# 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

# Overview

## Timeline

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

Project end date: 1/31/2013

Percent complete: 20%

## 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 to cubic meters

## Budget

- ❑ Total project funding
  - DOE share: $1.38 M
- ❑ Funding received in FY09: $400 K
- ❑ Funding for FY10: $400 K

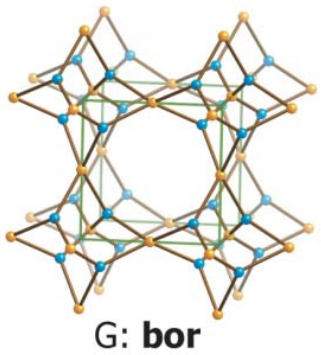
## Collaborating Partner

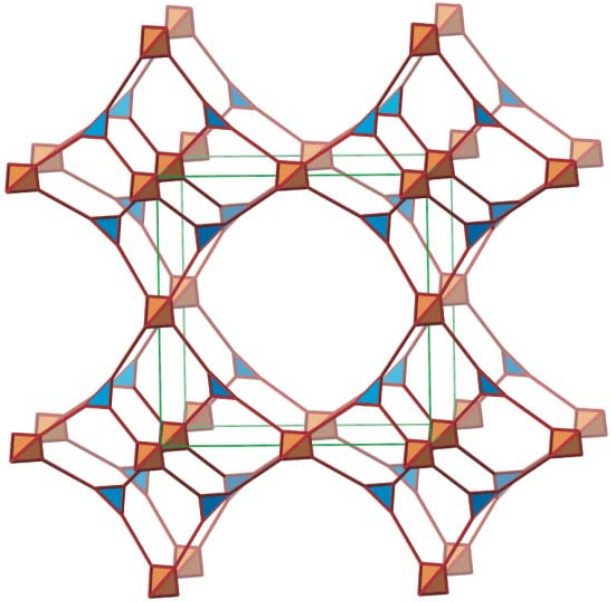
- ❑ BASF

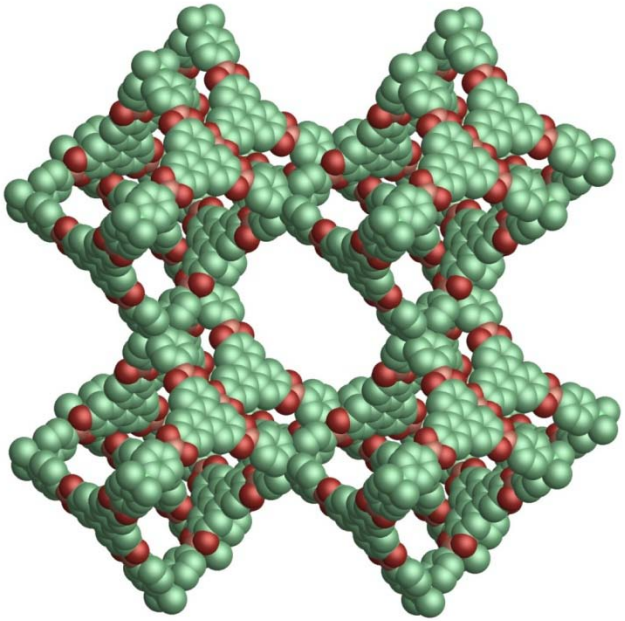
# Description of new materials

## Covalent Organic Frameworks (COFs)

- ❑ Control of structure, topology, and interpenetration
- ❑ Lightweight materials
- ❑ Design of functionalities
- ❑ Suitable towards light metal impregnation
- ❑ High-throughput material discovery is applicable



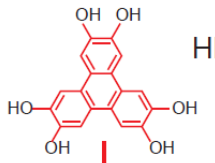





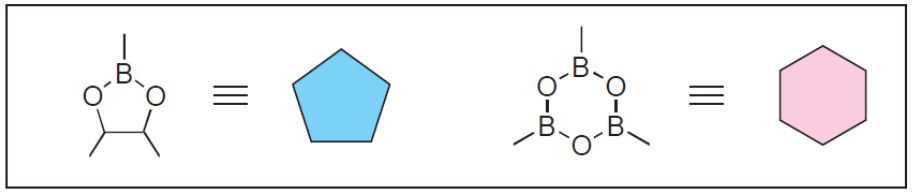
Science 2007

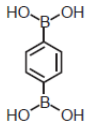
COF-108 ($d$ = 0.17 g cm$^{-3}$)

# Covalent Organic Frameworks (COFs)




HHTP

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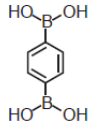


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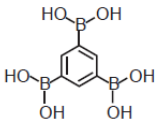


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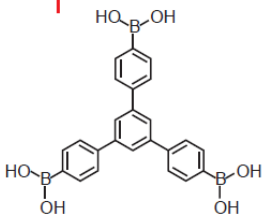


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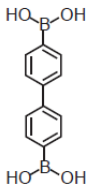


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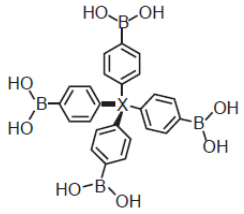
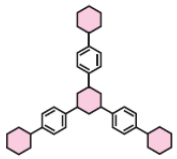
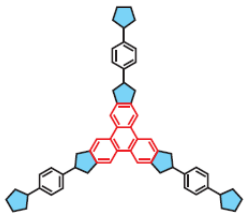
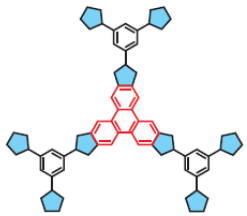
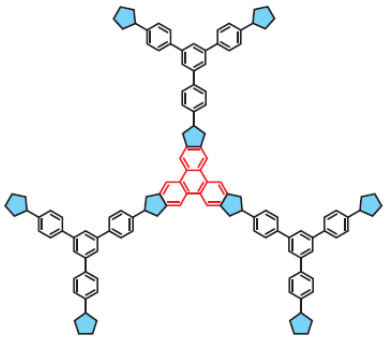


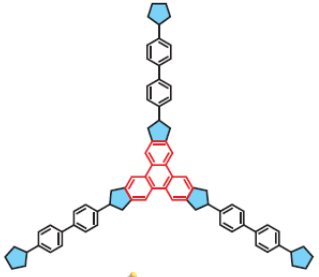

TBPM (X = C)
TBPS (X = Si)

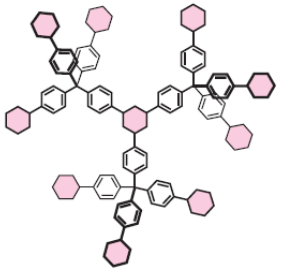


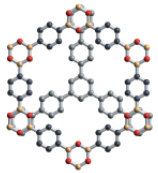




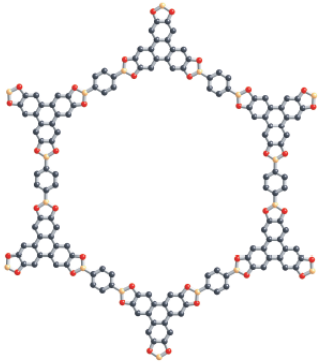




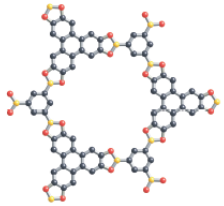




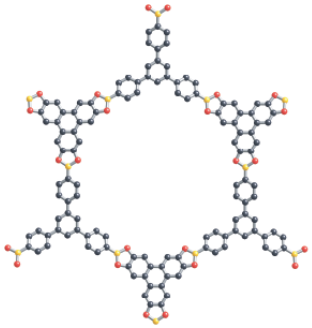
COF-1



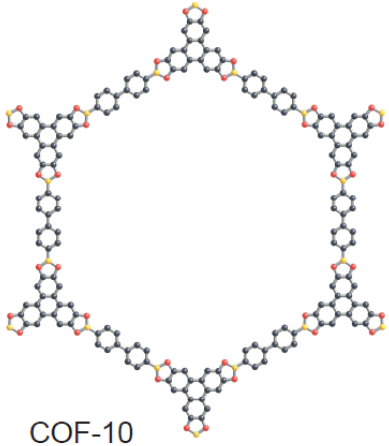
COF-5



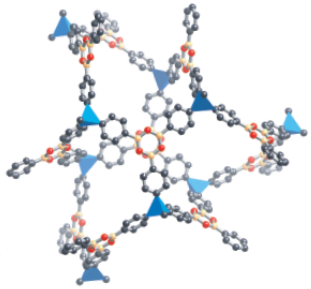
COF-6



COF-8

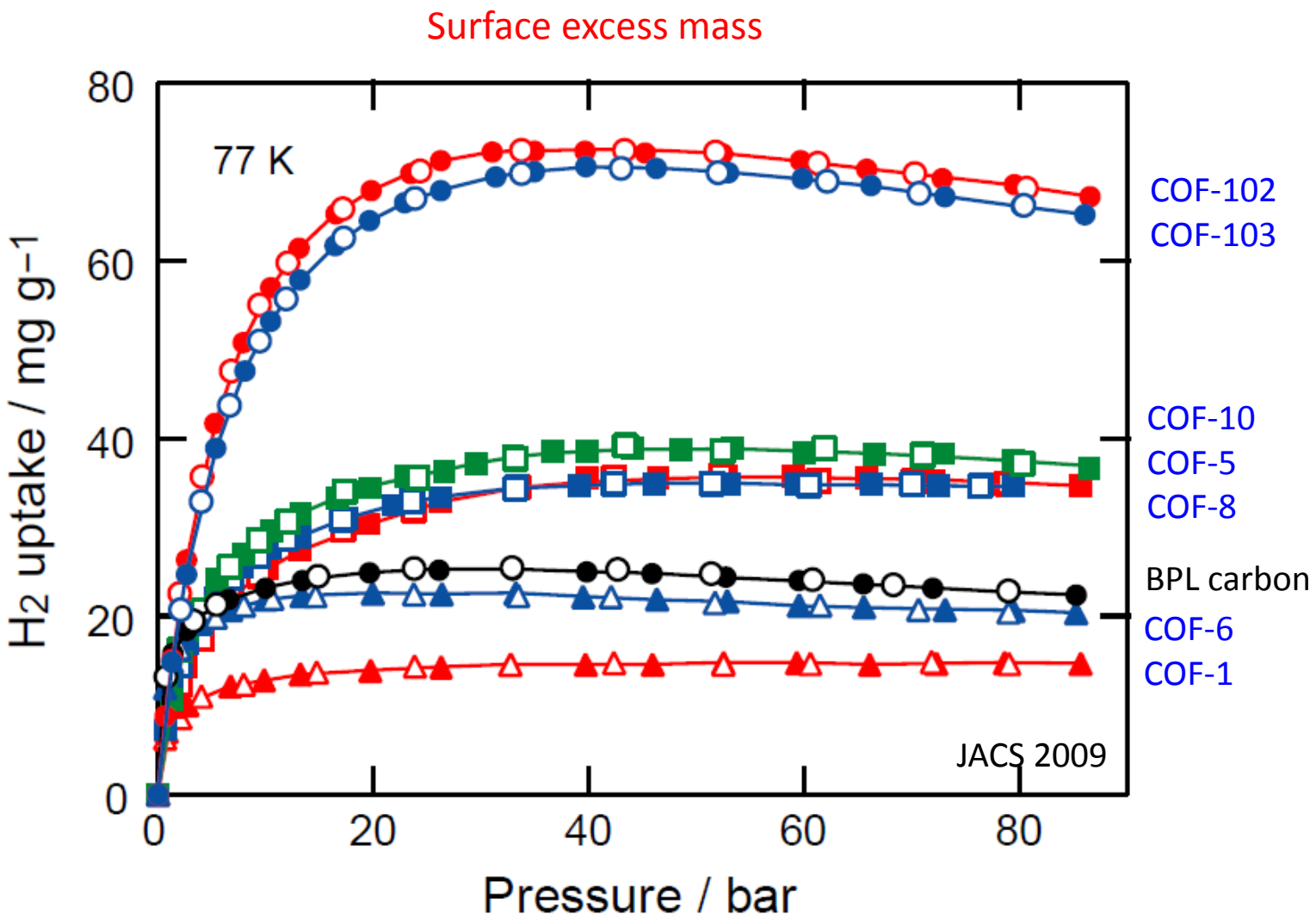


COF-10



COF-102 (X = C)
COF-103 (X = Si)

