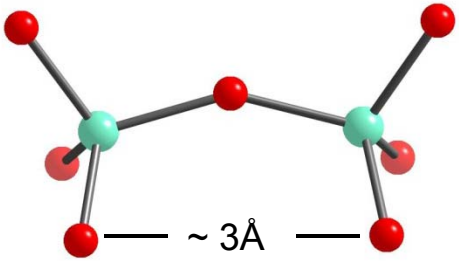
1



145 º
Si - O - Si

2

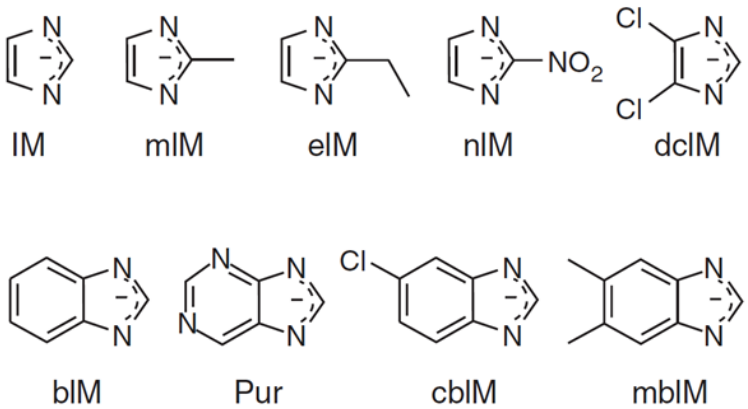




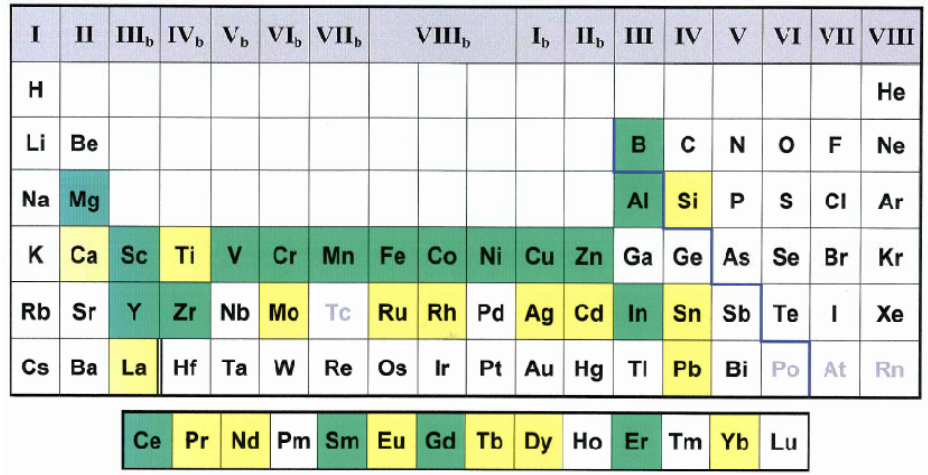
Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *PNAS,* **2006**, 103, 10186.

