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

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Project ID
ST022

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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

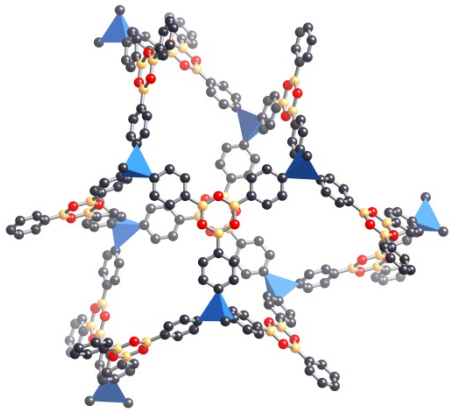
- ❑ Co-PI: William Goddard (Caltech)
- ❑ Fraser Stoddart (NW)
- ❑ Jaheon Kim (Soongsil University)
- ❑ BASF

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



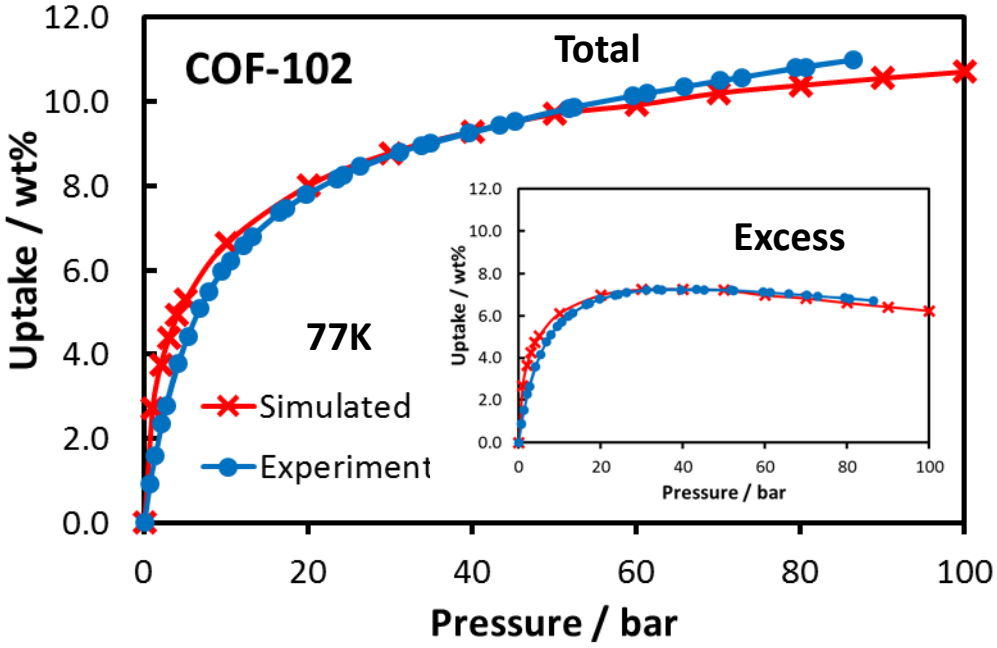
COF-102

Lightweight crystalline porous solids:

Covalent Organic Frameworks (COFs)

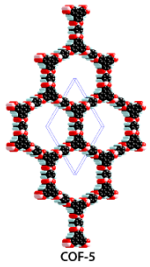
- Control of structure, topology, and interpenetration
- Lightweight materials
- Design of functionalities
- Suitable for metal impregnation

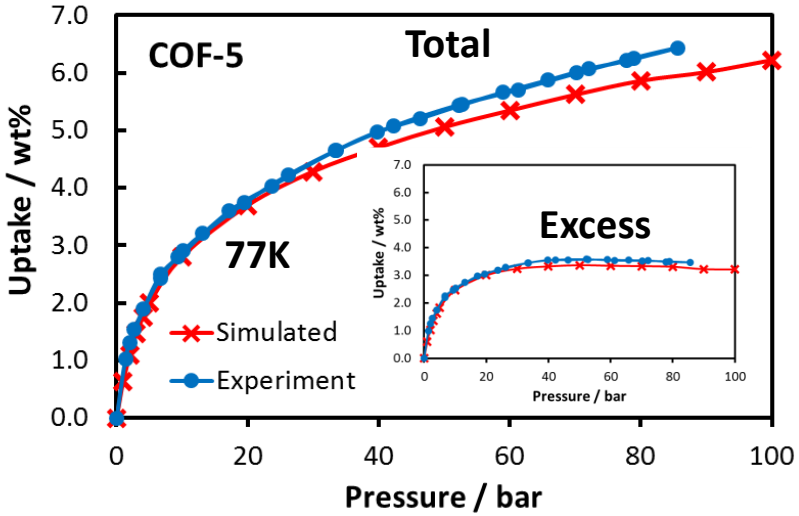
Theory and experiment agree
Thus can use Theory to identify the most promising metallated cases required to meet DOE requirements



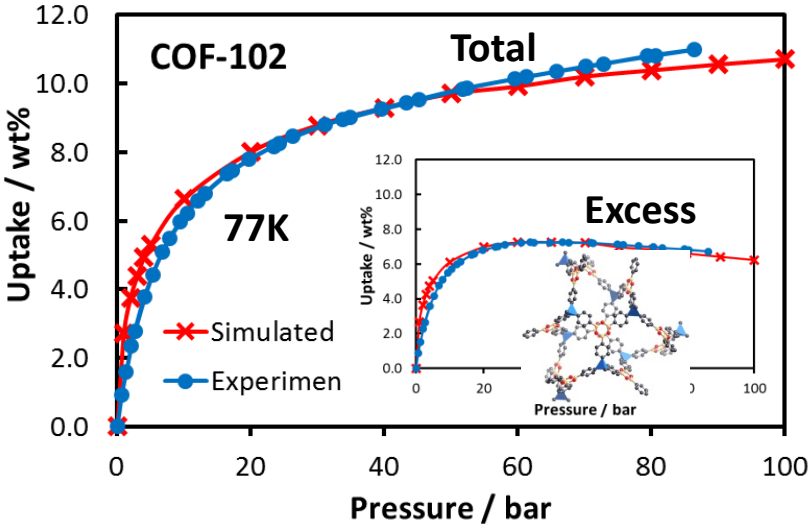
Excess and total H_2 uptakes in COF-102 and 103 are almost the same as that in MOF-177. However, binding energy is not high enough to meet the DOE targets. *JACS*, **2009** (exp).

Validation of theory by compare to Experiment: COFs





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



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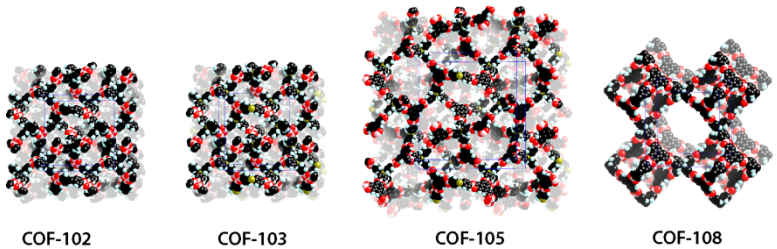
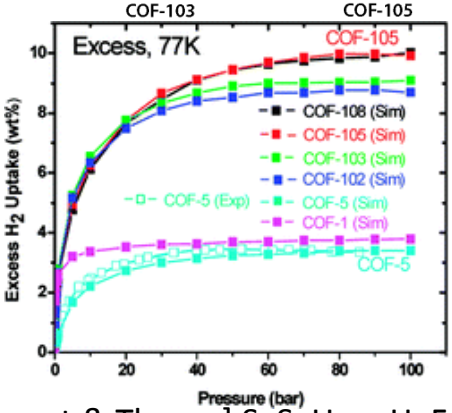
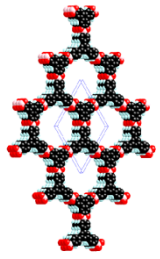
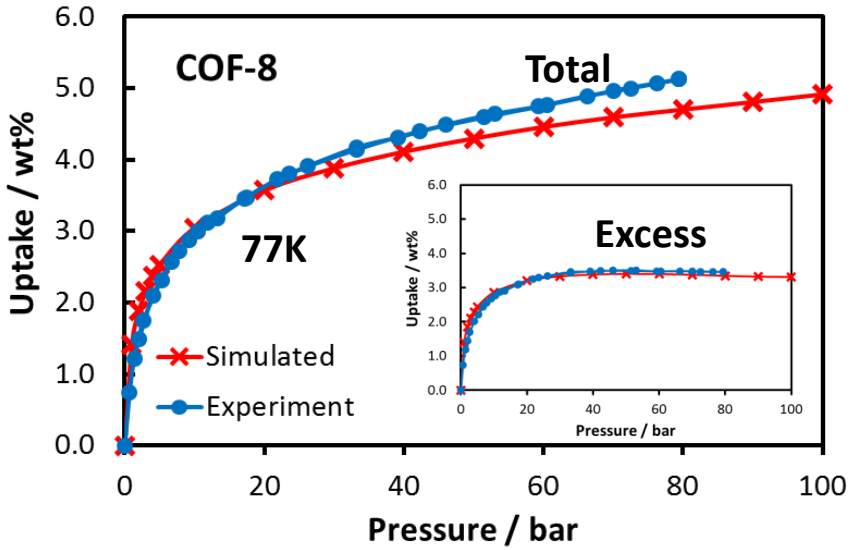




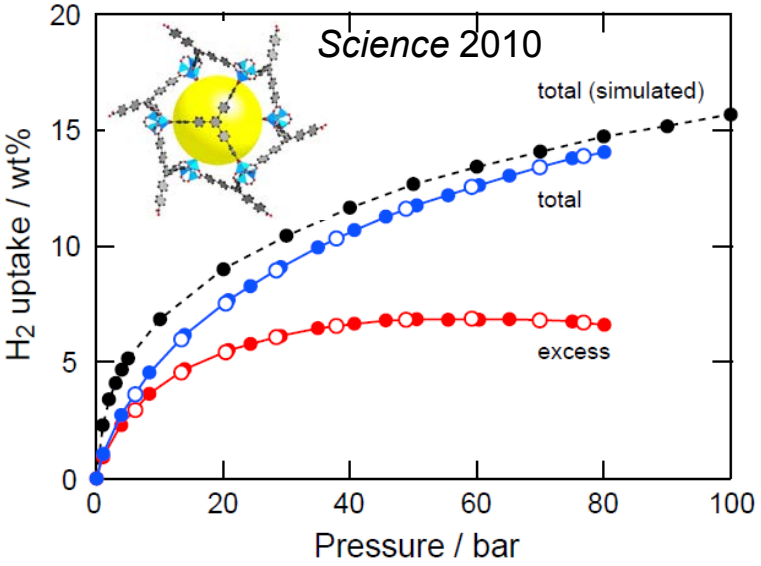




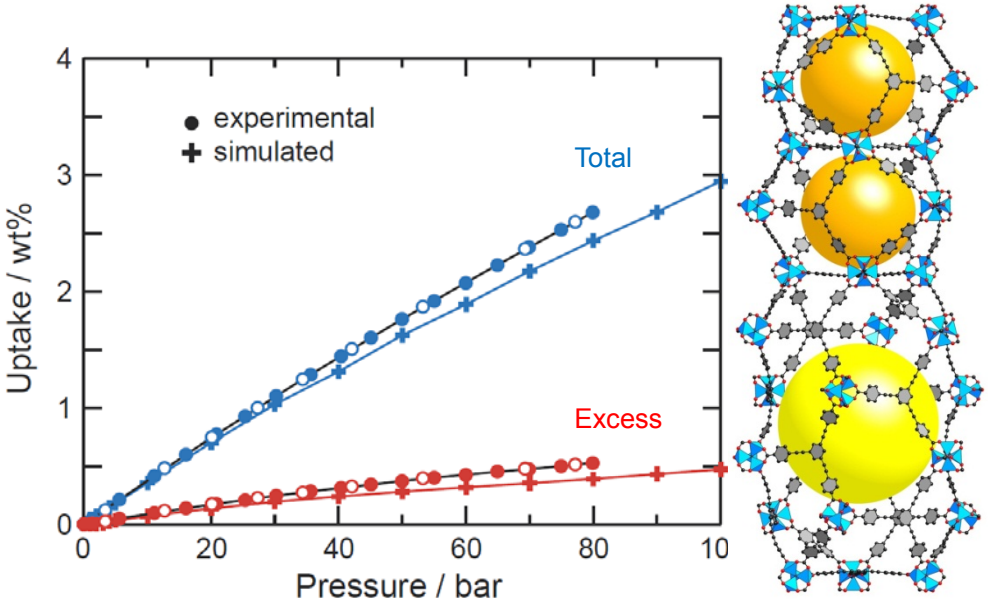
Furukawa et al, *JACS*, **2009** (exp).

