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

Omar M. Yaghi

Department of Chemistry
UC Berkeley

William A. Goddard III

Materials and Process Simulation Center
Caltech

May 16, 2012

Project ID
ST022

Overview

Timeline

Project start date: 9/1/2008 (funded from 4/1/2009)

Project end date: 1/31/2013

Percent complete: 65%

Barriers

Barriers addressed

- ❑ Improved gravimetric and volumetric density of hydrogen uptake
- ❑ Improved hydrogen binding energy
- ❑ Synthetic scale up of COFs to cubic meters

Budget

- ❑ Total project funding
  - DOE share: $1.38 M
  - Contractor Share: $405,499
- ❑ Funding received in FY11: $284,425
- ❑ Funding for FY12: $225 K

Collaborating Partner

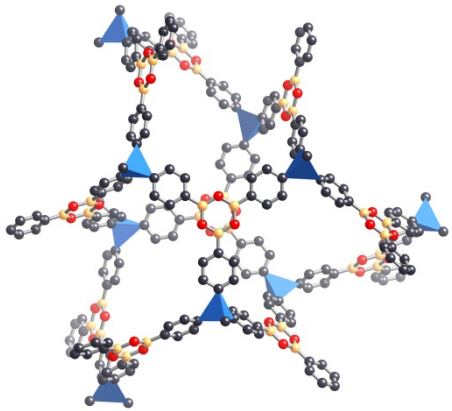
- ❑ Co-PI: William Goddard (Caltech)
- ❑ Fraser Stoddart (NW)
- ❑ Jaheon Kim (Soongsil University)
- ❑ BASF

Relevance

Overall project objectives:

Develop new materials to meet DOE system H_2 storage targets

- Theoretical prediction of H_2 storage capacities to guide chemistry
- Synthesize lightweight crystalline porous solids for the metalation
- Measure H_2 uptake and adsorption enthalpy



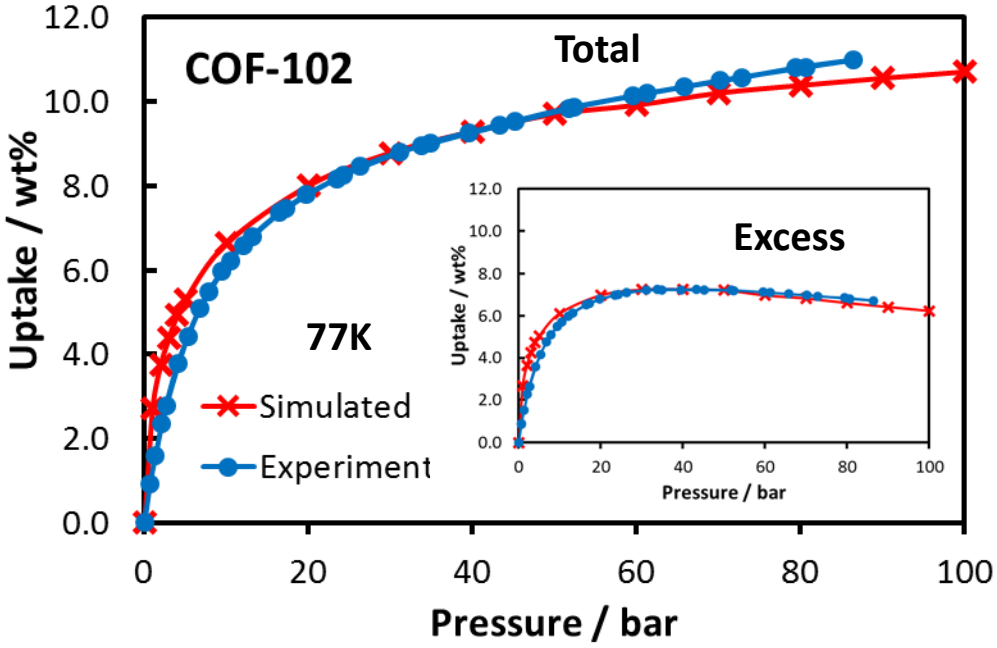
COF-102

Lightweight crystalline porous solids:

Covalent Organic Frameworks (COFs)

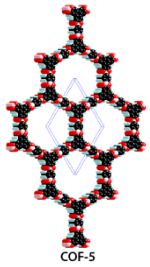
- Control of structure, topology, and interpenetration
- Lightweight materials
- Design of functionalities
- Suitable for metal impregnation

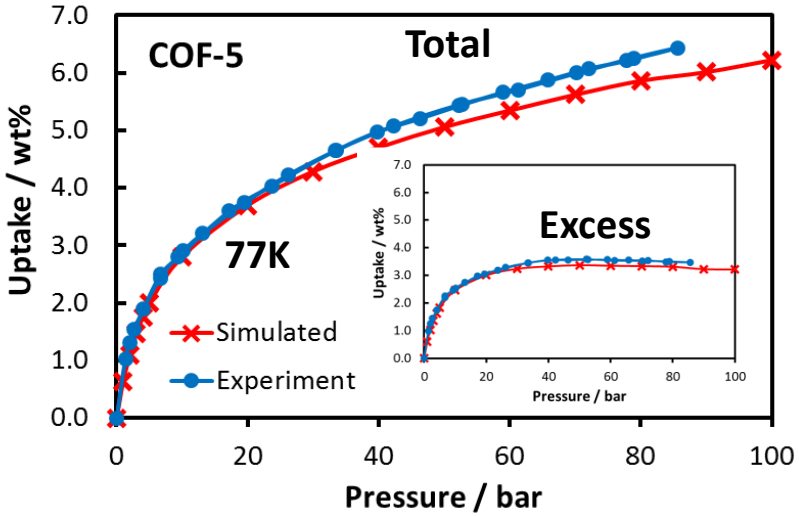
Theory and experiment agree
Thus can use Theory to identify the most promising metallated cases required to meet DOE requirements



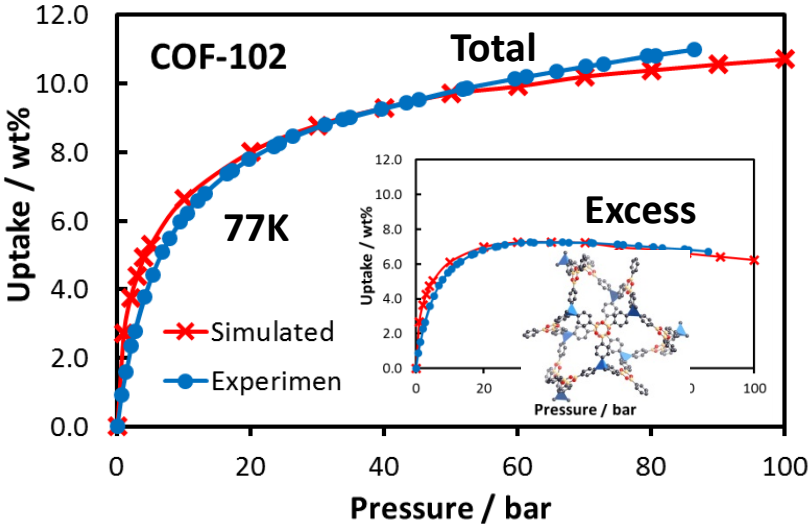
Excess and total H_2 uptakes in COF-102 and 103 are almost the same as that in MOF-177. However, binding energy is not high enough to meet the DOE targets. *JACS*, **2009** (exp).

Validation of theory by compare to Experiment: COFs

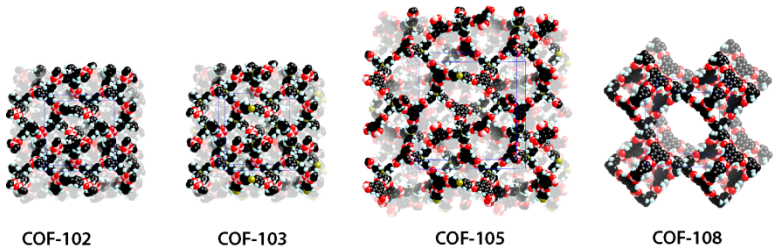


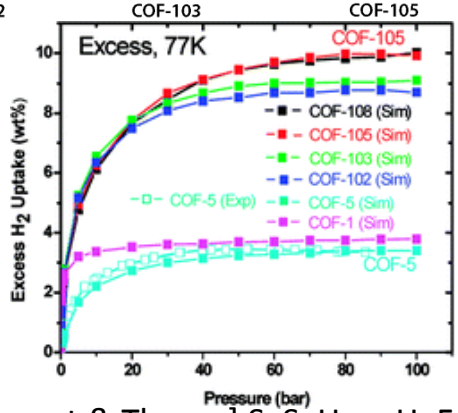


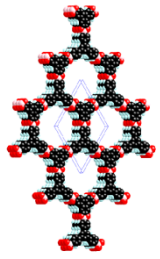
Furukawa et al, *JACS*, **2009** (exp).

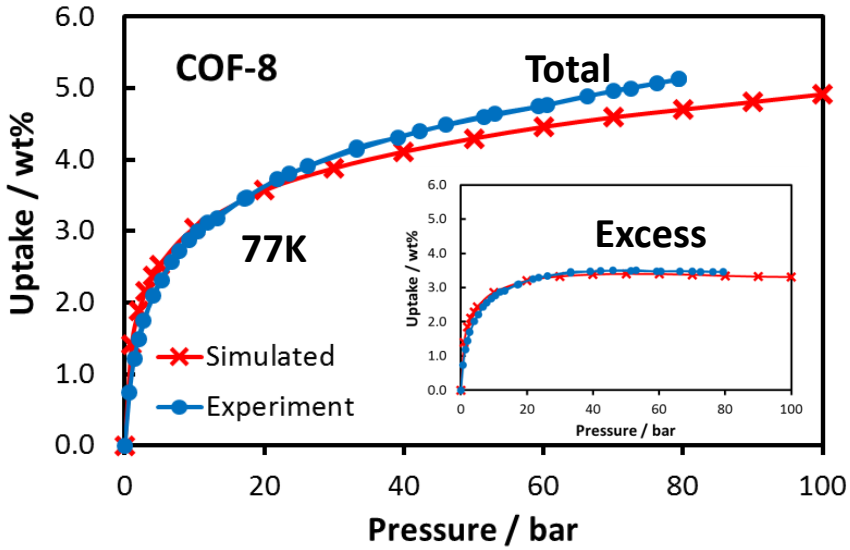


Furukawa et al, *JACS*, **2009** (exp).





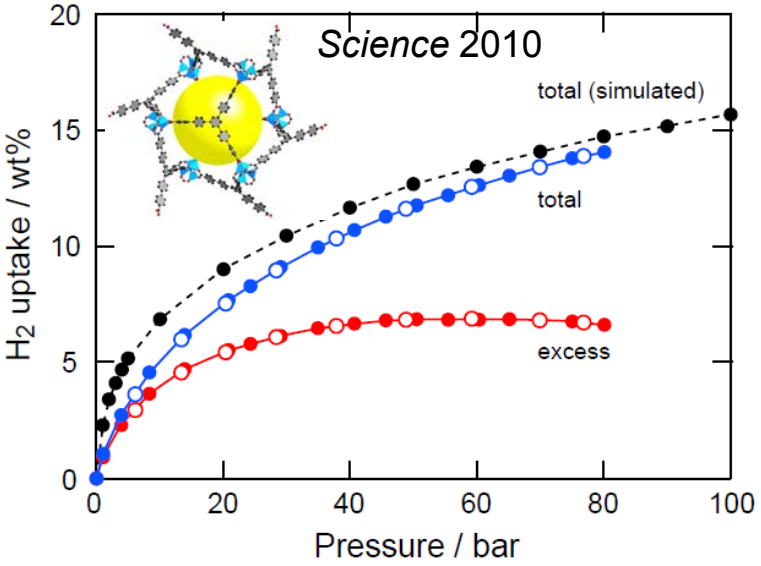




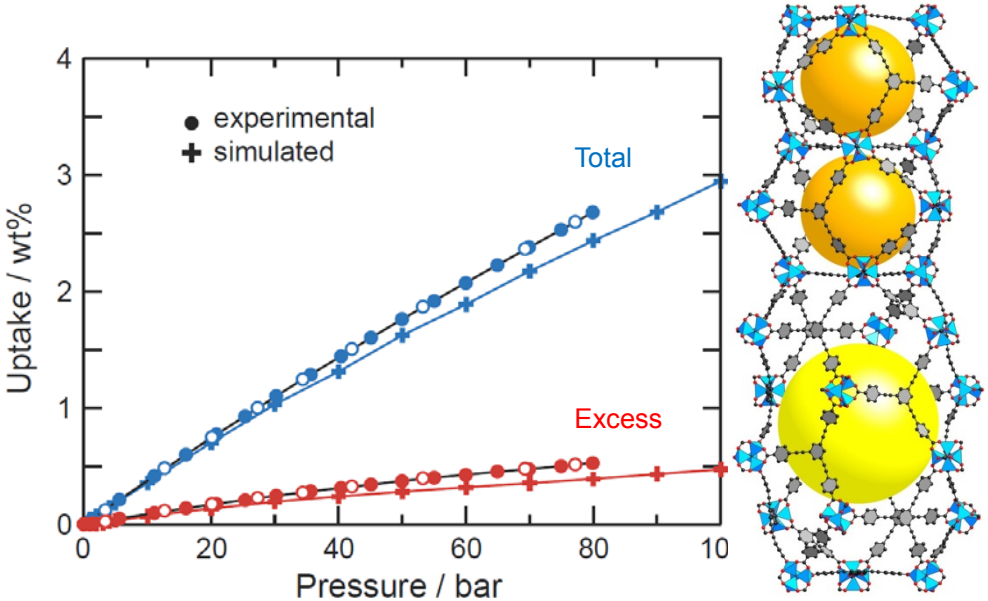
Furukawa et al, *JACS*, **2009** (exp).