Synthesis of ZIFs

Extensive class of functionalized linkers



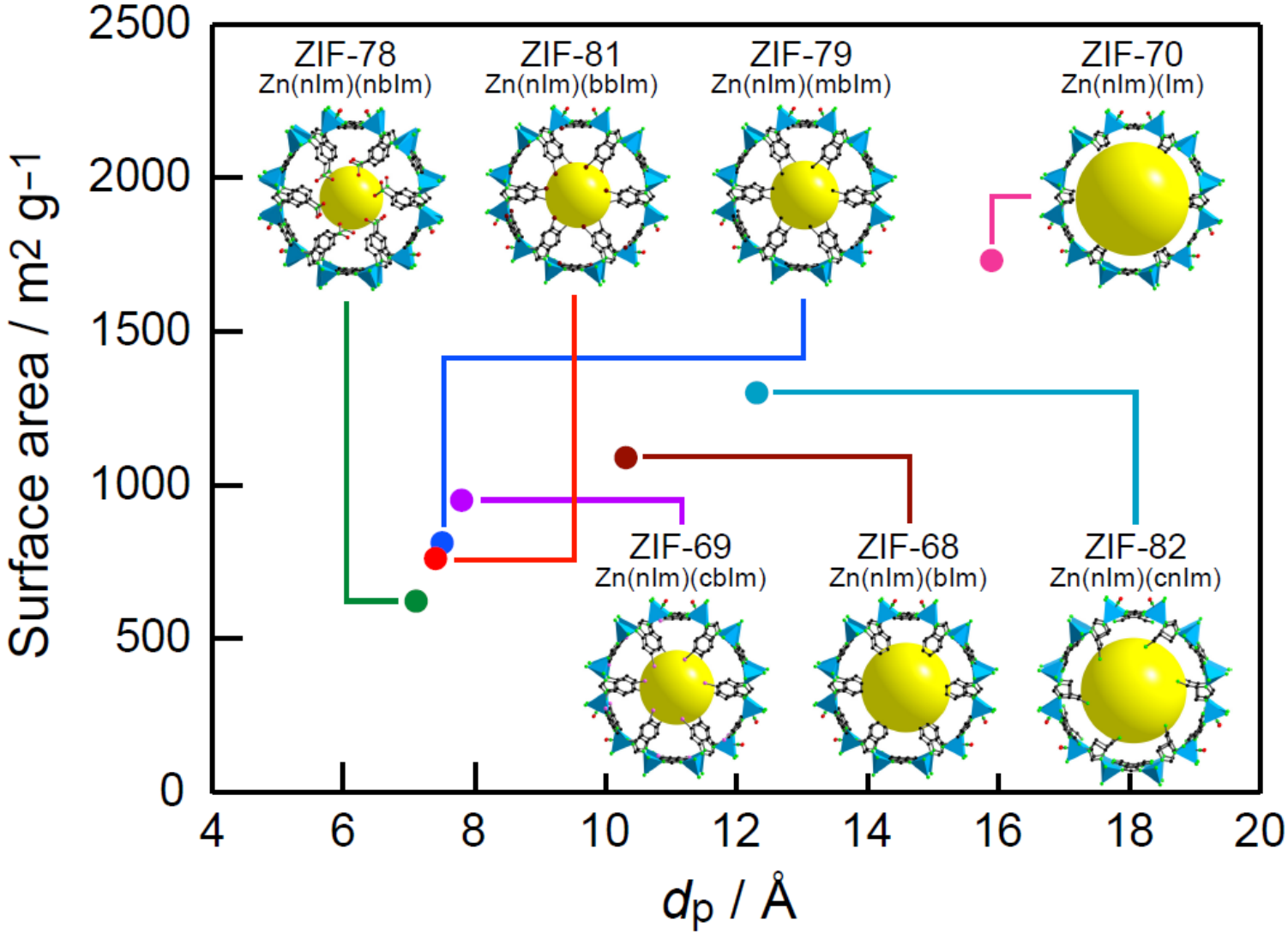
Various metal sources



- Design of composition (metal centers and organic linkers). Synthesis and structural characterization is well worked out.
- Control of structure, topology, interpenetration and porosity.
- High-throughput technique is available for quick screening.