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

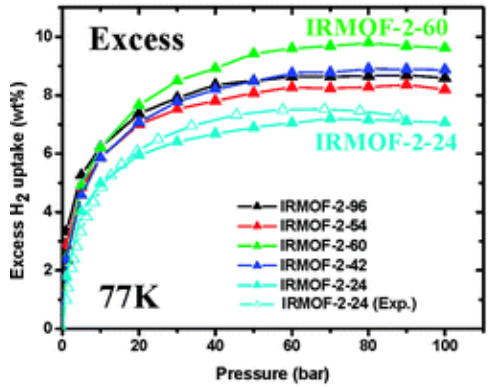
Validation of theory by compare to Experiment: MOFs



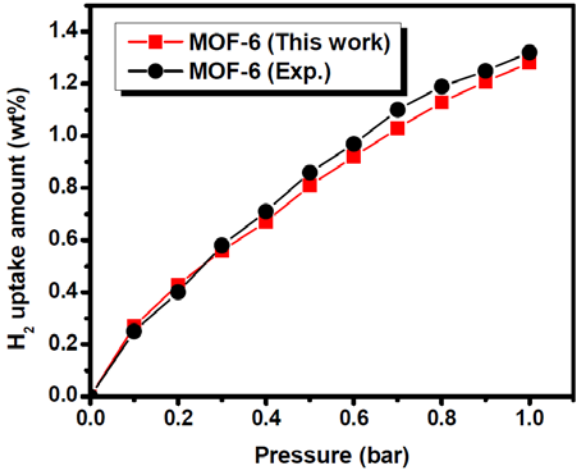
14 wt% total hydrogen uptake in MOF-200



2.7 wt% total hydrogen uptake in MOF-210



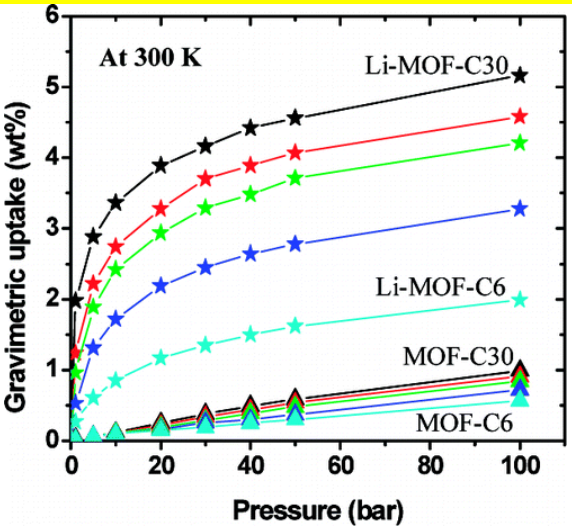
[Experiment] Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc. 128,* 3494 **(2006)** .
[Theory] S. S. Han, William A. Goddard III, *J. Phys. Chem. C 112,* 13431 **(2008).**

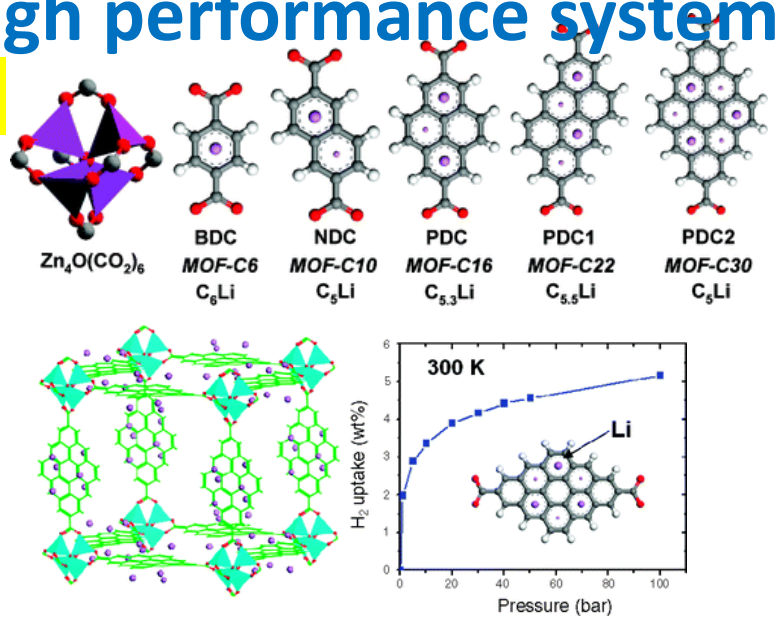


[Experiment] J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc. 128*, 1304 ***(2006).***
[Theory] S. S. Han, William A. Goddard III, *J. Am. Chem. Soc. 129,* 8422 ***(2007).***

Previous predictions of high performance systems

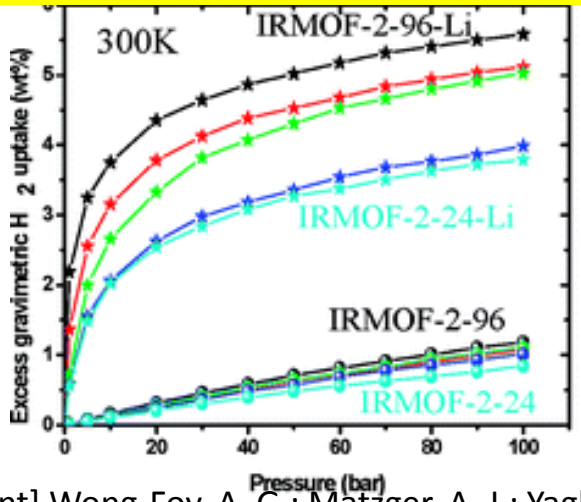
Li–MOF-C30 achieves over 5 wt % at 100 bar.

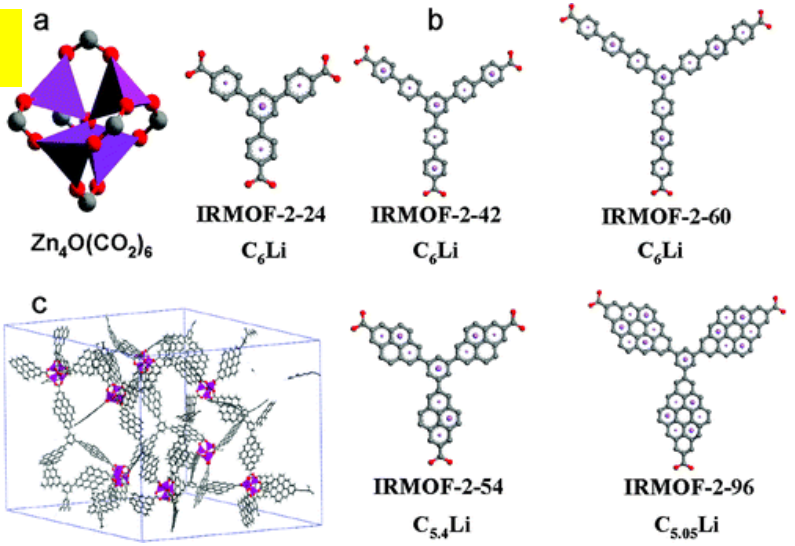




[Theory] S. S. Han, William A. Goddard III, *J. Am. Chem. Soc. 129,* 8422 ***(2007).***

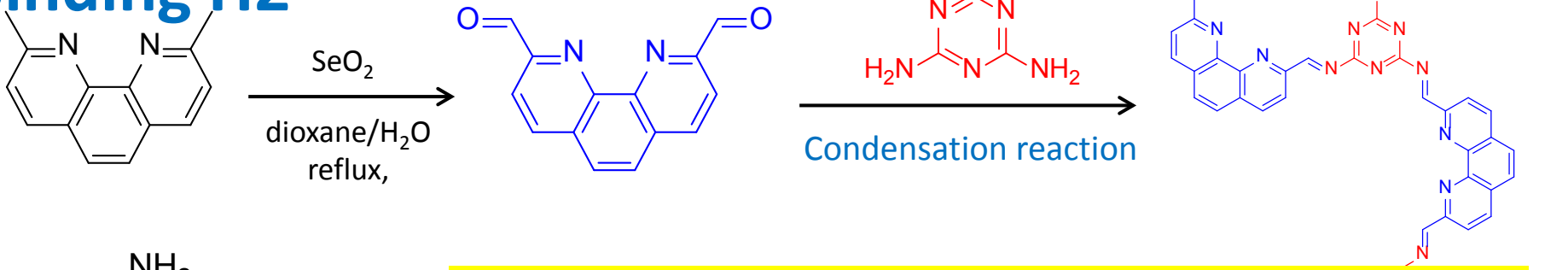
Li–MOF-C30 achieves over 5.5 wt % at 100 bar.