[Experiment & Theory] S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard III, *J. Am. Chem. Soc. 130*, 35, 11580 ***(2008).***

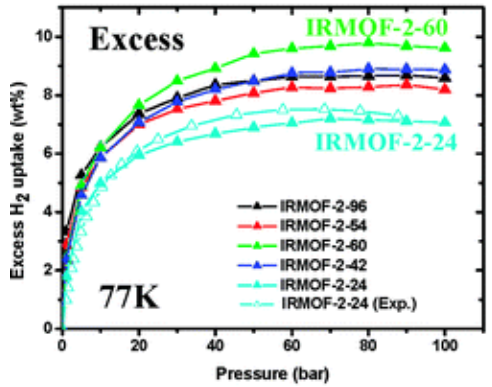
Validation of theory by compare to Experiment: MOFs



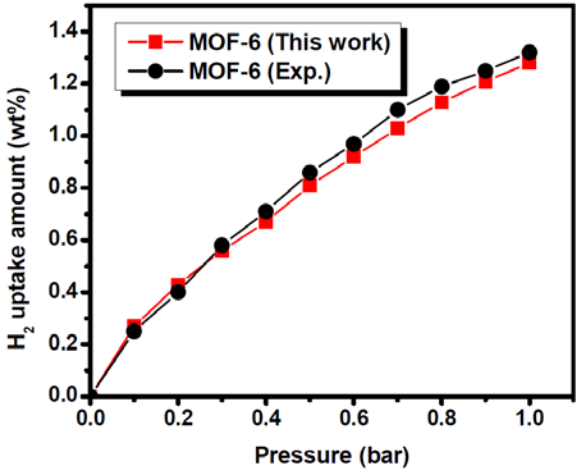
14 wt% total hydrogen uptake in MOF-200



2.7 wt% total hydrogen uptake in MOF-210



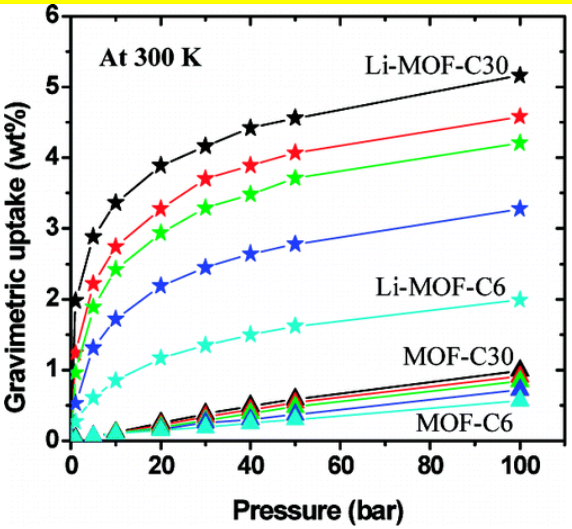
[Experiment] Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc. 128,* 3494 **(2006)** .
[Theory] S. S. Han, William A. Goddard III, *J. Phys. Chem. C 112,* 13431 **(2008).**

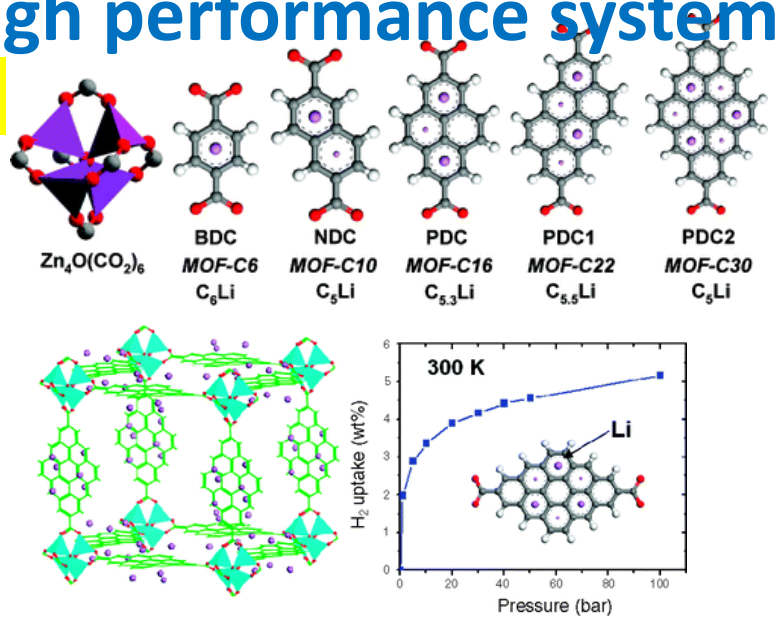


[Experiment] J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc. 128*, 1304 ***(2006).***
[Theory] S. S. Han, William A. Goddard III, *J. Am. Chem. Soc. 129,* 8422 ***(2007).***

Previous predictions of high performance systems

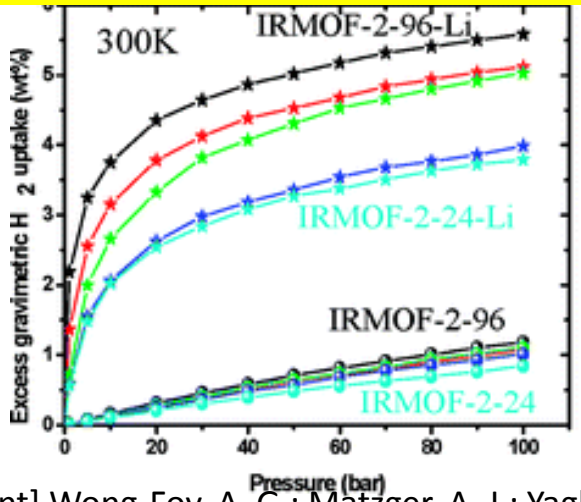
Li–MOF-C30 achieves over 5 wt % at 100 bar.

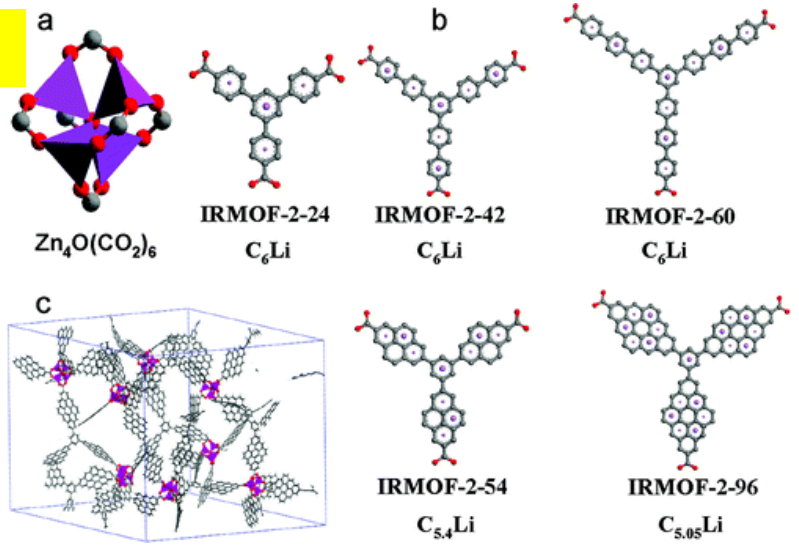




[Theory] S. S. Han, William A. Goddard III, *J. Am. Chem. Soc. 129,* 8422 ***(2007).***

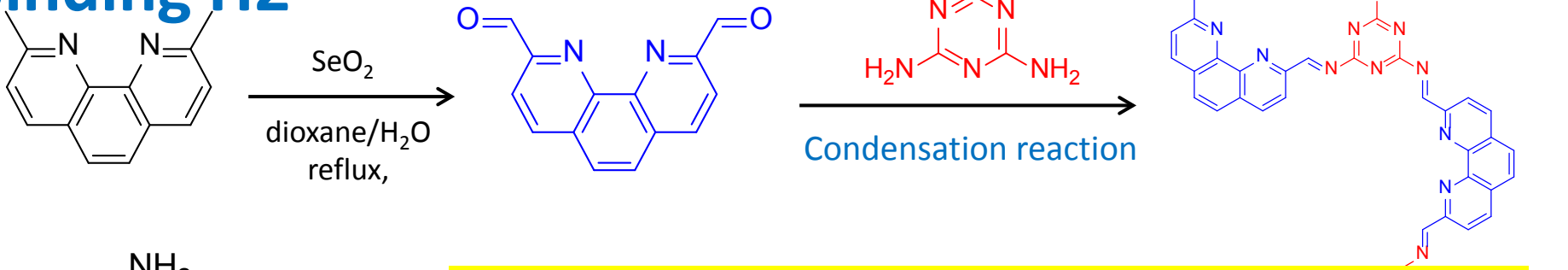
Li–MOF-C30 achieves over 5.5 wt % at 100 bar.

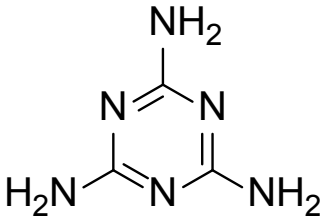




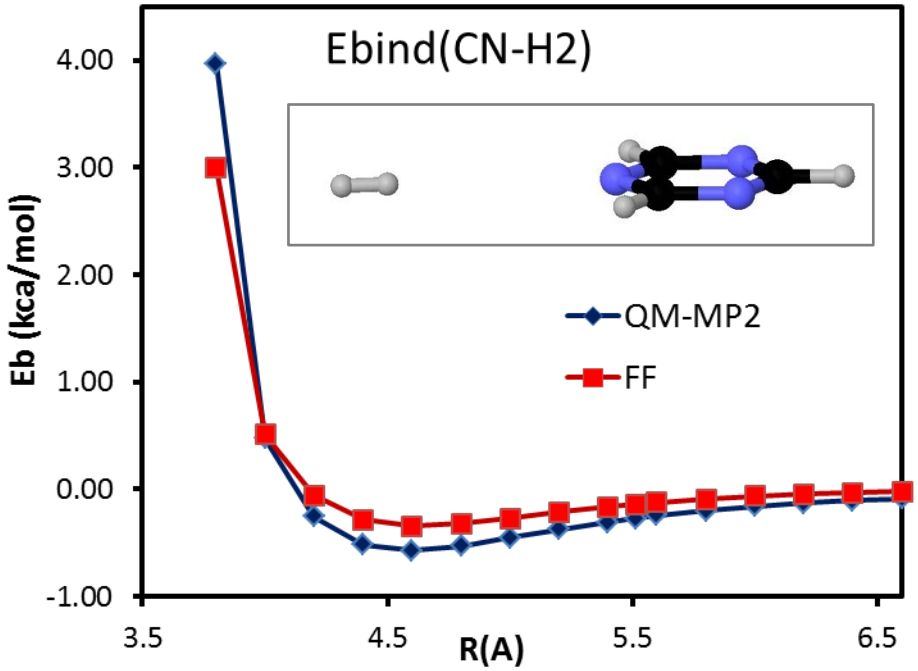
[Experiment] Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc. 128,* 3494 **(2006)** .
[Theory] S. S. Han, William A. Goddard III, *J. Phys. Chem. C 112,* 13431 **(2008).**