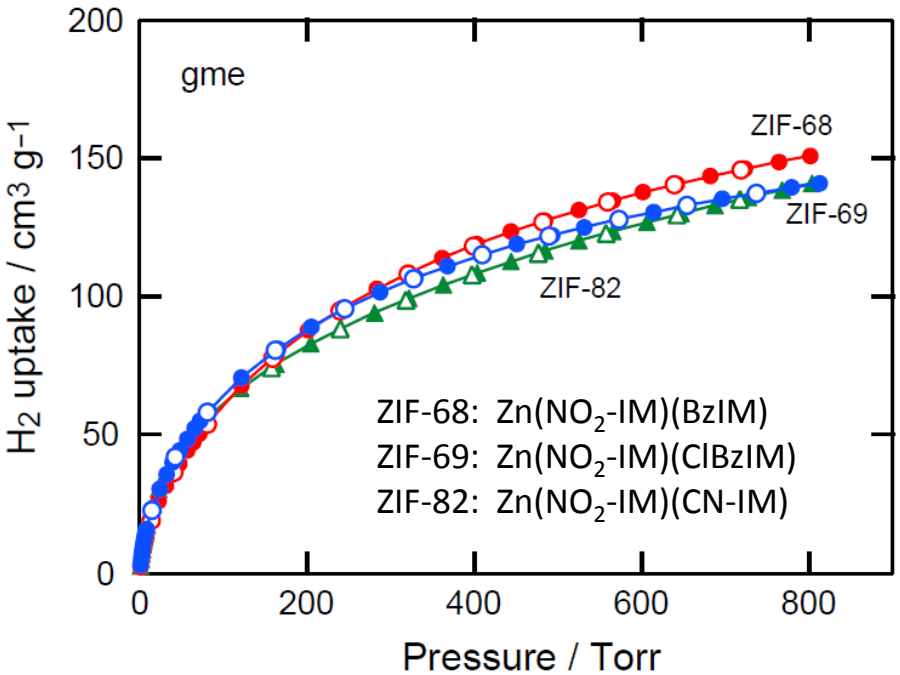
More than 50 ZIFs have been discovered by high-throughput methods.

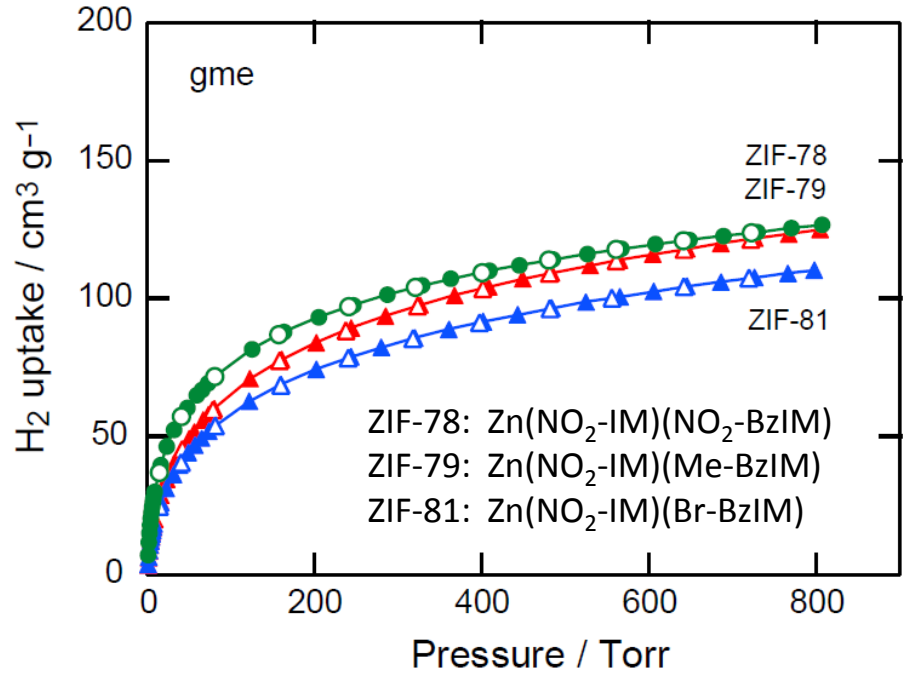
Designed porosity and functionality in ZIFs