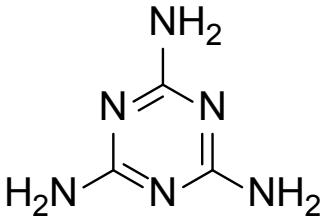




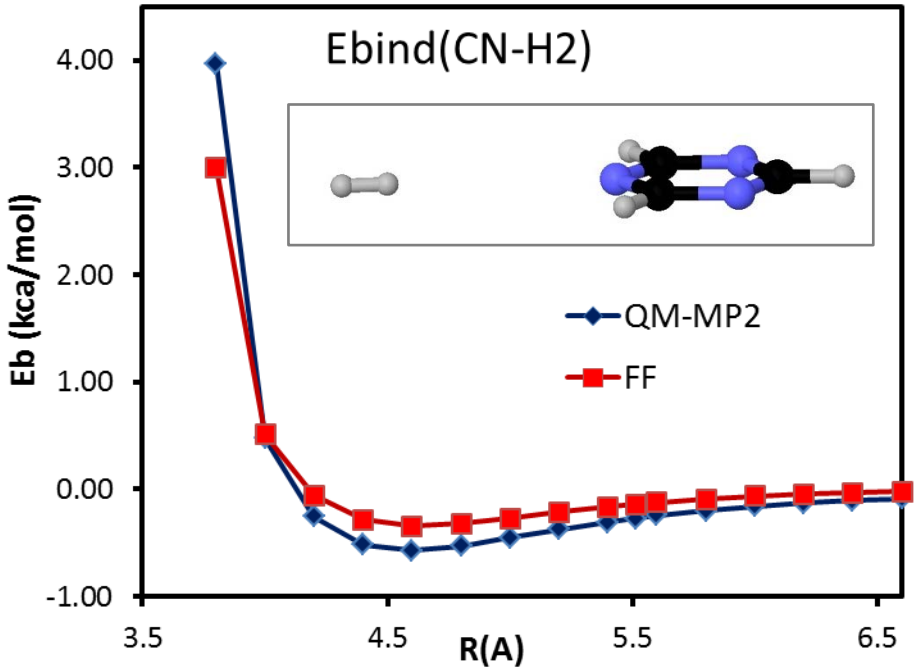
[Experiment] Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M. *J. Am. Chem. Soc. 128,* 3494 **(2006)** .
[Theory] S. S. Han, William A. Goddard III, *J. Phys. Chem. C 112,* 13431 **(2008).**

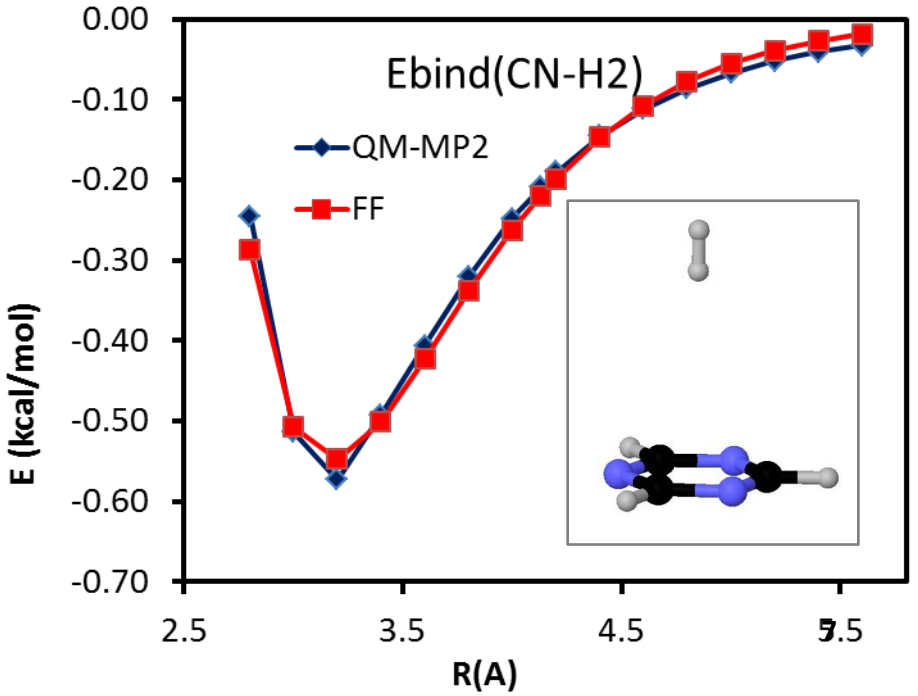
Design of COFs with metal binding sites for binding H2



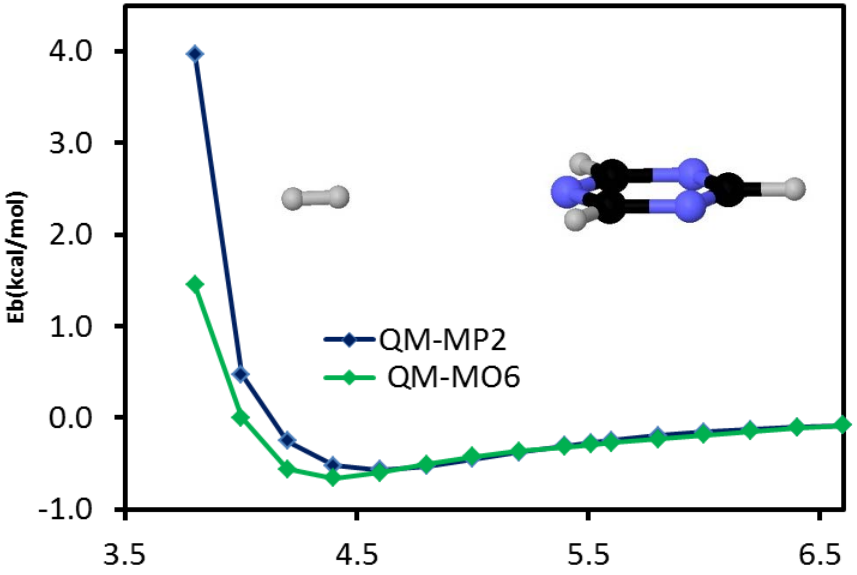


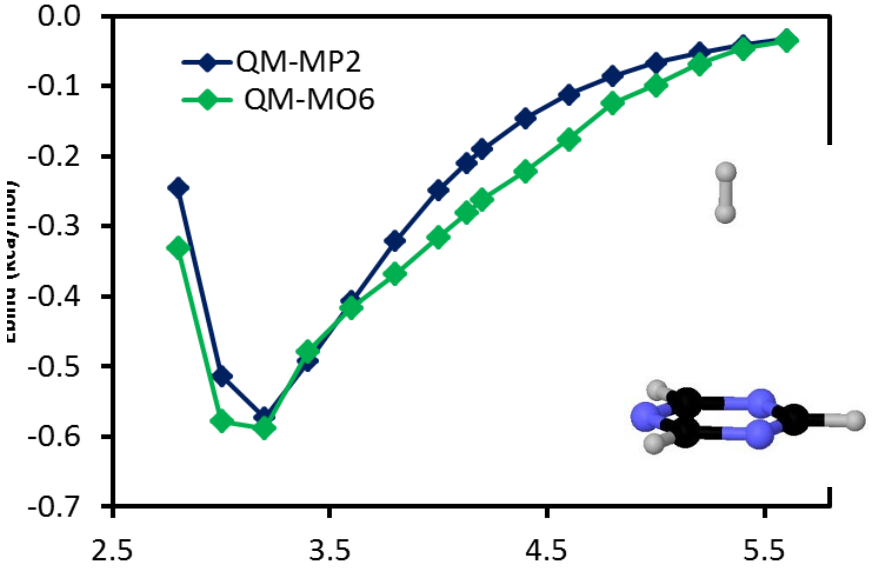
- We have constructed the FF for this class of COFs based on MP2 calculations
- We used this FF to predict promising systems.

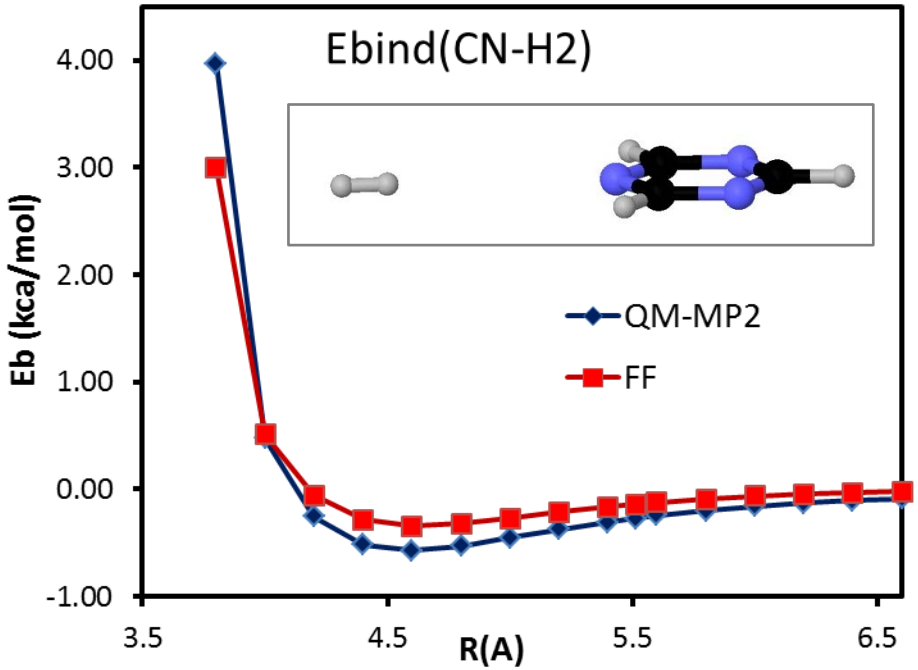


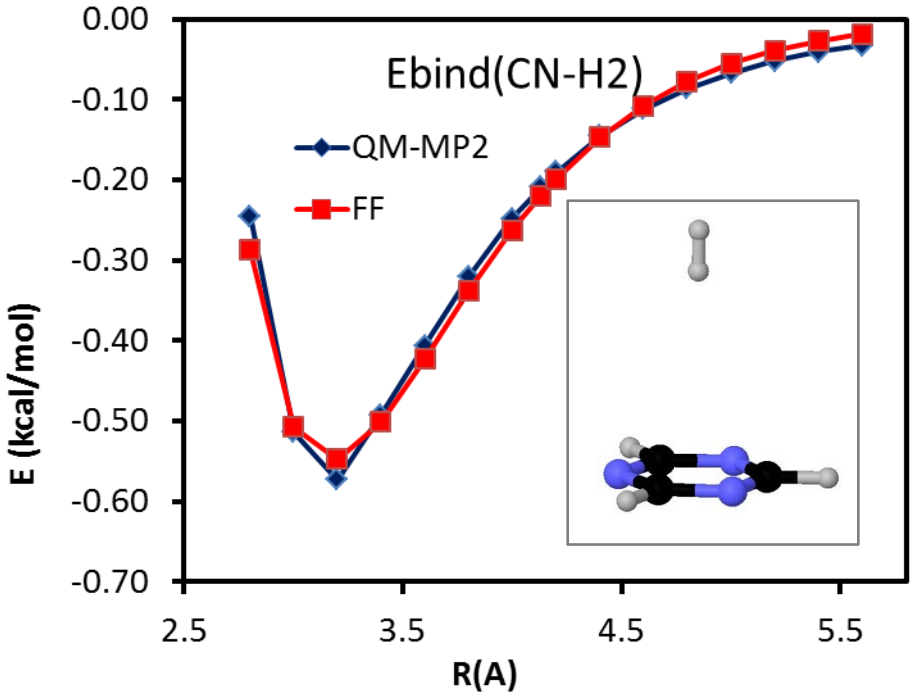


Development of 1st principles Force Field for Designing of COFs with metal binding sites