# High-pressure $H_2$ isotherms of COFs at 77 K




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

# Objectives (FY09-10)

Room temperature $H_2$ storage in COFs to meet DOE 2015 Targets

- Synergistic work between Yaghi (UCLA) and Goddard (Caltech)
- Build high-throughput preparation setups for COF synthesis (high temperature and pressure)
- Develop chemistry to realize stable frameworks
- Introduce potential metal binding sites through the COF synthesis
- Determine atomistic connectivity of COFs using an *ab initio* charge-flipping method using PXRD data
- Predict adsorption enthalpy of $H_2$ on various metal sites

# Milestones (FY10)

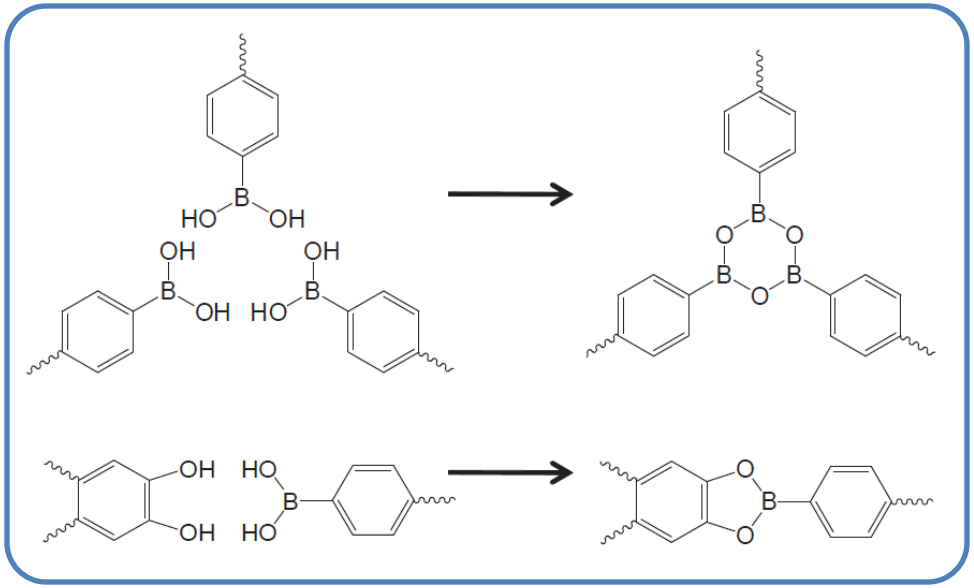
1. Discover new COFs utilizing high-throughput methods and explore $H_2$ uptake properties of COFs in the same parameter range.

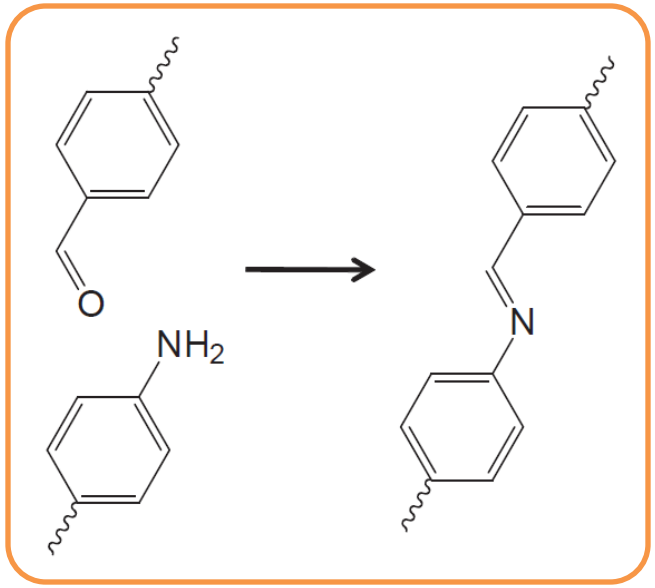
2. Investigate pressure and temperature dependence of $H_2$ uptake in metalated COFs over the parameter range specified in DOE YR2015 guidelines (5.5 wt % and 40 g $L^{-1}$ up to 100 bar, -40/85 C). Compare with predictions from theory.

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

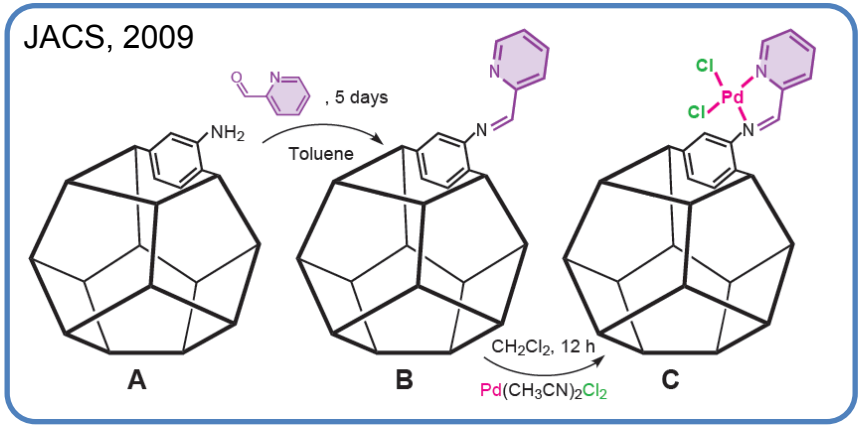
# Strategy

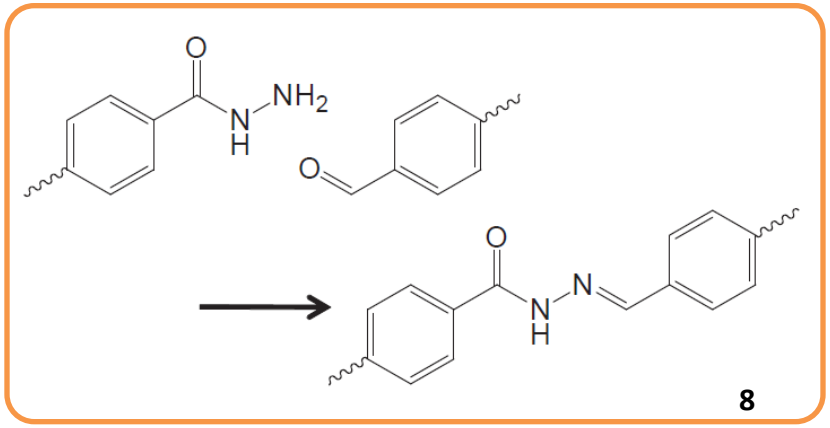
## Improve the framework stability against impurity (e.g. water)