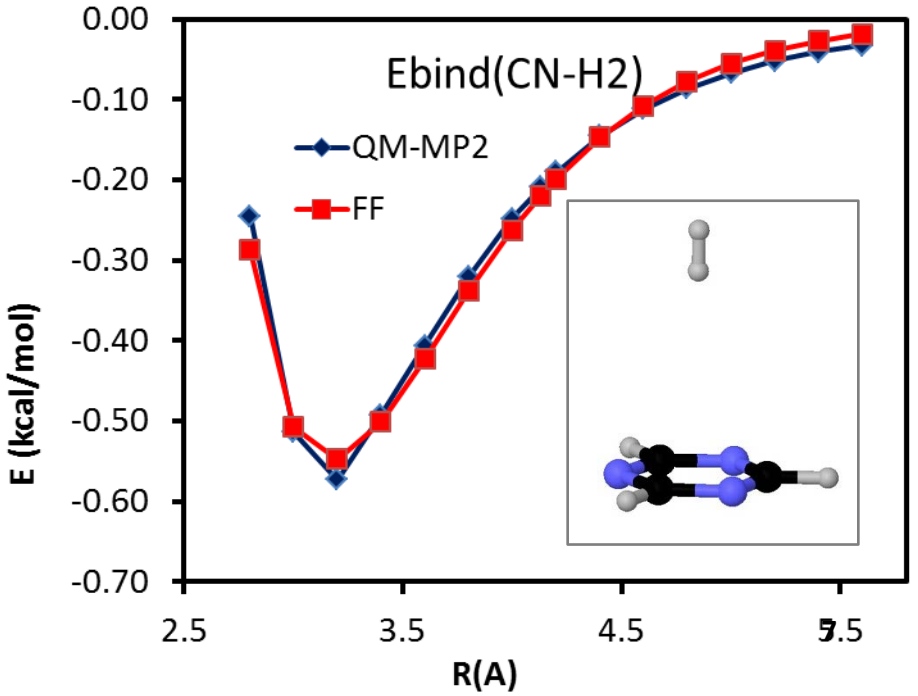
Design of COFs with metal binding sites for binding H2



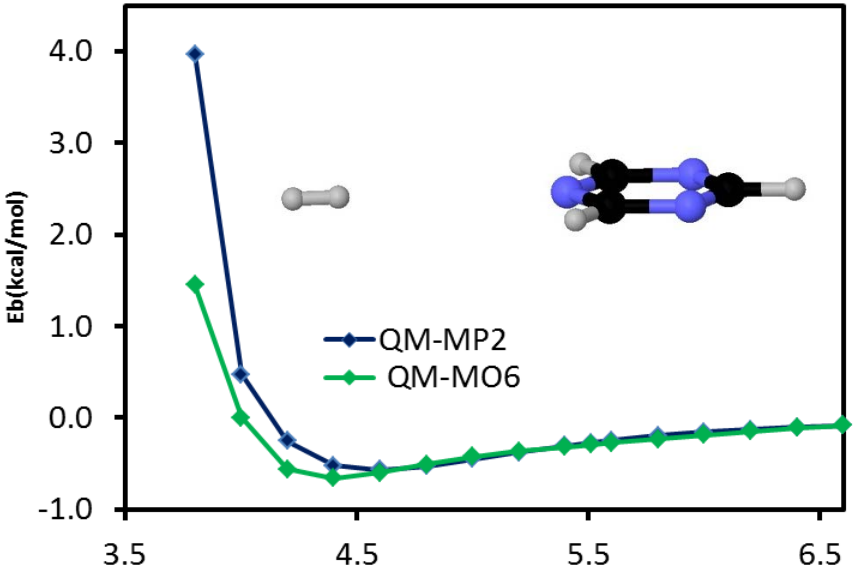


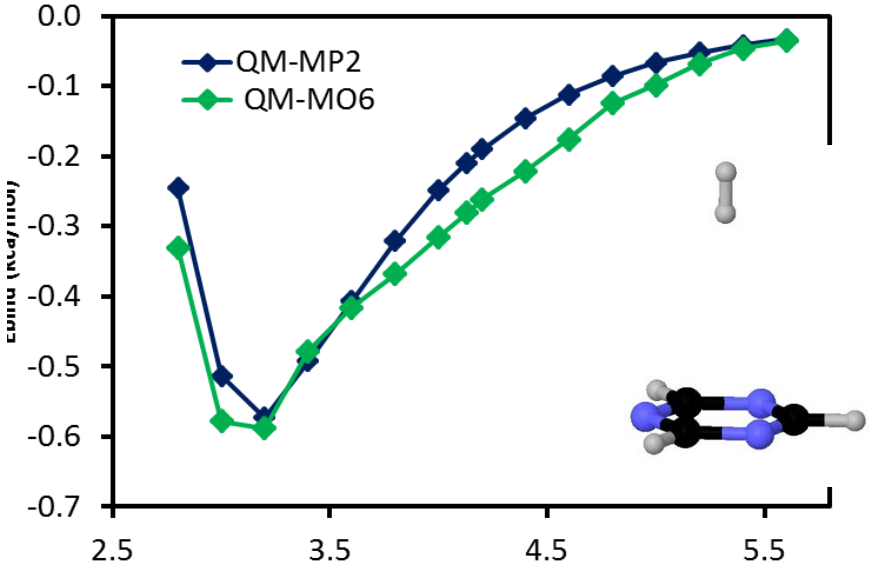
- We have constructed the FF for this class of COFs based on MP2 calculations
- We used this FF to predict promising systems.

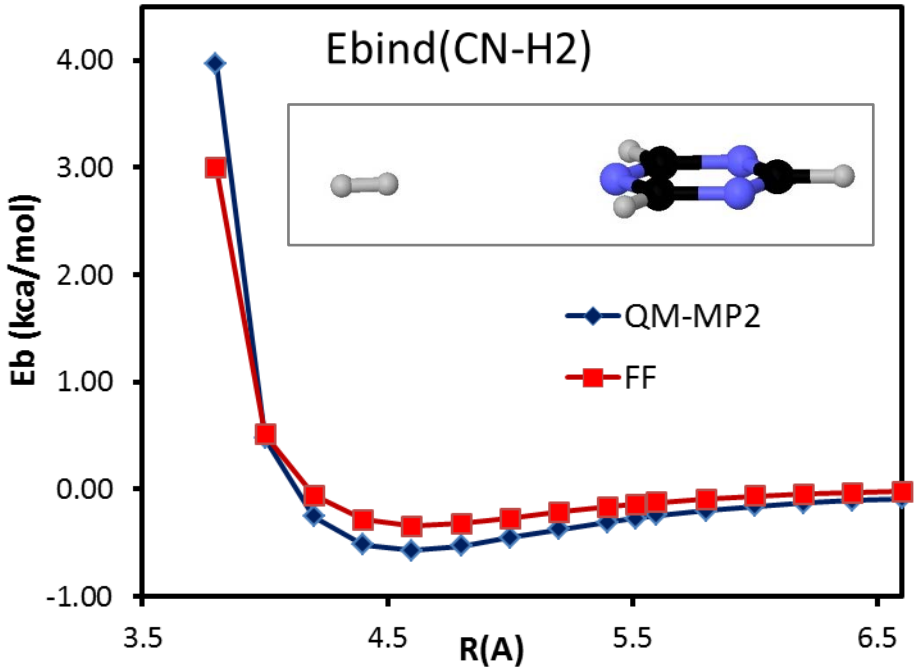


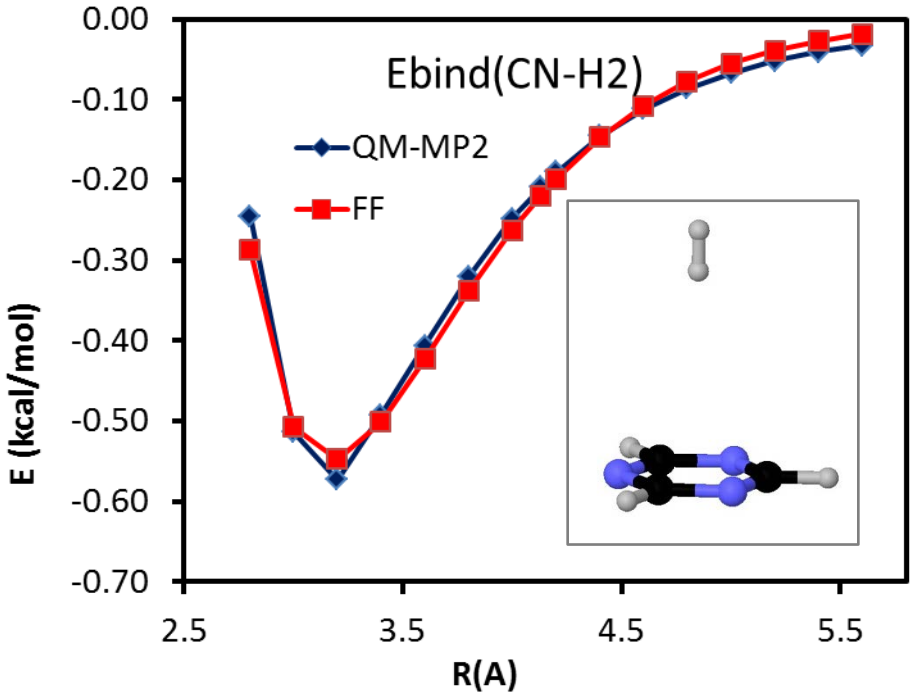


Development of 1st principles Force Field for Designing of COFs with metal binding sites



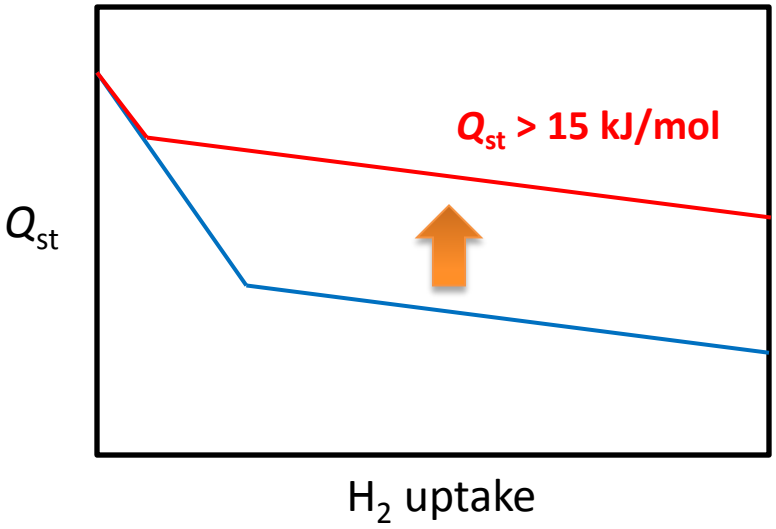


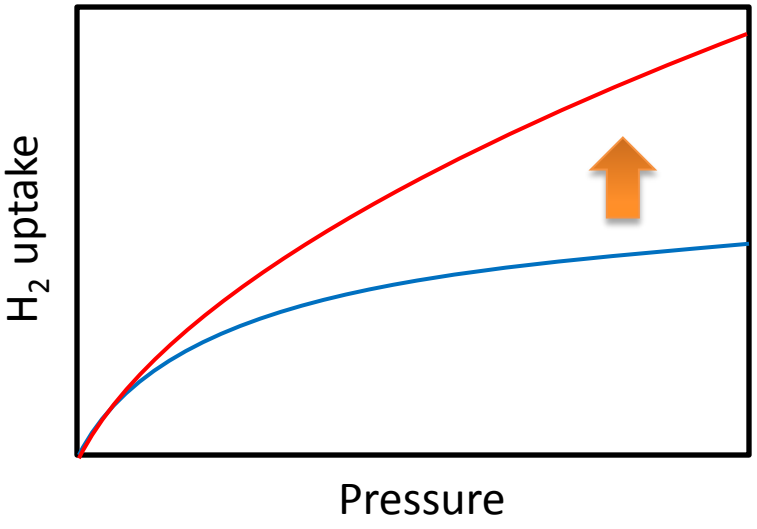




Strategy for achieving room temperature H_2 storage

How to increase binding energy (beyond the first 1-5 bar) and volumetric capacities to meet storage targets at room temperature?