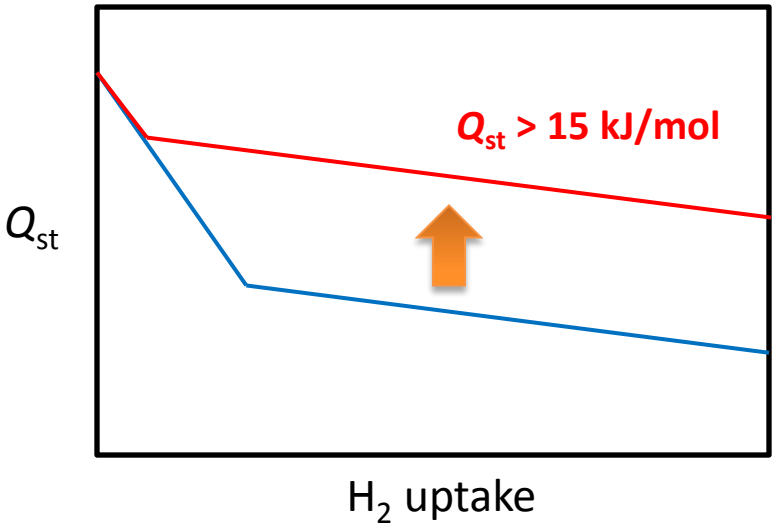


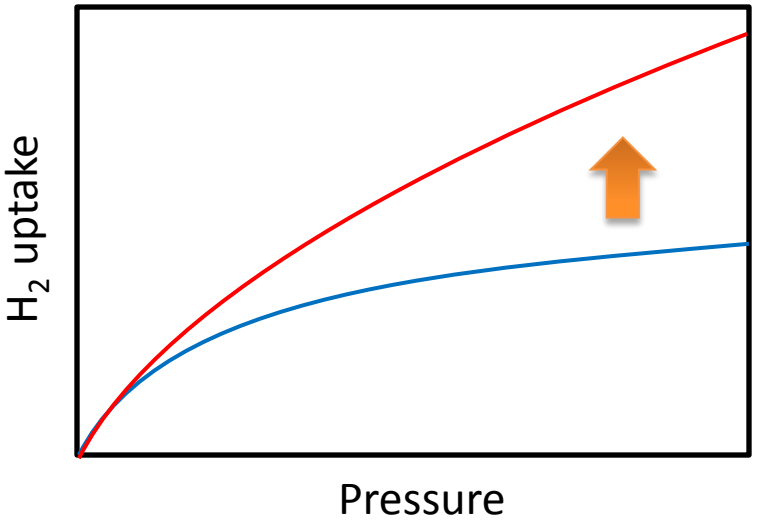




Strategy for achieving room temperature H_2 storage

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.

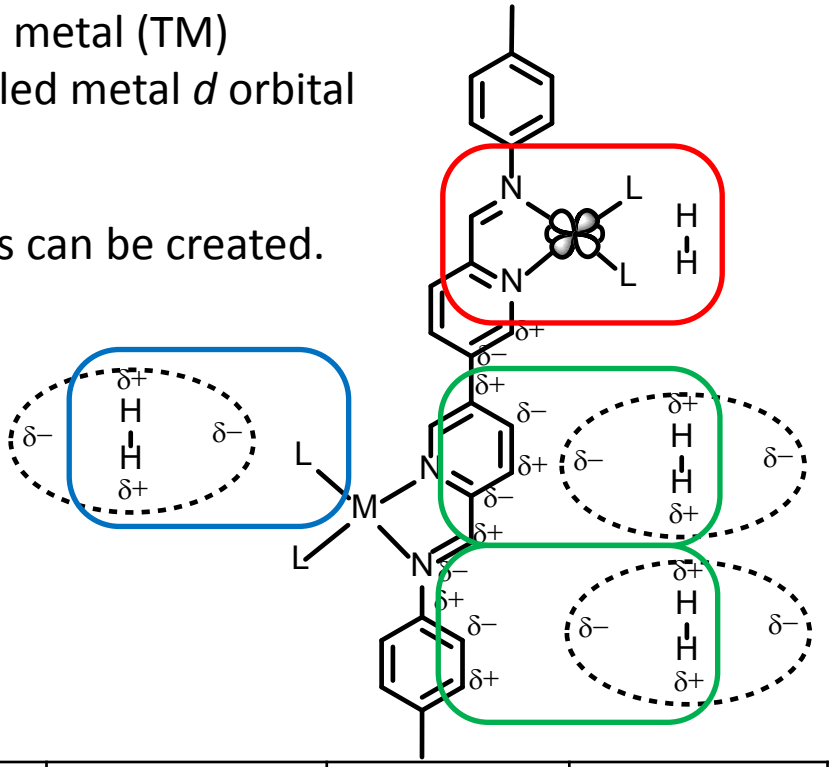
Need Materials with multiple H_2 adsorption sites (but not too strong) achieve 300K binding

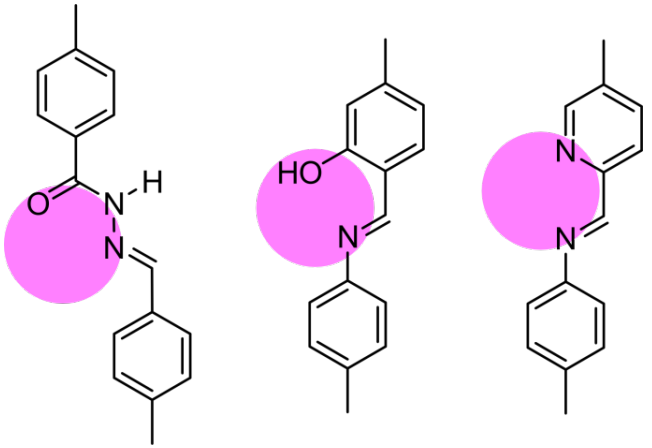
Approach: Create multiple hydrogen binding sites by metalation of COFs

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)



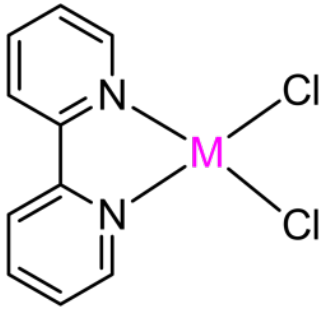


These units are ideal for binding metals controllably

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

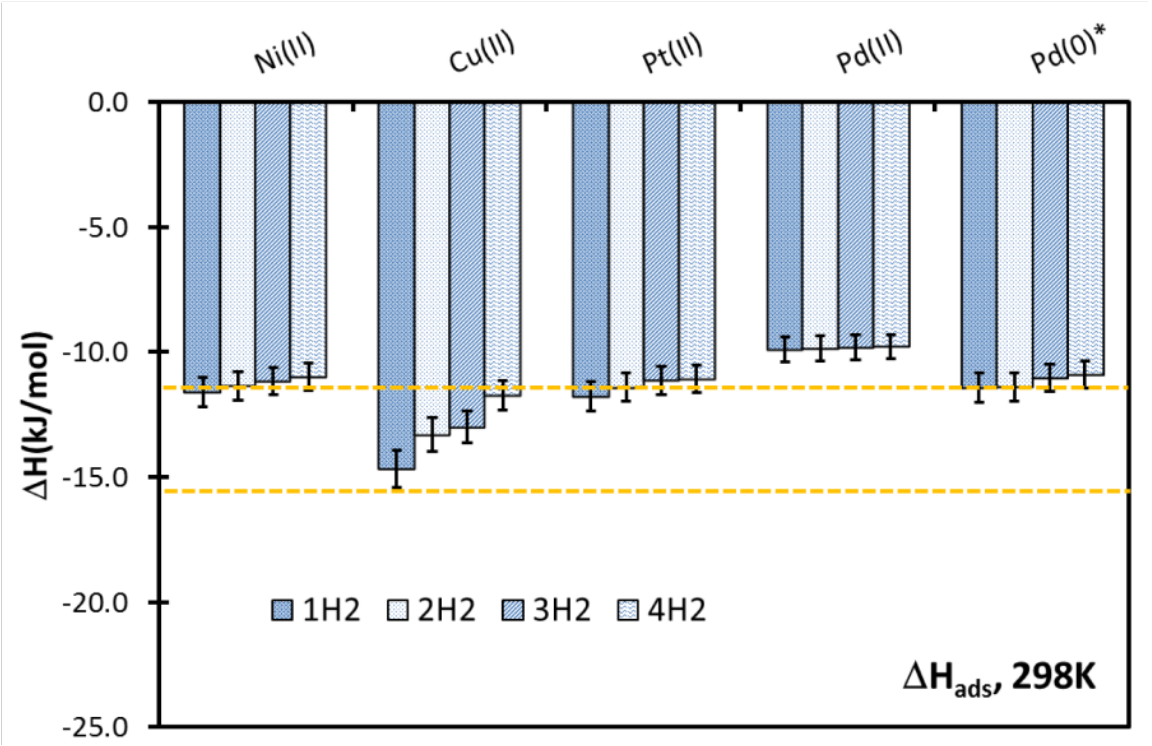
[a] *PCCP*, **2006**, *8*, 1357-1370. [b] *Langmuir*, **2006**, *107*, 1688-1700. [c] *Chem. Rev.*, **2007**, *107*, 4152-4205.