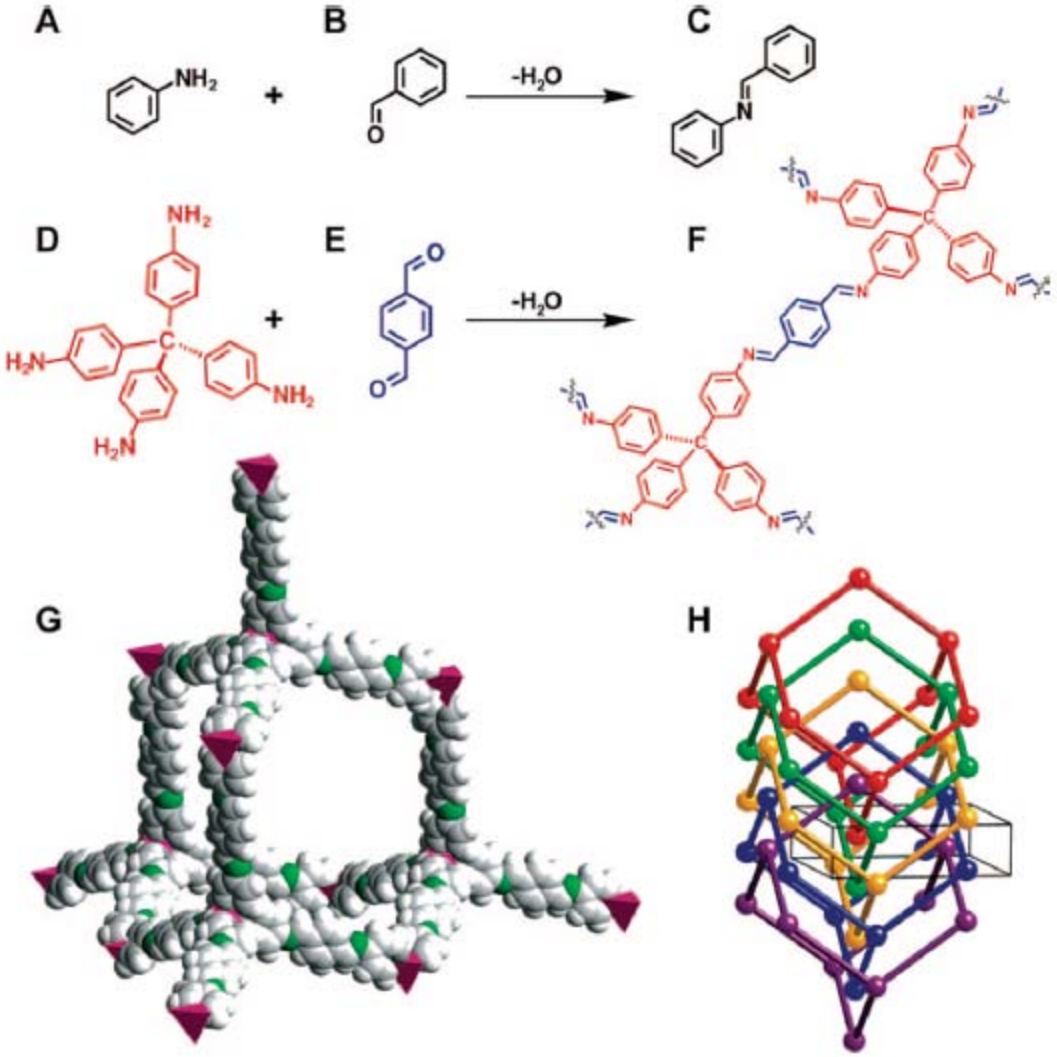


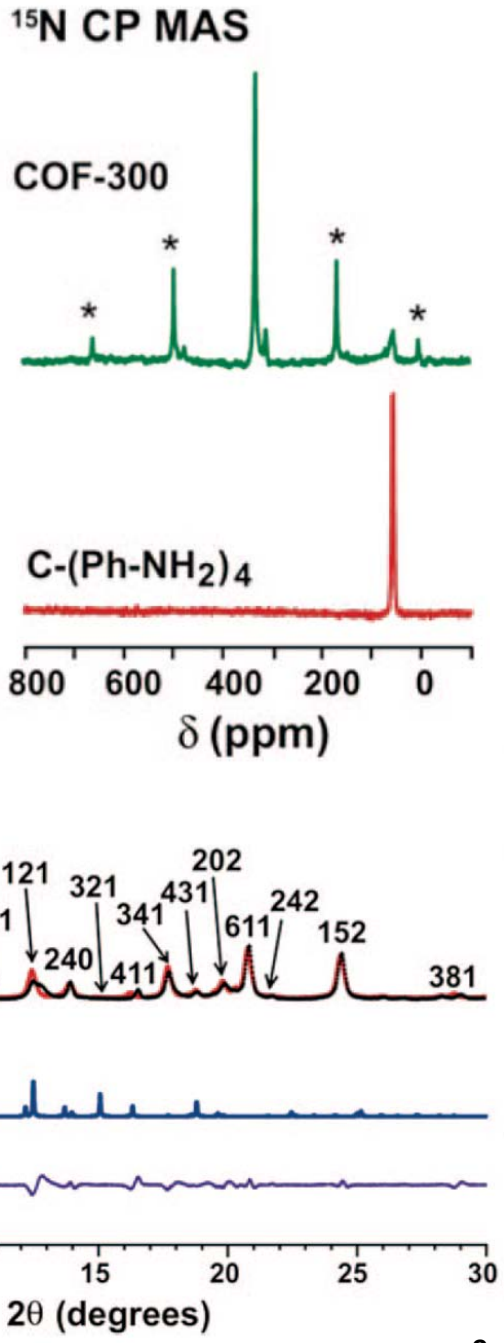

## Introduce metal binding sites through the COF formation



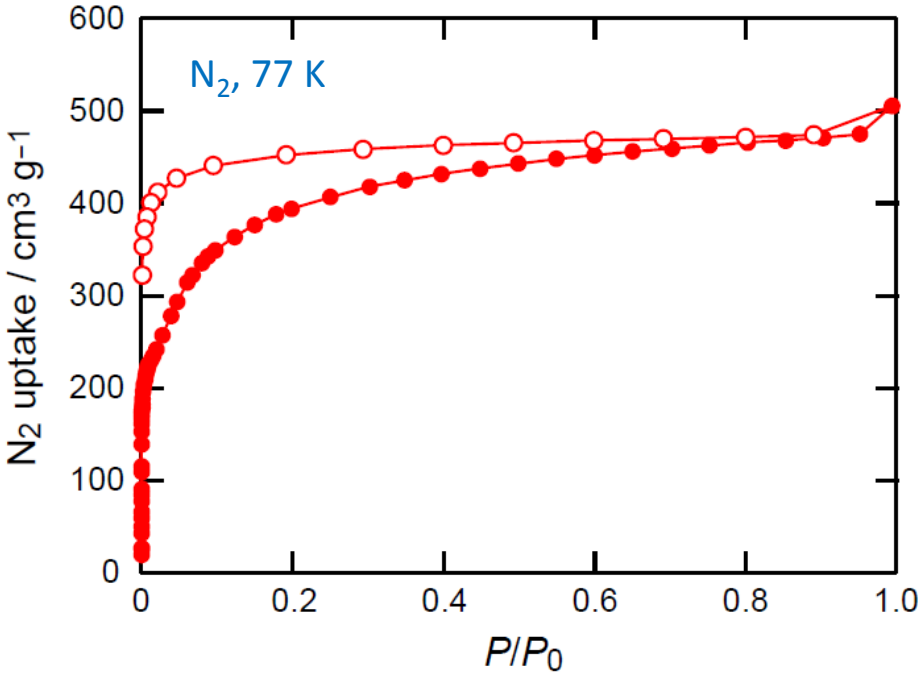
# Imine-Linked 3-D Porous COF

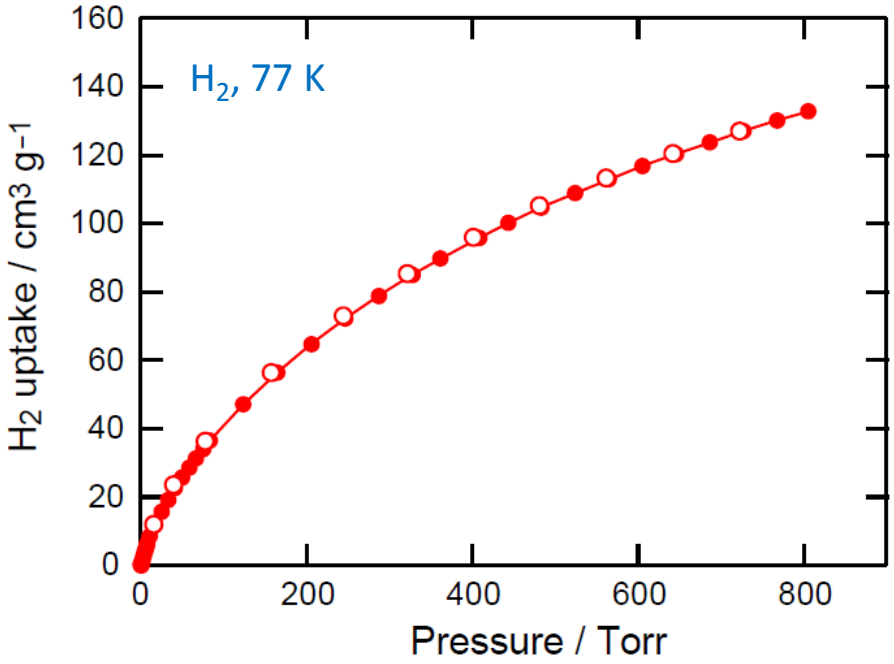


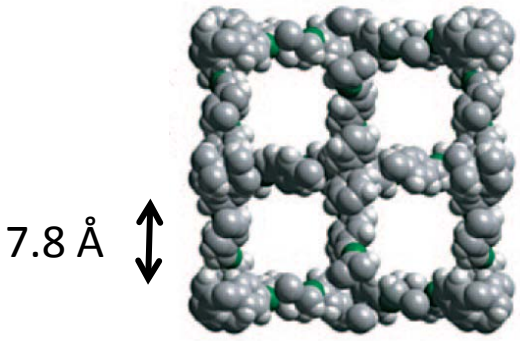




*J. Am. Chem. Soc.*, **2009**, *131*, 4570-4571

# $N_2$ and $H_2$ isotherms for COF-300

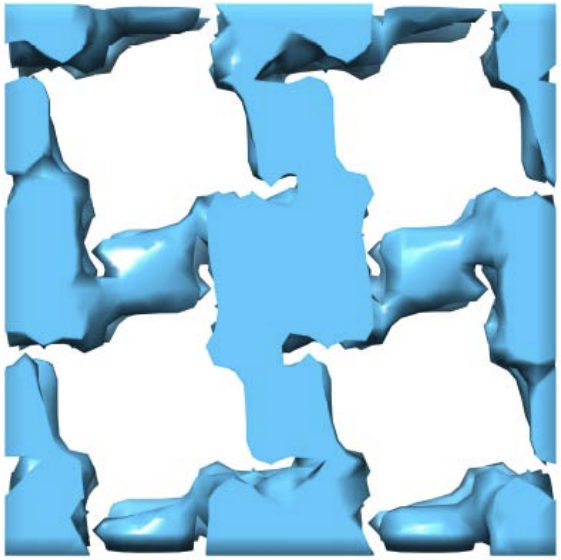


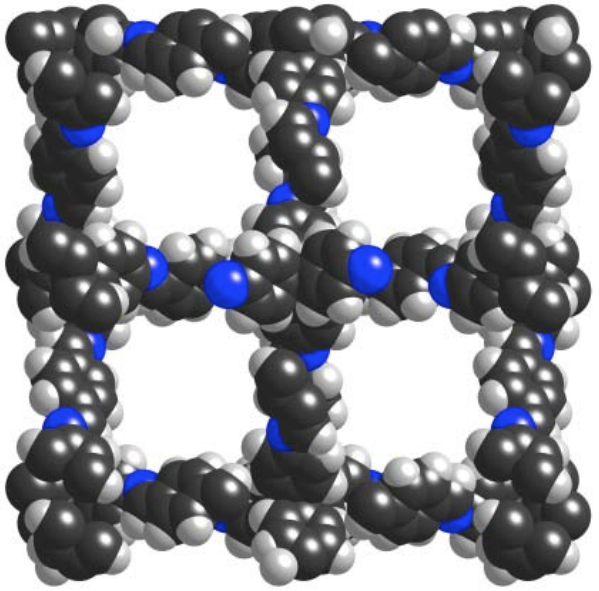




Permanent porosity was observed.
(BET SA = 1360 $m^2/g$, pore volume = 0.72 $cm^3/g$)
1.1 wt% $H_2$ uptake at 1 bar and 77 K

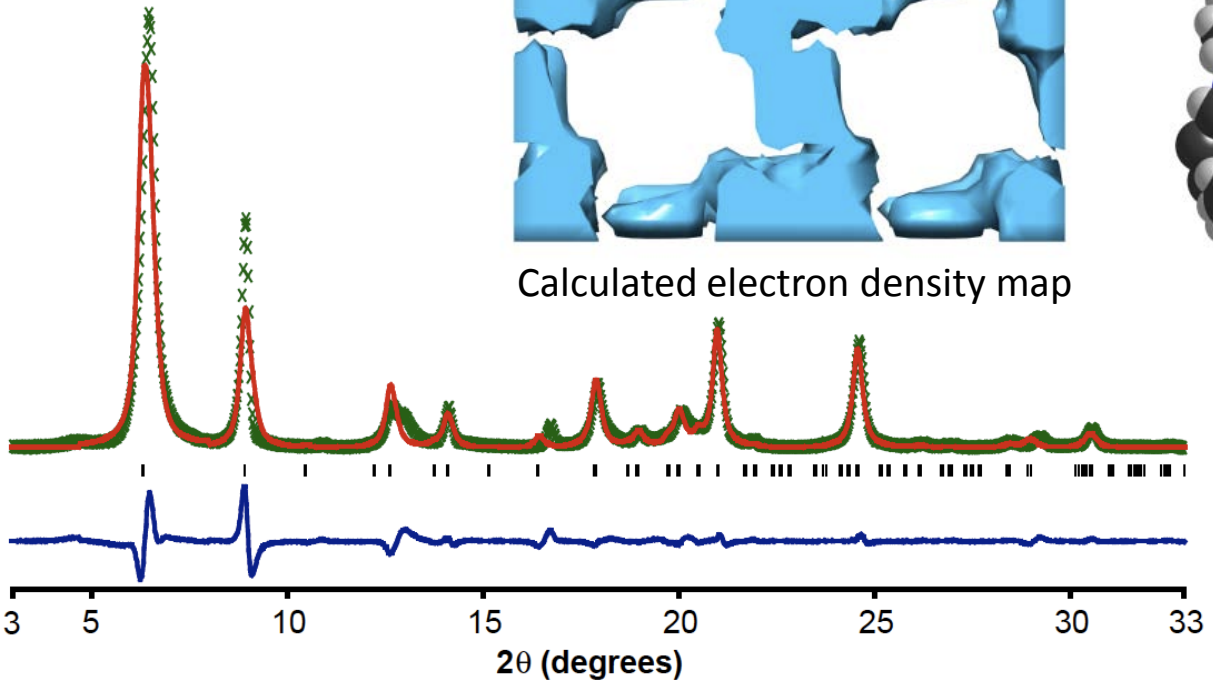
# Pore structure from low resolution PXRD data



