DOE Hydrogen Program

A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs/ZIFs 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: 35%

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
  - Contractor share: $0.41 M
- ❑ Funding received in FY10: $300 K
- ❑ Funding for FY11: $284 K

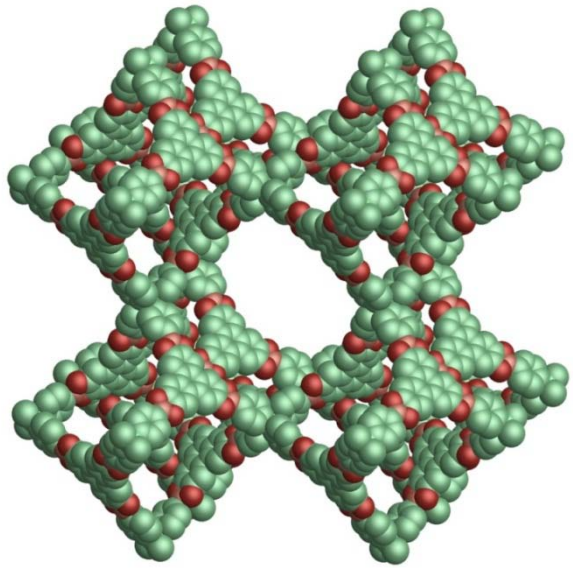
Collaborating Partner

- ❑ Fraser Stoddart (NW)
- ❑ Jaheon Kim (Soongsil University)
- ❑ BASF

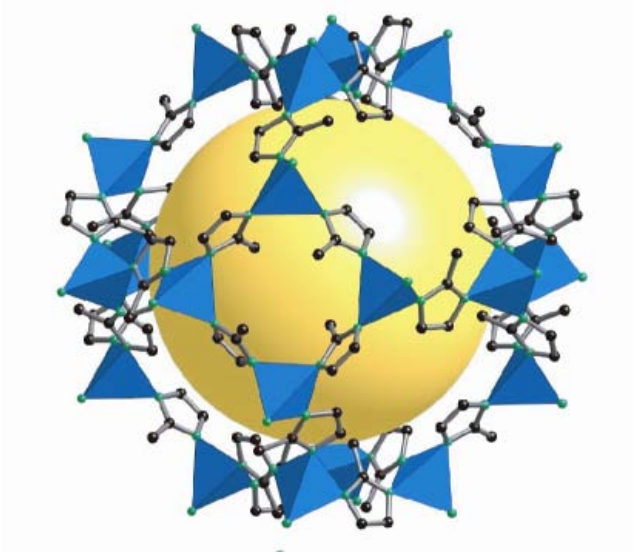
Description of new materials

Covalent Organic and Zeolitic Imidazolate Frameworks (COFs and ZIFs)