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



2,2'-bipyridine

BPY+$TMCl_2$



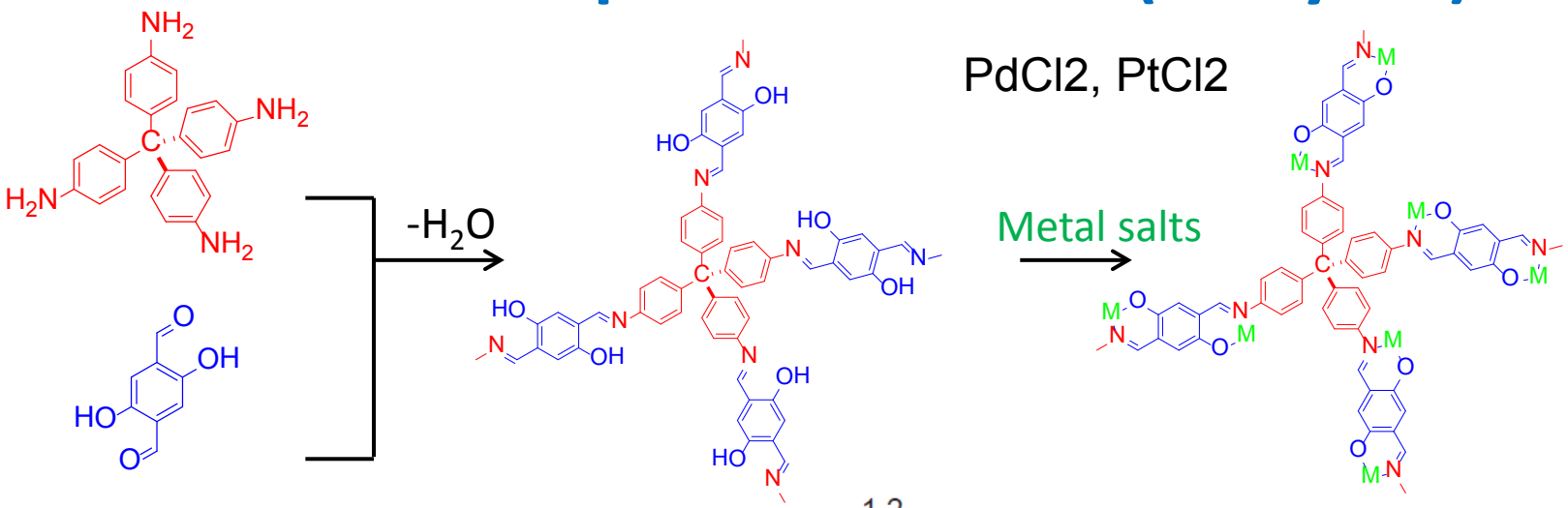
Accomplishments (this year)**:**

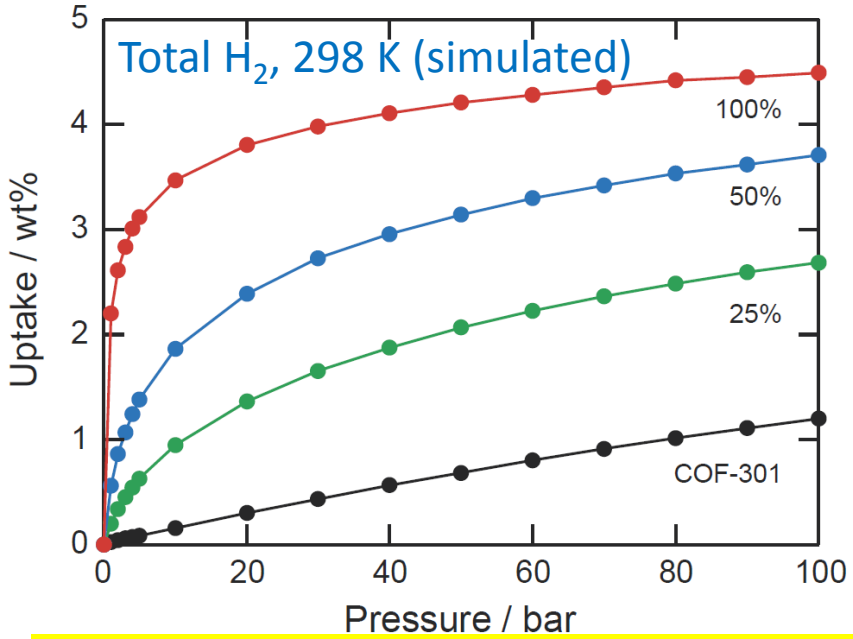
- The binding energy for third and fourth H_2 near the metal site was estimated.
- Similar binding energy (ΔH_{ads}) is observed for the first row transition metals and Pd.
- We found ΔH_{ads} is nearly the same even after 4 H_2 molecules are adsorbed.
- 30 to 40 H_2 can bind to the linker + MCl_2 moiety,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

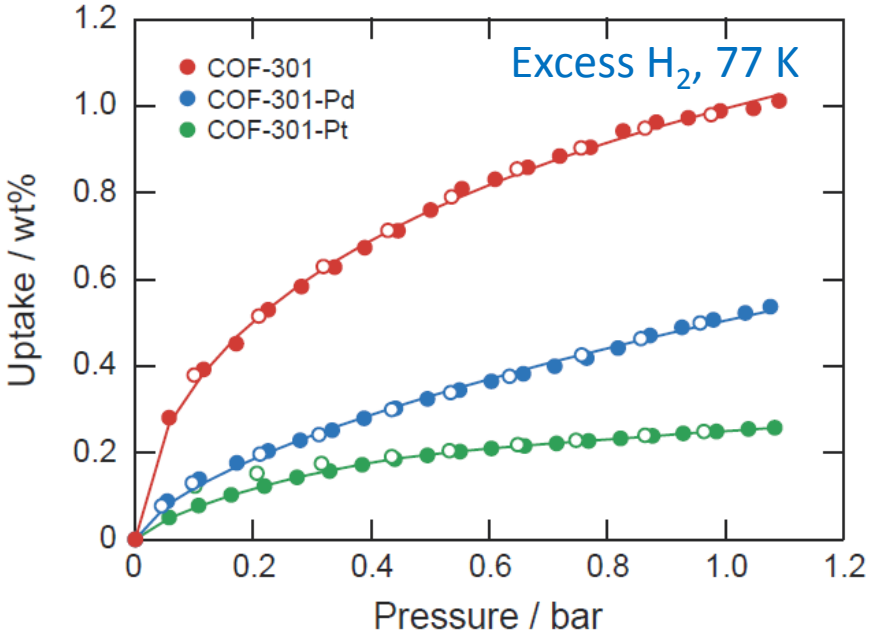
Approach:

- 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)



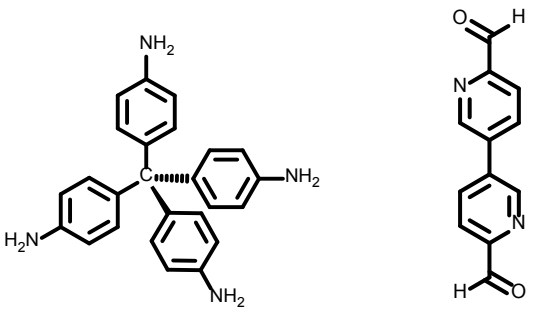




- Metalated materials maintain reduced porosity
- Experimental H_2 uptake was much smaller than predicted one, because of unreacted metal salts in pores

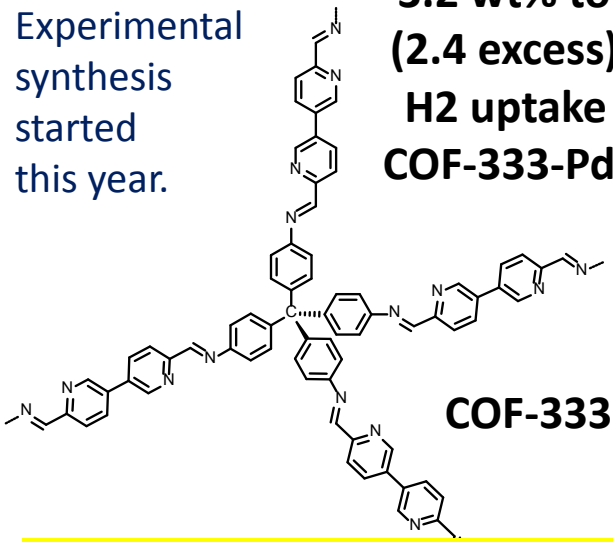
New approach: functionalization of COF-300

Theory

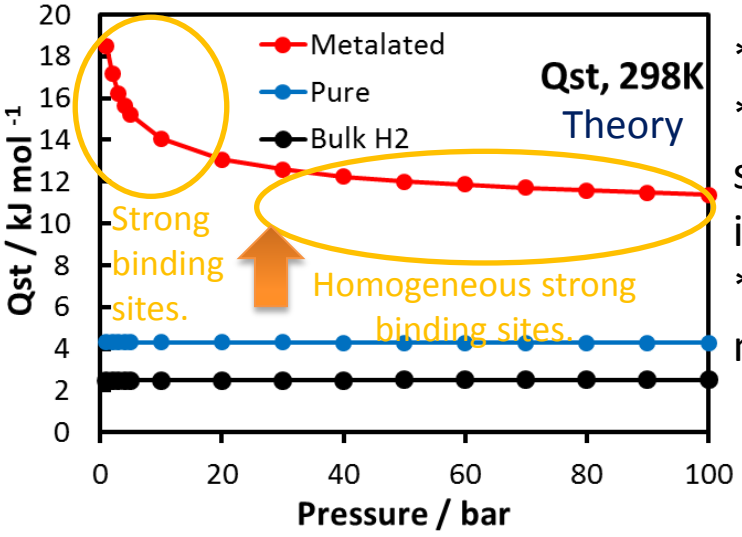


Experimental synthesis started this year.

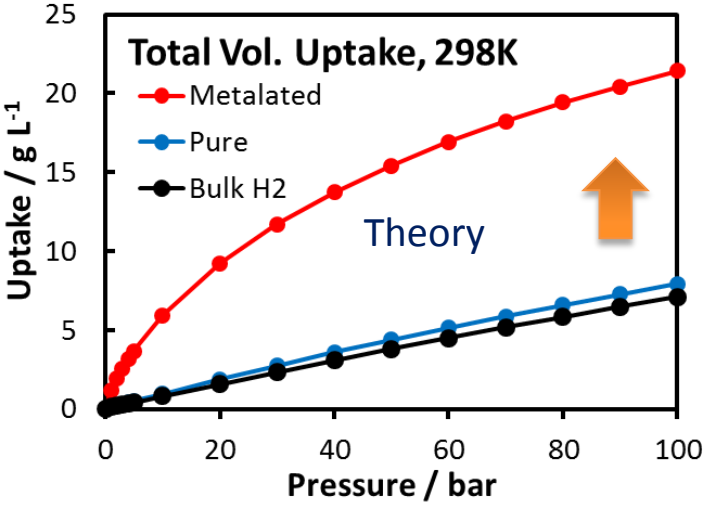
3.2 wt% total (2.4 excess)RT H2 uptake in COF-333-PdCl2

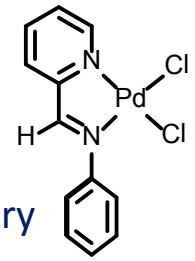


COF-333

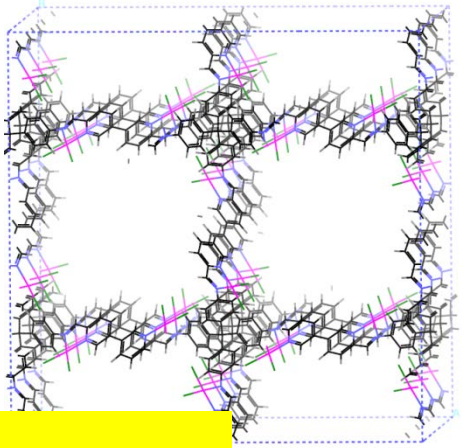


*Multiple sites.
*Stronger binding sites where the $PdCl_2$ is exposed to the pore
*Higher Qst for the metalated framework.



