

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%

Budget

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

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

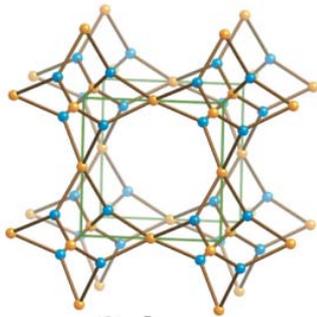
Collaborating Partner

- BASF

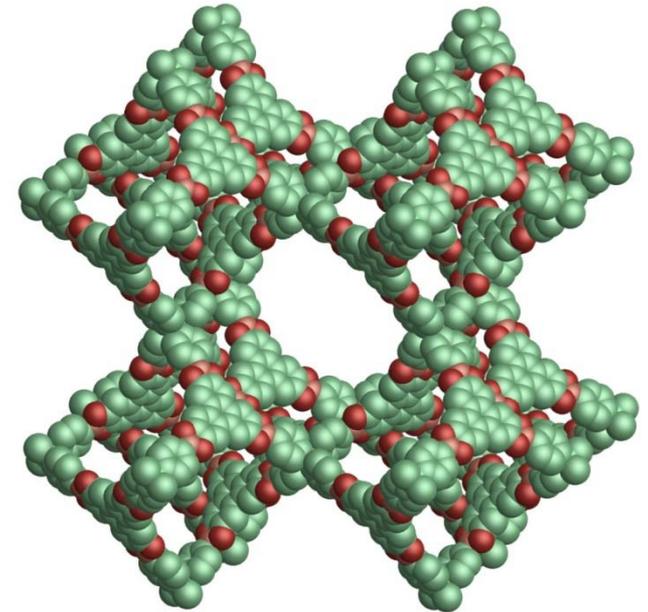
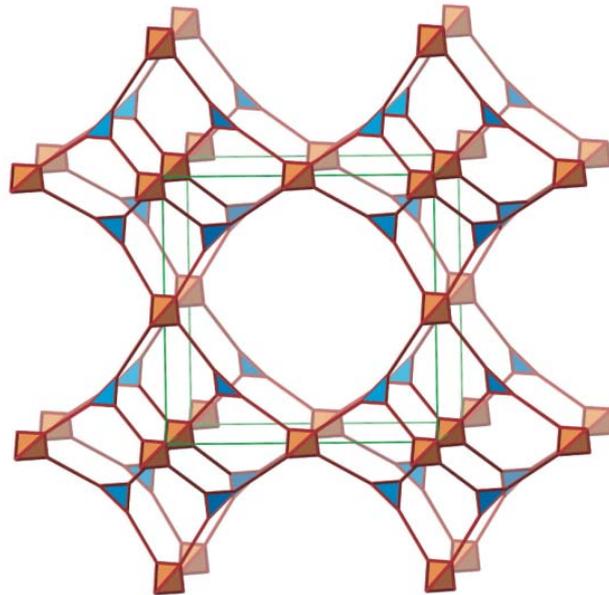
Description of new materials

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

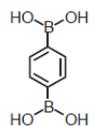
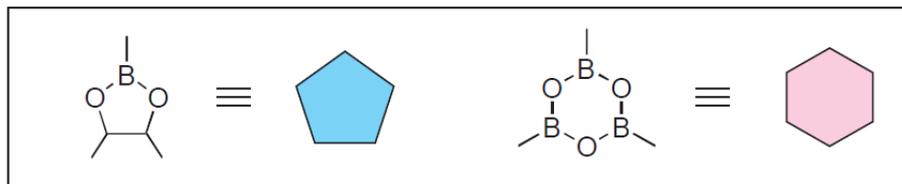
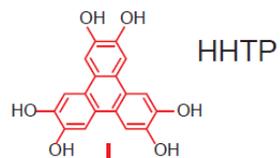


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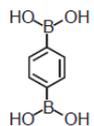


COF-108 ($d = 0.17 \text{ g cm}^{-3}$)

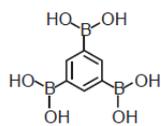
Covalent Organic Frameworks (COFs)



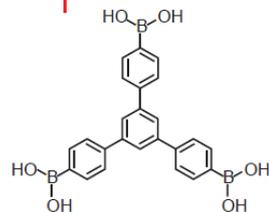
BDPA



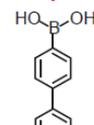
BDBA



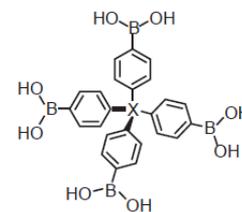
BTBA



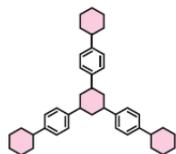
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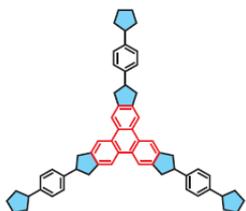
BPDA



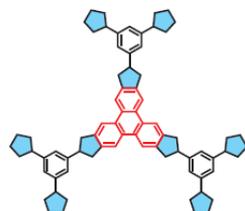
TBPM (X = C)
TBPS (X = Si)



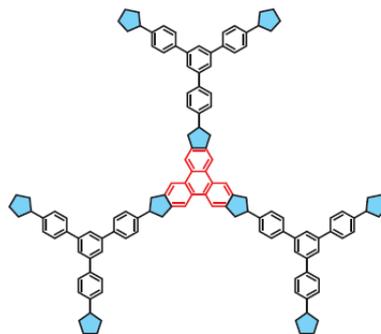
COF-1



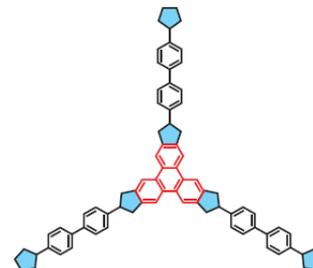
COF-5



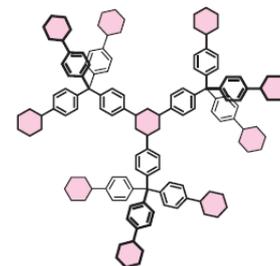
COF-6



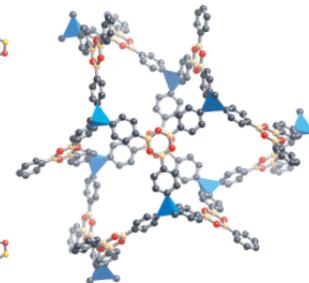
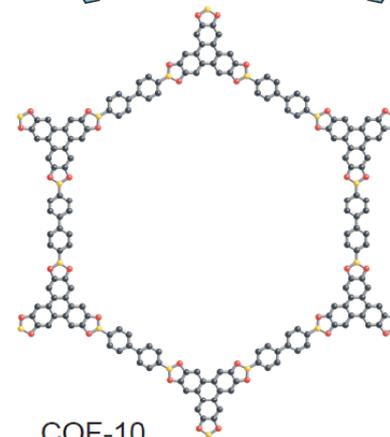
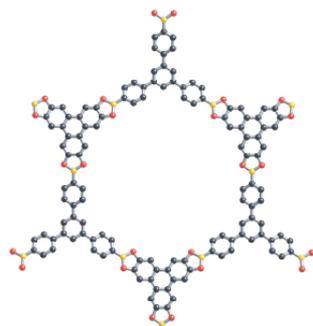
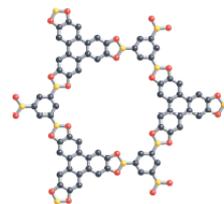
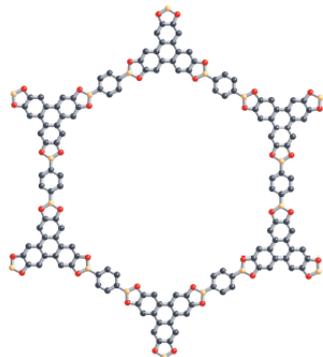
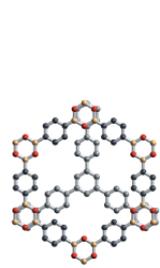
COF-8



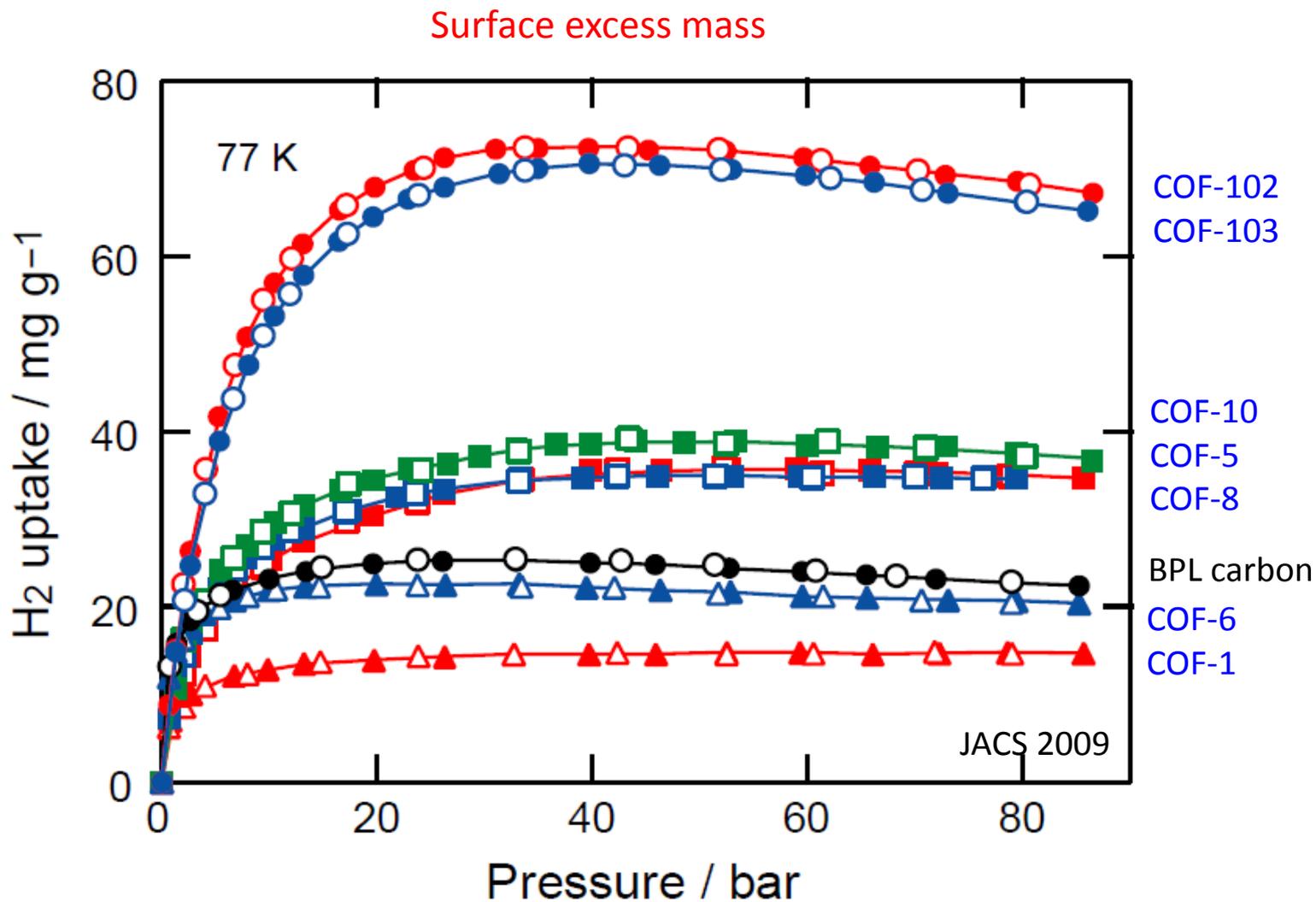
COF-10



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



High-pressure H₂ isotherms of COFs at 77 K



H₂ uptake in 3D COFs is almost the same as that in MOF-177.