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

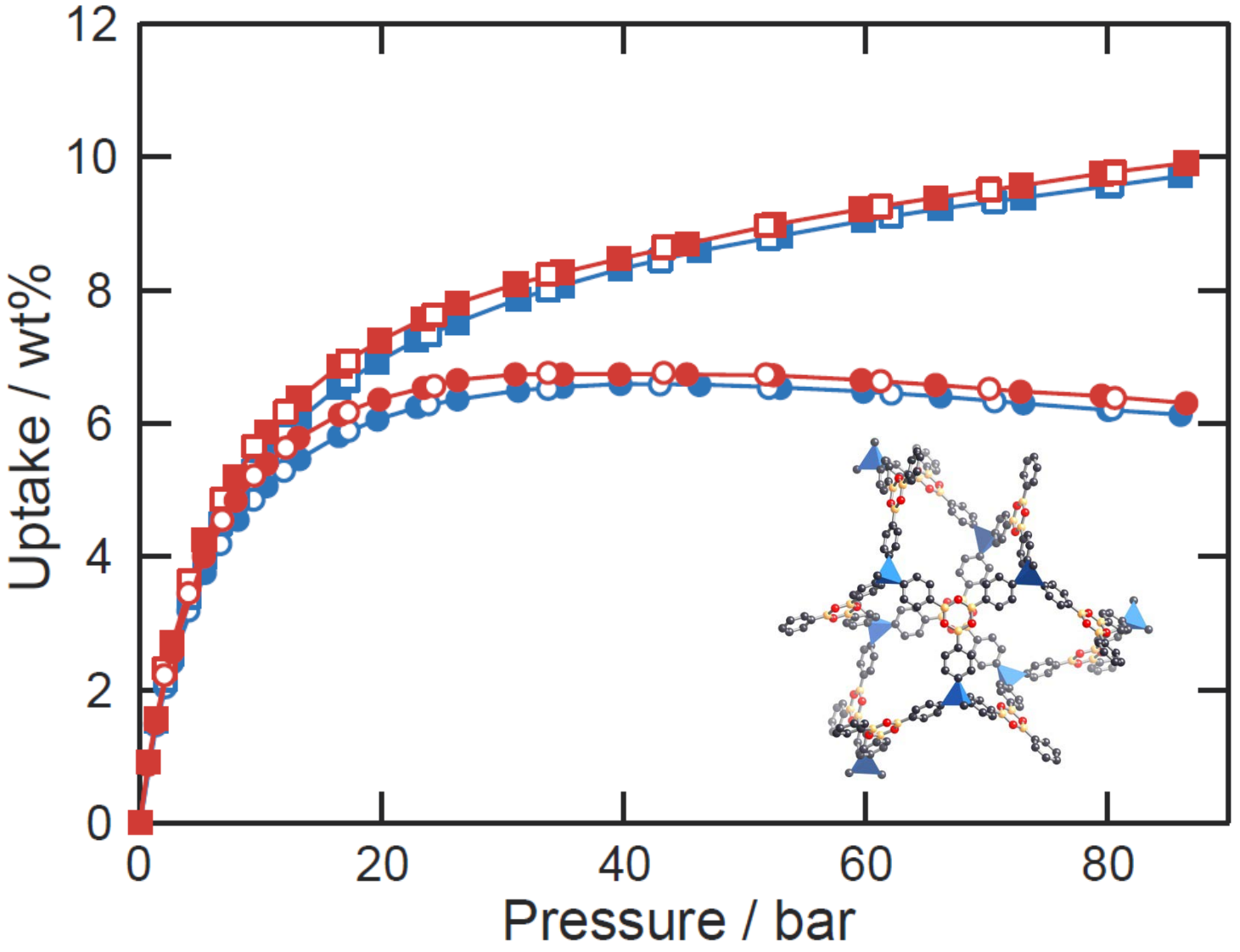


COF-108



ZIF-8

High-pressure H_2 isotherms of COFs at 77 K



JACS 2009

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

Objectives (FY10-11)

Accomplishments in last year:

- Predicted adsorption enthalpy of H_2 on various metal sites
- Began computation of H_2 uptake isotherms with developed Force Field
- Develop chemistry to realize stable frameworks
- Introduce potential metal binding sites through the COF synthesis

This year:

- ❑ Design new COFs with strong H_2 binding sites
- ❑ Predict H_2 uptake isotherm for designed frameworks with developed Force Field
- ❑ Prepare stable frameworks with potential metal binding sites
- ❑ Implement metalation experiments and evaluate the H_2 adsorption property
- ❑ Prepare mixed-metal ZIFs

Milestones (FY11)

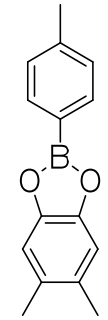
1. Discover new COFs with potential metal binding sites and explore H_2 uptake properties of COFs.

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.

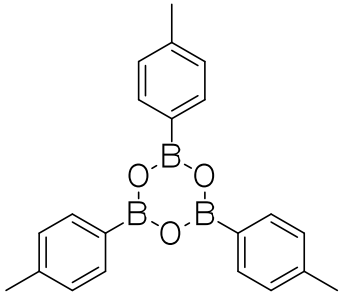
3. Develop new force fields for modeling adsorption properties of COFs. Test models using reported adsorption data for a range of known COFs.

4. Design new architectures of promising materials for hydrogen storage that are favorable thermodynamically.

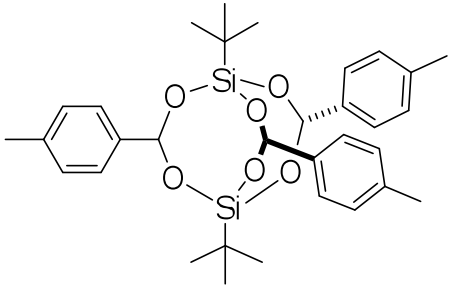
Strategy



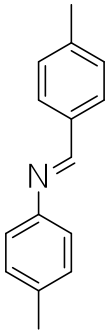
COF-5



COF-1

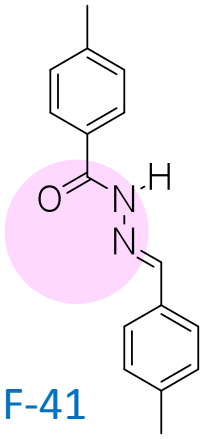


COF-202

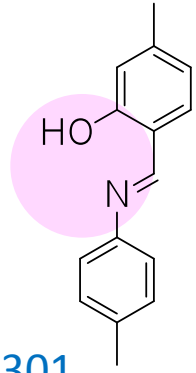


COF-300

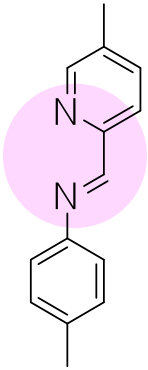
- ❑ Improve the framework stability against impurity (e.g. water)
- ❑ Introduce metal binding sites through the COF formation



COF-41

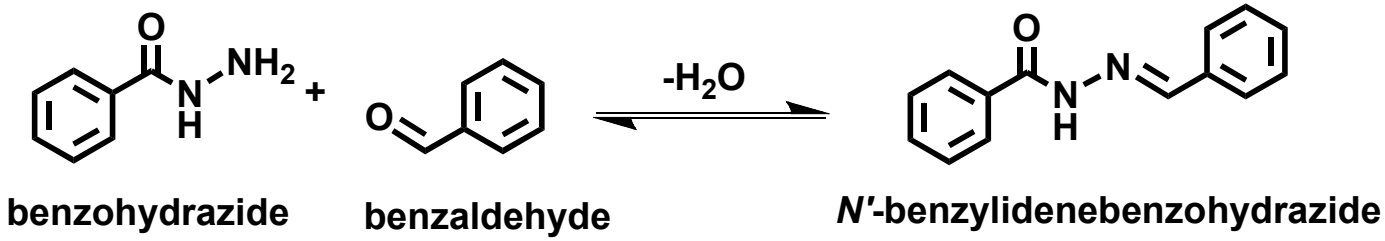


COF-301



Postmodified MOF (JACS, 2009)