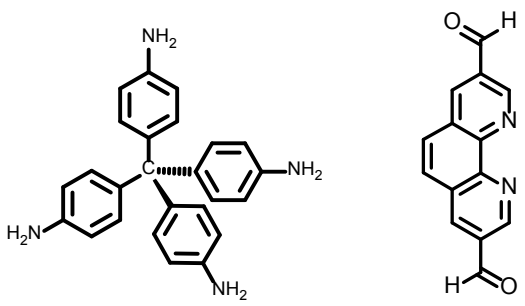


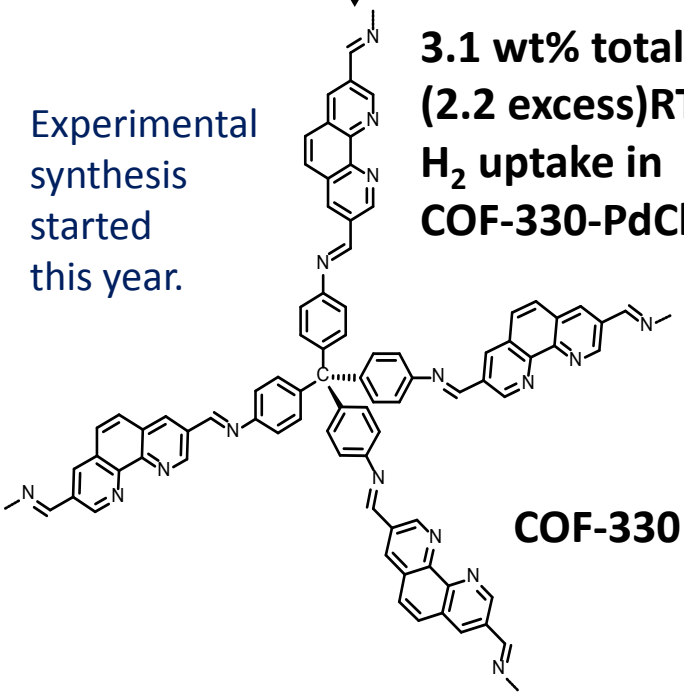
Theory



- 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



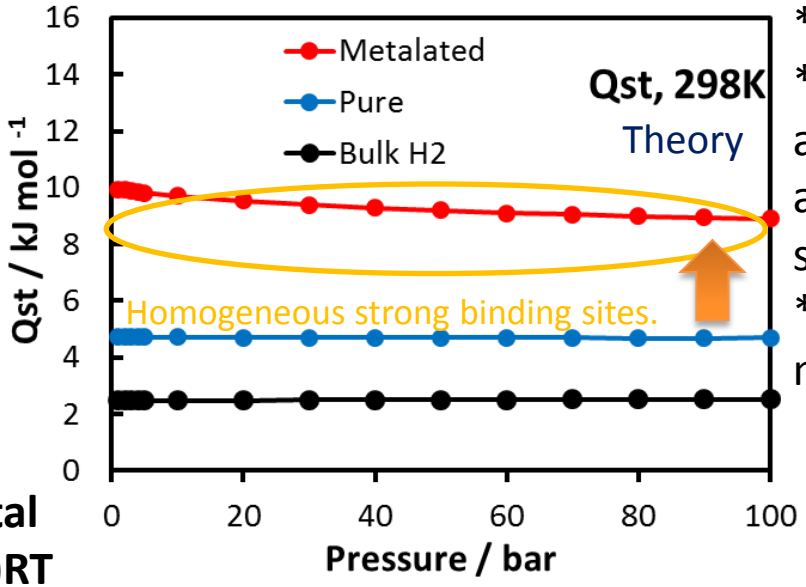


COF-330

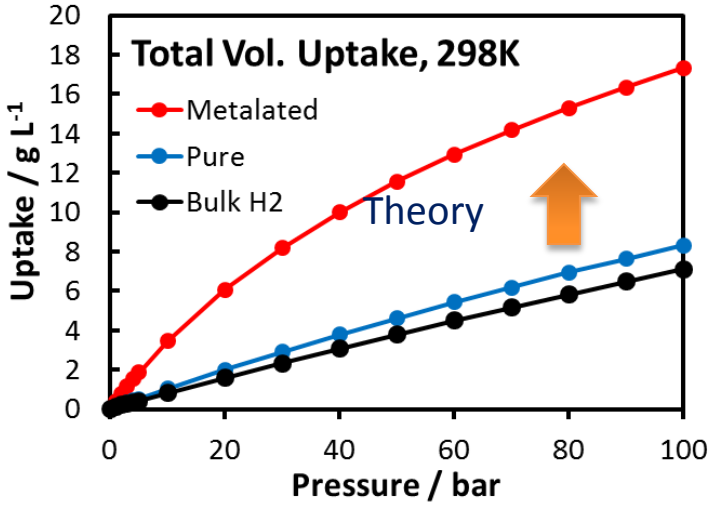
Experimental synthesis started this year.

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

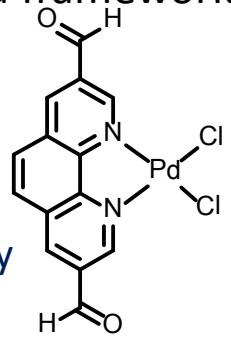
Theory

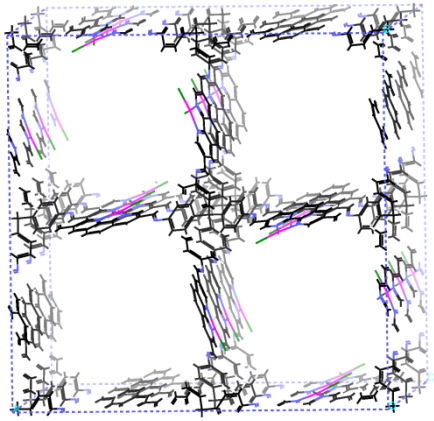


*Multiple sites.
*The metalated sites are not very accessible and the Qst improves slightly.
*Higher Qst for the metalated framework.



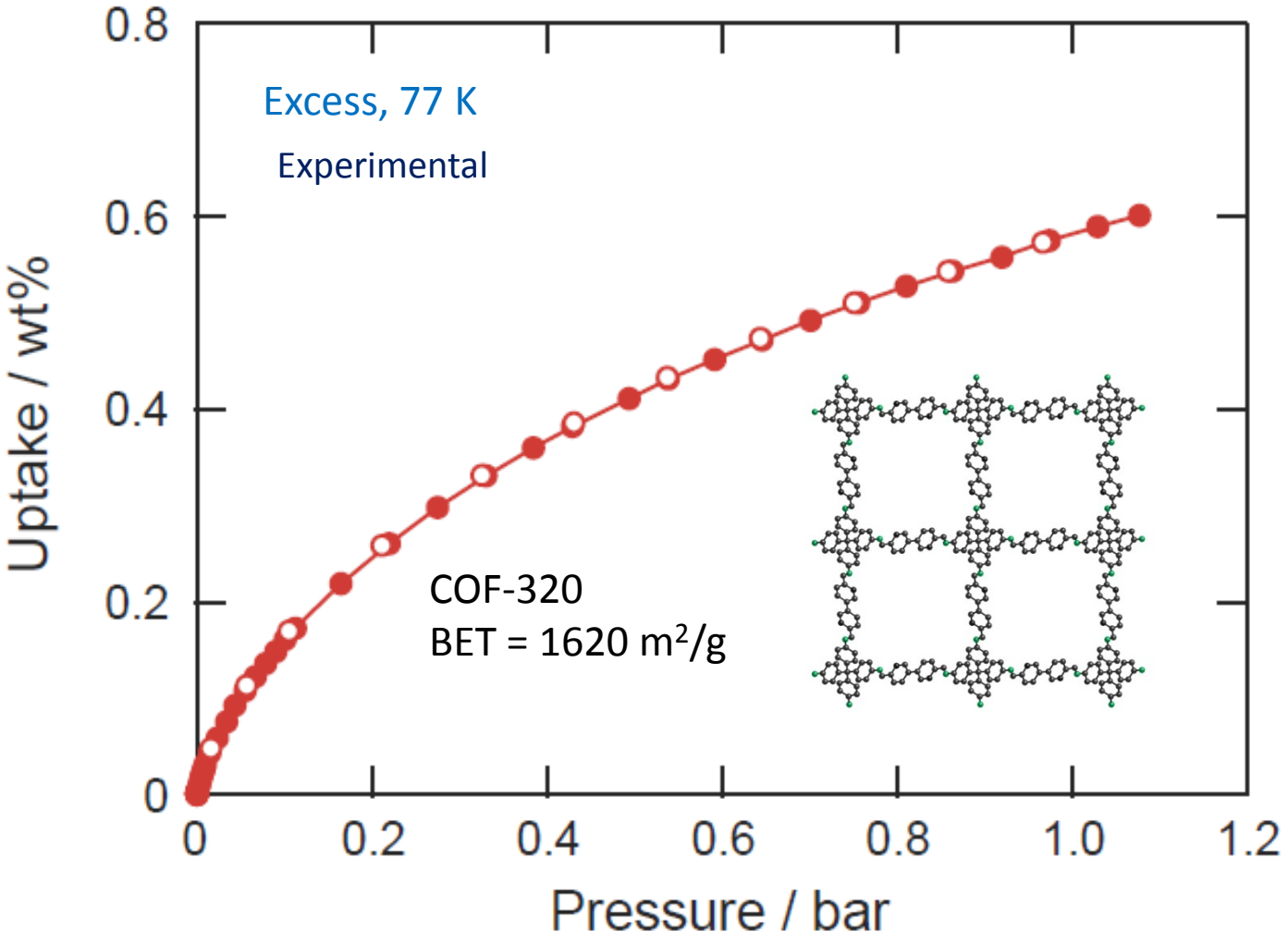
Theory

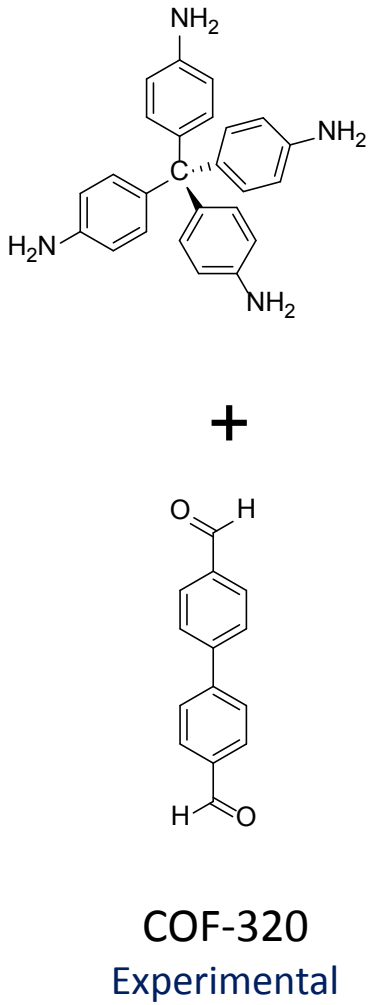




Metalation of phenanthroline moieties increases by 200% in the volumetric capacity and by 50% in the gravimetric capacity to the pristine material.

Preliminary excess H_2 uptake by COF-320 at 77 K

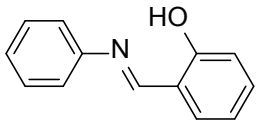
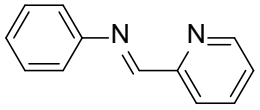
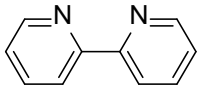
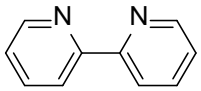
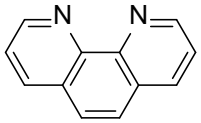




COF-320
Experimental

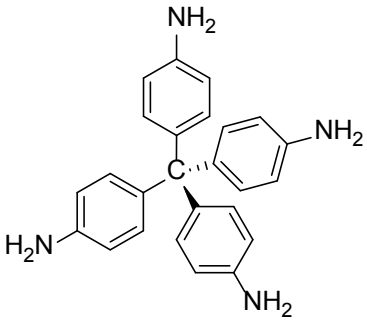
BET area of COF-320 is larger than COF-300 and 301, but H_2 uptake is smaller than these materials. Activation procedures must be optimized.