- Heterogeneity always reduce delivery amount of H_2.
- Assuming that 40 g H_2/L is stored through one-to-one binding in MOF-5, 207 H_2 binding sites are necessary per unit cell (= correspond to 6.3 wt% H_2 uptake).
- But there are only 328 C, O, and Zn (non-hydrogen) atoms per MOF-5 unit cell.
- If each phenyl group in MOF-5 hold two metal Li and if each Li bind 4.3 H_2 molecules, we can achieve 40 g/L (= 6.0 wt%) uptake.

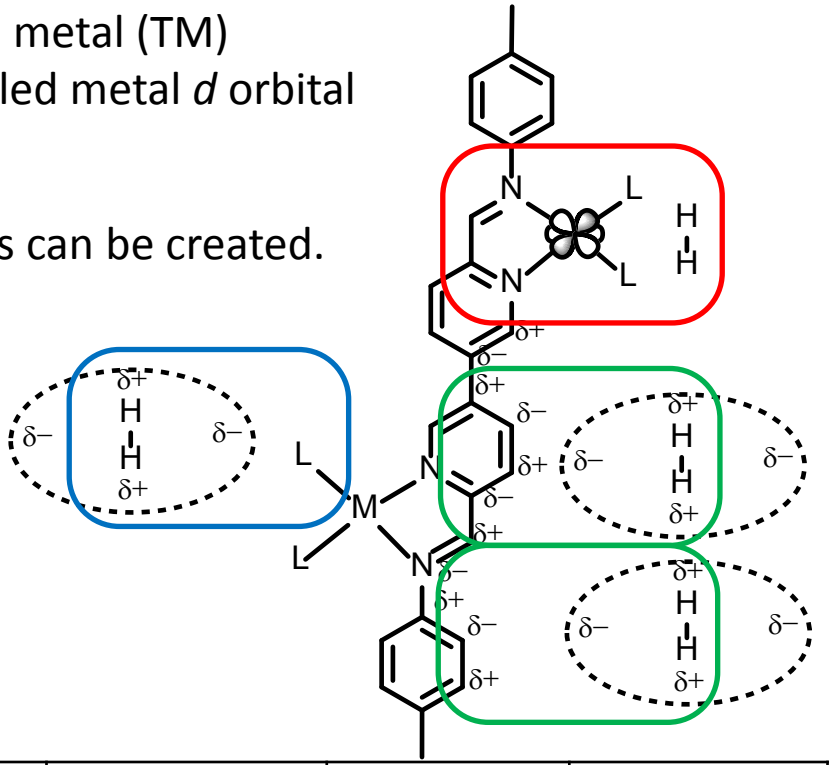
Need Materials with multiple H_2 adsorption sites (but not too strong) achieve 300K binding

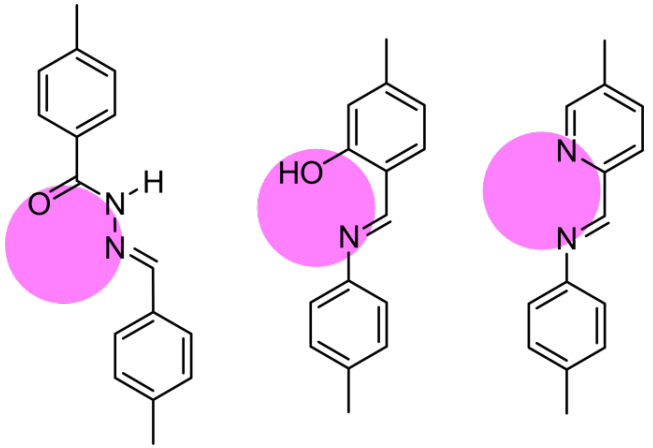
Approach: Create multiple hydrogen binding sites by metalation of COFs

H_2 is a weak Lewis base that can bind to transition metal (TM) because of the *back bonding* of electron from a filled metal *d* orbital to the antibonding orbital of H_2.

By metalating organic linkers multiple binding sites can be created.

- Estimate binding energy of H_2
- Effect of the oxidation state of TM
- Effect of the leaving groups (L)



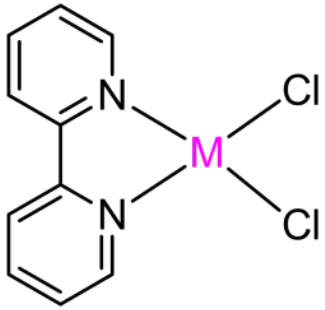


These units are ideal for binding metals controllably

Interaction	Charge - Quadrupole	Dispersive	Orbital interaction
Typical values (kJ/mol)	3.5 [a]	5-6 [b]	20-160 [c]

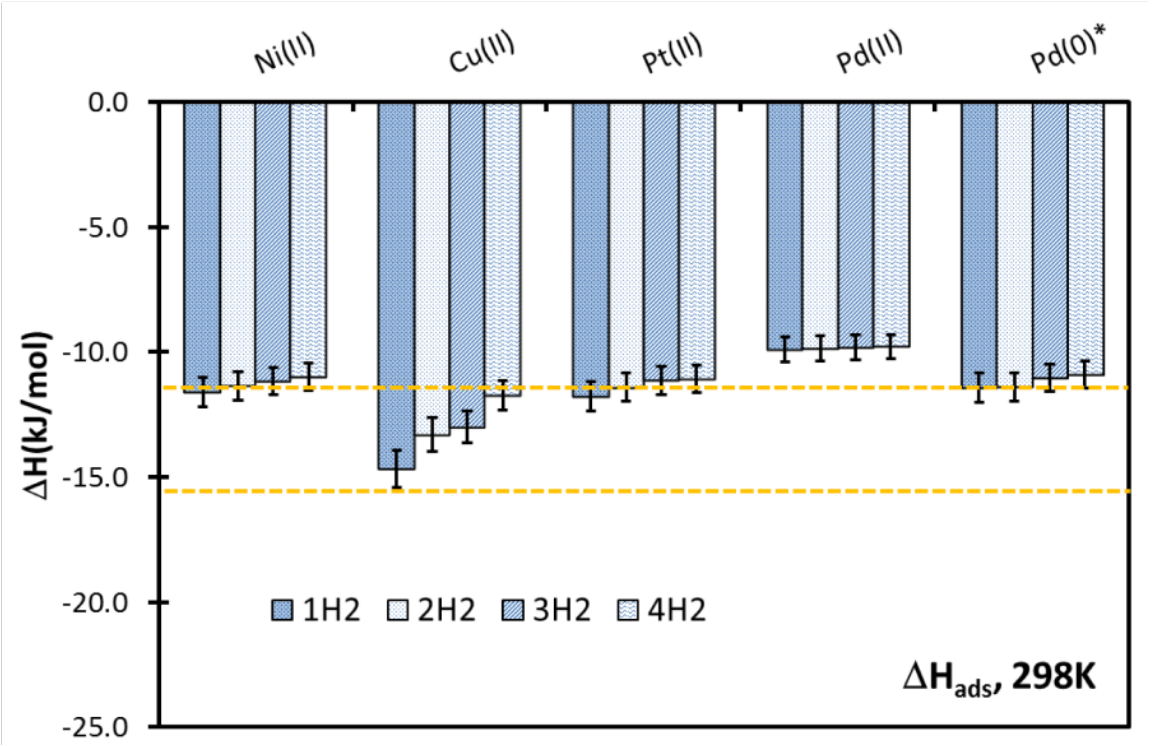
[a] *PCCP*, **2006**, *8*, 1357-1370. [b] *Langmuir*, **2006**, *107*, 1688-1700. [c] *Chem. Rev.*, **2007**, *107*, 4152-4205.

Accomplishments: found cases in which Binding energy is nearly the same after adsorption of 4 H_2 molecules



2,2'-bipyridine

BPY+$TMCl_2$



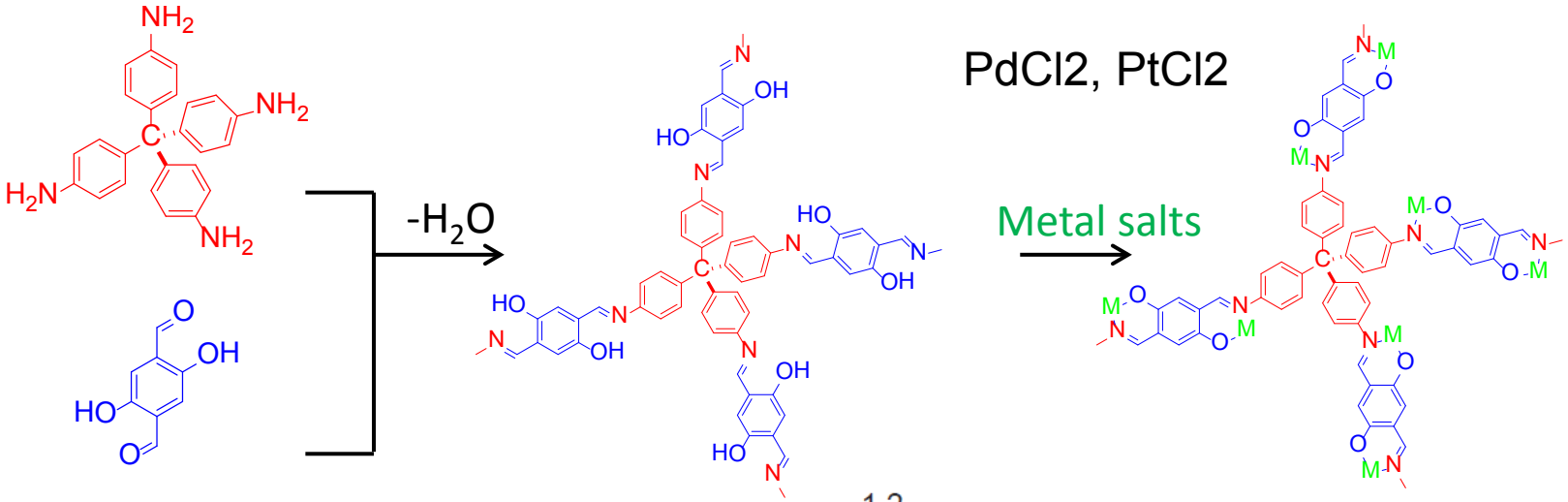
Accomplishments (this year)**:**

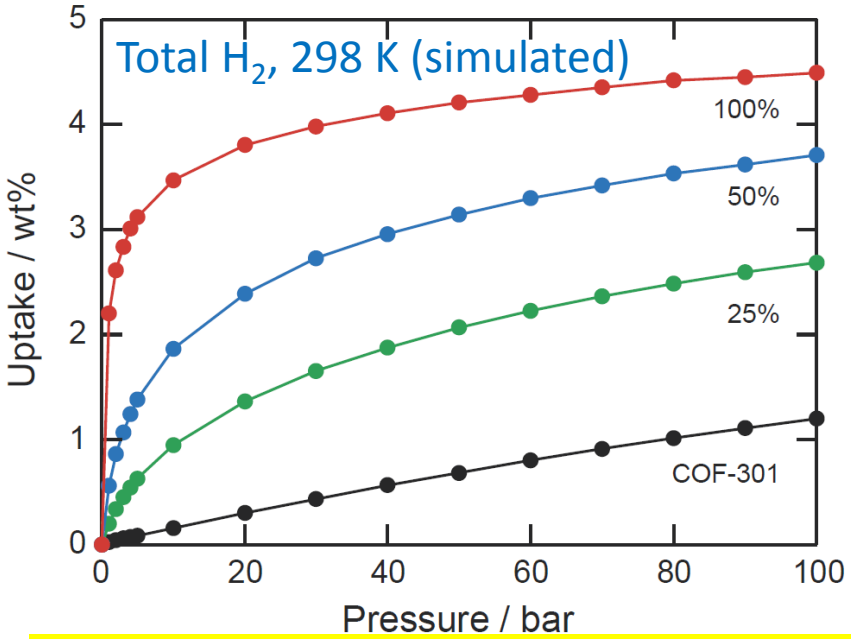
- The binding energy for third and fourth H_2 near the metal site was estimated.
- Similar binding energy (ΔH_{ads}) is observed for the first row transition metals and Pd.
- We found ΔH_{ads} is nearly the same even after 4 H_2 molecules are adsorbed.
- 30 to 40 H_2 can bind to the linker + MCl_2 moiety, if there is enough space.