Hydrazone condensation

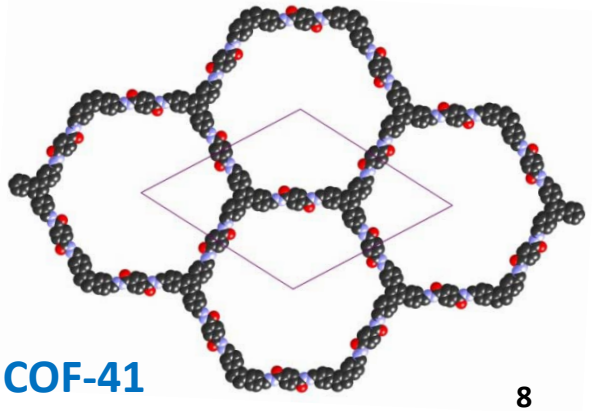


benzohydrazide benzaldehyde *N'*-benzylidenebenzohydrazide

- Obtained hydrazone chemically stable in water and basic conditions.
- Polyacylhydrazones have been prepared showing monomer exchange under mild conditions.
- Potential metal binding sites

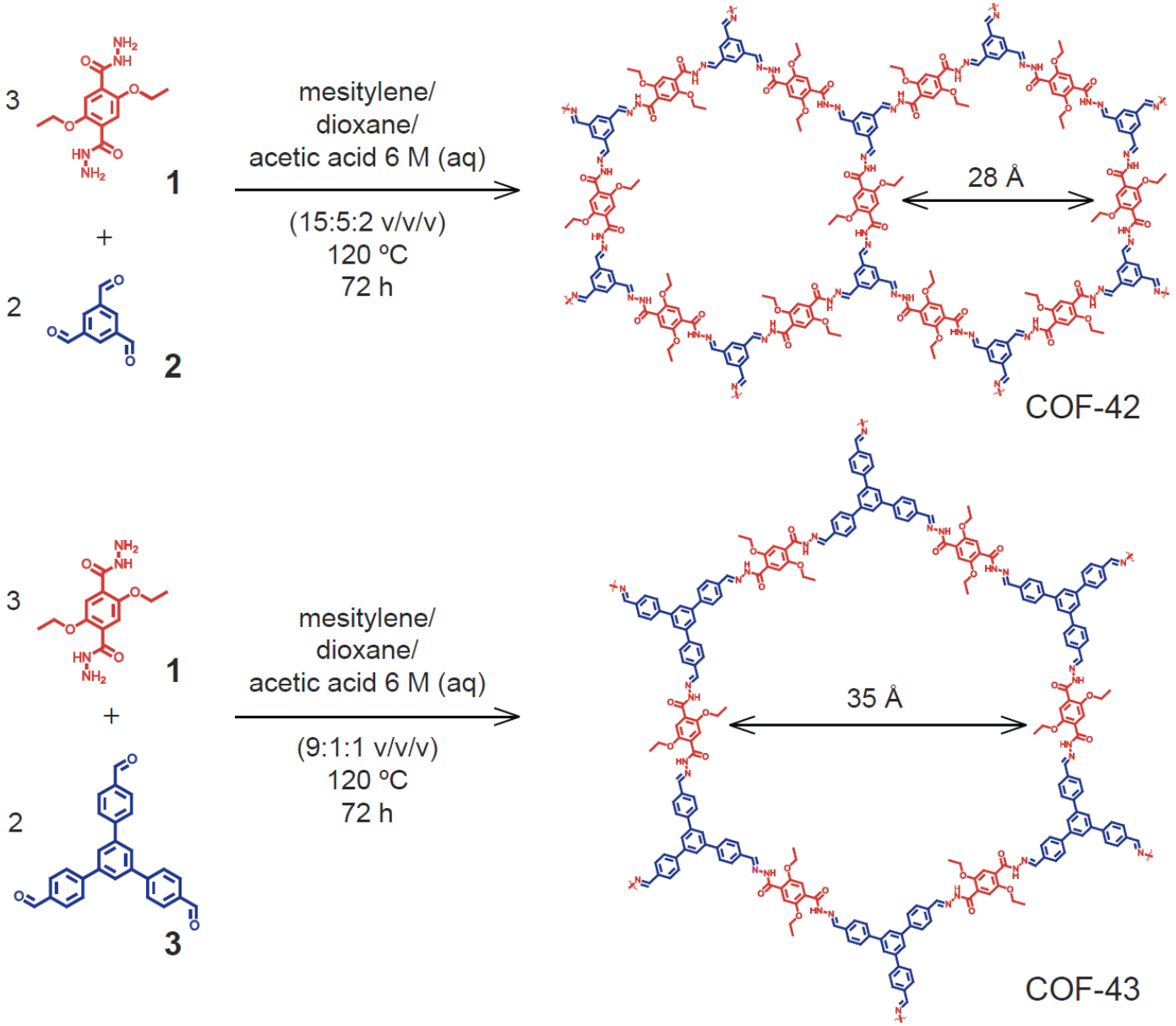
Last year, we prepared hydrazone COF (COF-41)