Objectives (FY09-10)

Room temperature H₂ storage in COFs to meet DOE 2015 Targets

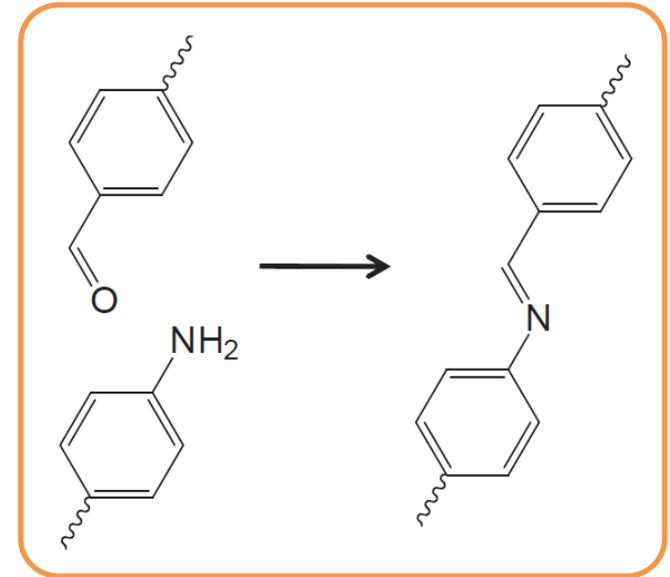
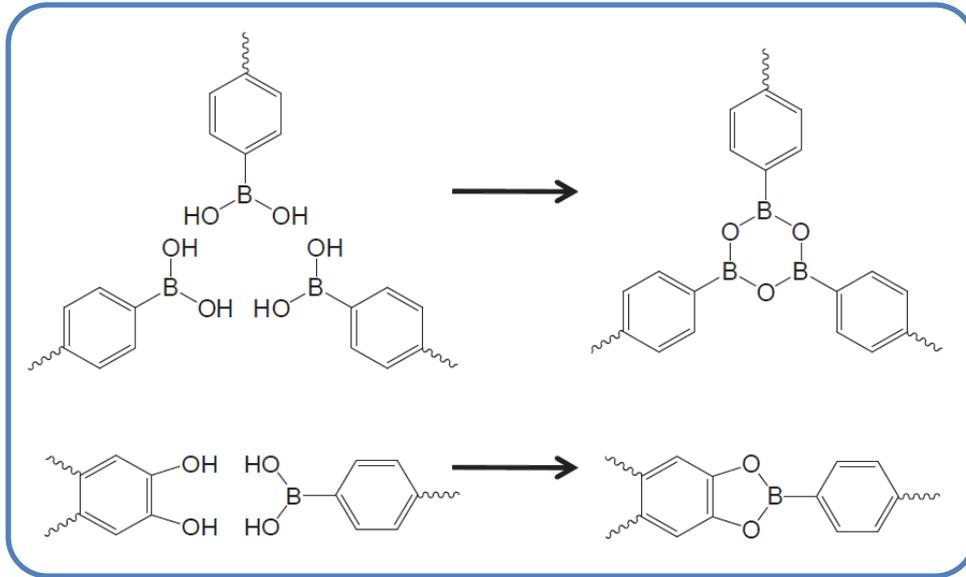
- ❑ Synergistic work between Yaghi (UCLA) and Goddard (Caltech)
- ❑ Build high-throughput preparation setups for COF synthesis (high temperature and pressure)
- ❑ Develop chemistry to realize stable frameworks
- ❑ Introduce potential metal binding sites through the COF synthesis
- ❑ Determine atomistic connectivity of COFs using an *ab initio* charge-flipping method using PXRD data
- ❑ Predict adsorption enthalpy of H₂ on various metal sites

Milestones (FY10)

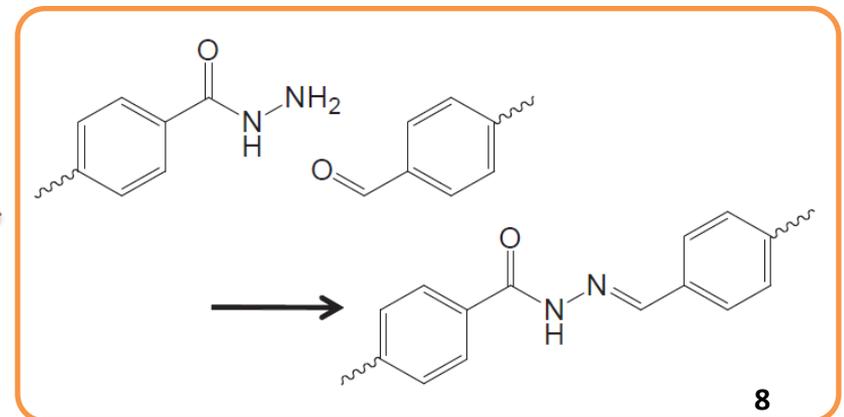
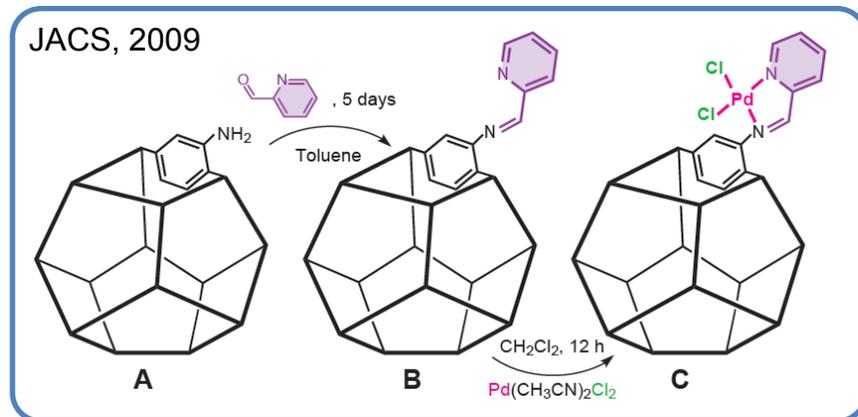
1. Discover new COFs utilizing high-throughput methods and explore H₂ uptake properties of COFs in the same parameter range.
2. Investigate pressure and temperature dependence of H₂ uptake in metalated COFs over the parameter range specified in DOE YR2015 guidelines (5.5 wt % and 40 g L⁻¹ up to 100 bar, -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

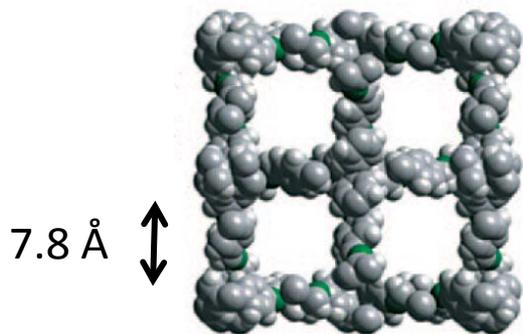
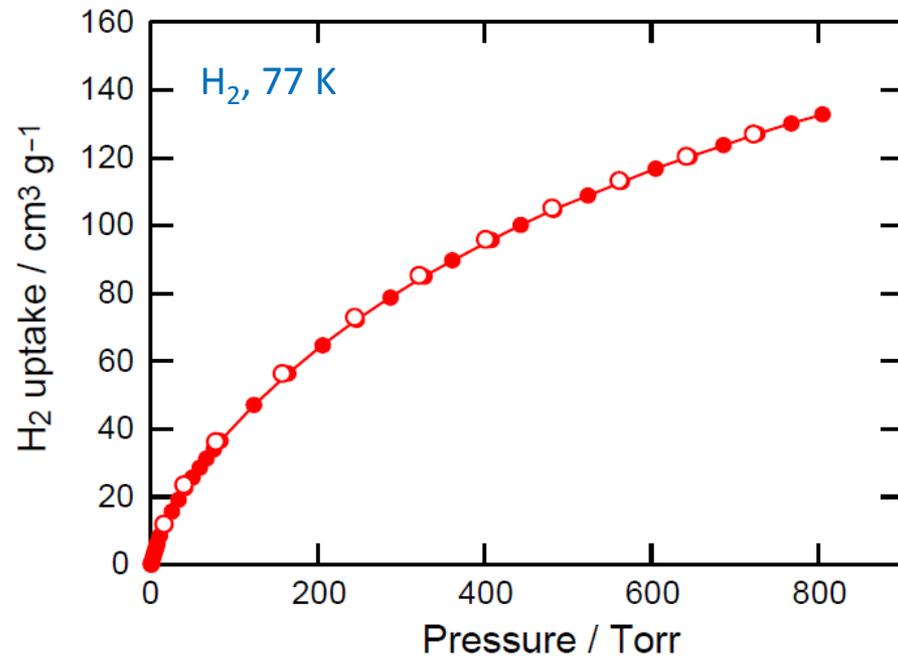
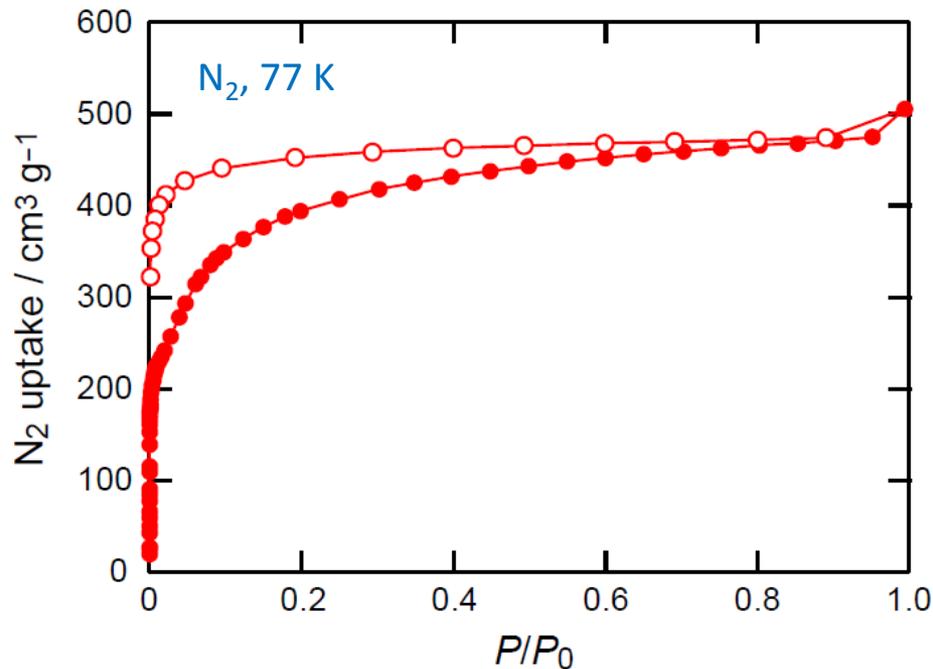
Improve the framework stability against impurity (e.g. water)



Introduce metal binding sites through the COF formation



N₂ and H₂ isotherms for COF-300

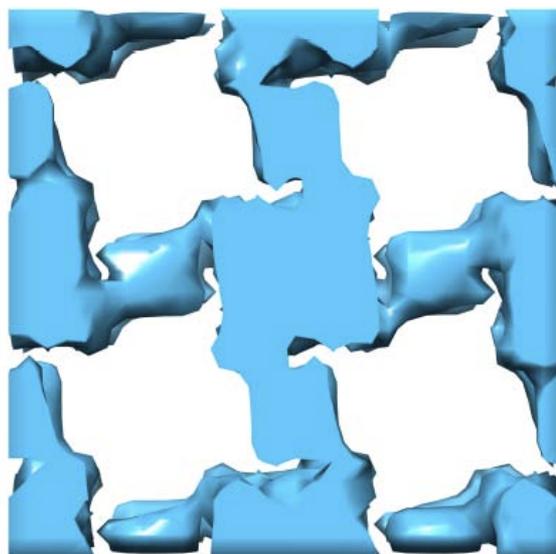


Permanent porosity was observed.