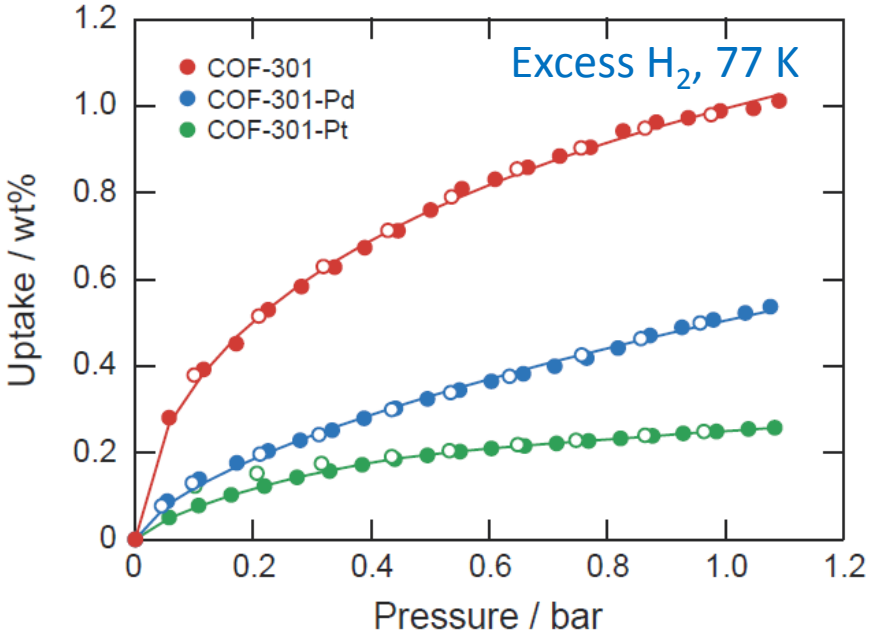
Approach:

- Need to design new COF materials, which can provide enough space to confine H_2 without losing metal density per volume.

Our first attempts on COF-301 (last year)

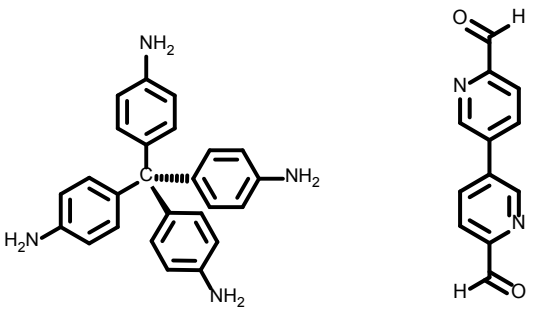






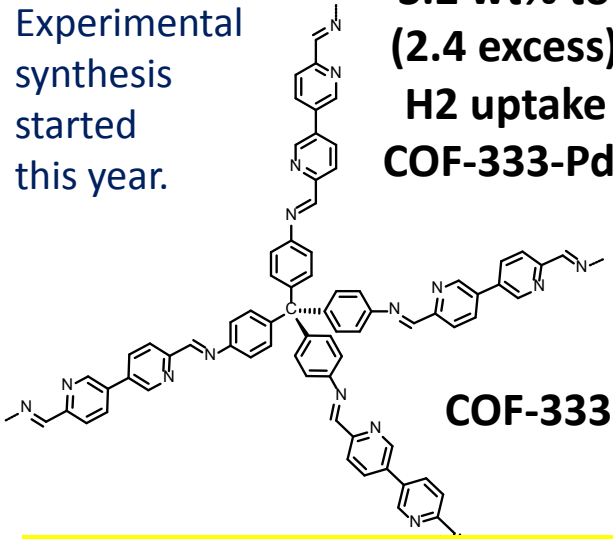
- Metalated materials maintain reduced porosity
- Experimental H_2 uptake was much smaller than predicted one, because of unreacted metal salts in pores

New approach: functionalization of COF-300



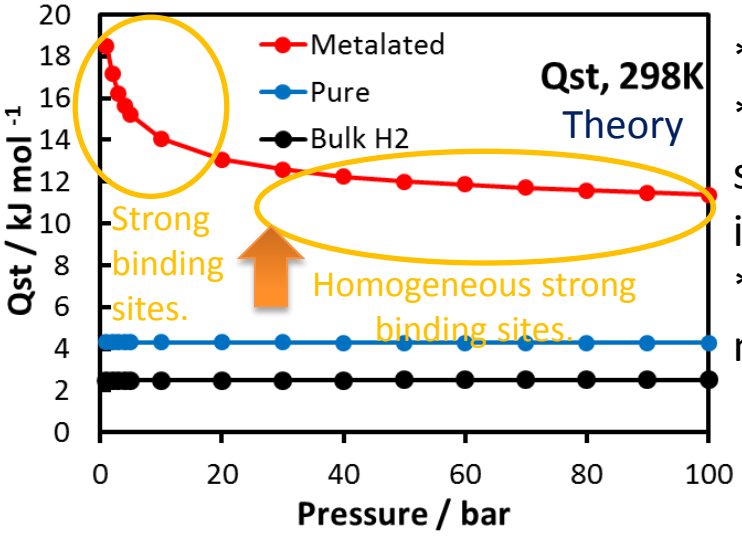
Experimental synthesis started this year.

3.2 wt% total (2.4 excess)RT H2 uptake in COF-333-PdCl2

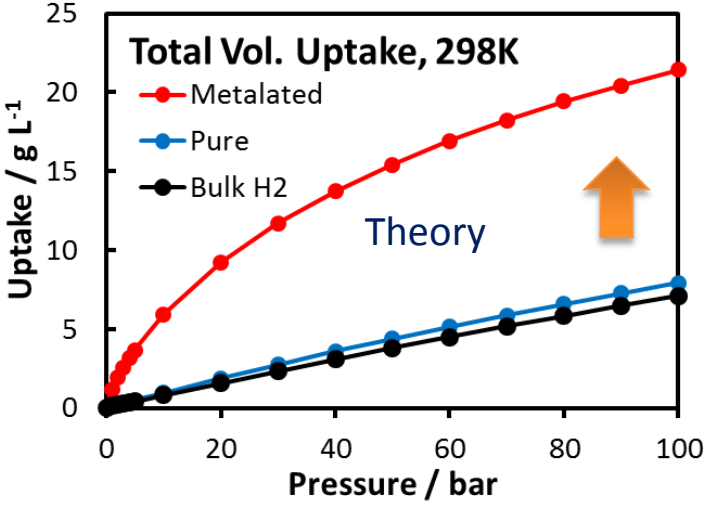


COF-333

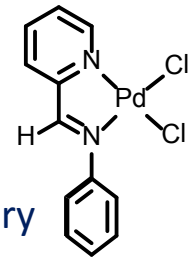
Theory

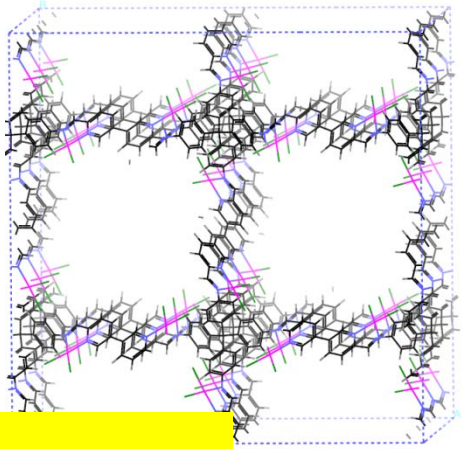


*Multiple sites.
*Stronger binding sites where the $PdCl_2$ is exposed to the pore
*Higher Qst for the metalated framework.



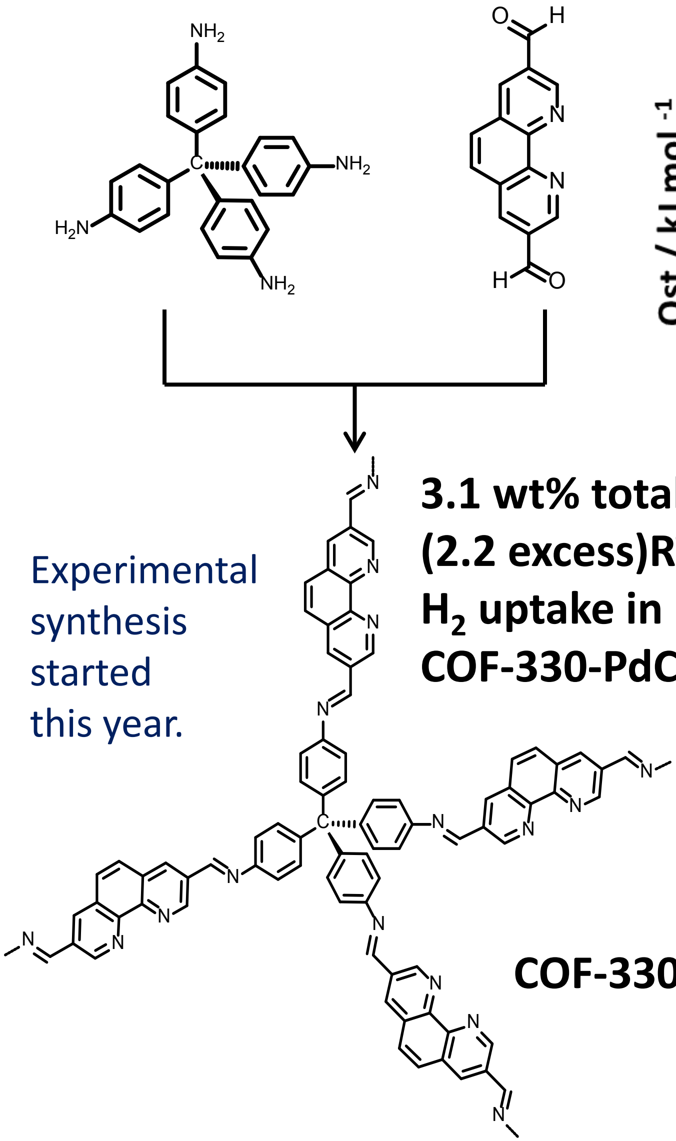
Theory





- Higher initial Q_{st} is expected compared to COF-330.
- Metalation increases by ~300% in the volumetric capacity and by ~50% in the gravimetric capacity because of higher density of metals in the structure.

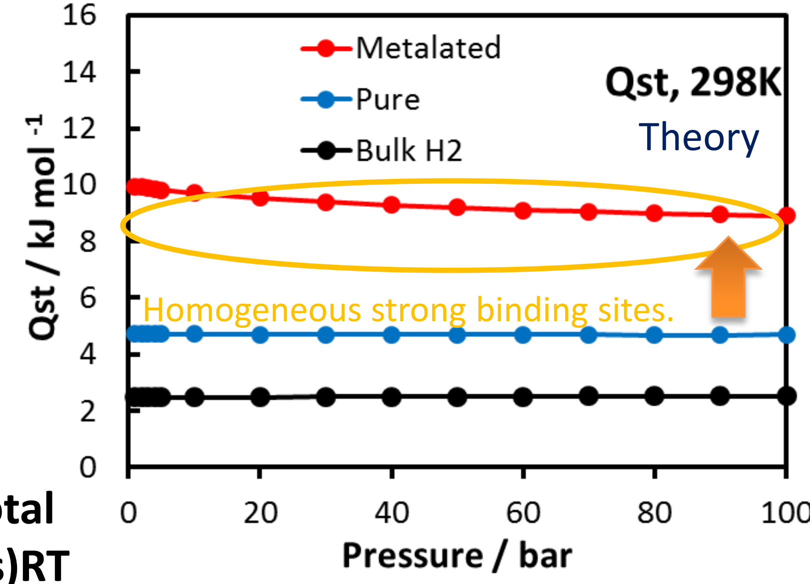
New approach: functionalization of COF-300

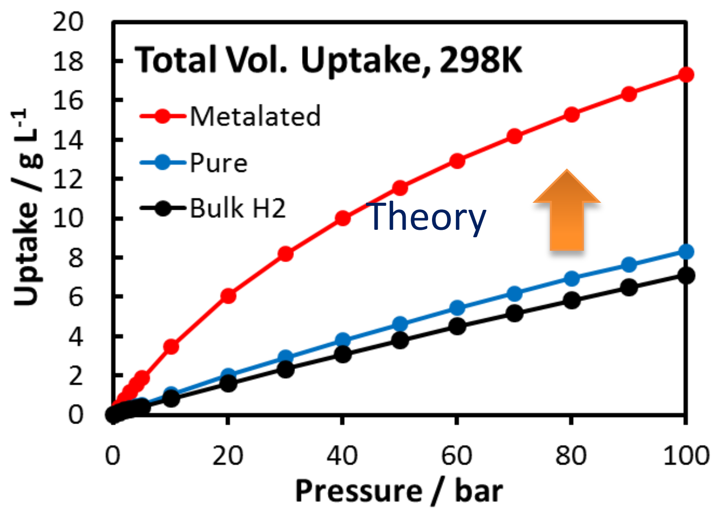


Experimental synthesis started this year.