- Crystalline porous solid
- Stable in air
- BET surface area was 110 m^2/g

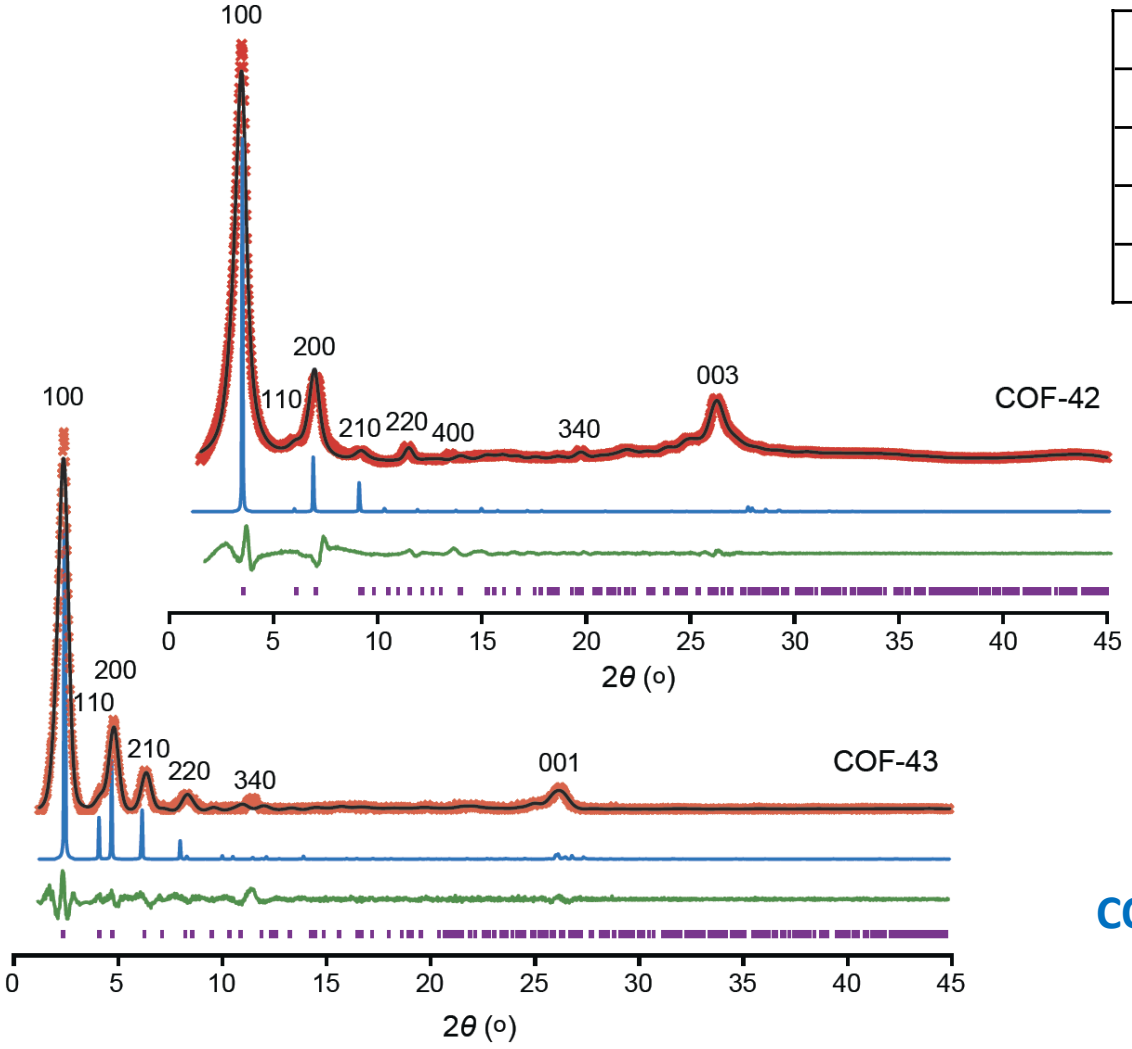


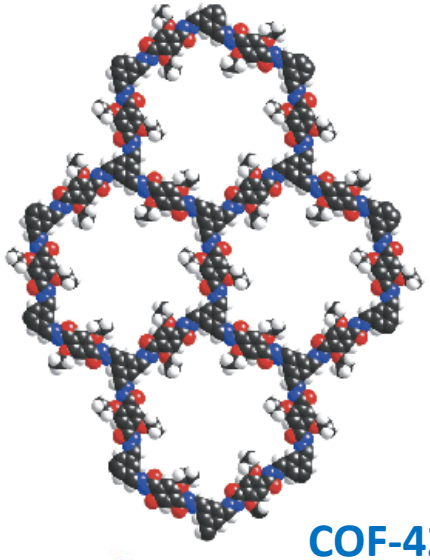
COF-41

Synthesis of COFs based on hydrazone linkages