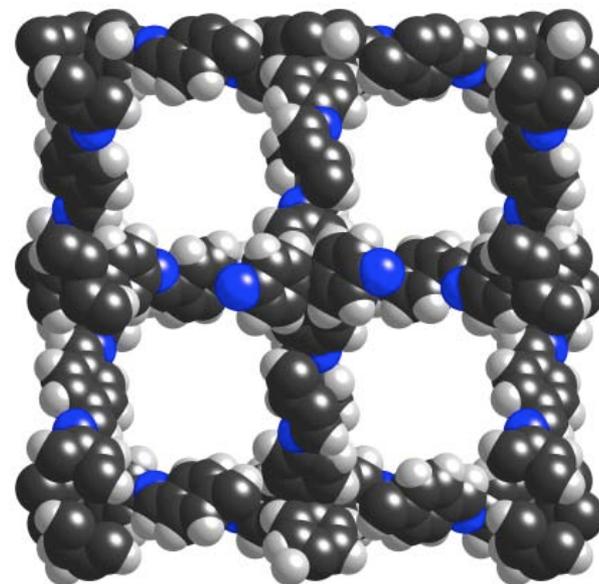
(BET SA = 1360 m²/g, pore volume = 0.72 cm³/g)

1.1 wt% H₂ uptake at 1 bar and 77 K

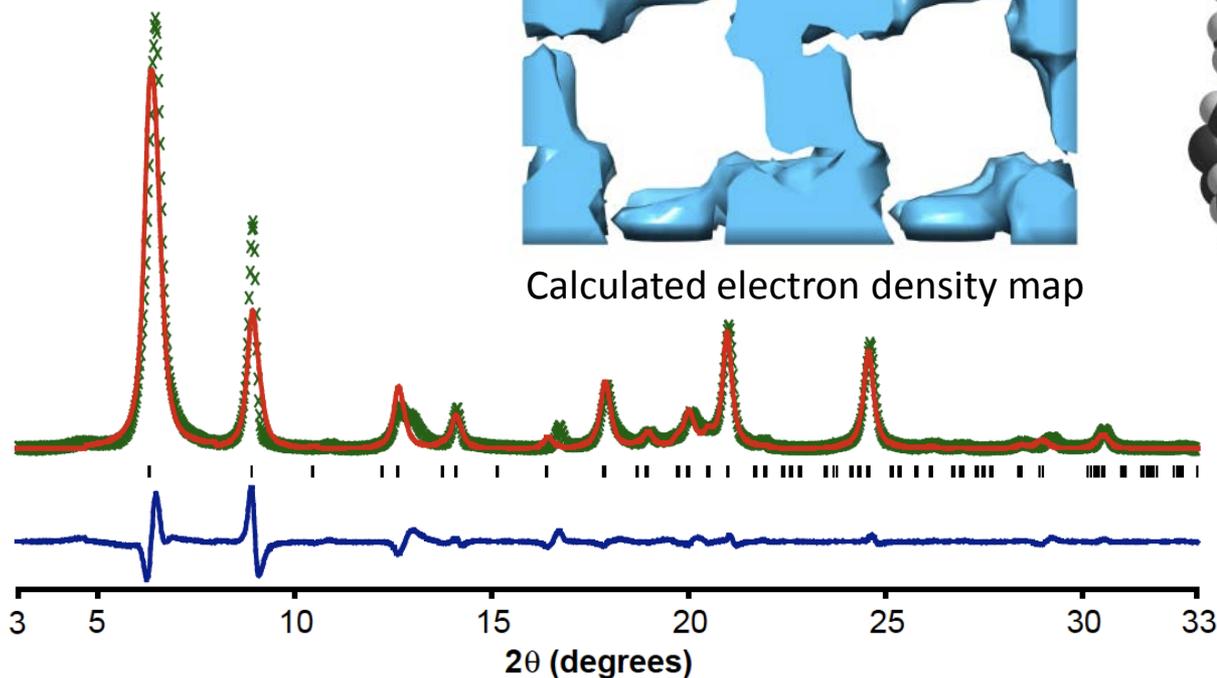
Pore structure from low resolution PXRD data



Calculated electron density map



Space filling model of COF-300

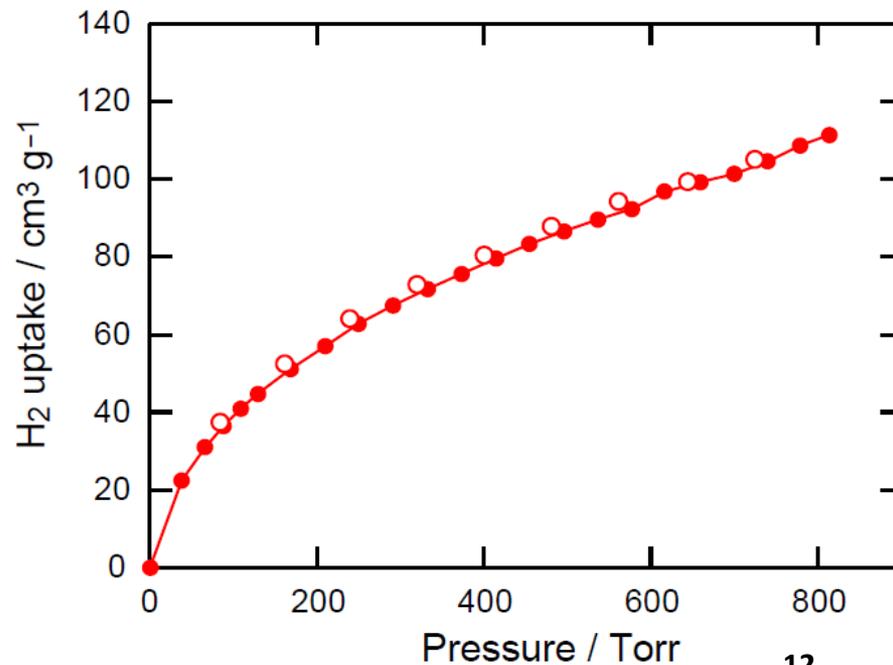
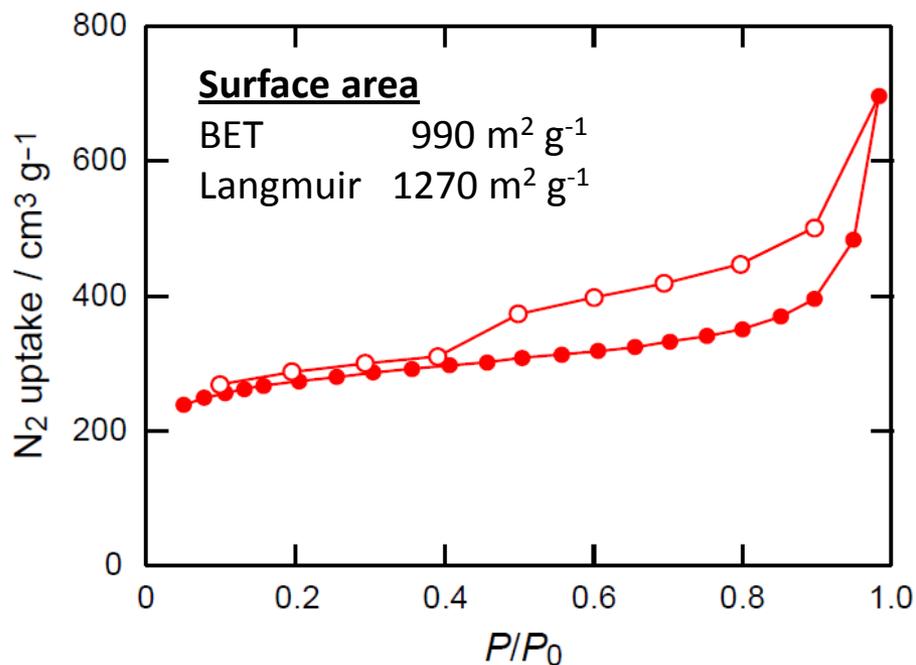
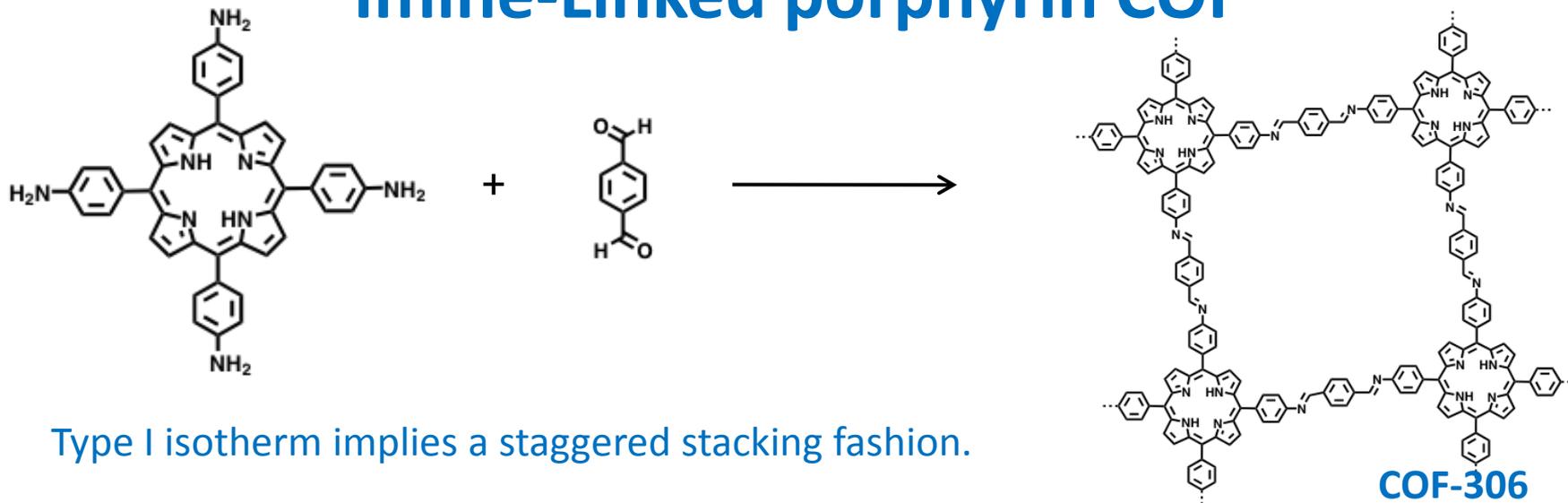