Calculated electron density map



Space filling model of COF-300

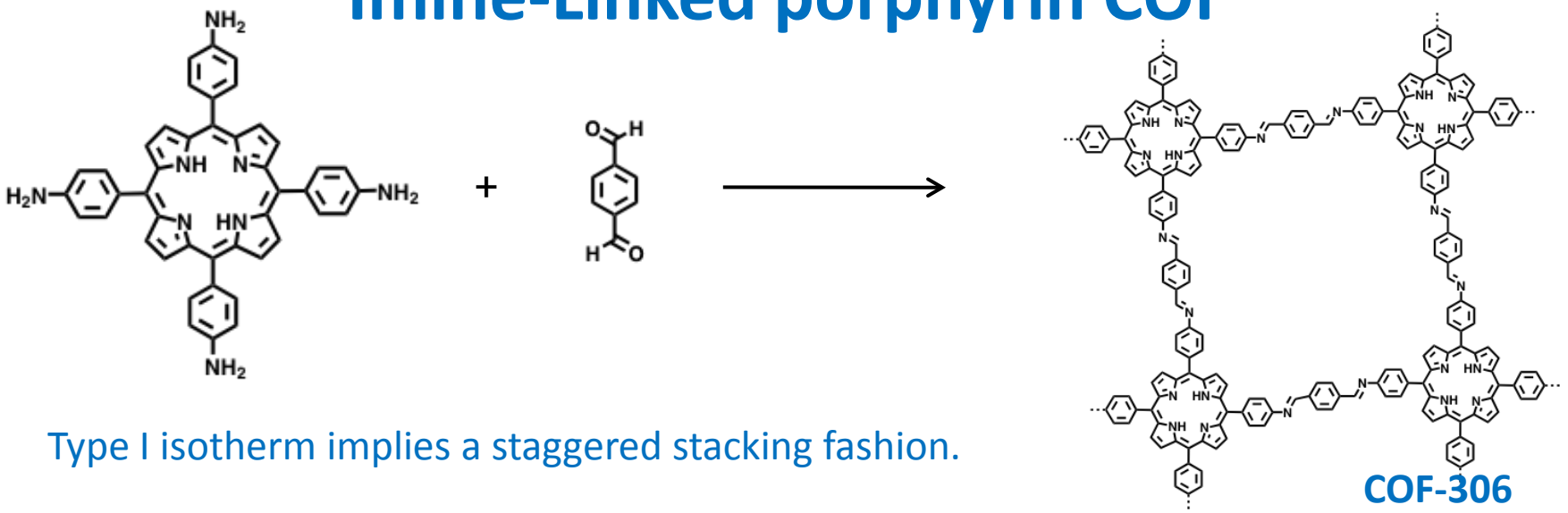



Refined powder X-ray diffraction pattern (resolution 2.0 Å) of activated COF-300

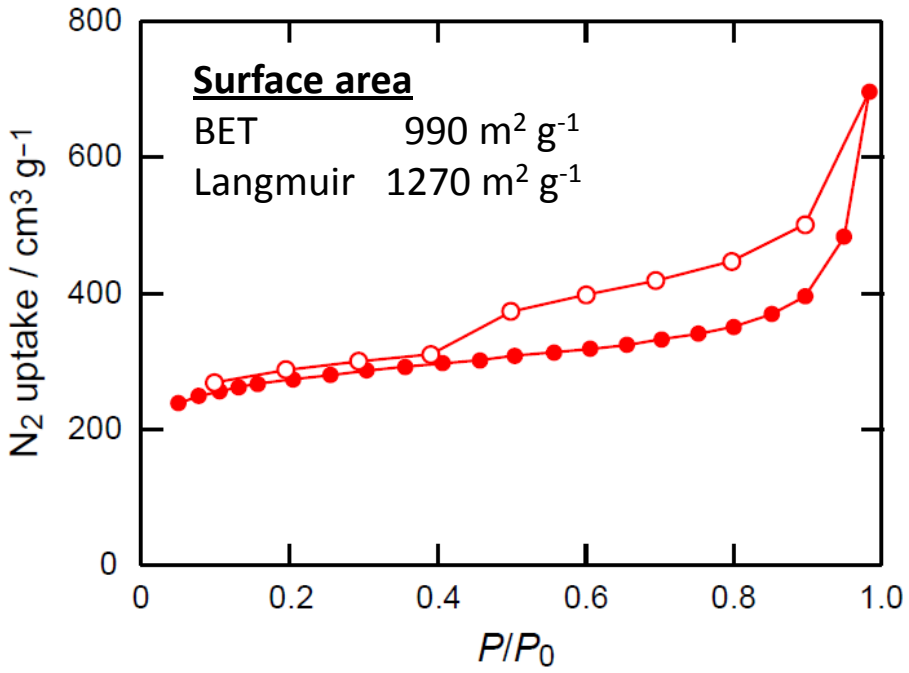
*ab initio* charge-flipping method was applied to determine the pore structure with extracted intensities.

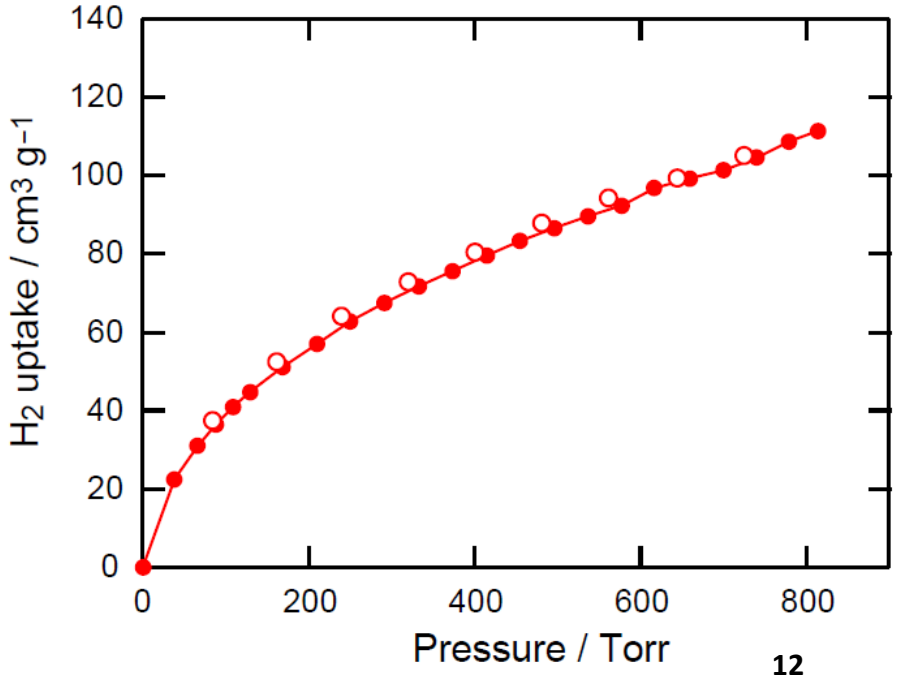
- Unit cell parameters are required.
- No information related to the connectivity and space group is necessary.

# Imine-Linked porphyrin COF

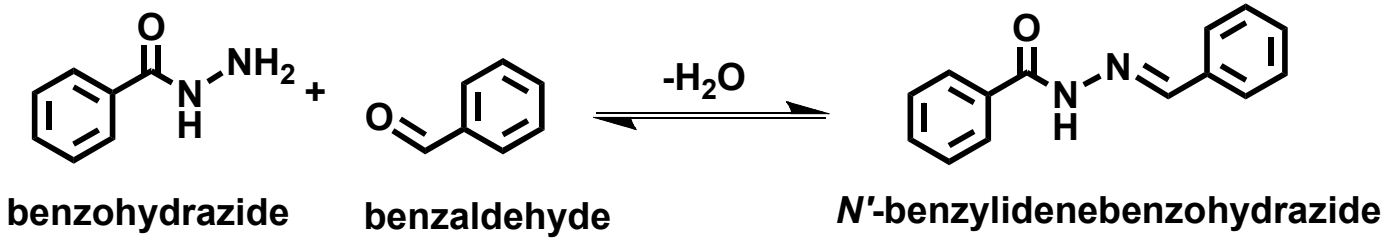



Type I isotherm implies a staggered stacking fashion.



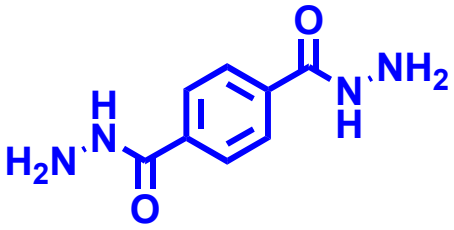
# Hydrazone condensation



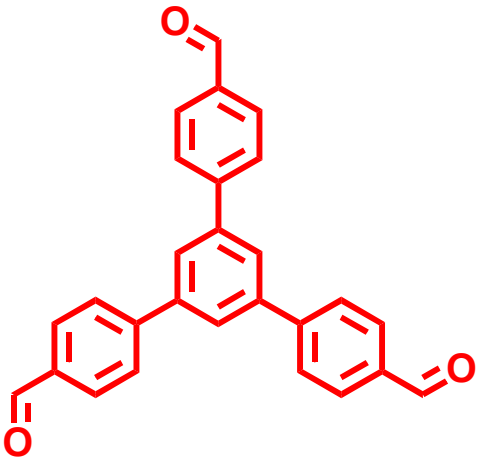

benzohydrazide benzaldehyde ***N'*-benzylidenebenzohydrazide**

- Contains imine and amide functionalities
- Obtained hydrazone chemically stable in water and basic conditions.
- Polyacylhydrazones have been prepared showing monomer exchange under mild conditions.
- Hydrazides are very easy to make.
- Potential metal binding sites

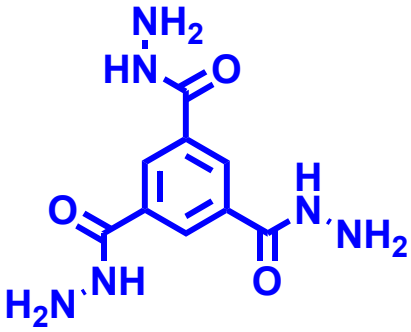
# Building blocks



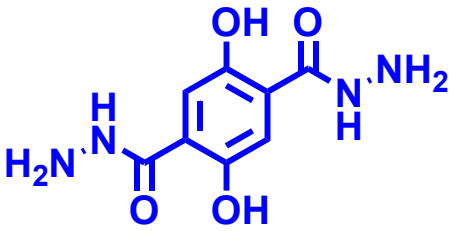
terephthalohydrazide



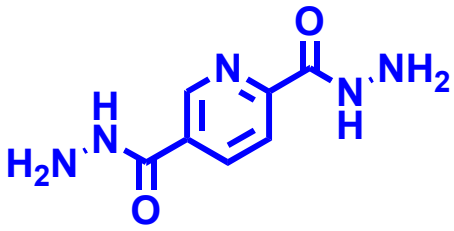
1,3,5-tris(4-formyl-phenyl)-benzene



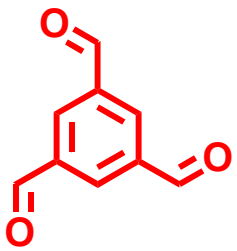
benzene-1,3,5-tricarbohydrazide



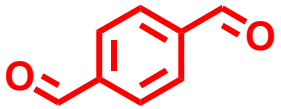
2,5-dihydroxyterephthalohydrazide



pyridine-2,5-dicarbohydrazide

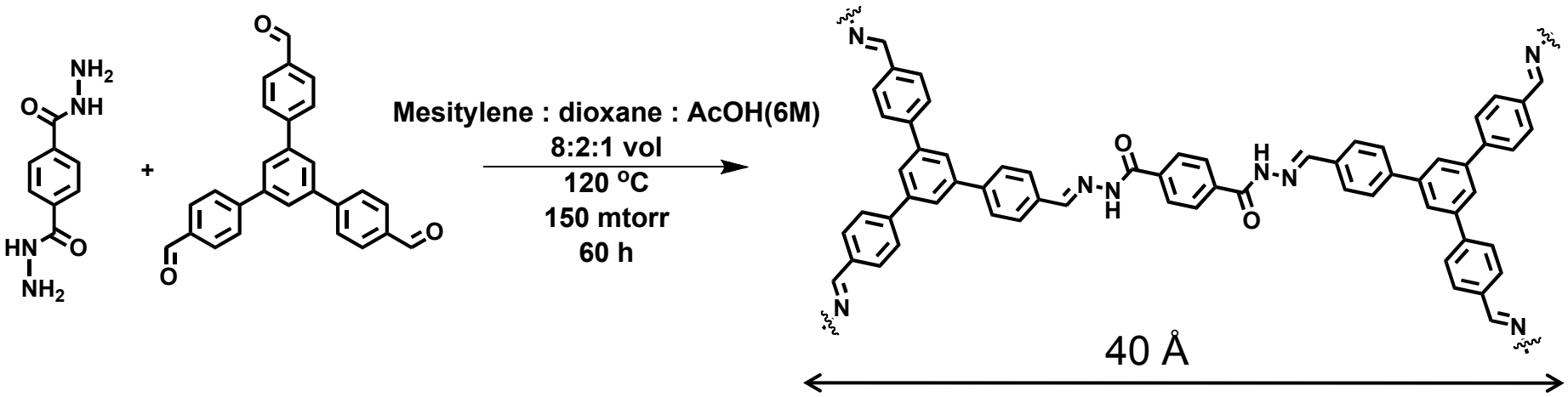


benzene-1,3,5-tricarbaldehyde



terephthalaldehyde

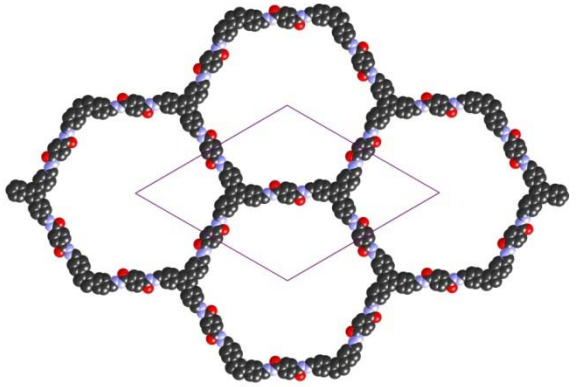
# Typical example: COF-41




Expected pore size is large enough to hold metal complexes.