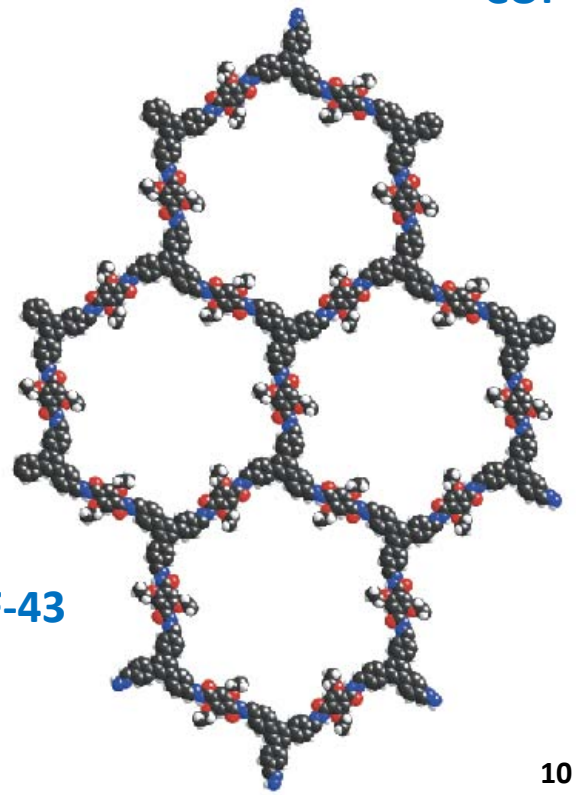


PXRD patterns of COF-42 and 43



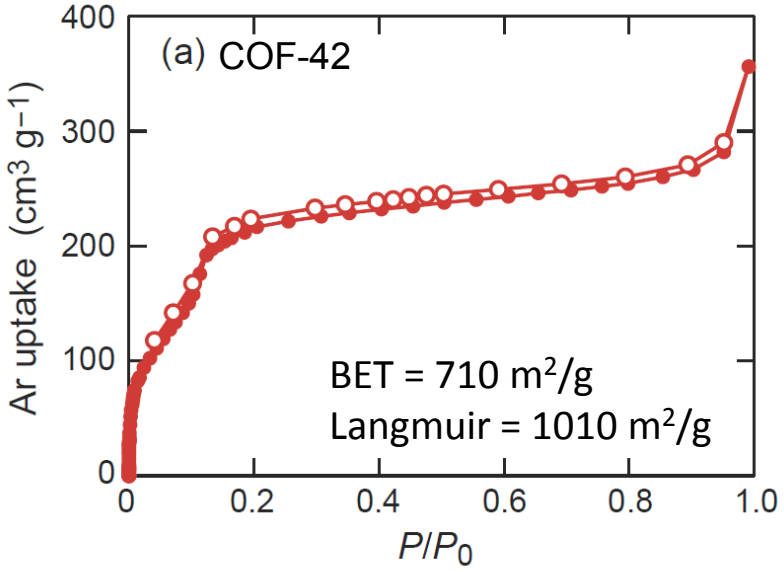


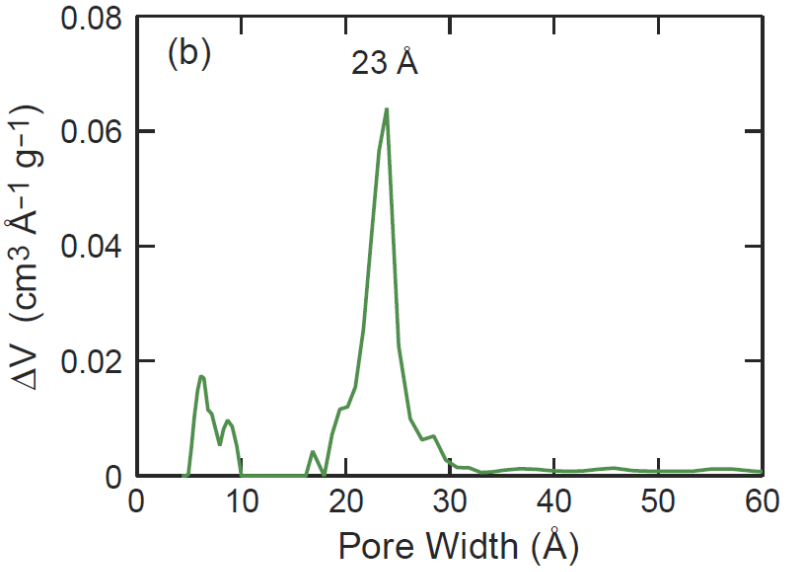
COF-42

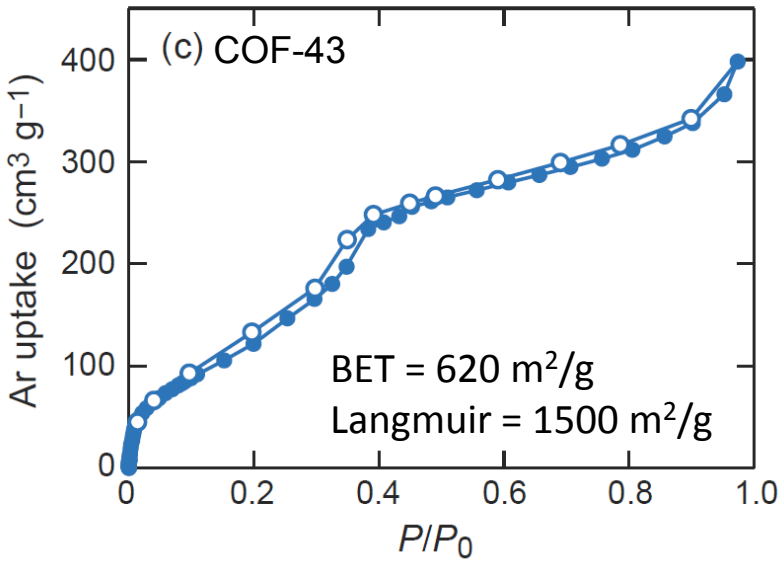