Refined powder X-ray diffraction pattern (resolution 2.0 Å) of activated COF-300

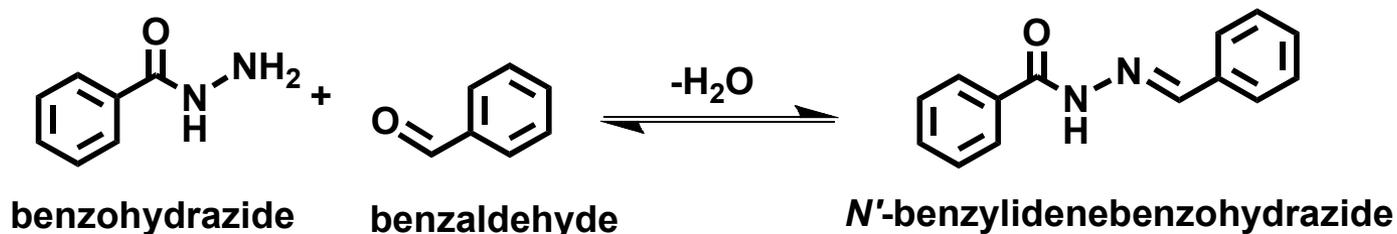
ab initio charge-flipping method was applied to determine the pore structure with extracted intensities.

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

Imine-Linked porphyrin COF

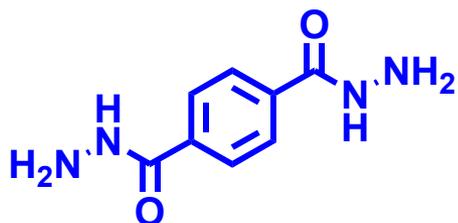


Hydrazone condensation

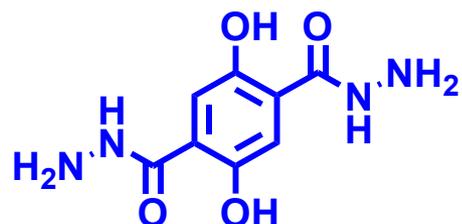


- Contains imine and amide functionalities
- Obtained hydrazone chemically stable in water and basic conditions.
- Polyacylhydrazones have been prepared showing monomer exchange under mild conditions.
- Hydrazides are very easy to make.
- Potential metal binding sites