3.1 wt% total (2.2 excess)RT H_2 uptake in COF-330-$PdCl_2$

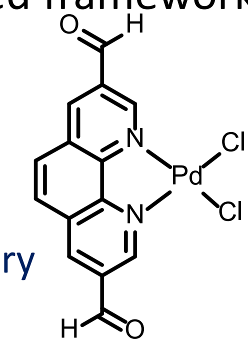
COF-330



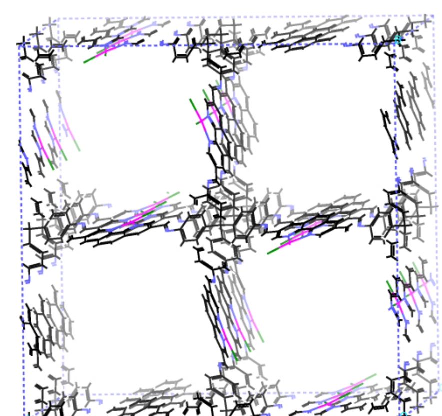


Theory

*Multiple sites.
*The metalated sites are not very accessible and the Qst improves slightly.
*Higher Qst for the metalated framework.

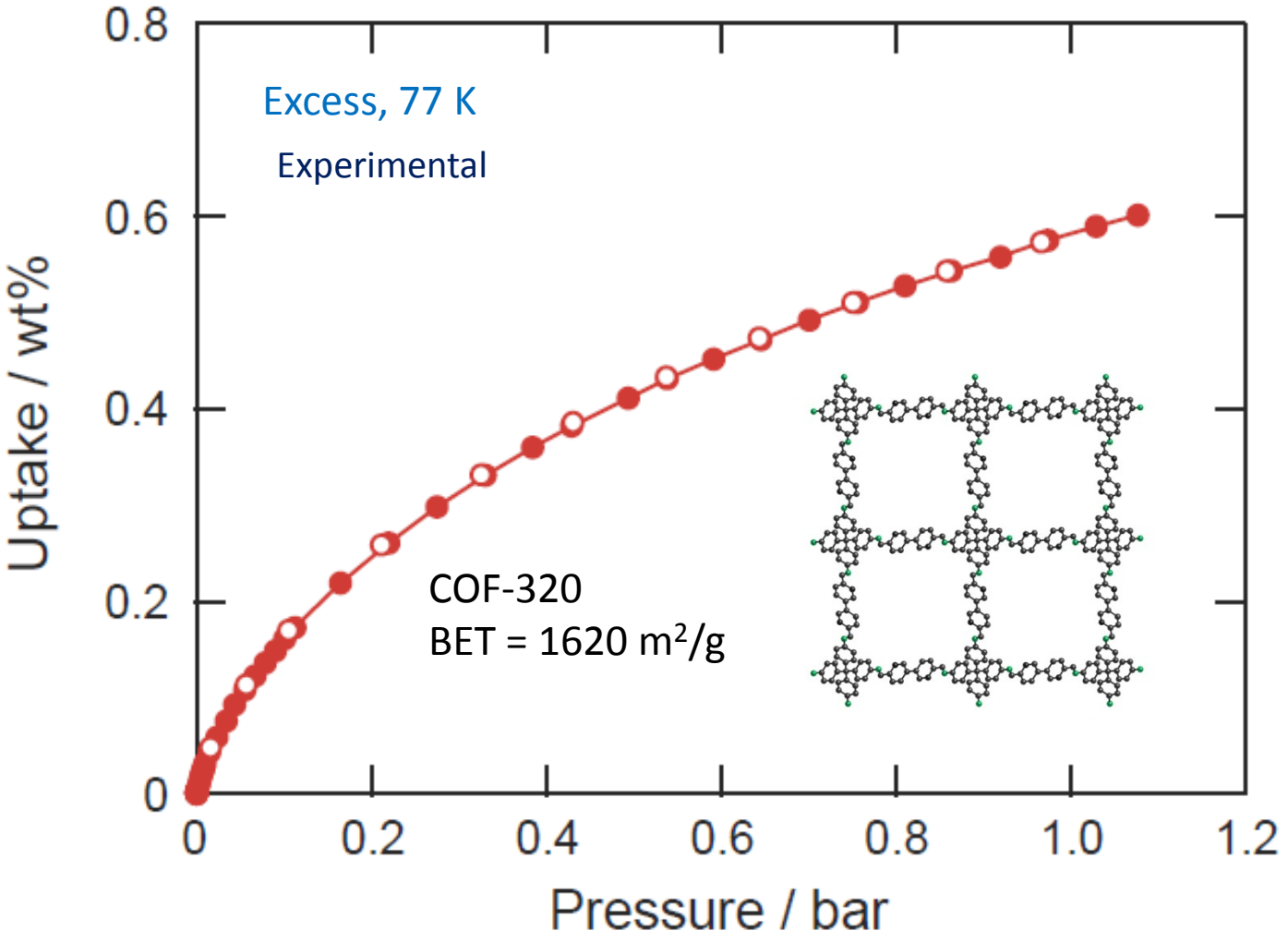


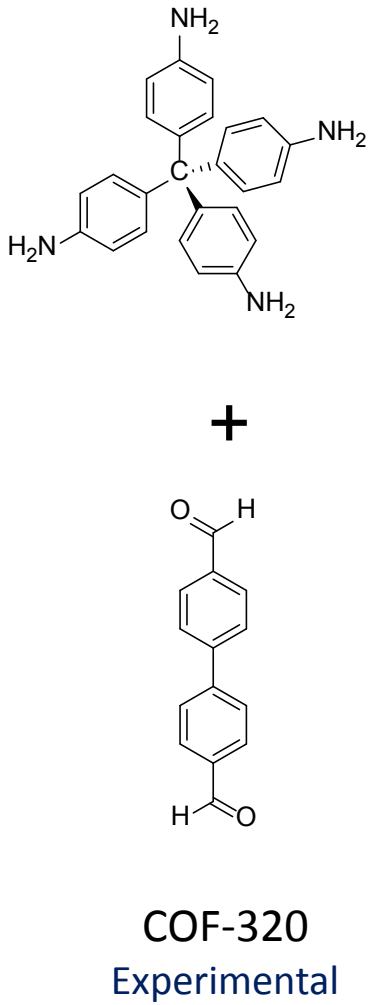
Theory



Metalation of phenanthroline moieties increases by 200% in the volumetric capacity and by 50% in the gravimetric capacity to the pristine material.

Preliminary excess H_2 uptake by COF-320 at 77 K

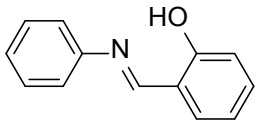
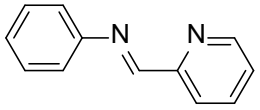
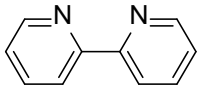
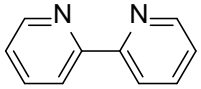
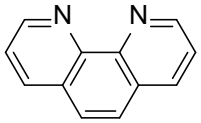




COF-320
Experimental

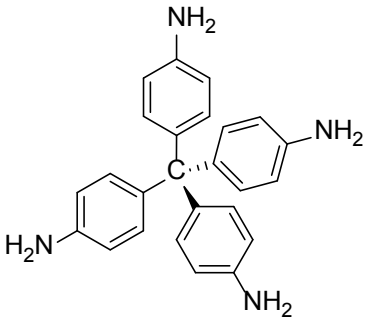
BET area of COF-320 is larger than COF-300 and 301, but H_2 uptake is smaller than these materials. Activation procedures must be optimized.

Literature: Large open pores are key to successful metalation

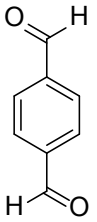
Compound	Metal binding site	Pore size	Metals impregnated	Porosity	Ref
COF-301		6 Å	$PdCl_2$ $PtCl_2$	Significant SA drop	AMR 2011
UMCM-1 derivative		20 Å	$PdCl_2$	ca. 60%	JACS 2008
MOF-253		8 Å	$Cu(BF_4)_2$ $PdCl_2$	Significant SA drop	JACS 2011
MOF-267		7 Å	Only low metalation yield	–	Unpublished
New MOF		12 Å	$Cu(BF_4)_2$ $PdCl_2$	ca. 50%	Unpublished

Larger pore diameter should be important for successful metalation reactions when binding constants are large enough to allow the metalation.

New approach: Successful isoreticular pore expansion and functionalization of COF-300

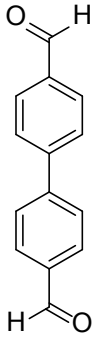


+

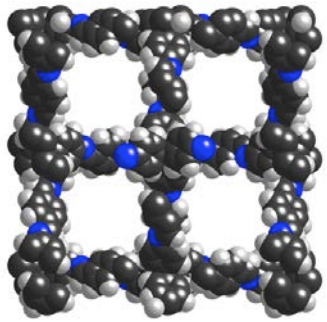


COF-300

expansion

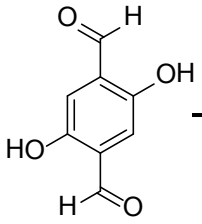


COF-320*



Space filling model of COF-300

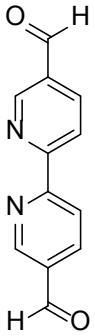
functionalization



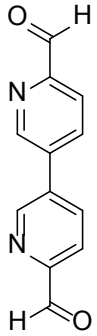
COF-301

MTV-COF*

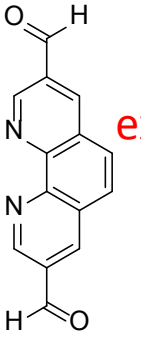
functionalization



COF-322

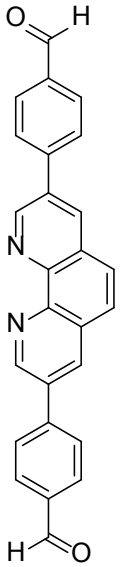


COF-333*



COF-330

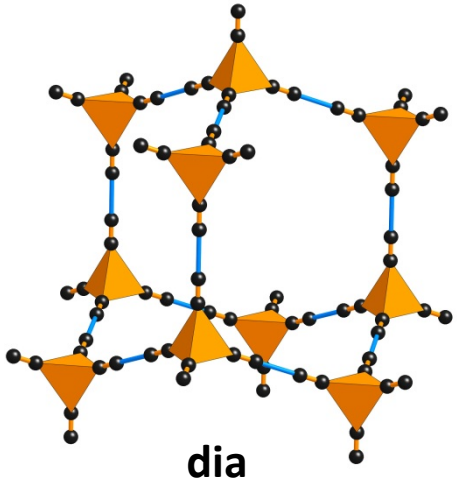
expansion



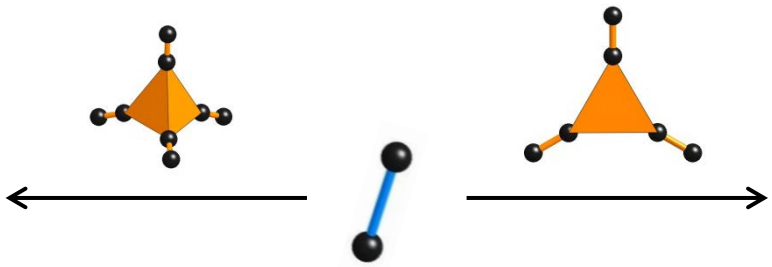
COF-340*

* Synthesis of these COF materials started this year.