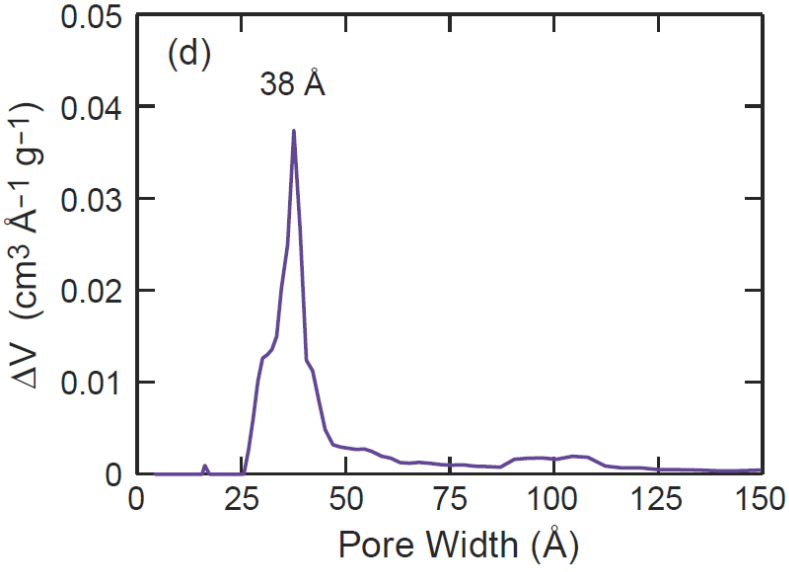
COF-43

Ar isotherms of COF-42 and COF-43



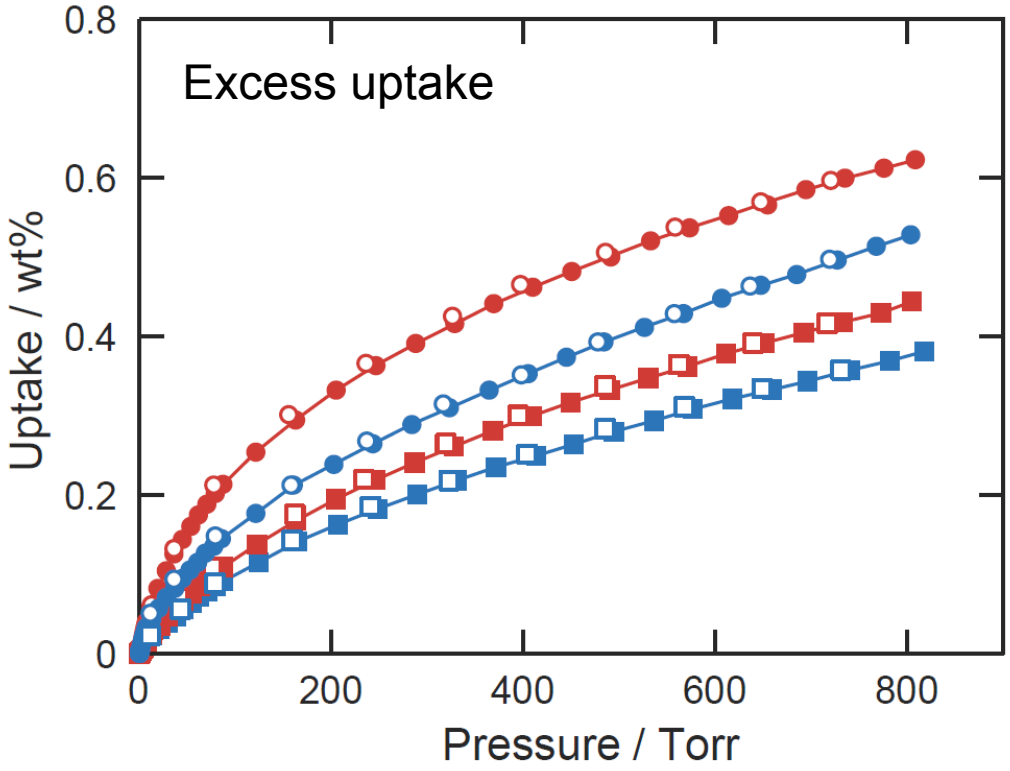






COF-42 shows 6.5 times higher BET area than COF-41.