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



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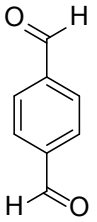
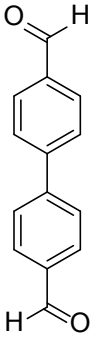
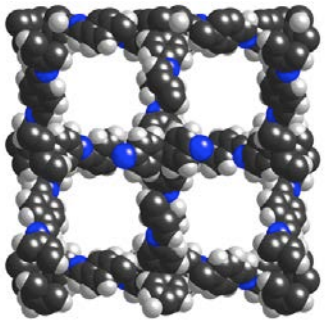


COF-300

expansion

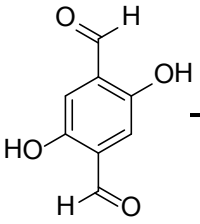


COF-320*



Space filling model of COF-300

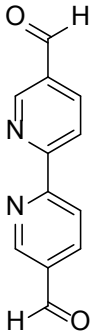
functionalization



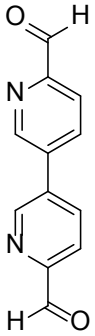
COF-301

MTV-COF*

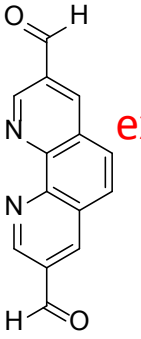
functionalization



COF-322

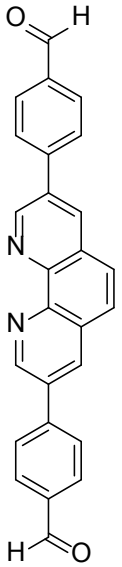


COF-333*



COF-330

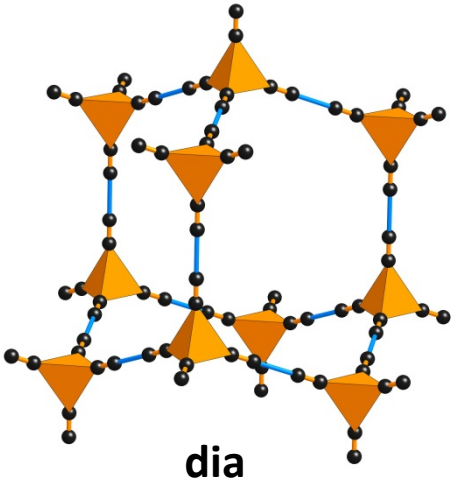
expansion



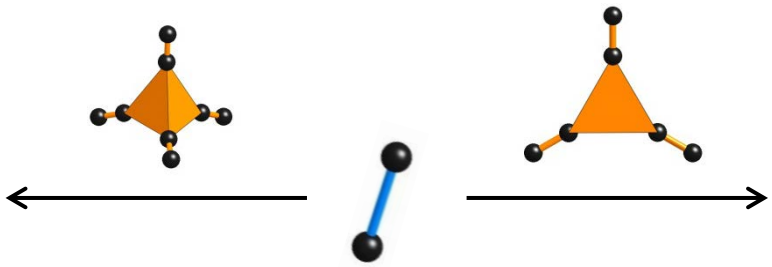
COF-340*

* Synthesis of these COF materials started this year.

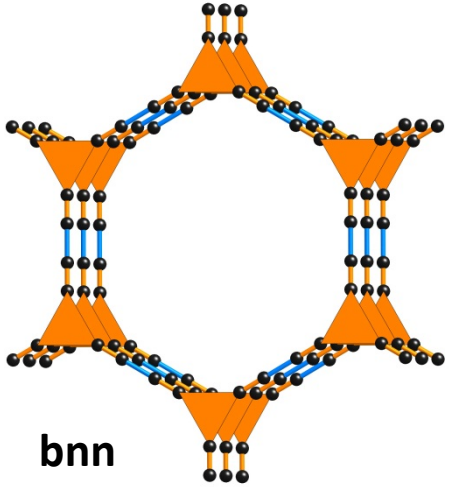
Accomplishments: Gram scale synthesis of organic links (1)



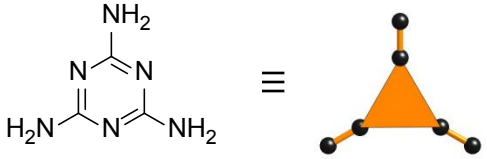
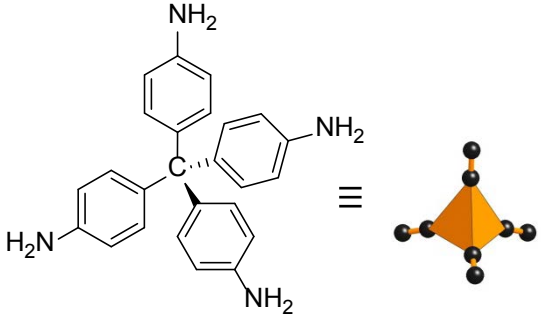
dia



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

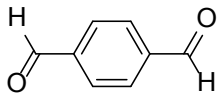
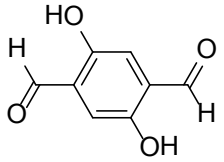
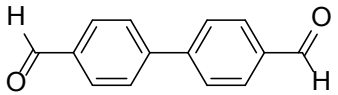
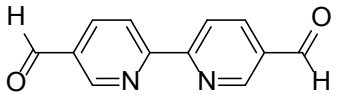
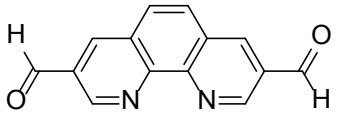
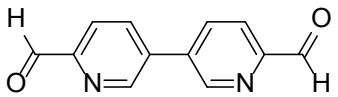
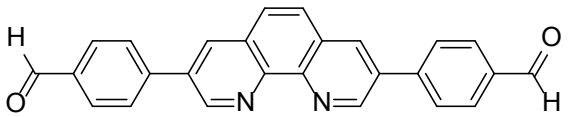


bnn

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*

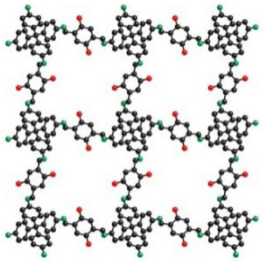
*Large scale synthesis was achieved this year.

Accomplishments: Gram scale synthesis of organic links (2)

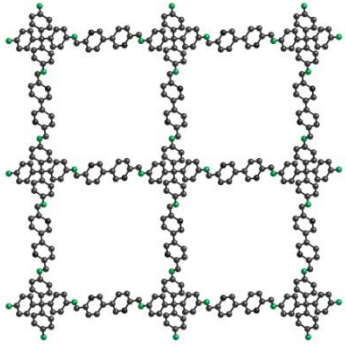
Structure (≡)	Link for COF-*n*	Synthetic steps	Scale available
	**COF-300**	Commercially available	> 10 gram scale
	**COF-301**	1 steps	gram scale
	**COF-320**	Commercially available	> 10 gram scale
	*COF-322*	1 step (based on a literature)	n/a
	*COF-330*	Developing synthetic conditions	n/a
	**COF-333**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

*Large scale synthesis was achieved this year.

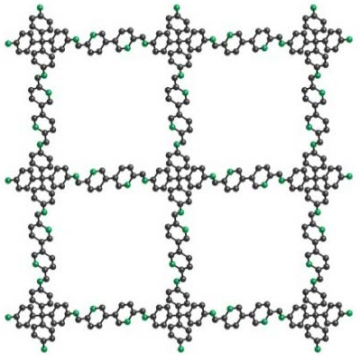
Successful synthesis of MOFs with expanded links



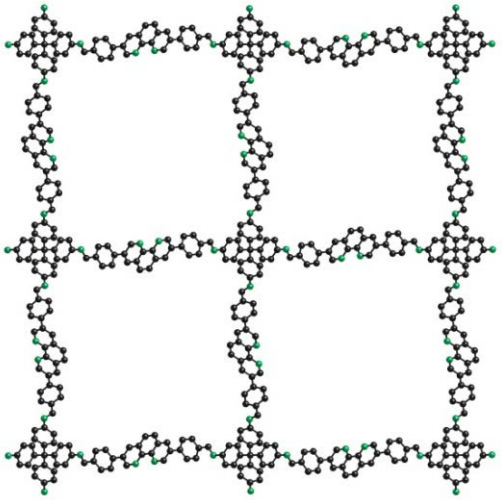
COF-301



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**

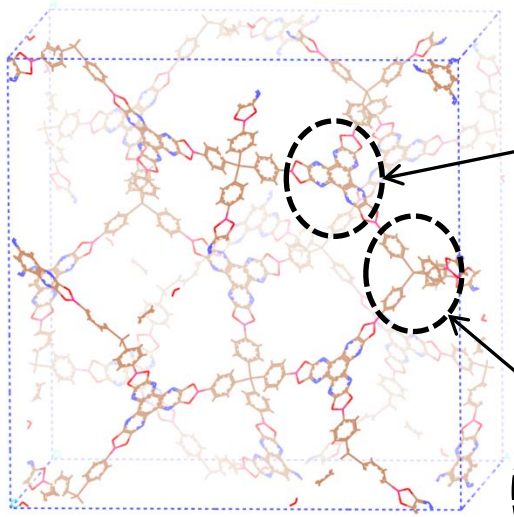
Metal binding sites are introduced through the condensation reaction and/or by use of linkers with phenanthroline/bipyridine units.

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.