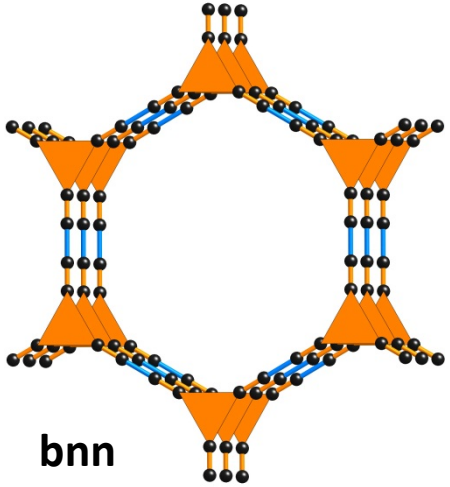
Accomplishments: Gram scale synthesis of organic links (1)



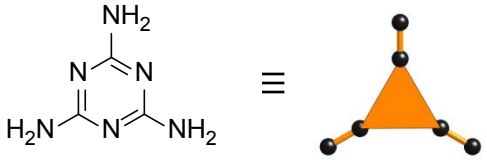
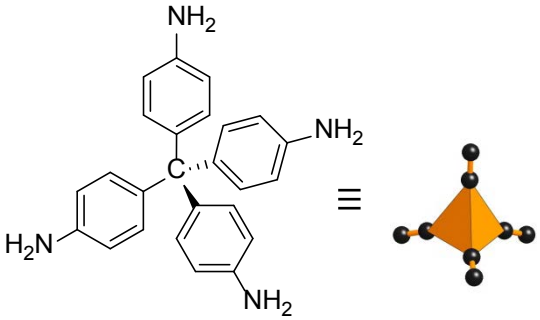
dia



Metal binding sites should be introduced into both 2D and 3D COFs.

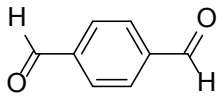
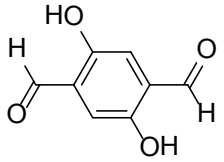
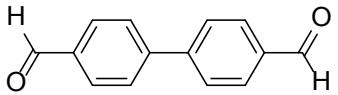
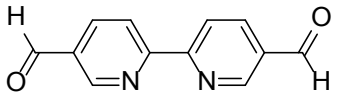
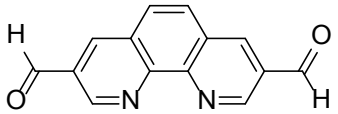
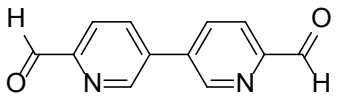
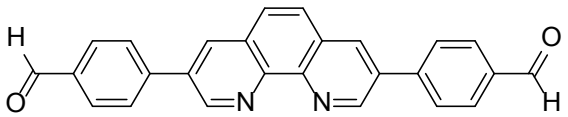


bnn

Structure	Link for COF-*n*	Synthetic steps	Scale available
	2D COFs 3D COFs	Commercially available	> 10 gram scale
	3D COFs (**dia**)	3 steps	gram scale*

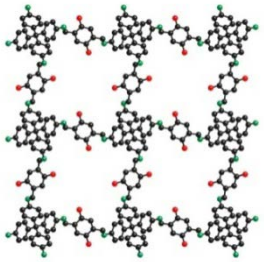
*Large scale synthesis was achieved this year.

Accomplishments: Gram scale synthesis of organic links (2)

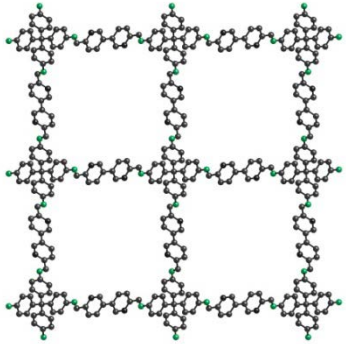
Structure (≡)	Link for COF-*n*	Synthetic steps	Scale available
	**COF-300**	Commercially available	> 10 gram scale
	**COF-301**	1 steps	gram scale
	**COF-320**	Commercially available	> 10 gram scale
	*COF-322*	1 step (based on a literature)	n/a
	*COF-330*	Developing synthetic conditions	n/a
	**COF-333**	2 steps	gram scale*
	**COF-340**	3 steps	gram scale*

*Large scale synthesis was achieved this year.

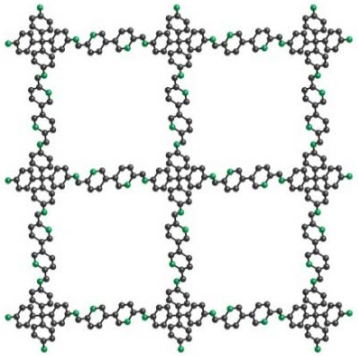
Successful synthesis of MOFs with expanded links



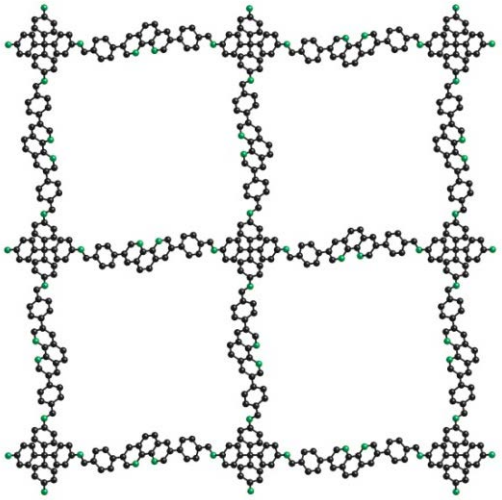
COF-301



COF-320



COF-333



COF-340

COF-*n*	Pore size (Å)	Metal binding site	Status	References
COF-300	8	n/a	Expt	JACS 2009
COF-301	6	Iminophenol	Expt and Calc	AMR 2011
COF-320	12	n/a	Expt	**AMR 2012**
COF-322	12	Bipyridine	Not started	
COF-330	12	Phenanthroline	Calc	**AMR 2011**
COF-333	12	Iminopyridine	Expt and Calc	**AMR 2011**
COF-340	19	Phenanthroline	Expt	**AMR 2011**

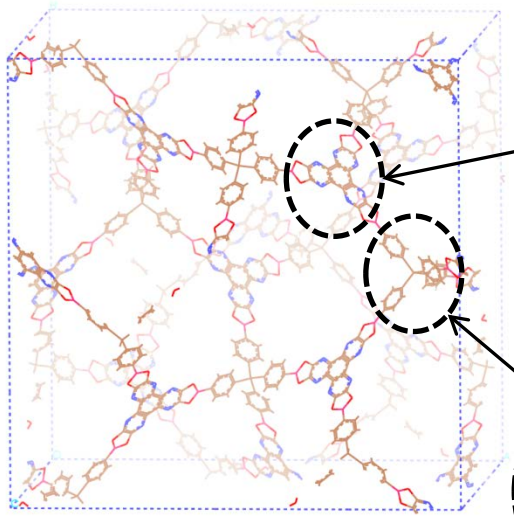
Metal binding sites are introduced through the condensation reaction and/or by use of linkers with phenanthroline/bipyridine units.

Summary of porosity data of COFs

COF-*n*	Experimental		Simulation		References
	BET SA (m^2/g)	Excess H_2 uptake at 1 bar and 77 K (wt%)	Total H_2 uptake at 100 bar and 298 K (wt%)	Initial Q_{st} (kJ/mol)	
COF-300	1360	1.1	n/a	n/a	JACS 2009
COF-301	840	1.0	1.2	6.0	AMR 2011
COF-320	1620	0.6	In progress	In progress	**AMR 2012**
COF-330	n/a	n/a	2.2	4.7	**AMR 2012**
COF-333	In progress	In progress	2.4	4.3	**AMR 2012**
COF-340	In progress	In progress	In progress	In progress	**AMR 2012**
COF-330-Pd*	n/a	n/a	3.1	9.9	**AMR 2012**
COF-333-Pd*	n/a	n/a	3.2	18.5	**AMR 2012**

* Doubly interpenetrating structures were used for both calculations.