H_2 isotherms of COF-42 and COF-43

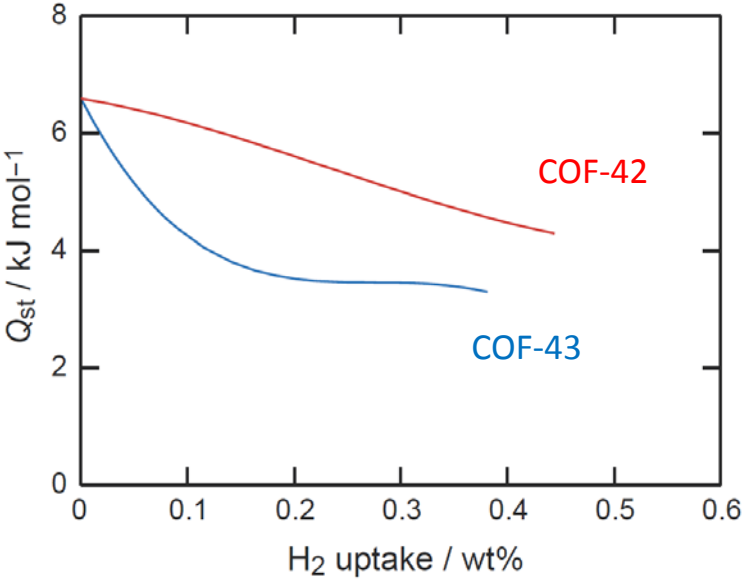


COF-42, 77 K

COF-43, 77 K

COF-42, 87 K

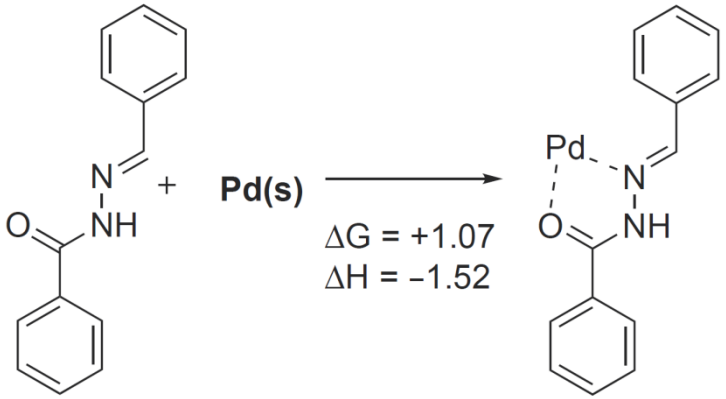
COF-43, 87 K

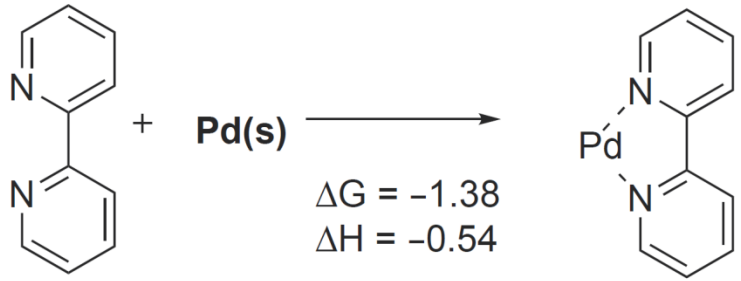


	BET SA (m^2/g)	H_2 uptake (wt%)	Q_{st} (kJ/mol)
COF-41*	110	n.d.	n.d.
COF-42	710	0.60	6.6
COF-43	620	0.51	6.6

*Reported last year

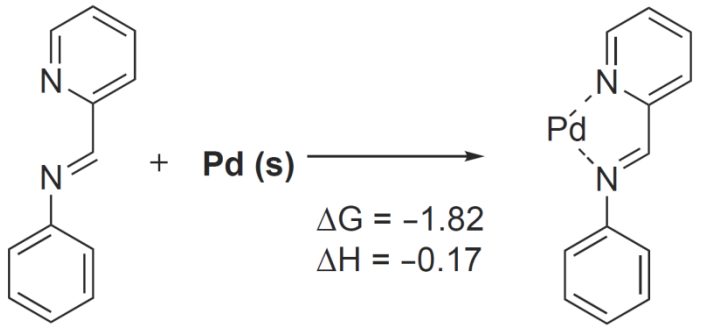
Calculated ΔG and ΔH of metalation reactions