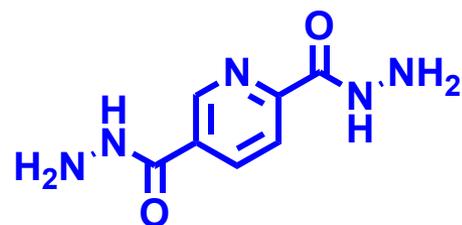
Building blocks



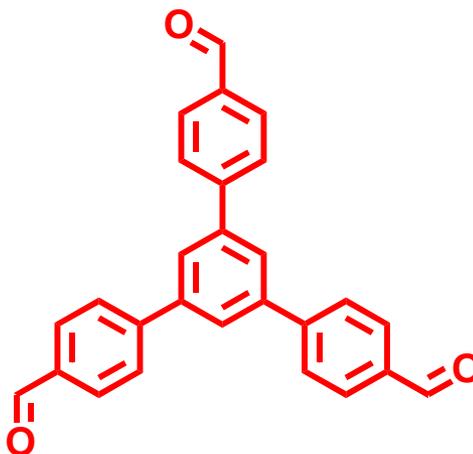
terephthalohydrazide



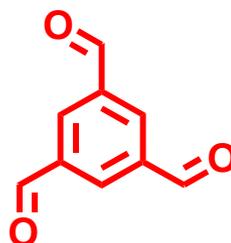
2,5-dihydroxyterephthalohydrazide



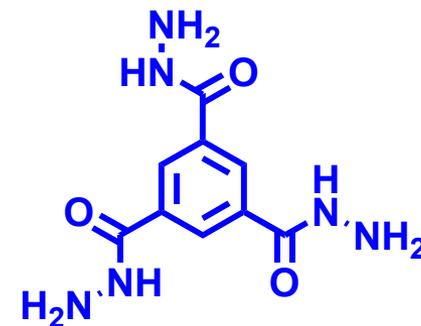
pyridine-2,5-dicarbohydrazide



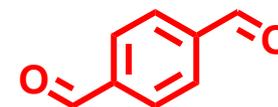
1,3,5-tris(4-formyl-phenyl)-benzene



benzene-1,3,5-tricarbaldehyde

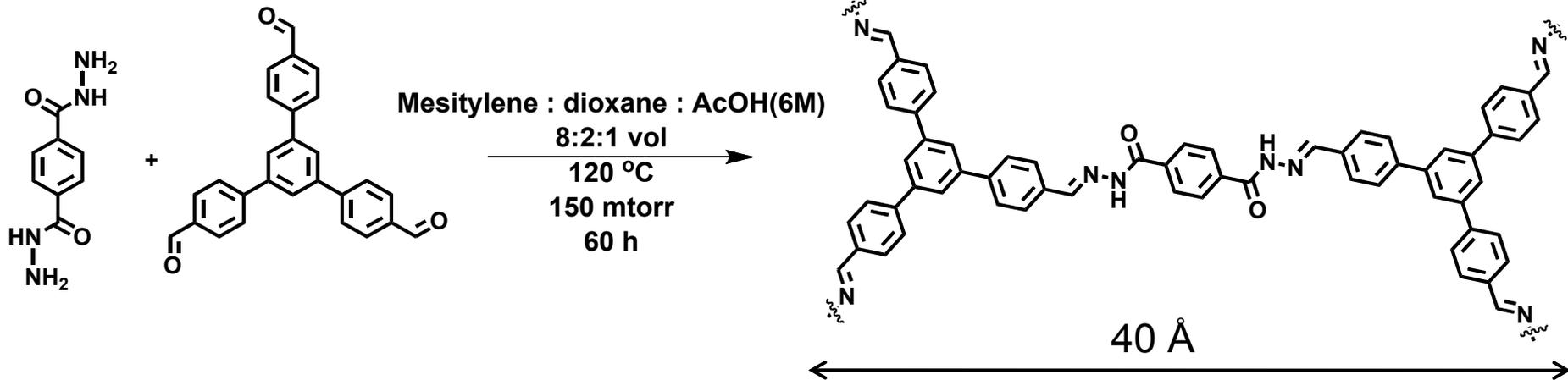


benzene-1,3,5-tricarbohydrazide



terephthalaldehyde

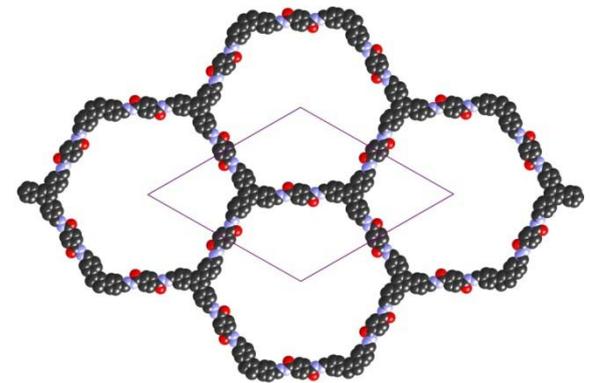
Typical example: COF-41



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



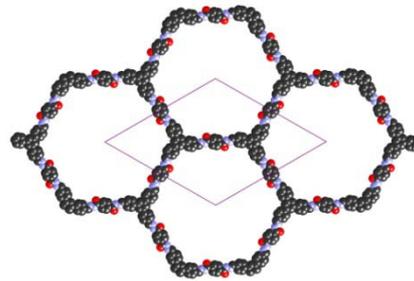
Proposed structure of COF-41

COF-41

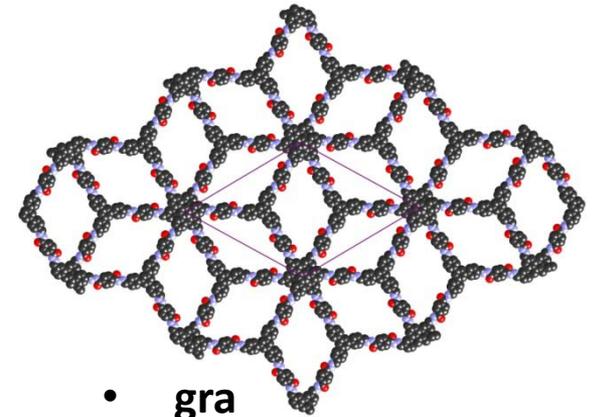
hexagonal P

$$a = 43.616(14) \text{ \AA}$$

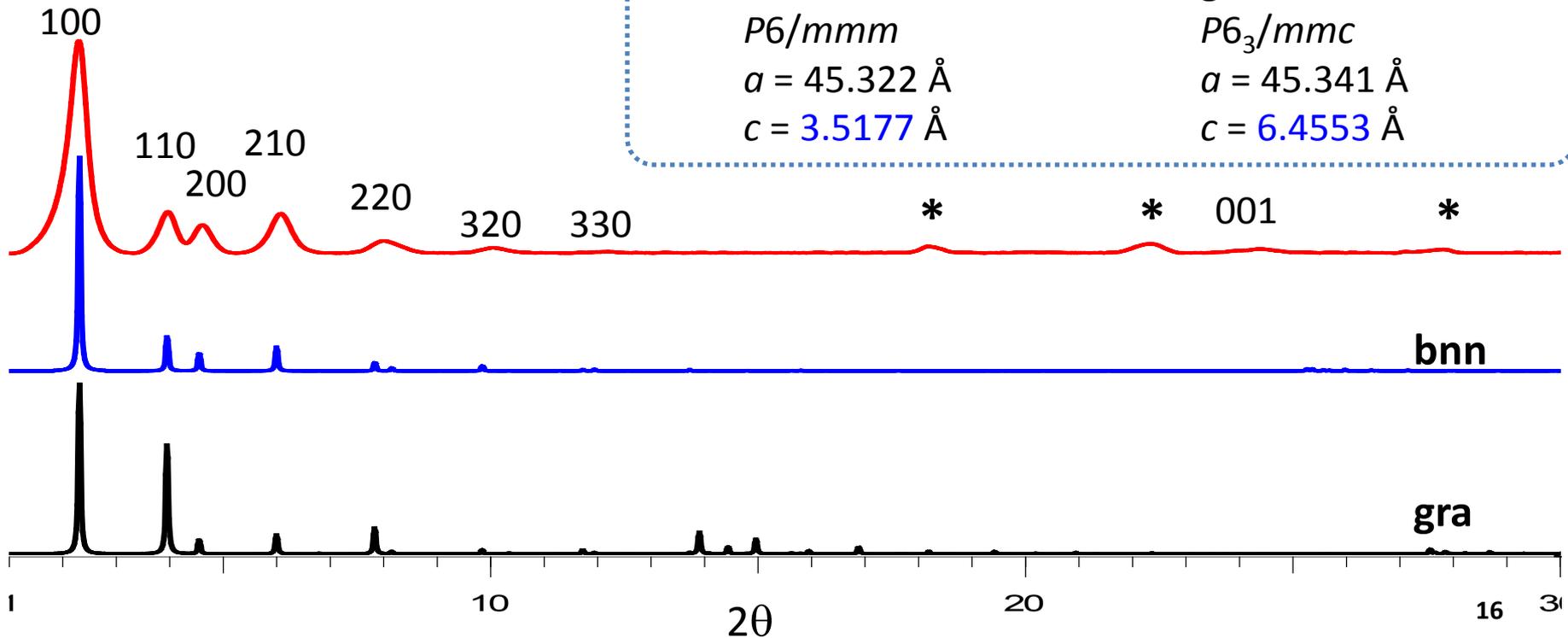
$$c = 3.6186(13) \text{ \AA}$$



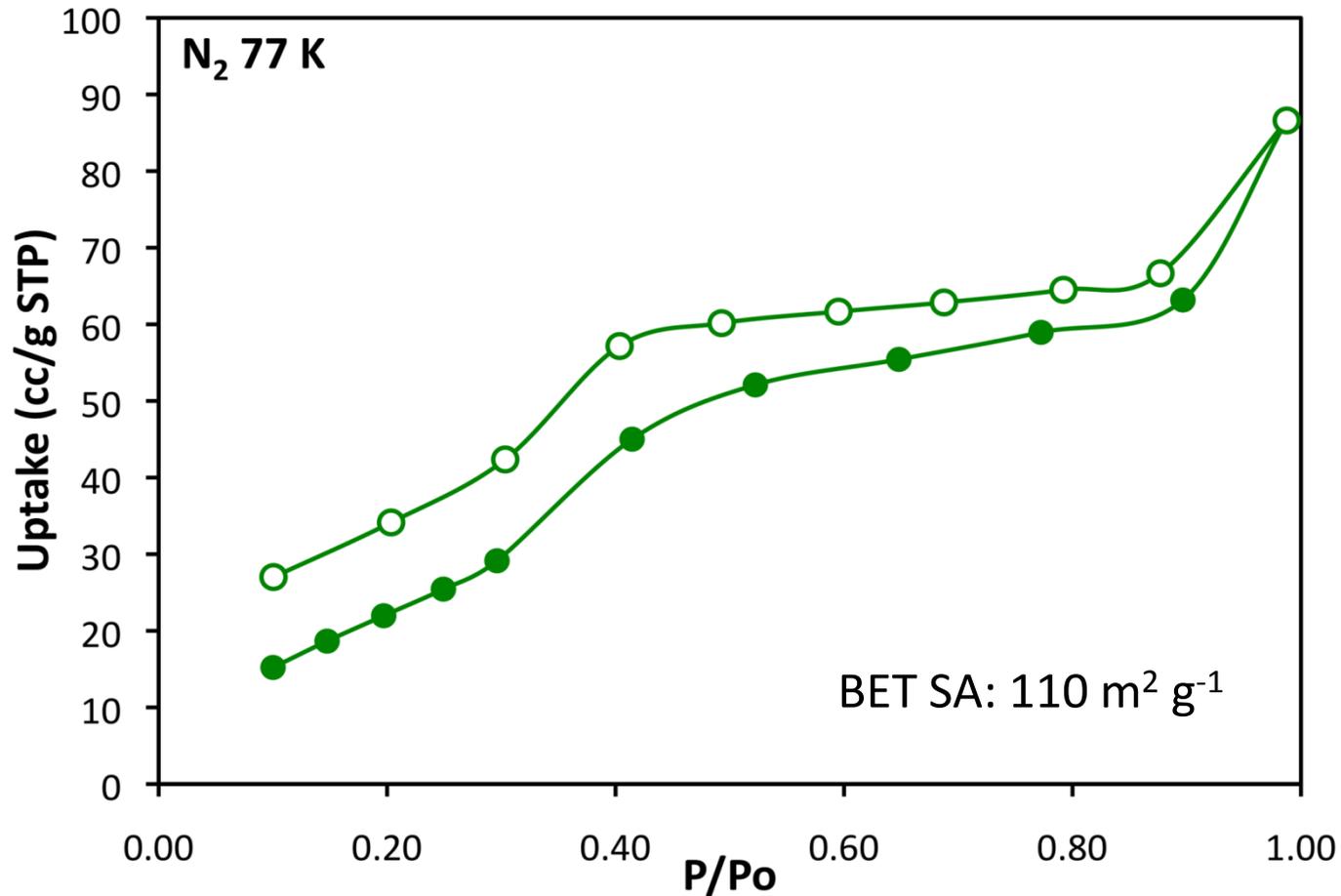
- **bnn**
P6/mmm
 $a = 45.322 \text{ \AA}$
 $c = 3.5177 \text{ \AA}$



- **gra**
P6₃/mmc
 $a = 45.341 \text{ \AA}$
 $c = 6.4553 \text{ \AA}$

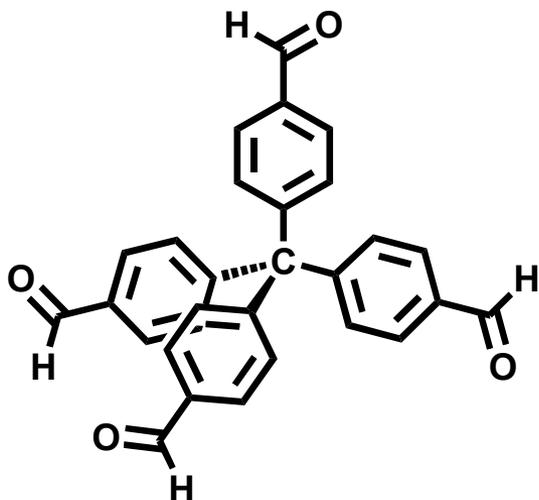


N₂ isotherm for COF-41

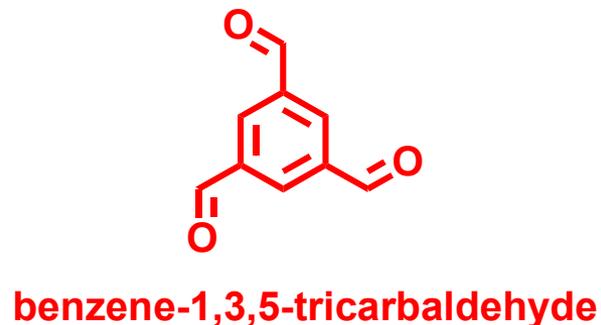
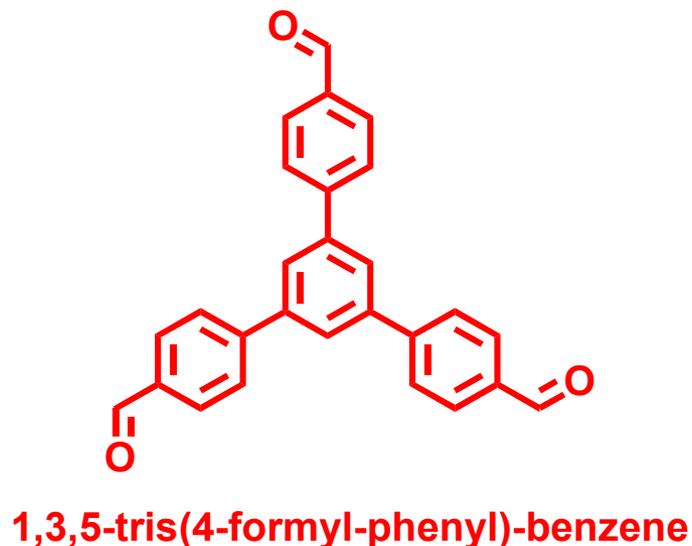


- Presence of mesopore → enough space for metal impregnation
- Activation procedure needs to be optimized

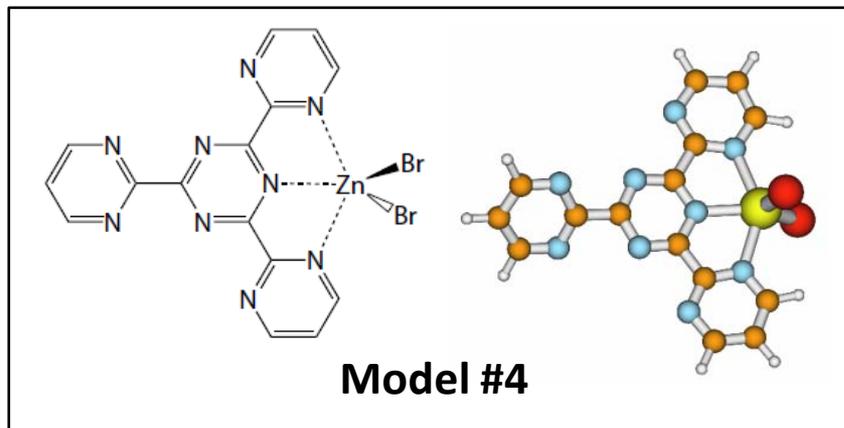
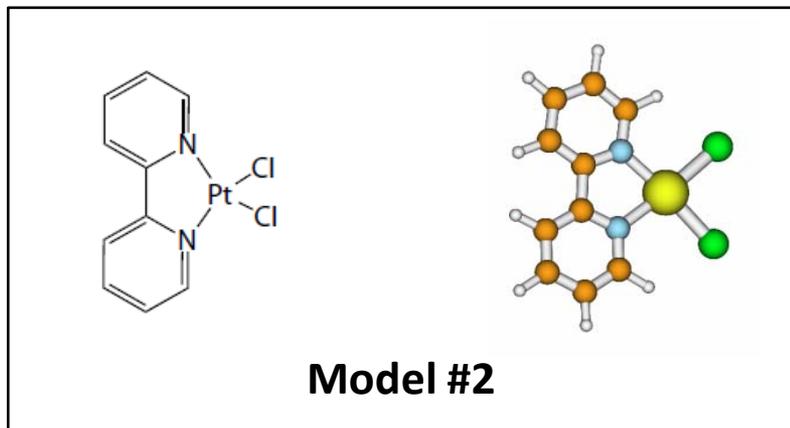
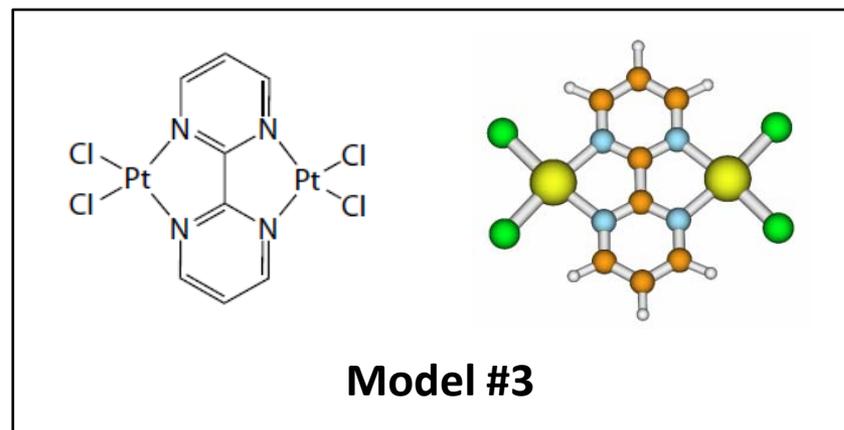
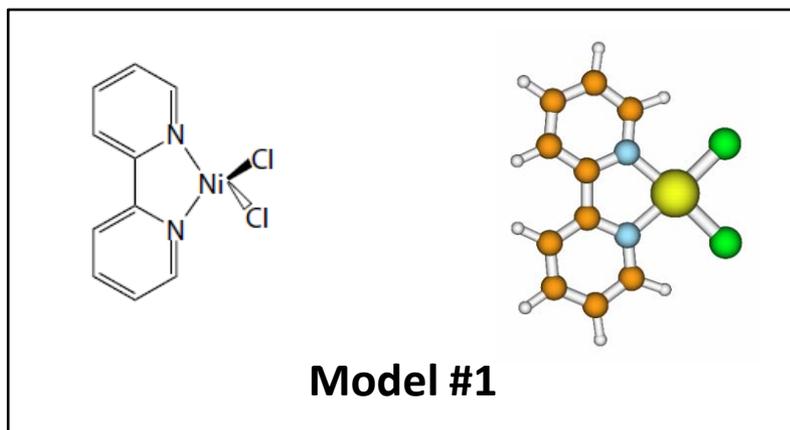
Future work: other building blocks (for 3D nets)