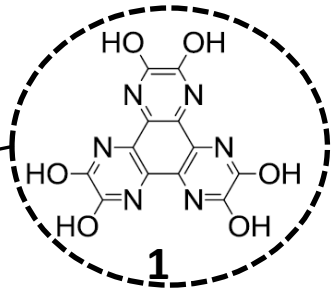
New Approach: Hexa-azatriphenylene COFs



1+3

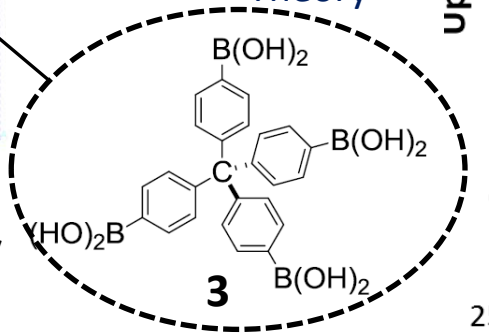
COF102-Hat-Pd

Metalation/ Pd



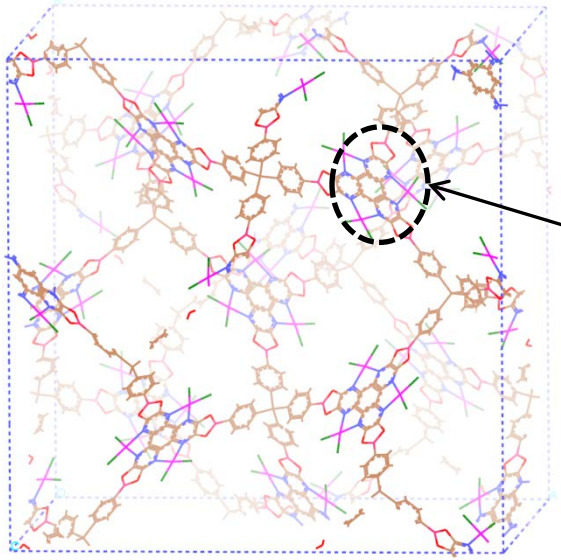
1

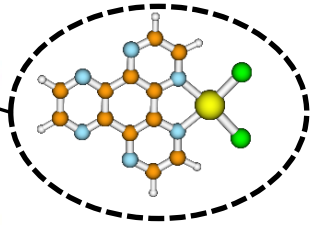
Theory



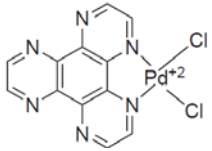
3

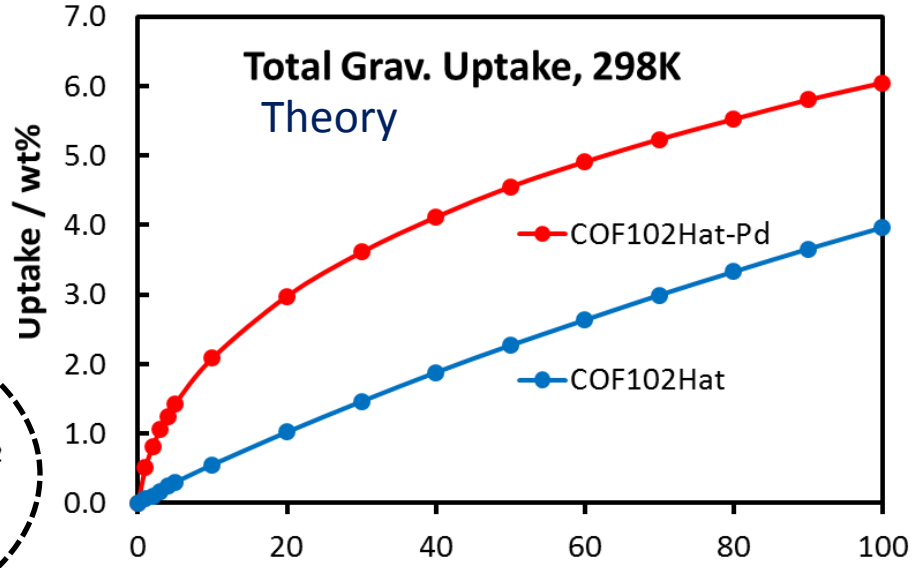
COF102-Hat



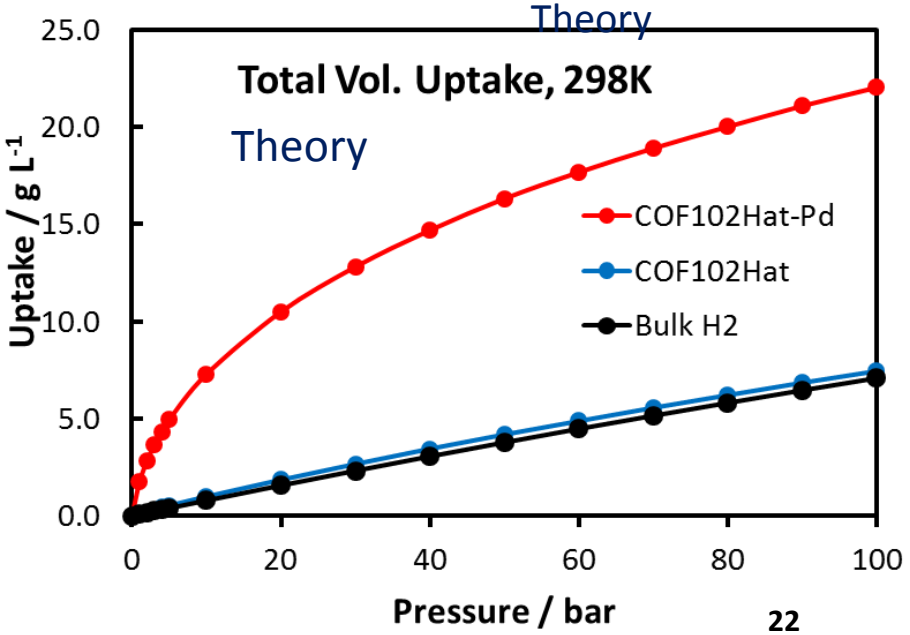


Theory



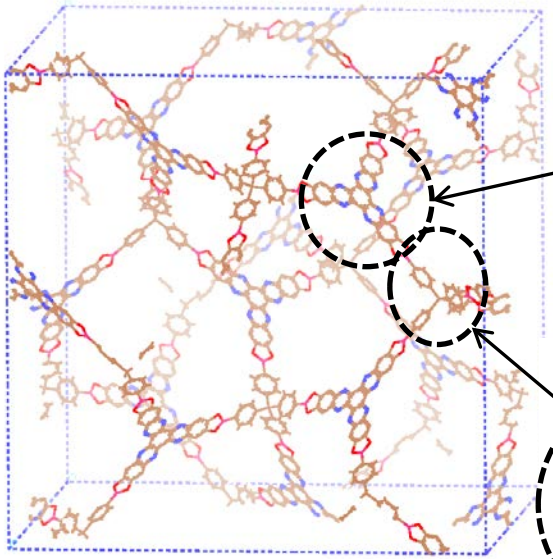


Theory



[Theory] JL Mendoza-Cortes, H. Furukawa, OM Yaghi, WA Goddard III, *In preparation.* ***(2012).***

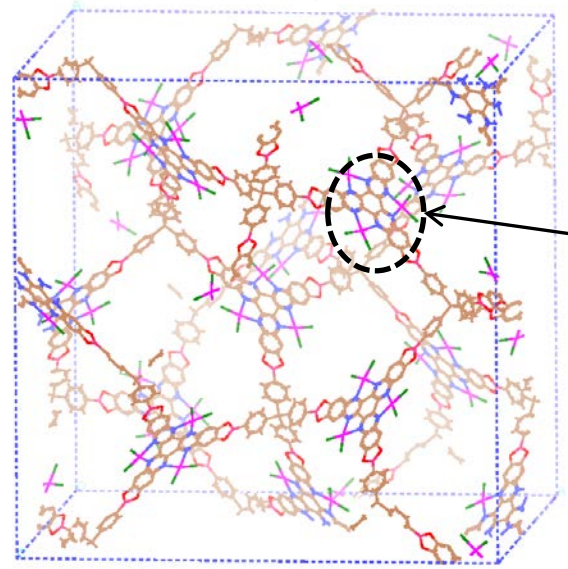
New Approach: Hexaazatribyphenylene COFs

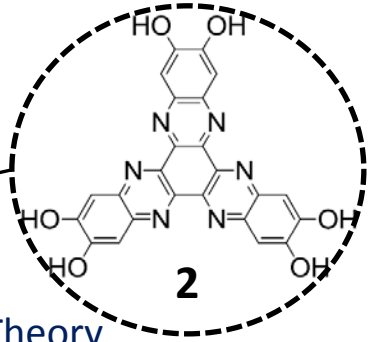


2+3

COF102-Hatb-Pd

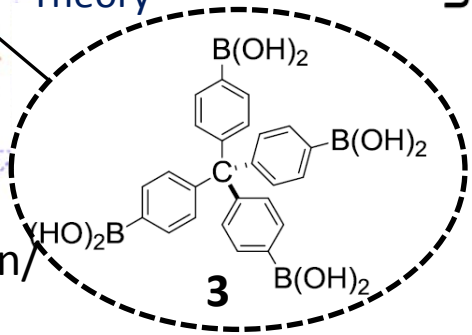
Metalation / Pd





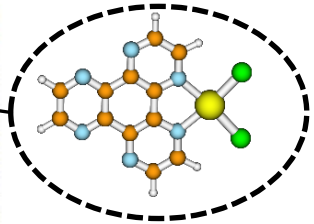
2

Theory

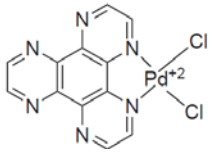


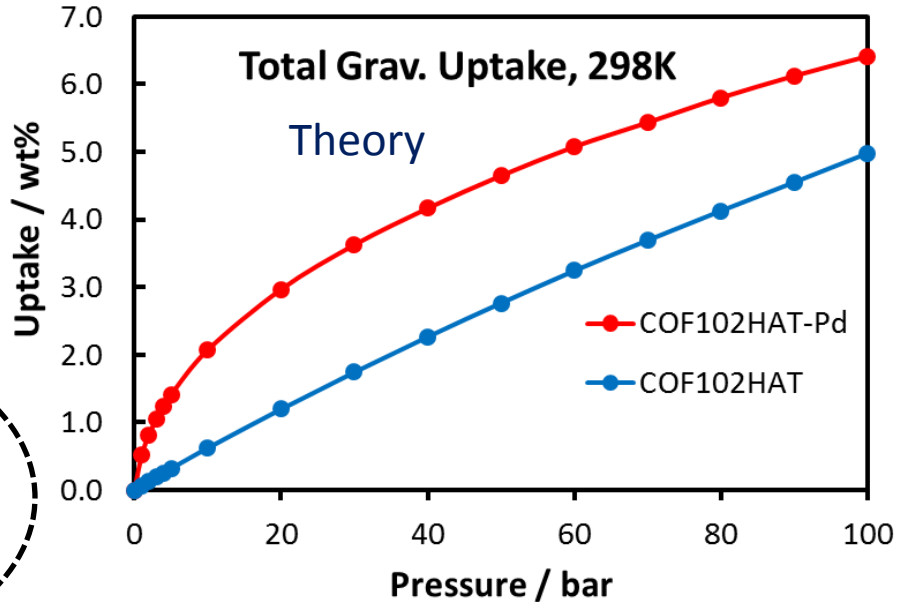
3

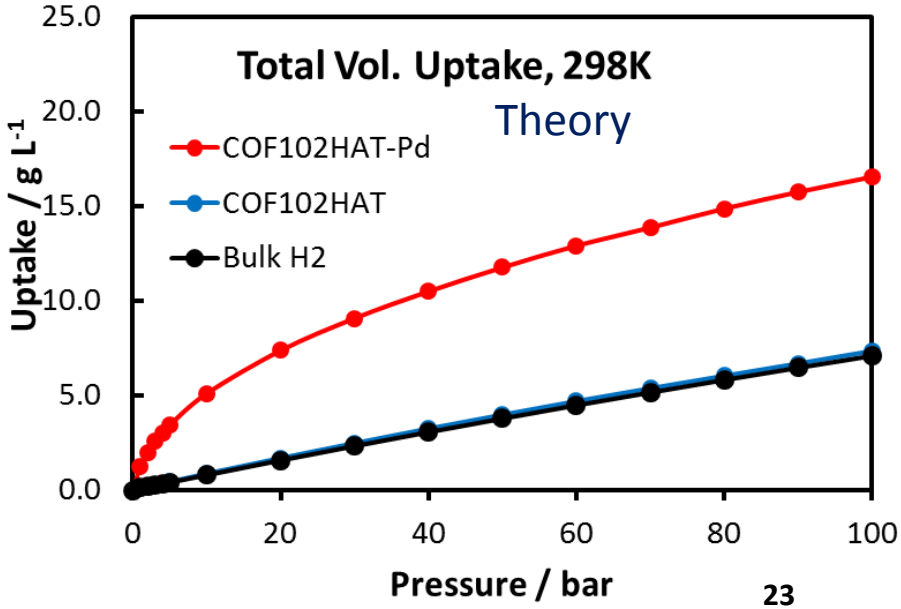
COF102-Hatby



Theory







[Theory] JL Mendoza-Cortes, H. Furukawa, OM Yaghi, WA Goddard III, *In preparation.* ***(2012).***

Summary

UCLA team

- Synthesized new air stable COFs through imine condensation (COF-320 and 340)
- Performed metalation experiments of COFs (MTV-COF, phenanthroline-MOF/COFs)
- Synthesized two low density COFs with triptycene unit (0.15-0.21 g/cm^3)
- Summary: synthesized COFs which are amenable to functionalization and in accordance to the predicted ones. If we metalate these, we expect room temperature storage (4 wt% total H_2 uptake).

Caltech team

- Metalation of phenanthroline moieties COF-330-PdCl2. Increases by 200% in the volumetric capacity and by 50% in the gravimetric capacity to the pristine material) leads to 3.1 wt% total (2.2 excess)RT H_2 uptake
- COF-333-PdCl2. Metalation increases by ~300% in the volumetric capacity and by ~50% in the gravimetric capacity because of higher density of metals in the structure). Leads to 3.2 wt% total (2.4 excess)RT H_2 uptake
- Predicted binding energy with all first row transition metals to identify best candidates
- COF-42, and 43 Calculated surface area of and predicted their H_2 isotherms (298 K, up to 100 bar)
- COF-Hat and COF-Hatby predicted H_2 isotherms both reach at least 6 wt% total (at least 4 wt% excess at 298 K, up to 100 bar).

Technology transfer/collaborations: Active relationship with collaboration partners and BASF (organic synthesis, material design, structural analysis) .

Review criterion

The GO/NO-GO criteria (September 2012)
Metalated COFs will be prepared. Target Q_{st}: 15 kJ/mol, target total H_2 uptake at 80 bar and room temperature: 4 wt% and 30 g/L.

To achieve room temperature hydrogen storage, we carried out systematic survey using both experiment and theory

- Designed and prepared low density COFs with potential metal binding sites.
- High throughput screening of H_2 binding energy with organic linkers and metals using quantum chemistry based Force Field
- identified metalated candidates that promise to approach DOE volumetric targets.
- Have not yet been successful in synthesizing these most promising targets, but hopeful of near term success

Work to be performed

Full characterization of new COFs (e.g. COF-320, 333, 340)

Recently prepared COFs will be fully characterized, including degree of interpenetration and stability.

- [Exp]Complete standard characterization (XRD, NMR, IR, EA, porosity tests, stability)
- [Exp]Large scale synthesis of organic links to prepare large quantity of COF samples.
- [Exp]Optimize the activation conditions for the best surface area. H_2 isotherms and Q_{st} data will be compared to the predicted data.

Metalation of COFs (e.g. COF-340, 42, and 43)

Based on the prediction by theory, promising TM will be impregnated into COFs

- [Theory] Predict effect of counter anions
- [Theory and Exp]Use weakly coordinating anions, such as BF_4^-, $CF_3SO_3^-$ and PF_6^-, which could be removed to create exposed metal surface.
- [Theory and Exp]Characterize metalated materials (metal binding fashion, surface area, H_2 uptake, Q_{st})
- [Theory] Develop the vdW-FF for the entire row of early transition metals from our current results
- [Theory] use 2PT approach to calculate phase diagram for H2 inside the pores H2 including counter anions. Also get diffusion coefficients
- [Exp]Optimize the metalation condition and loading amount for high-pressure H_2 tests at room temperature.
- [Exp]High-pressure H_2 isotherms will be measured using best performers.