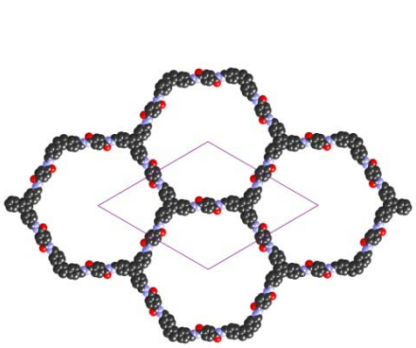
- White-yellow product.
- Hot filtration & rinse with boiling dioxane & cold THF.
- Distance between $C_3$ centers: 26.2 Å.

| FT-IR | ν (C=N) 1 | ν (C=N) 2 |
|---|---|---|
| COF-41 | 1558 | 1273 |
| Model | 1550 | 1288 |

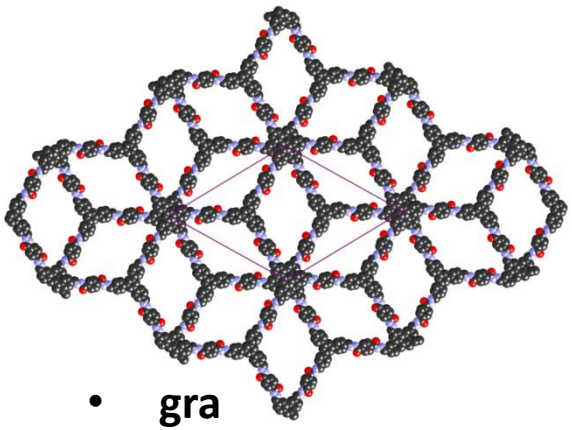


# Proposed structure of COF-41

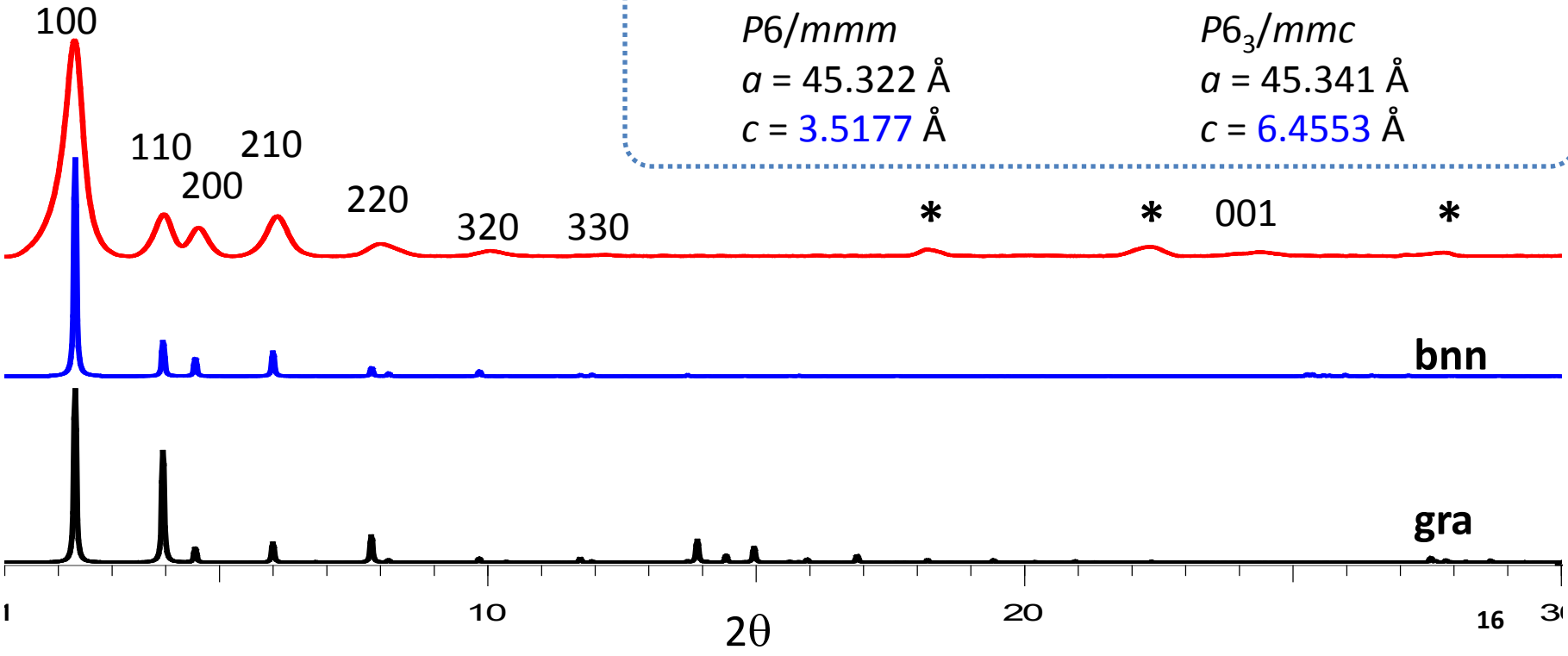
**COF-41**
hexagonal P
*a* = 43.616(14) Å
*c* = 3.6186(13) Å



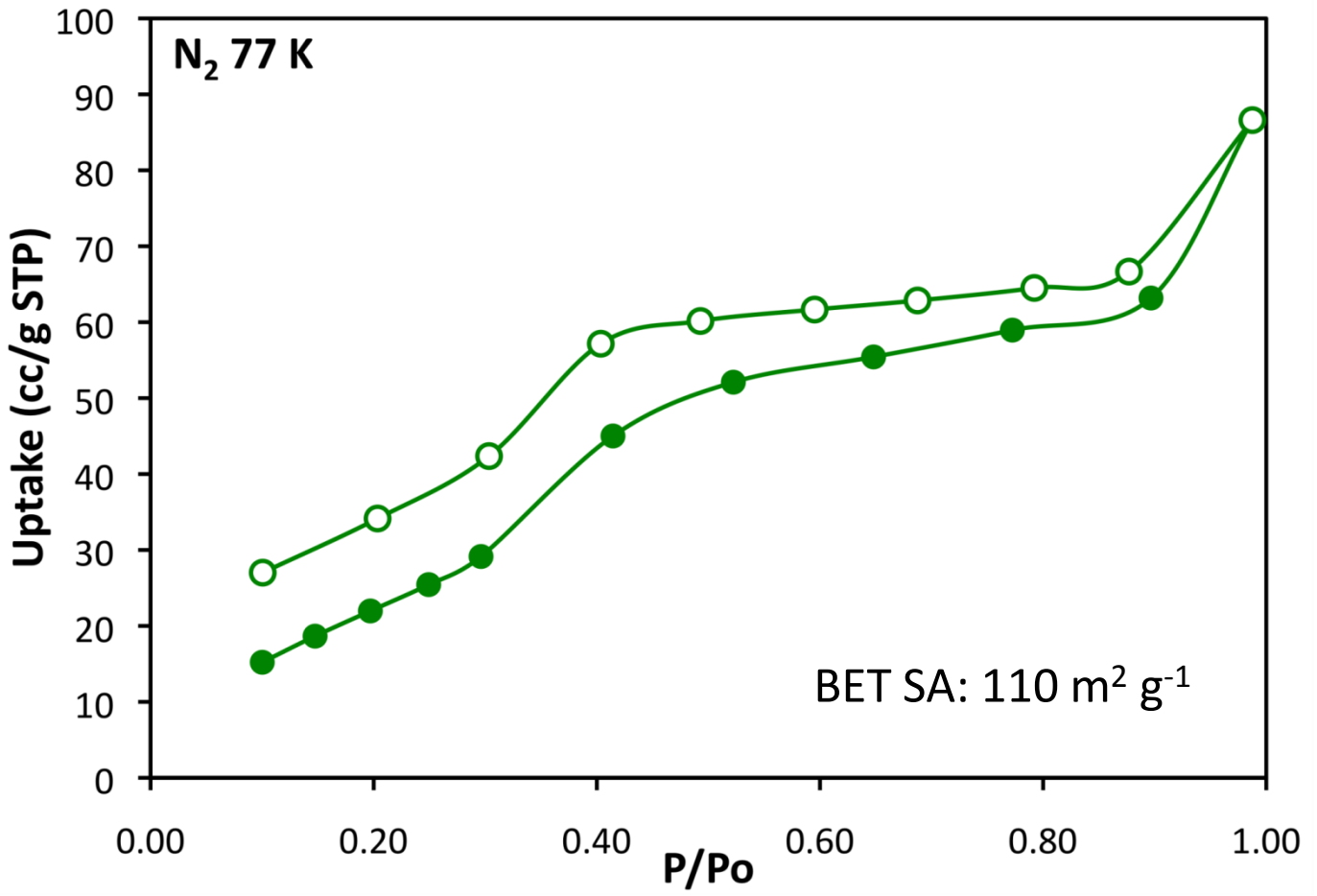
- **bnn**
  *P6/mmm*
  *a* = 45.322 Å
  *c* = 3.5177 Å



- **gra**
  *P6*$_3$*/mmc*
  *a* = 45.341 Å
  *c* = 6.4553 Å

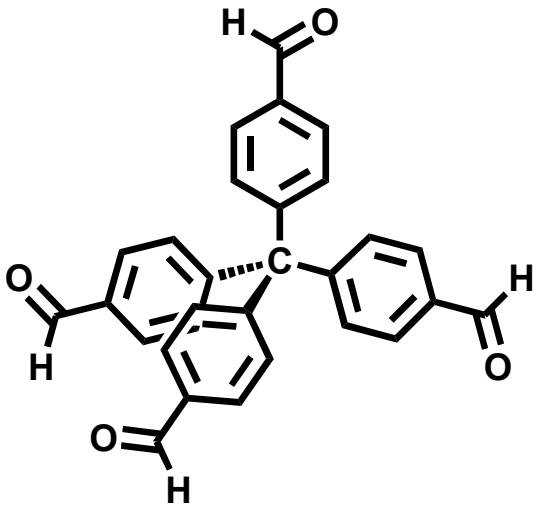


# $N_2$ isotherm for COF-41

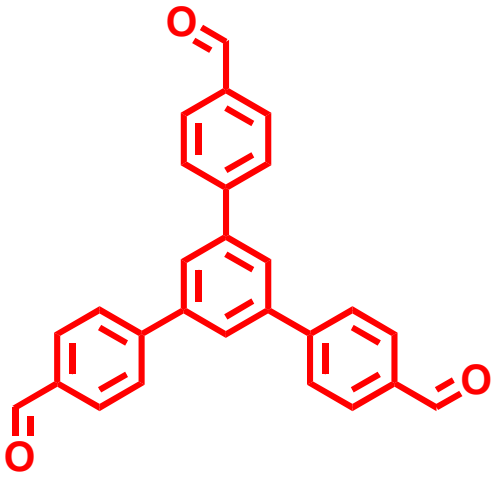



- Presence of mesopore ➔ enough space for metal impregnation
- Activation procedure needs to be optimized

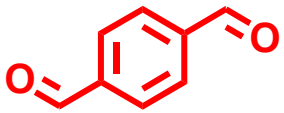
# Future work: other building blocks (for 3D nets)