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

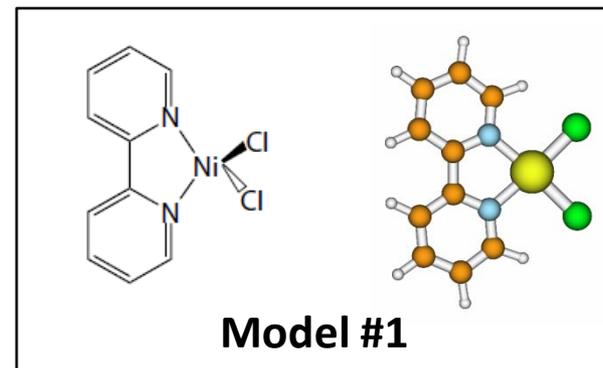
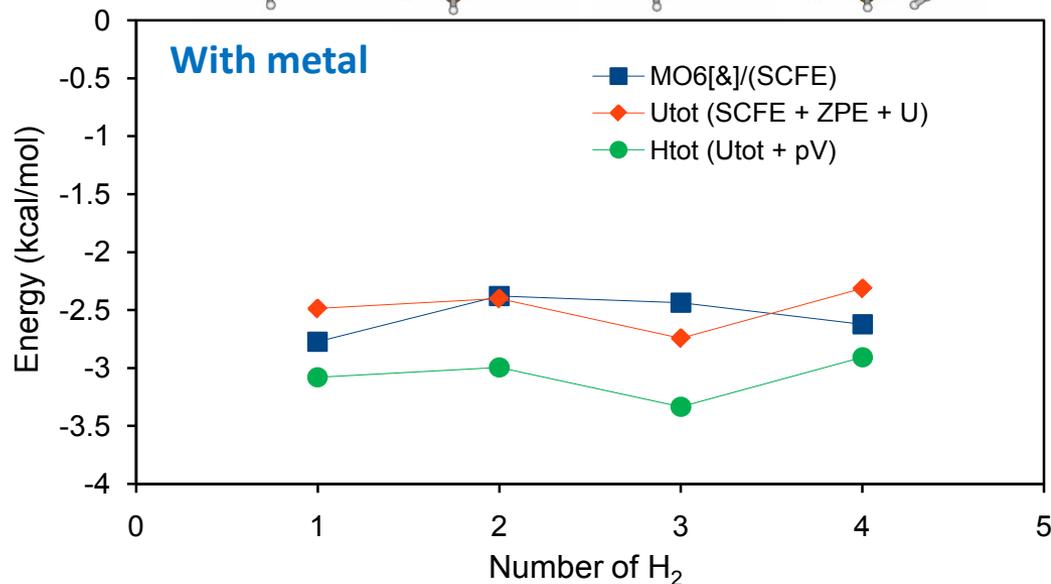
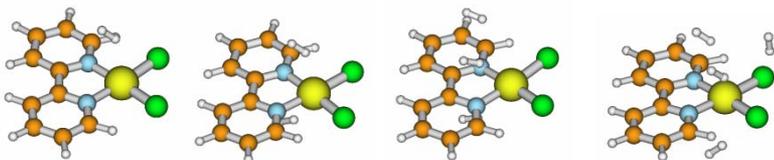


Coordination with theory: Examined model systems

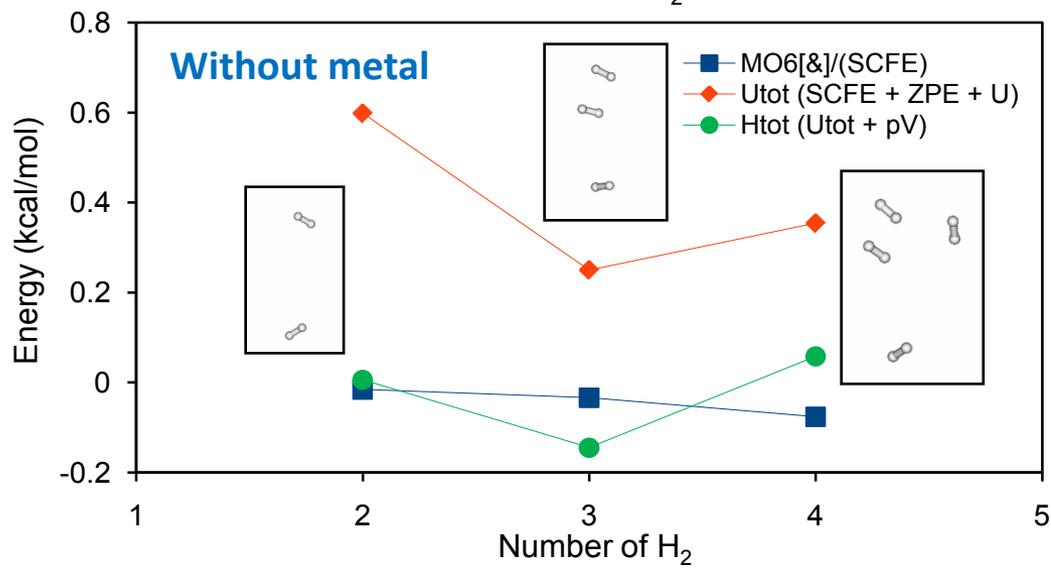


- ❑ Four plausible model systems were tested.
- ❑ Calculated MO, U_{total} and H_{total} for each model.
- ❑ The DFT-MO6 functional was used to calculate the non covalent interactions with the basis set LACVP to calculate optimization.
- ❑ Adsorption enthalpy of these models is ranging from 3 to 4 kcal/mol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

Theoretical prediction of binding energy #1

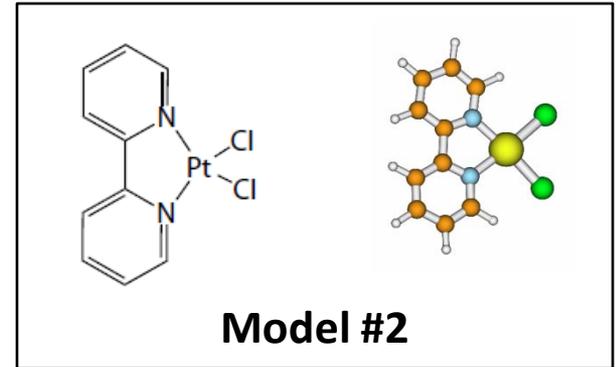


The binding energy is almost constant with the addition of H₂.



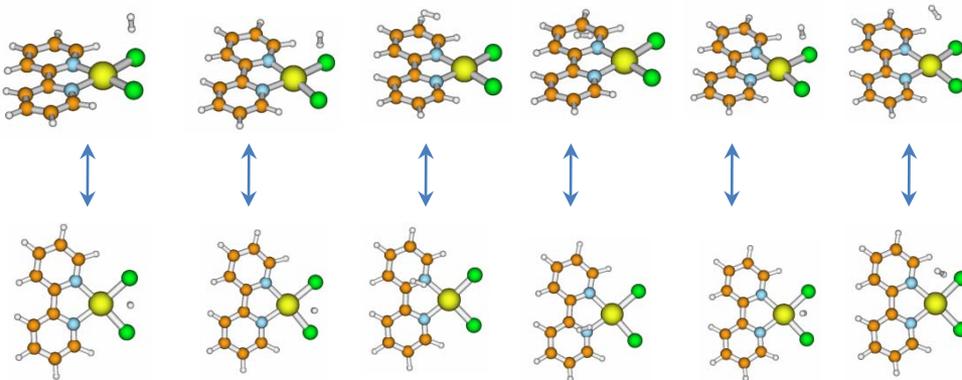
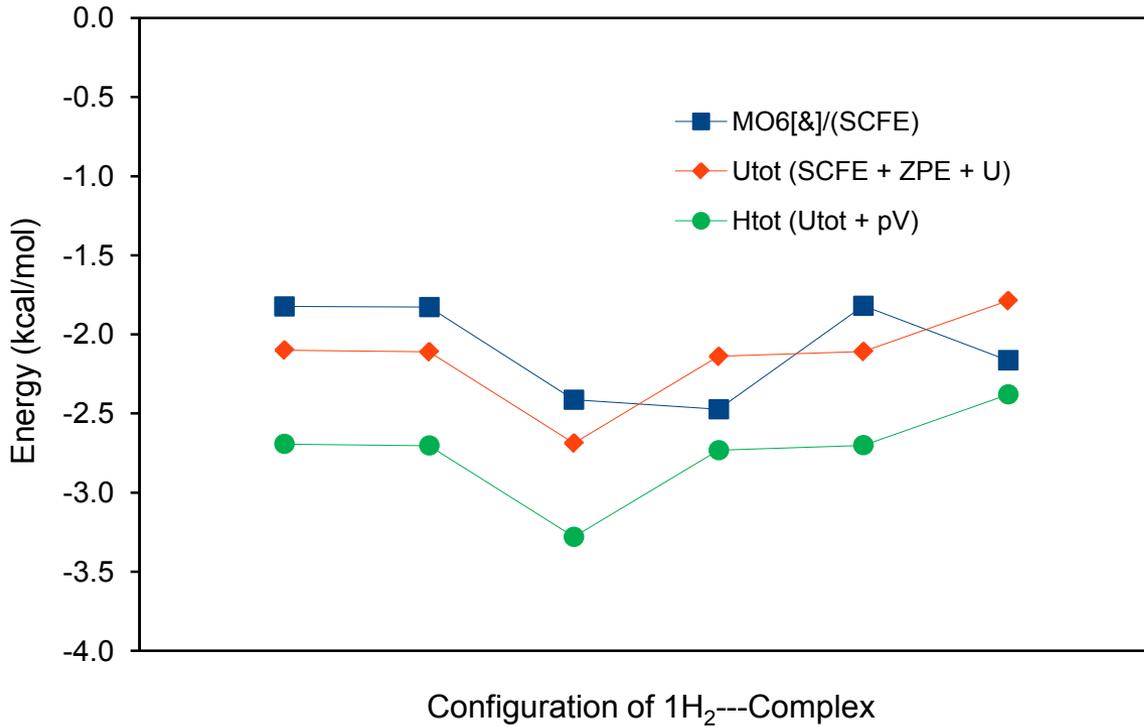
H₂-H₂ interaction of the metal-complex is stable than that of the bipyridine system.