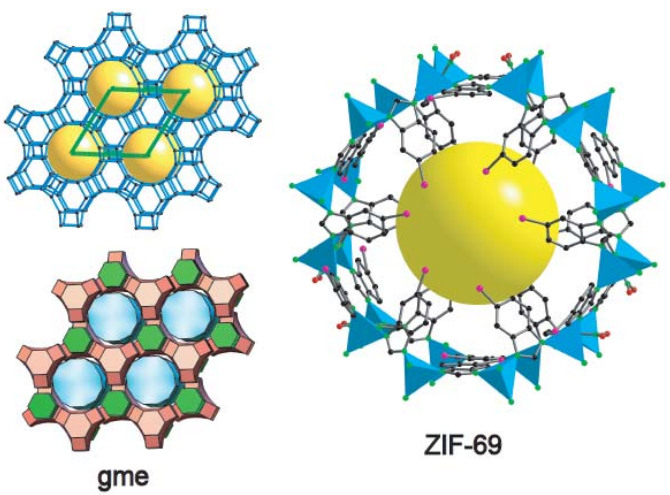


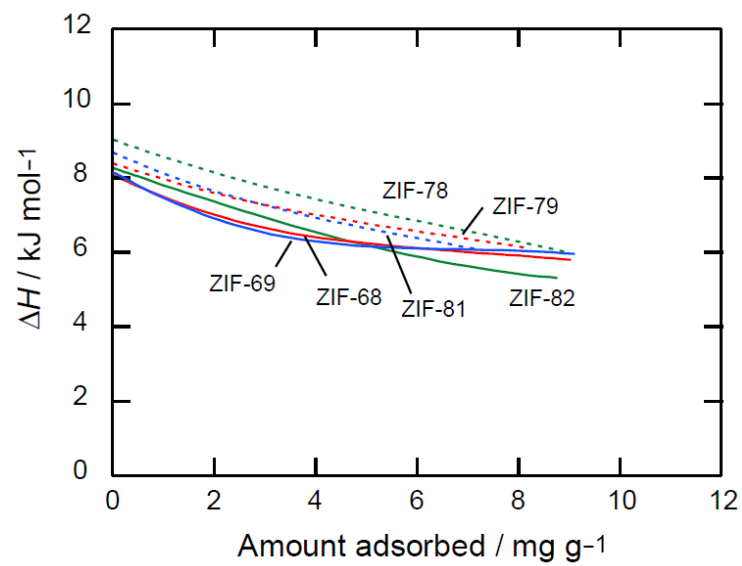
R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe, O. M. Yaghi, *JACS* **2009**, *131*, 3875-3877.