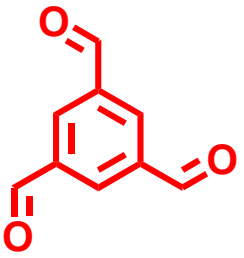

4,4',4'',4'''-methanetetrayltetrabenzaldehyde




1,3,5-tris(4-formyl-phenyl)-benzene

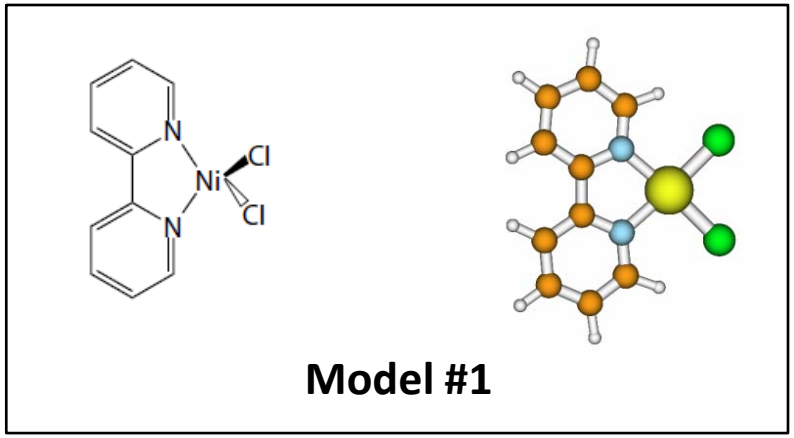



terephthalaldehyde

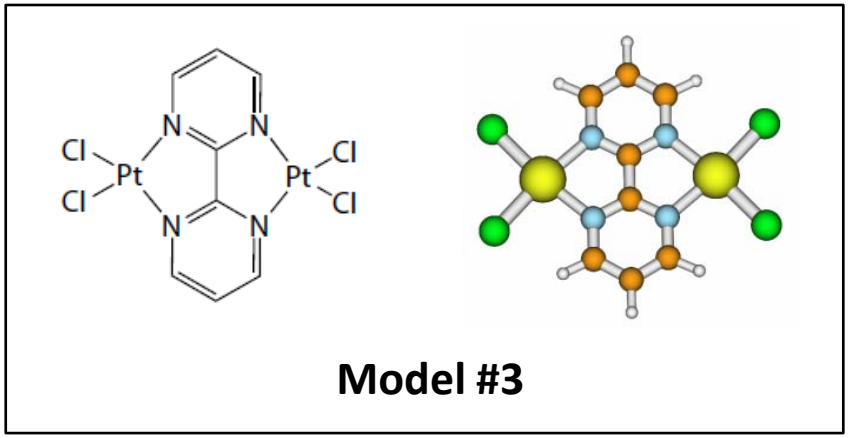



benzene-1,3,5-tricarbaldehyde

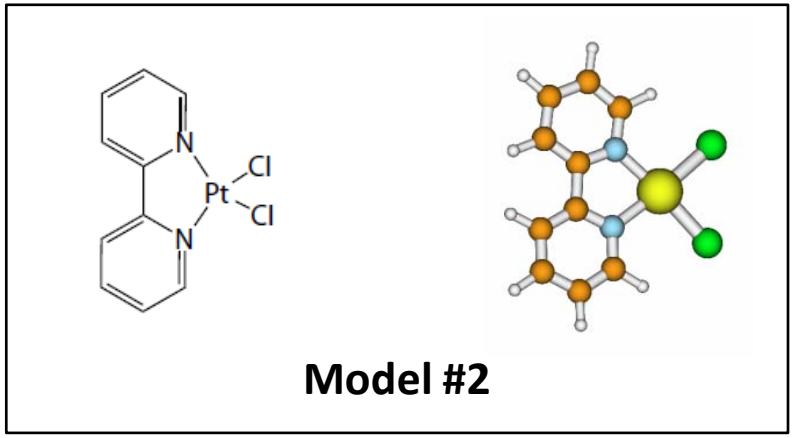
# Coordination with theory: Examined model systems



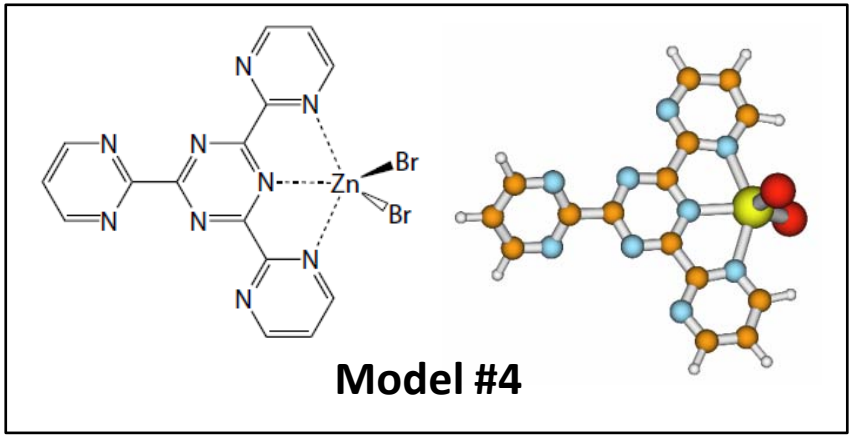

**Model #1**




**Model #3**



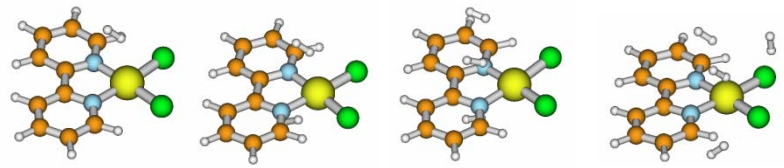

**Model #2**

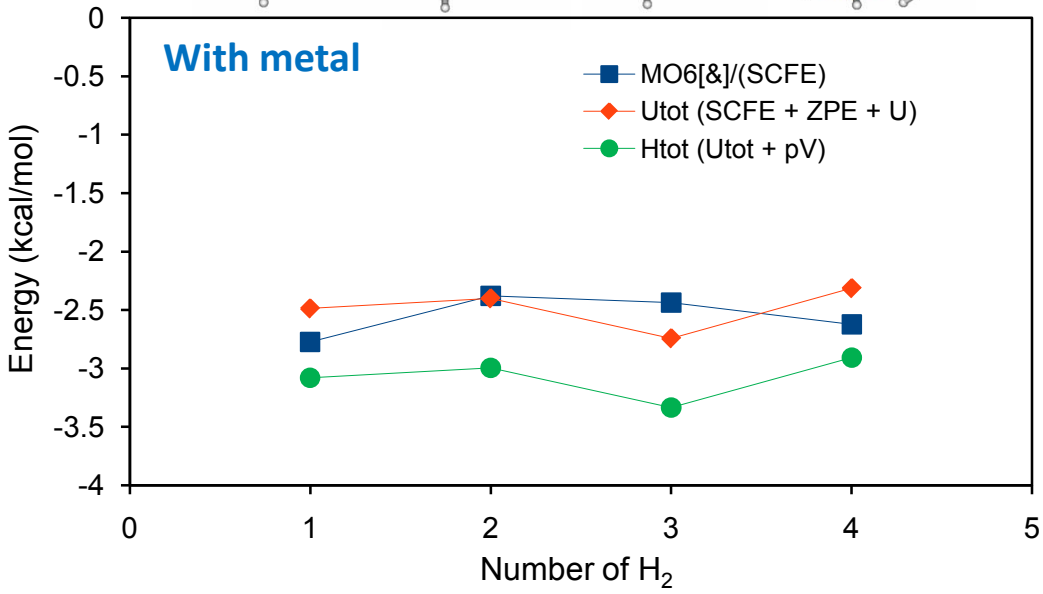


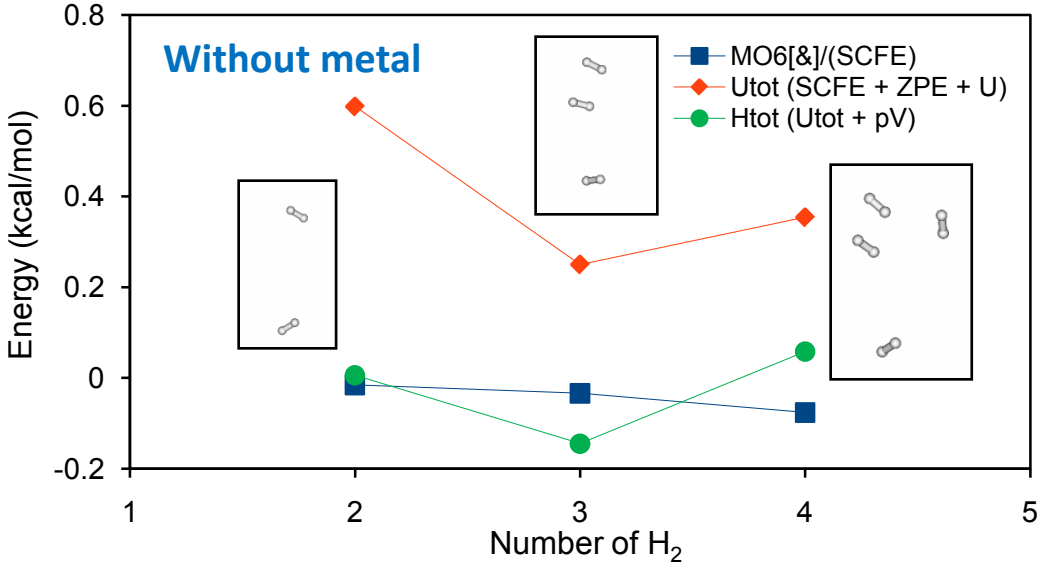

**Model #4**

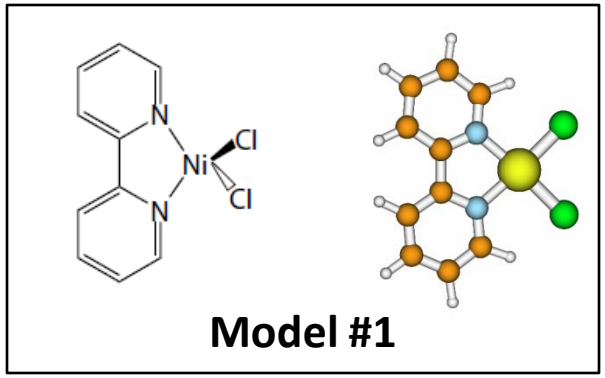
- Four plausible model systems were tested.
- Calculated MO, $U_{total}$ and $H_{total}$ for each model.
- The DFT-MO6 functional was used to calculate the non covalent interactions with the basis set LACVP to calculate optimization.
- Adsorption enthalpy of these models is ranging from 3 to 4 kcal/mol (12-17 kJ/mol )