Theoretical prediction of binding energy #2

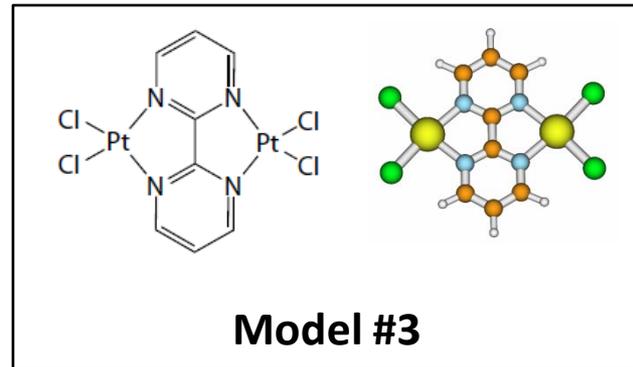
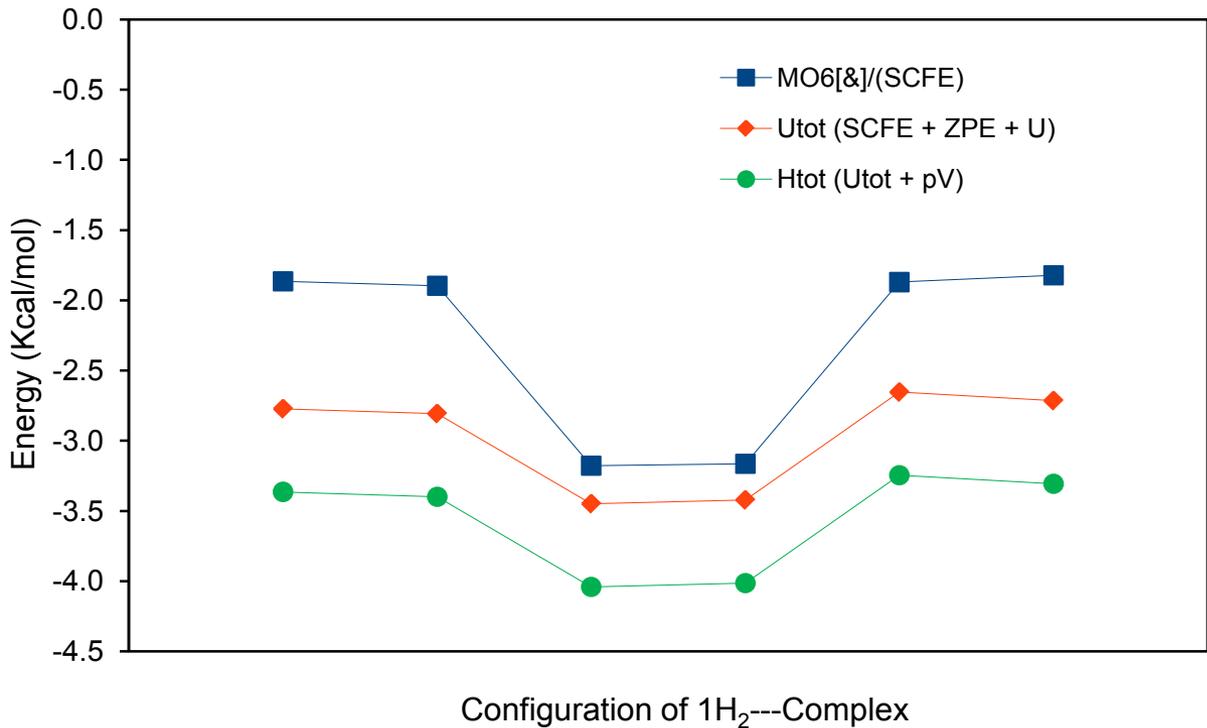


The most favorable interaction is observed over the bond of N-Pt, which is the same as N-Ni system (Model #1).

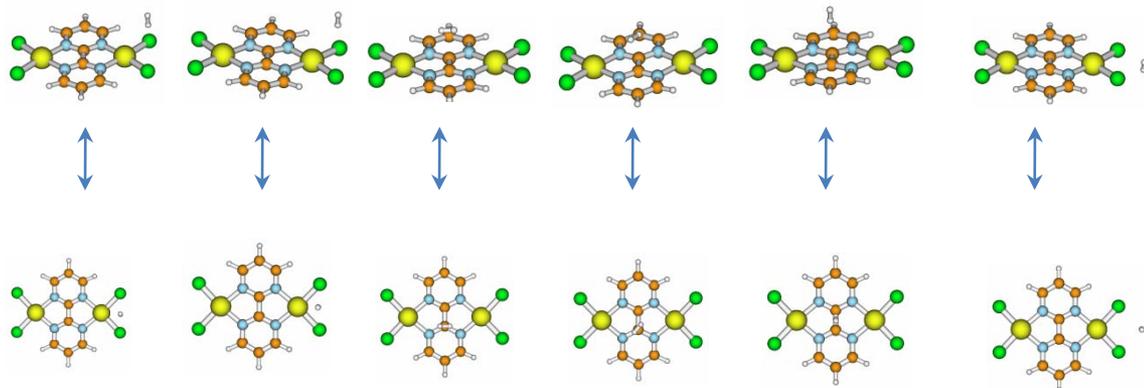
Predicted binding energy is smaller than Model #1 (ca. 1 kcal/mol).



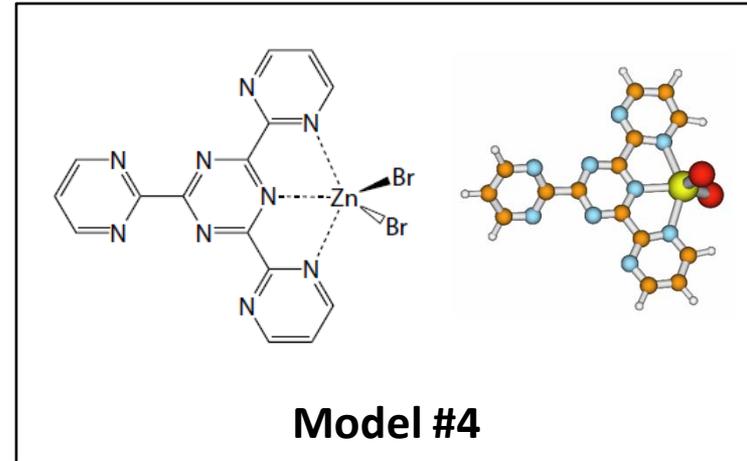
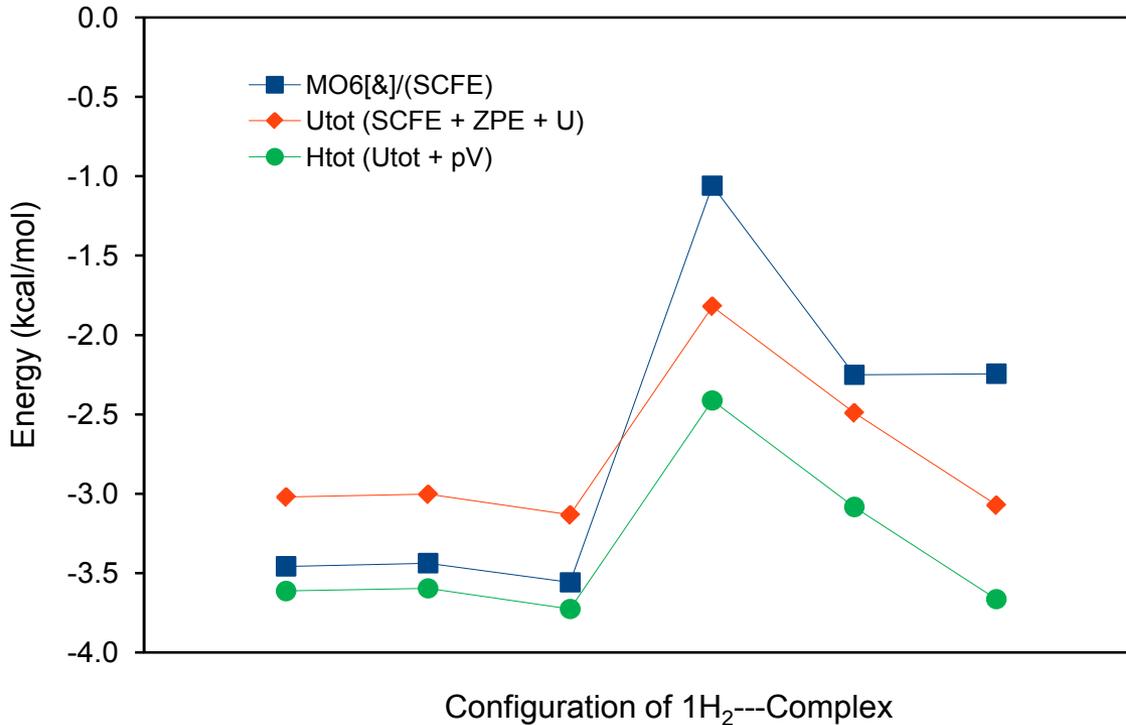
Theoretical prediction of binding energy #3



Favorable interaction is observed when H₂ molecule locates over C atom of the five membered ring.