Accomplishment: H_2 uptake in ZIFs

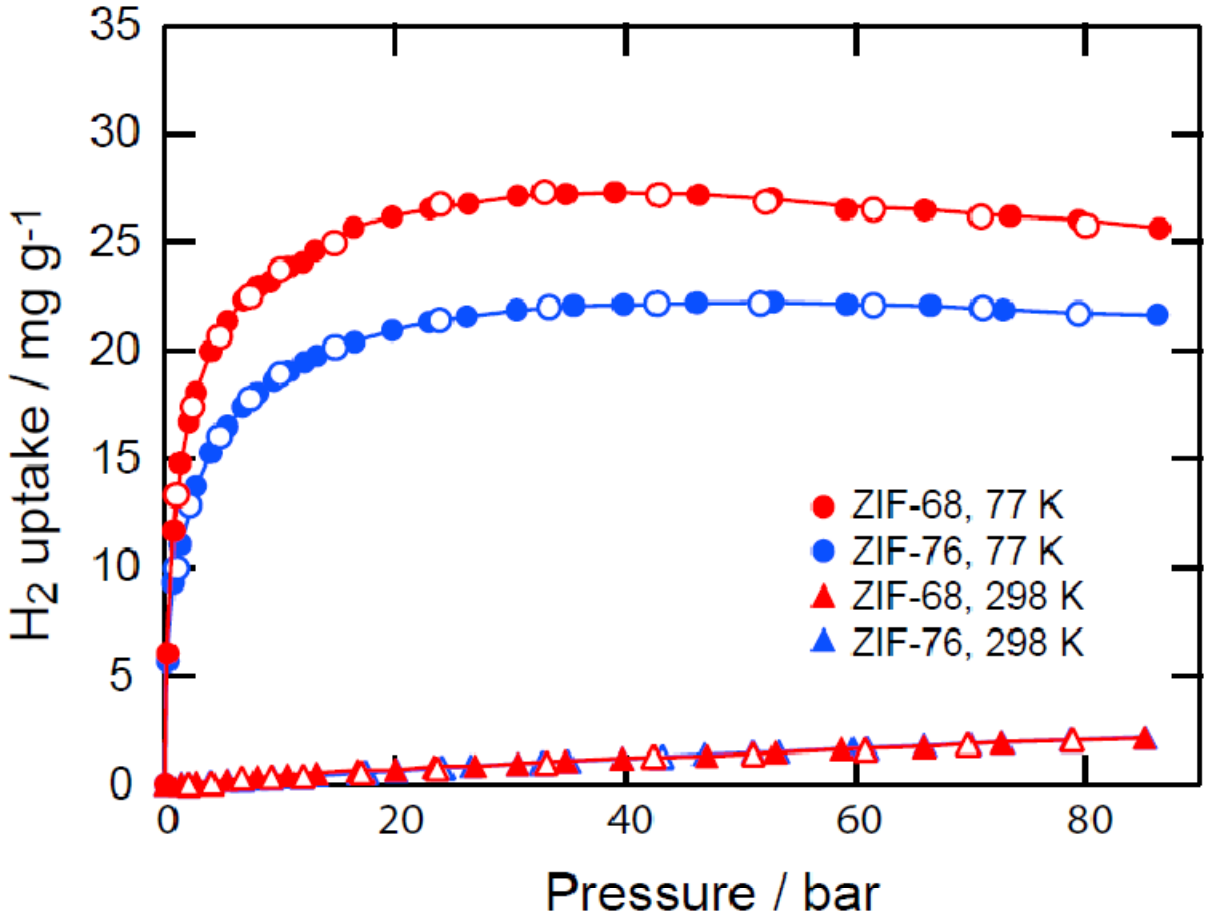


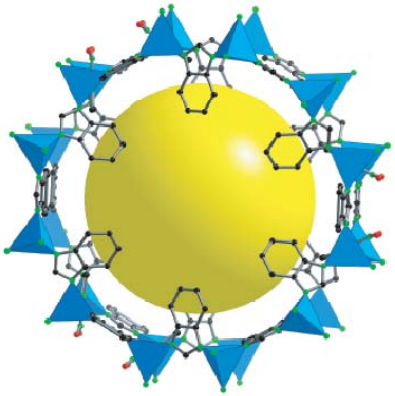




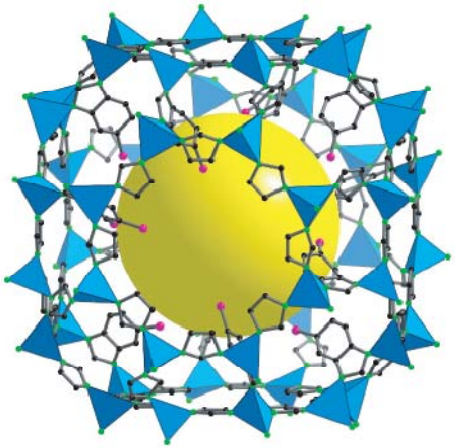


Accomplishment: High pressure H_2 isotherms of ZIFs





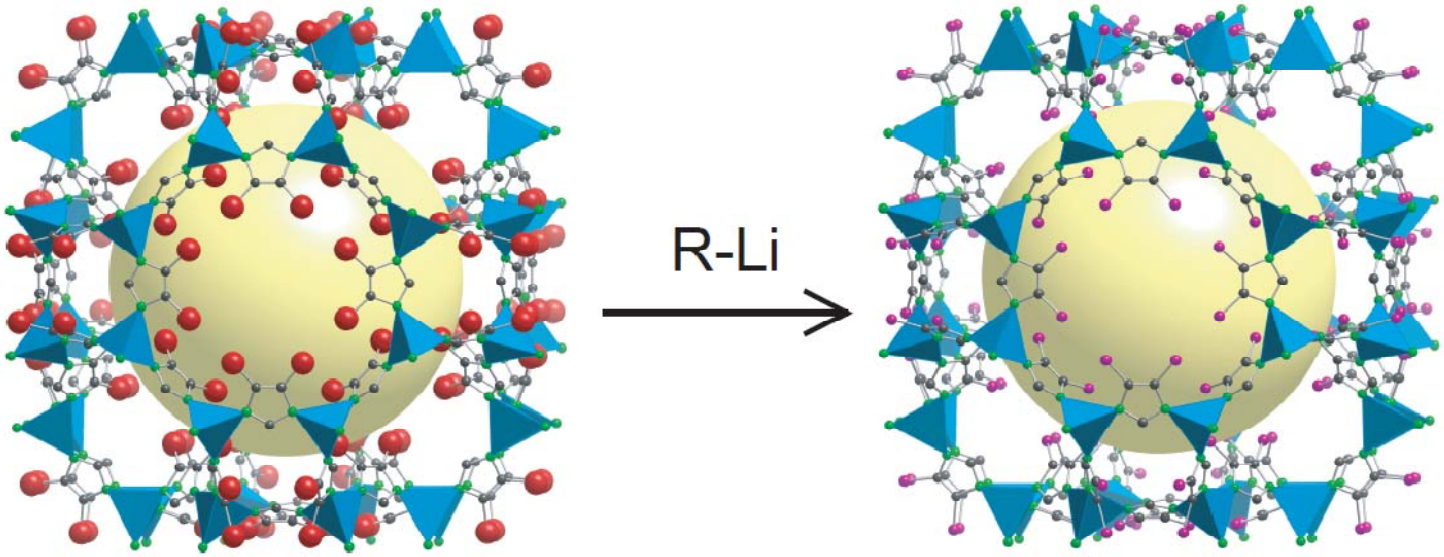
ZIF-68

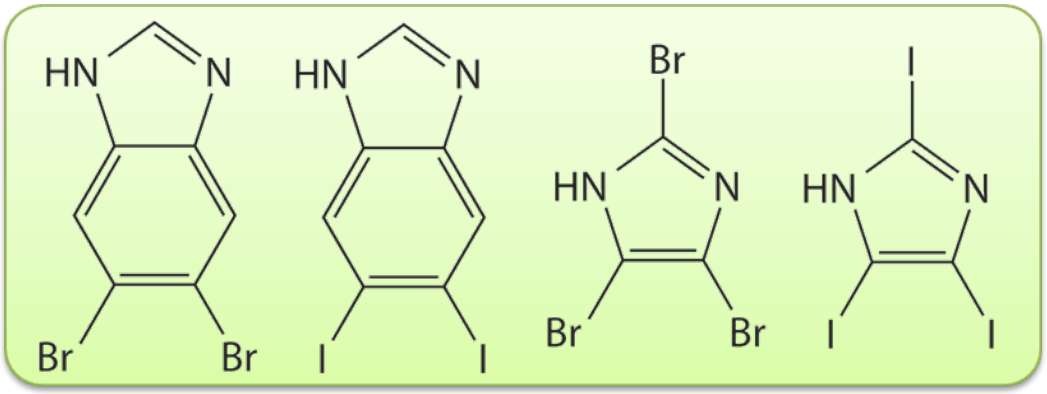


ZIF-76

Poor H_2 uptake at room temperature.

Approach 3: Post-synthesis modification of ZIFs
(e.g. potential halogen-lithium exchange)





+

$Zn(NO_3)_2$
or
$Co(NO_3)_2$

Summary

Relevance: For room temperature hydrogen storage, a systematic survey was started experimentally as well as theoretically.

Approach: Aim at increasing strong binding sites for maximum hydrogen uptake capacity without losing pore volume.

Technical accomplishments and progress:

- High pressure H_2 uptake behavior in COFs
- Synthesis of new ZIFs for metal impregnation
- Began modeling study for optimal materials

Technology transfer/collaborations: Active relationship with collaboration partners and BASF.

Proposed future research:

- Employ light weight metals to create strong binding sites.
- Material design based on theoretical prediction.