# Theoretical prediction of binding energy #1





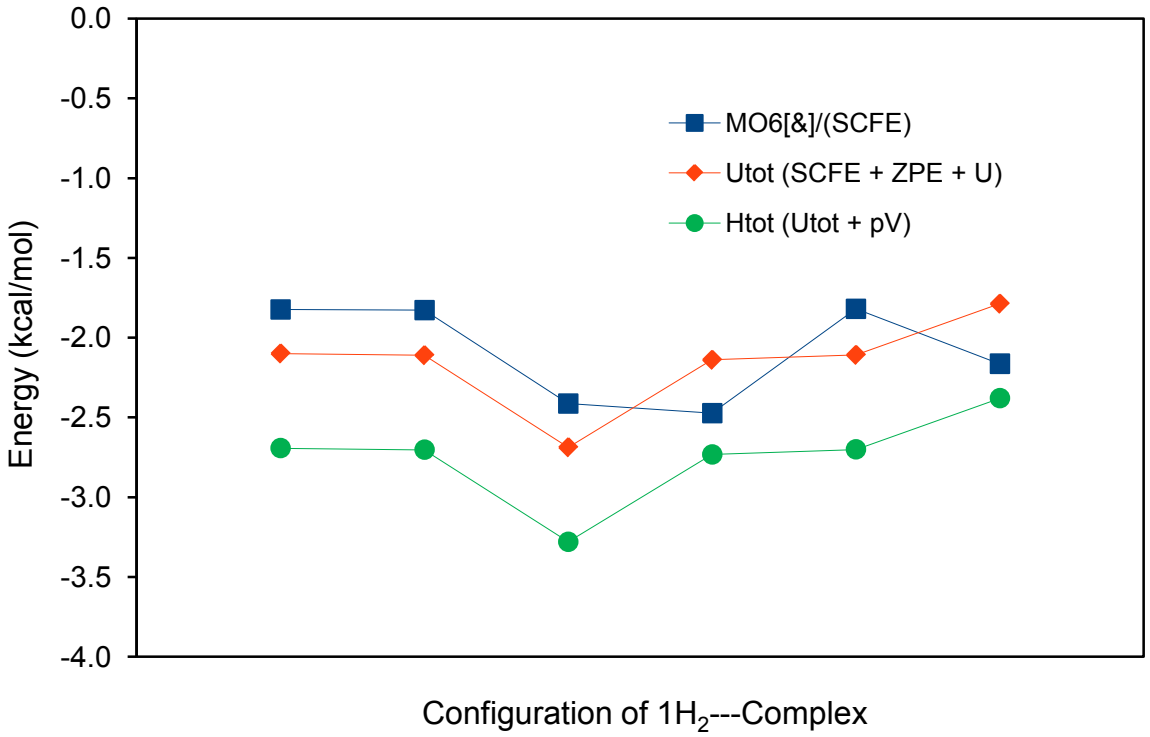



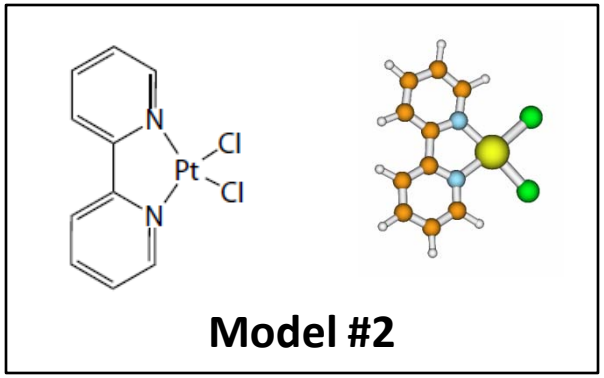




The binding energy is almost constant with the addition of $H_2$.

$H_2$-$H_2$ interaction of the metal-complex is stable than that of the bipyridine system.

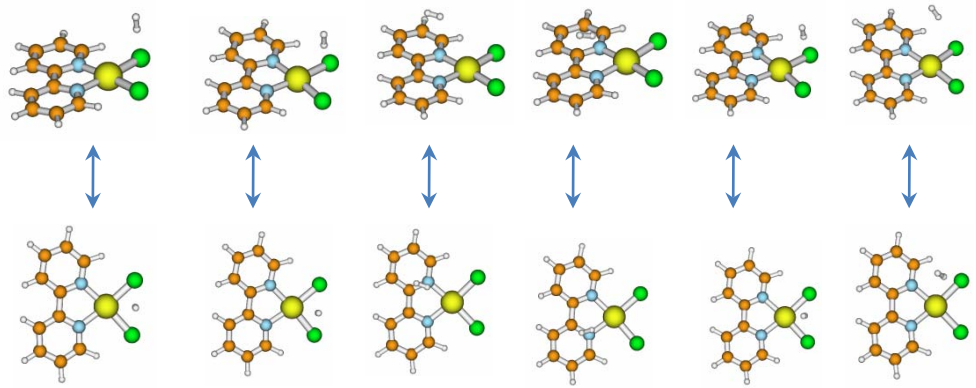
# Theoretical prediction of binding energy #2



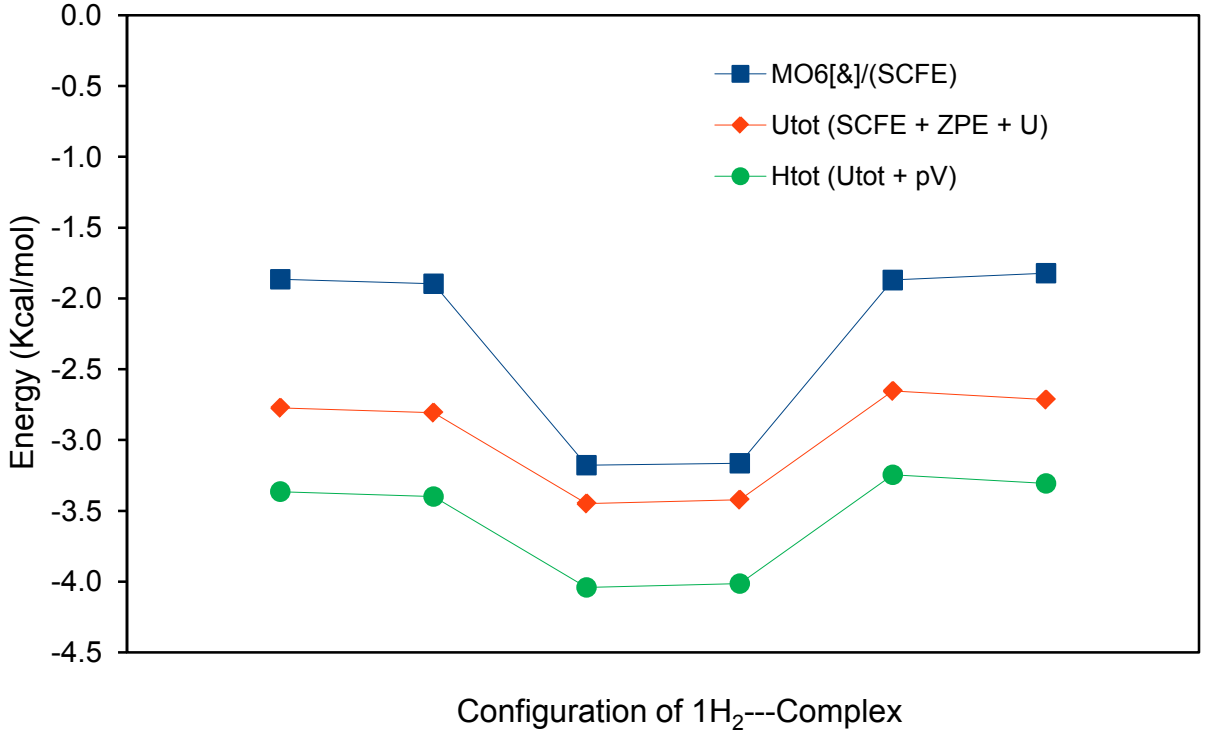

**Model #2**

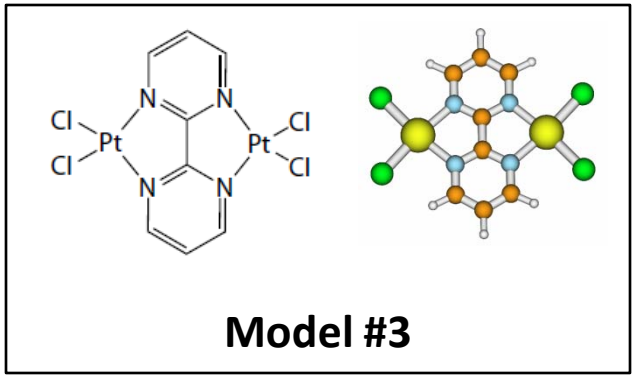
The most favorable interaction is observed over the bond of N-Pt, which is the same as N-Ni system (Model #1).



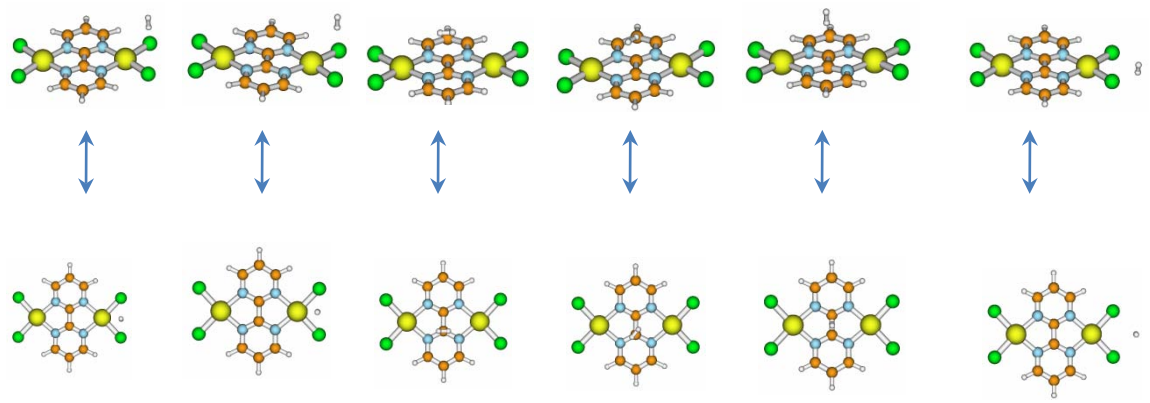
Predicted binding energy is smaller than Model #1 (ca. 1 kcal/mol).

# Theoretical prediction of binding energy #3



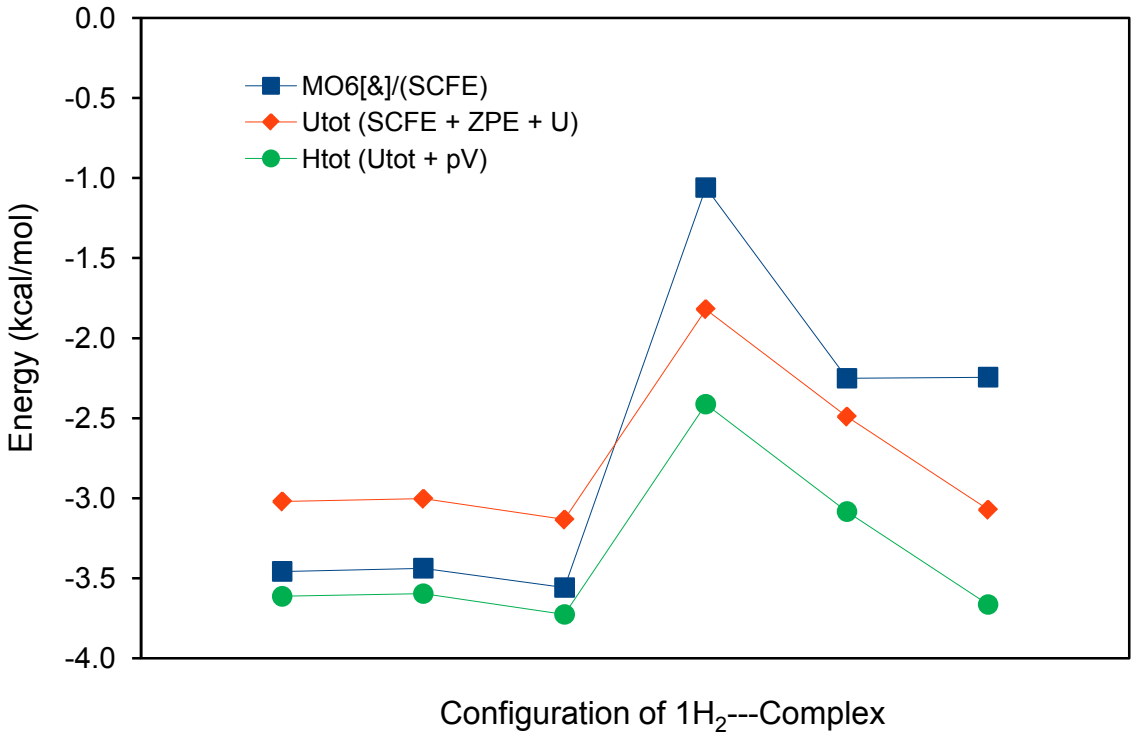



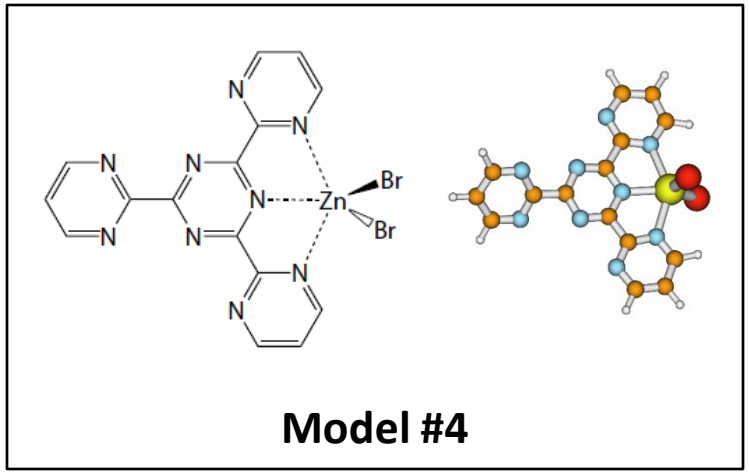

**Model #3**



Favorable interaction is observed when $H_2$ molecule locates over C atom of the five membered ring.