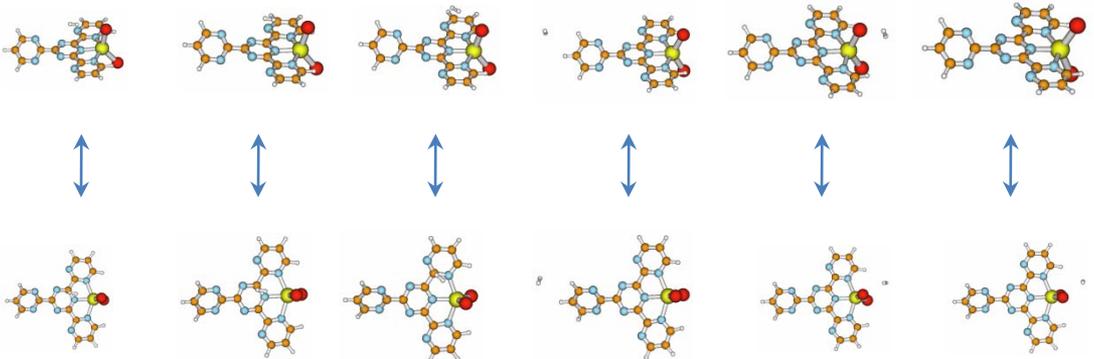


Theoretical prediction of binding energy #4

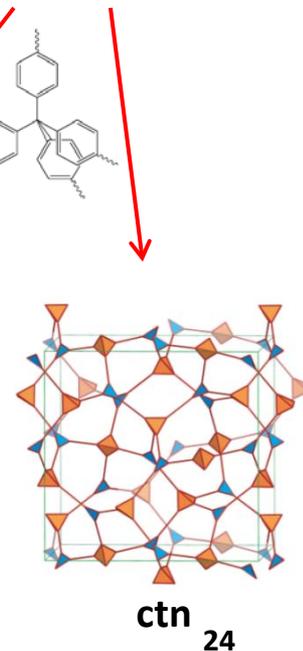
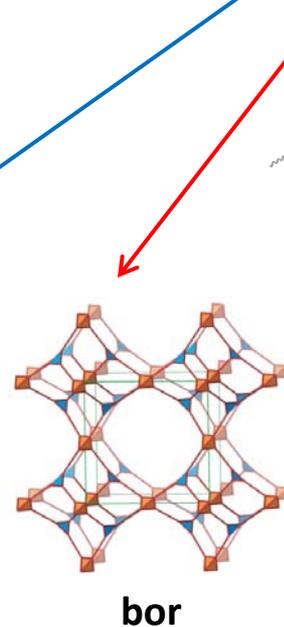
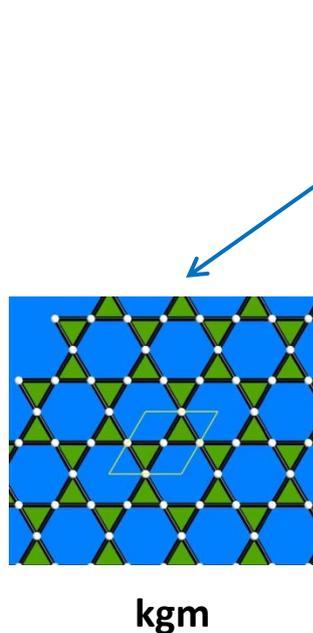
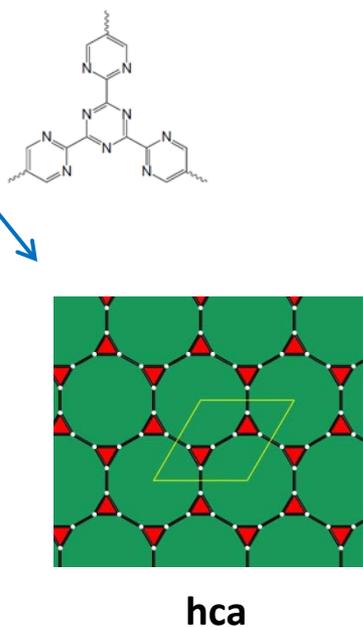
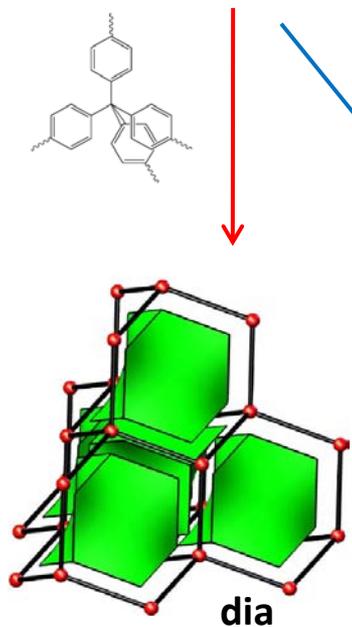
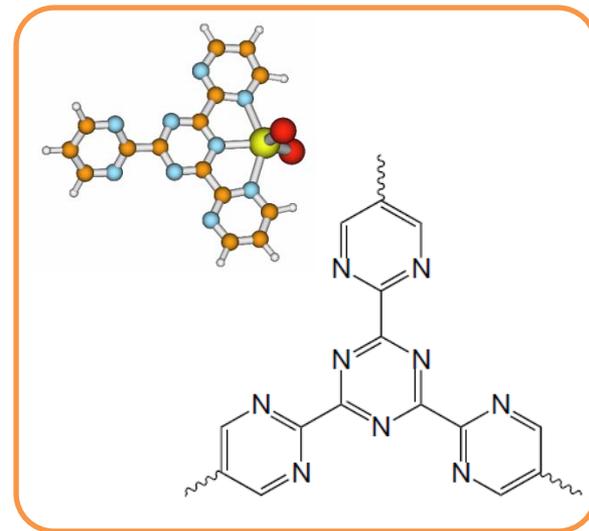
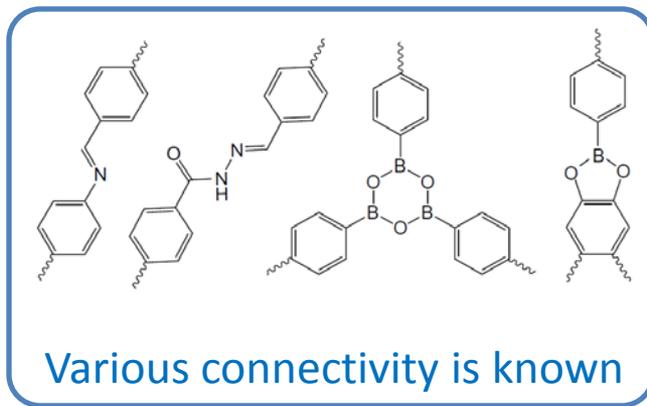
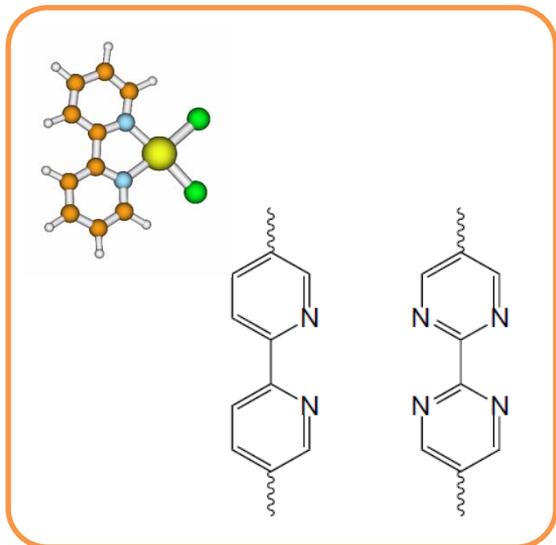


Adsorption sites of H₂ does not seem to be the metal itself.

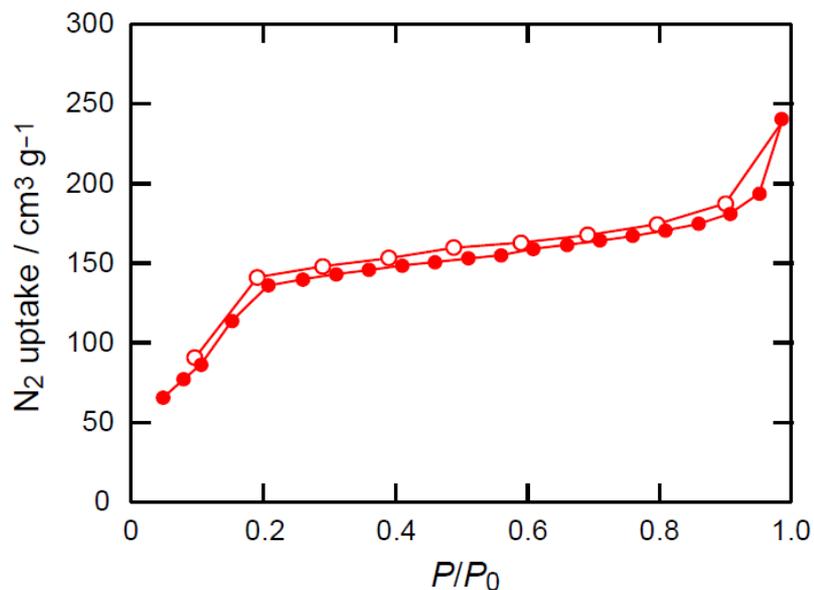
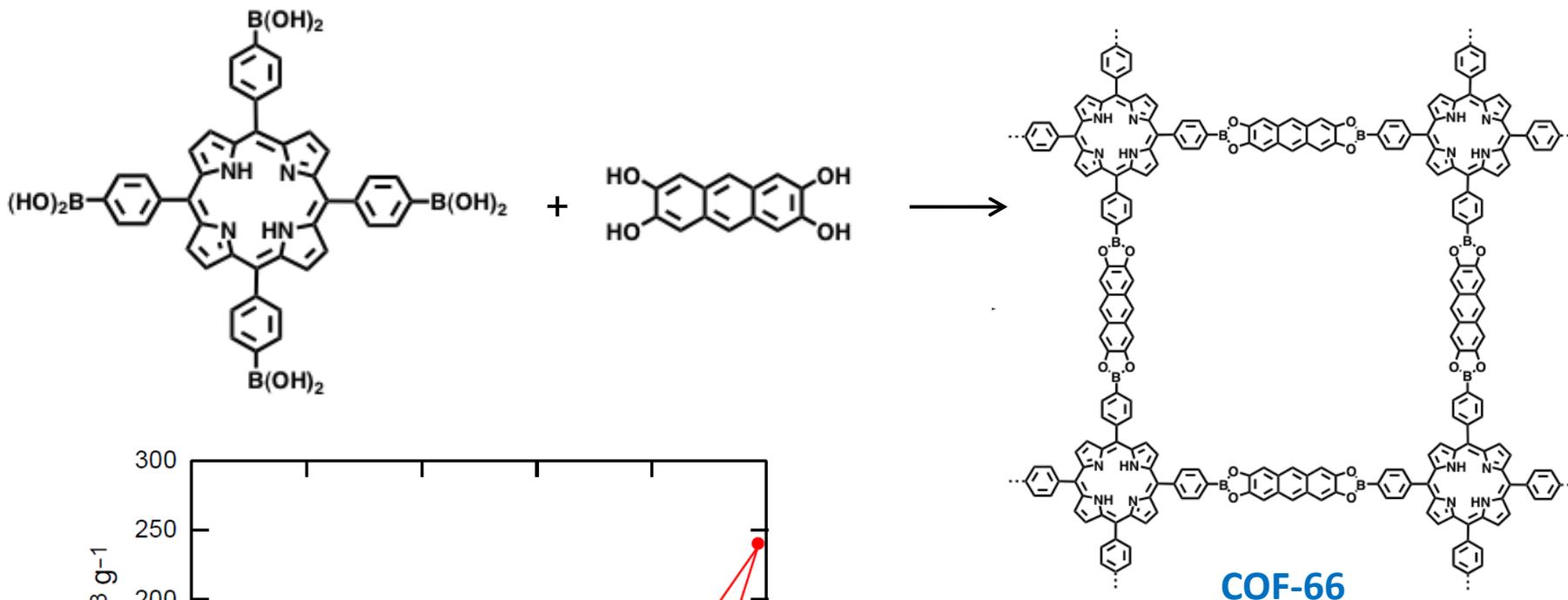
The most favorable interaction is observed when H₂ locates over the N-Zn bond.



Approach 1: Proposed COF connectivity for metalation



Approach 2: Intercalation of COFs with metals



- ☐ Permanent porosity was confirmed
- ☐ BET SA = $410 \text{ m}^2 \text{ g}^{-1}$
- ☐ 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.