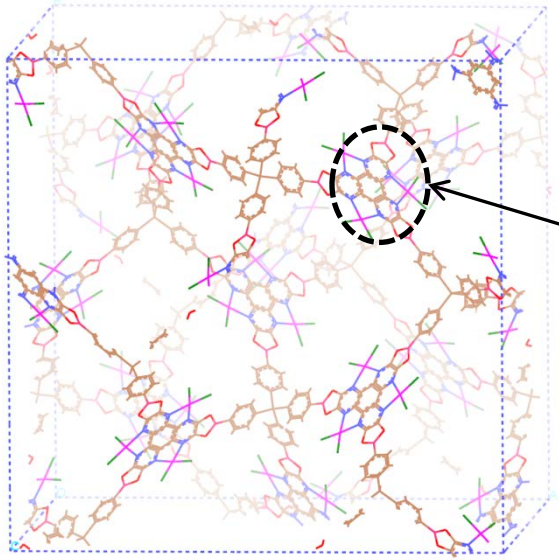
New Approach: Hexa-azatriphenylene COFs

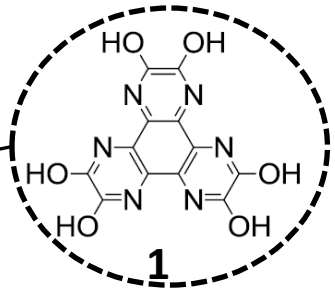


1+3

COF102-Hat-Pd

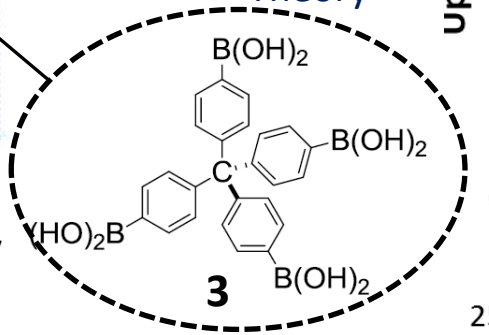
Metalation/ Pd





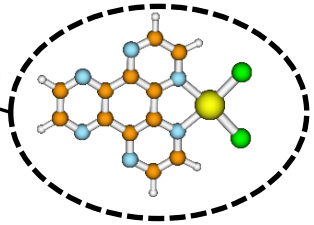
1

Theory

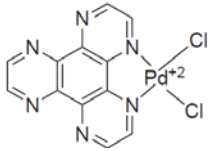


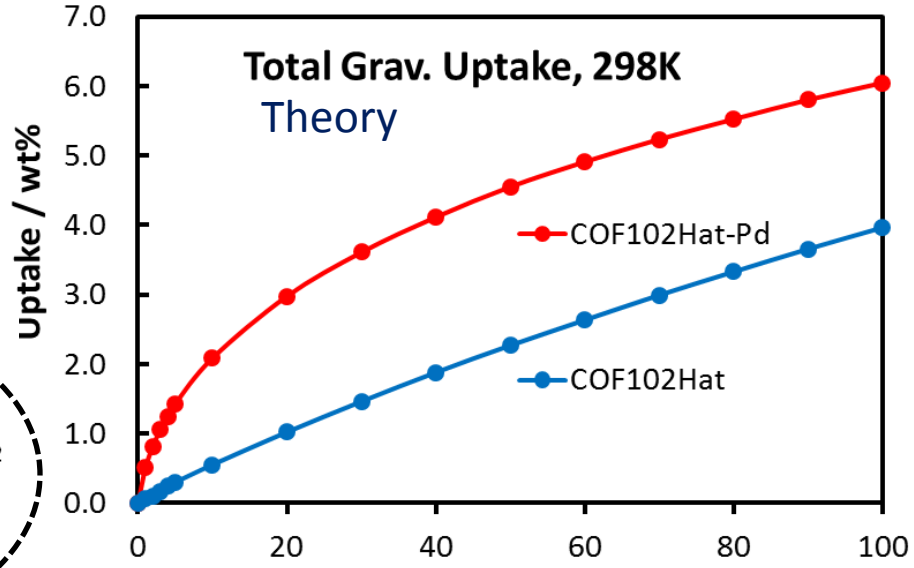
3

COF102-Hat

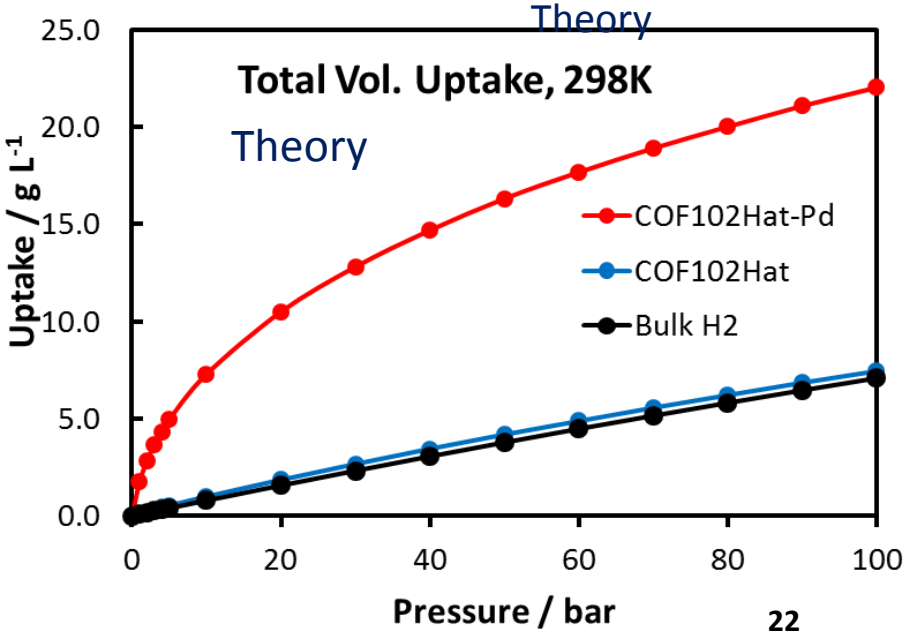


Theory



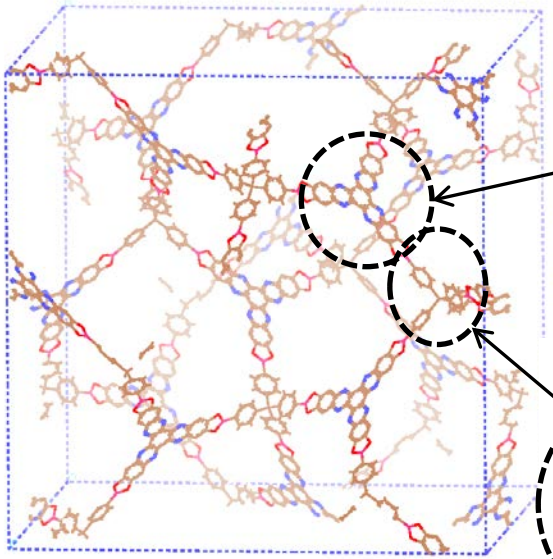


Theory



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

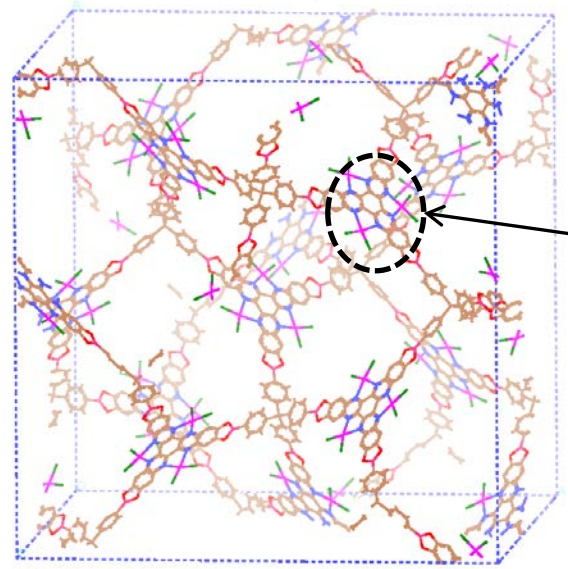
New Approach: Hexaazatribyphenylene COFs

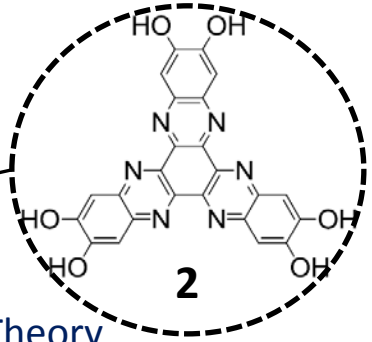


2+3

COF102-Hatb-Pd

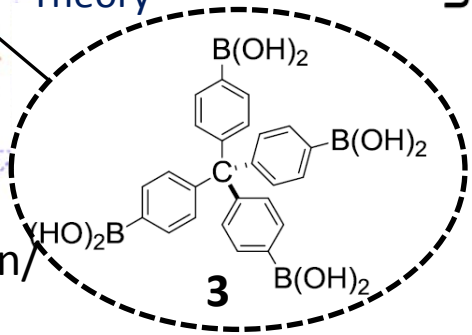
Metalation / Pd





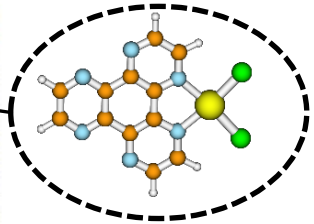
2

Theory

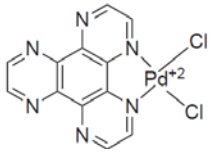


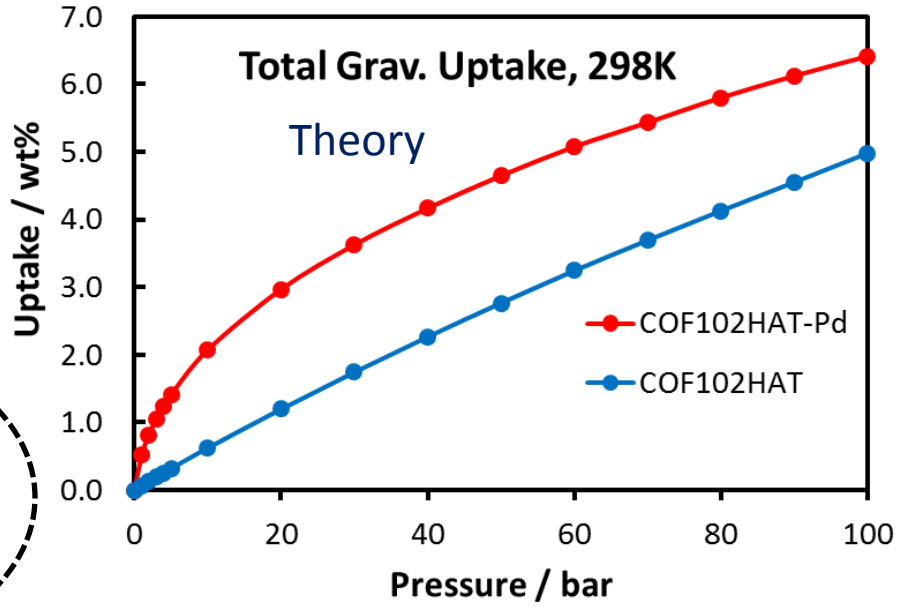
3

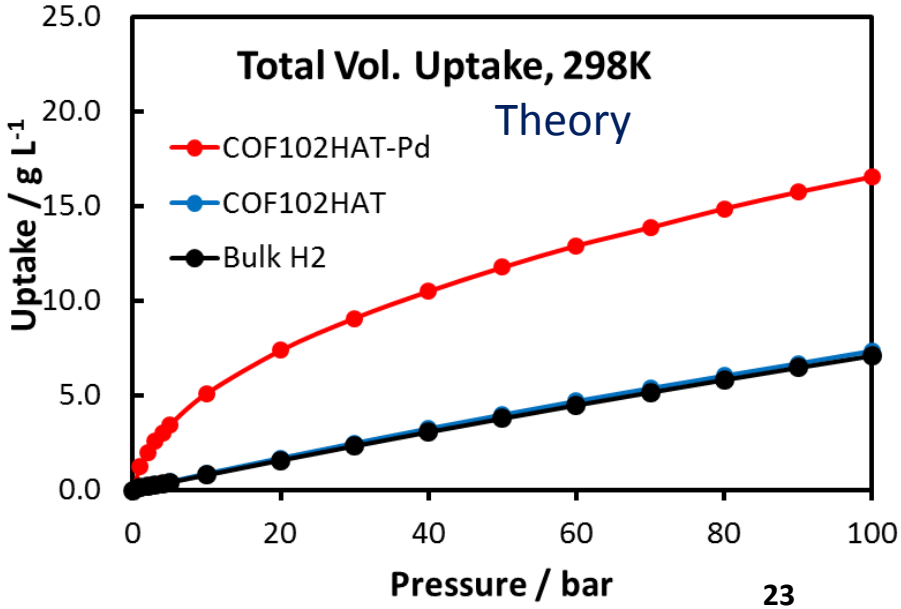
COF102-Hatby



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.