# Theoretical prediction of binding energy #4

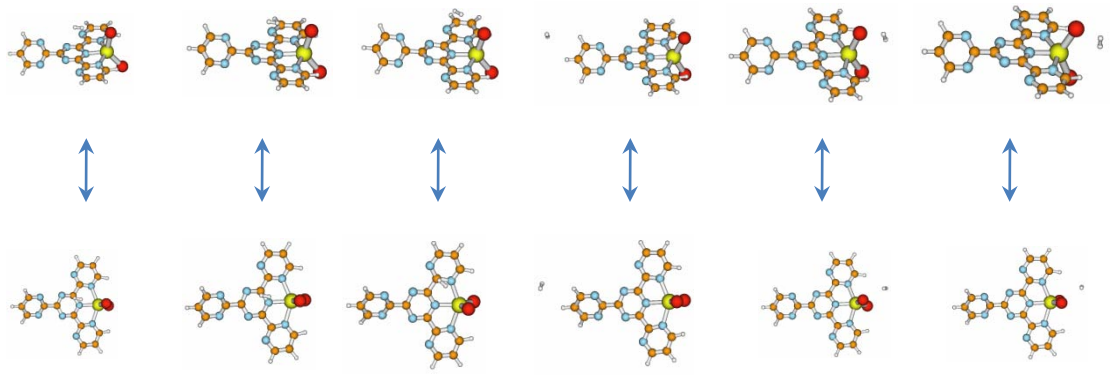


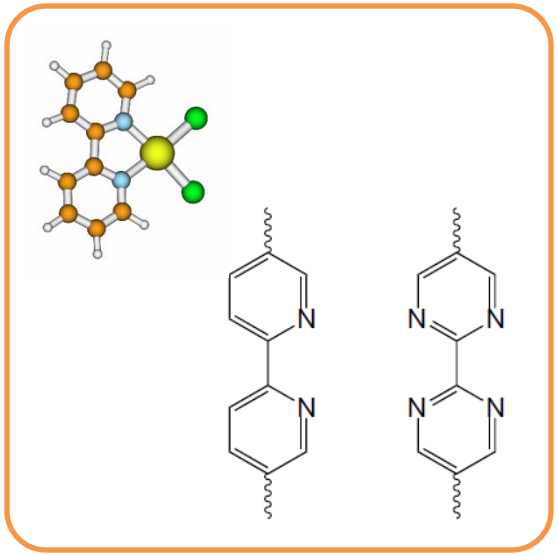

**Model #4**

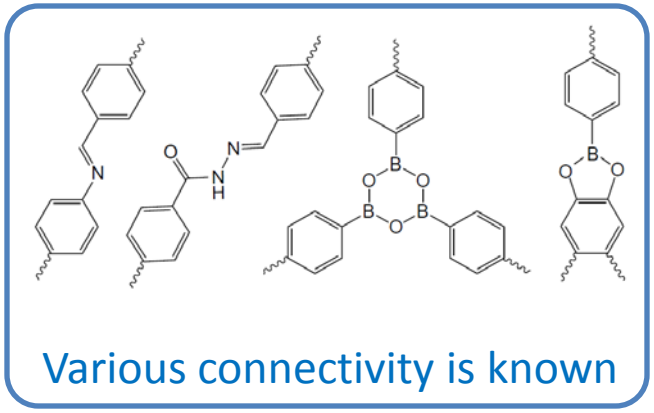
Adsorption sites of $H_2$ does not seem to be the metal itself.

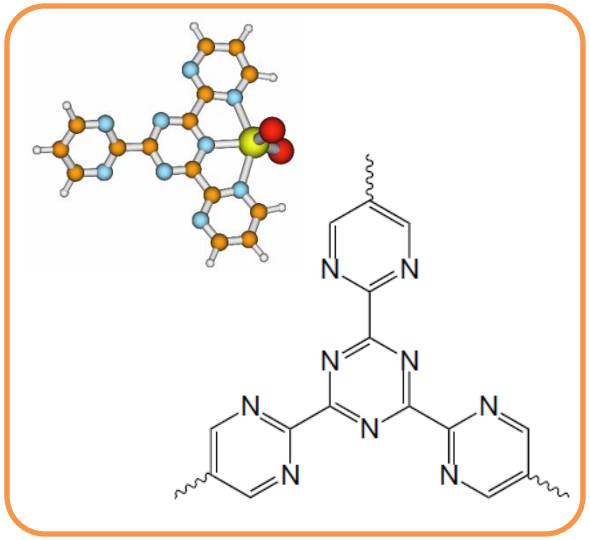
The most favorable interaction is observed when $H_2$ locates over the N-Zn bond.

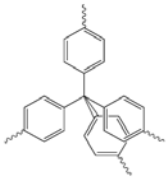


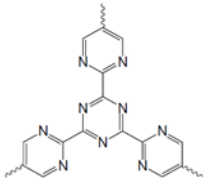
# Approach 1: Proposed COF connectivity for metalation

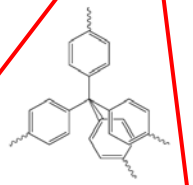


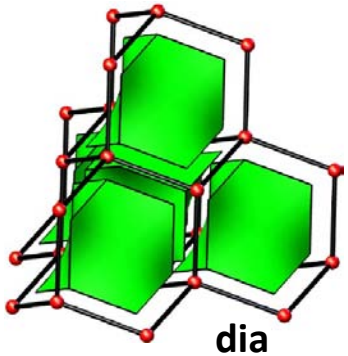


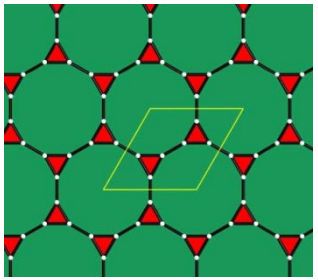




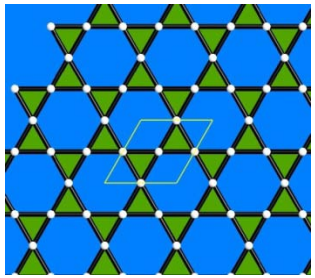




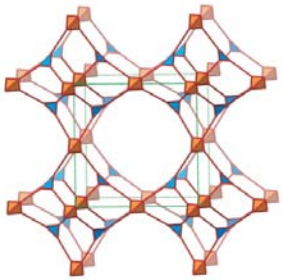
dia



hca



kgm



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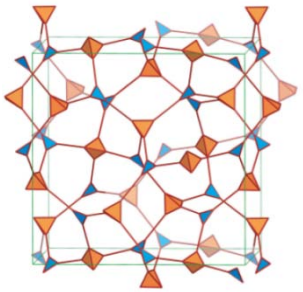
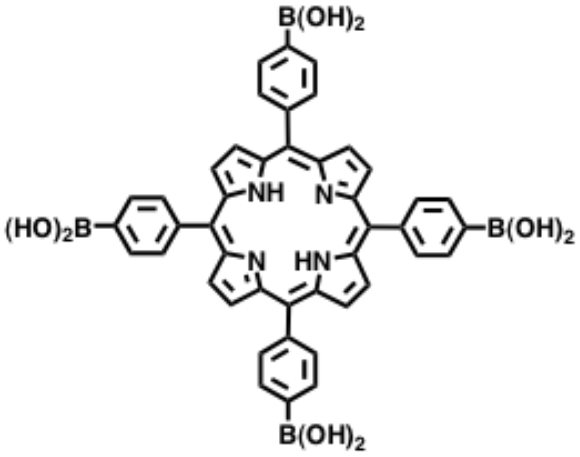


ctn

# Approach 2: Intercalation of COFs with metals

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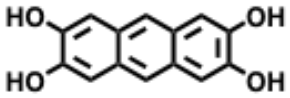
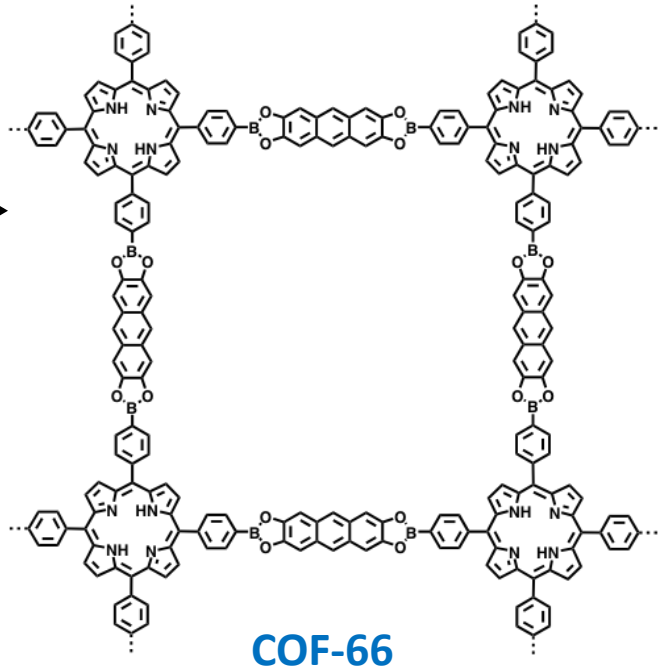
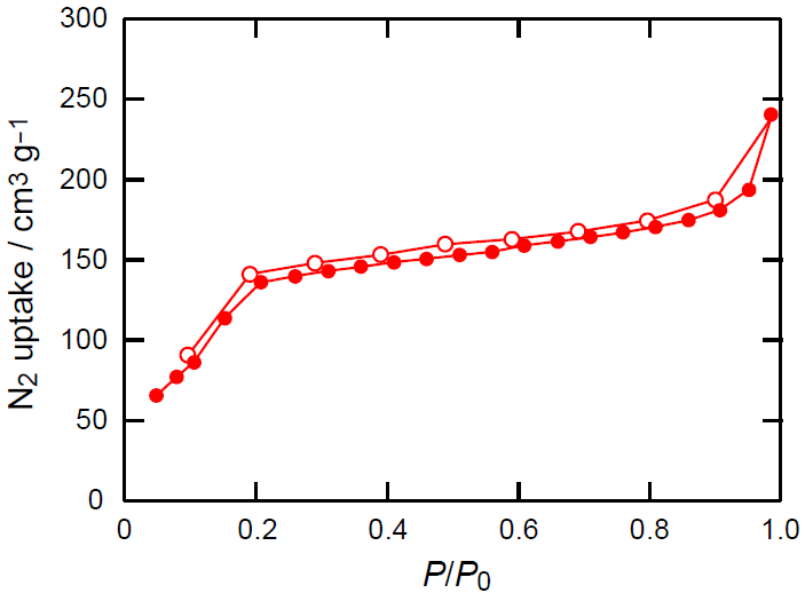


COF-66




- Permanent porosity was confirmed
- BET SA = 410 $m^2 g^{-1}$
- Presence of micropore filling (eclipse stacking)

Eclipse stacking fashion can be utilized for metal intercalation.

# 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:**

- Build high-throughput preparation setups
- Develop structural determination technique using *ab initio* charge-flipping method
- Synthesis of new COFs through hydrazone condensation
- Began modeling study for optimal binding energy

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

**Proposed future research:**

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