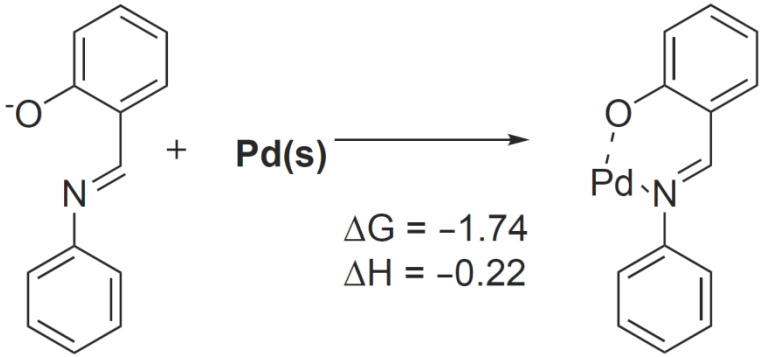


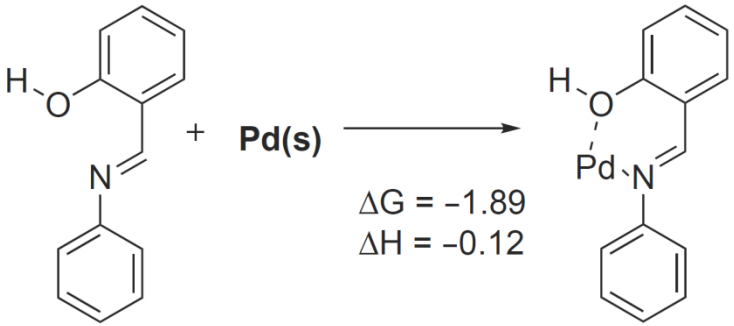


Unit: kcal/mol

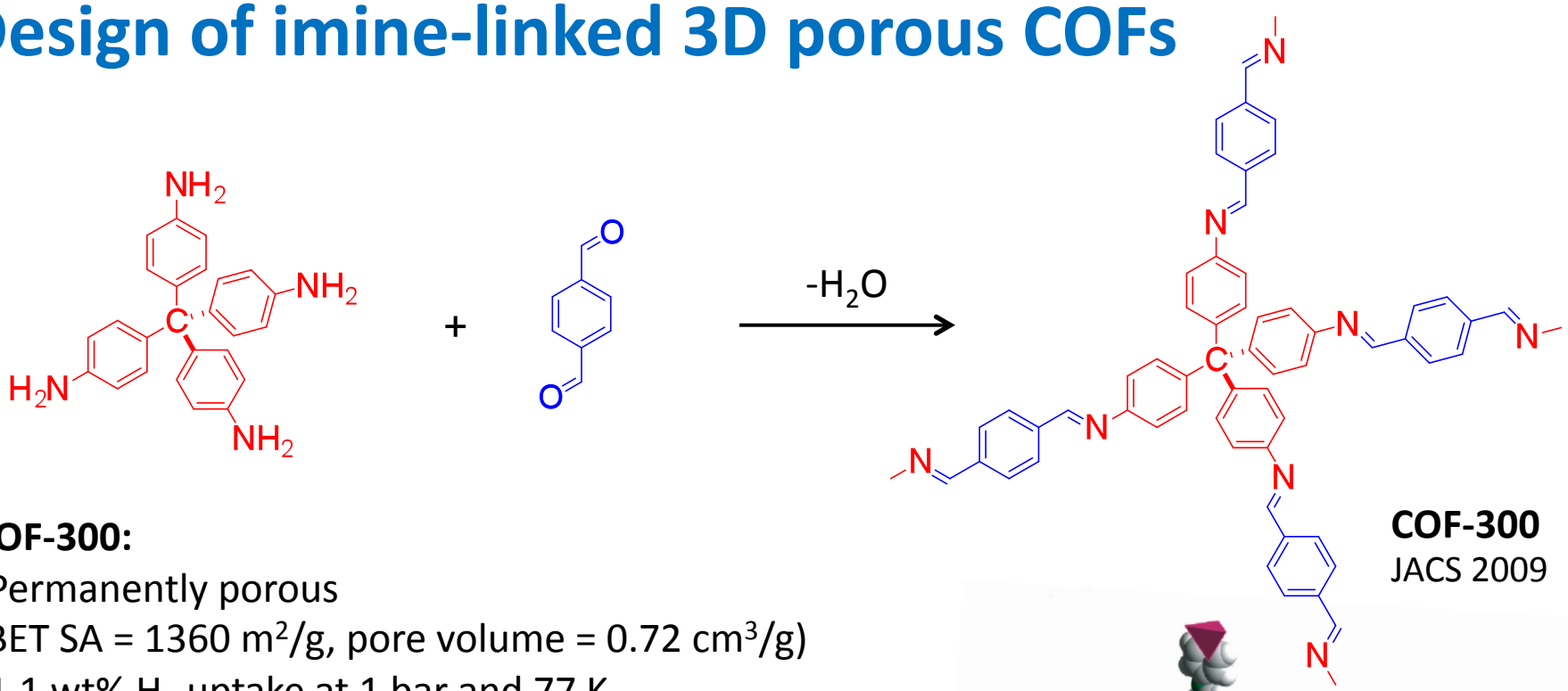
From the calculation, each linker can hold atomic Pd except the hydrozone.
➔ Design of imine-linked COFs







Design of imine-linked 3D porous COFs

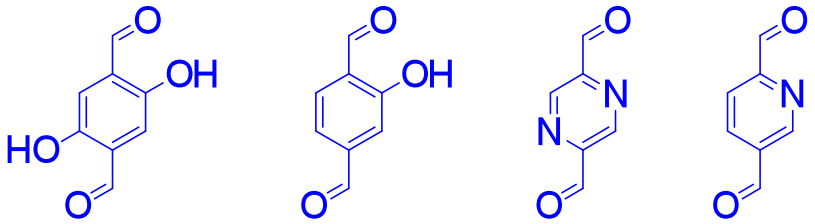


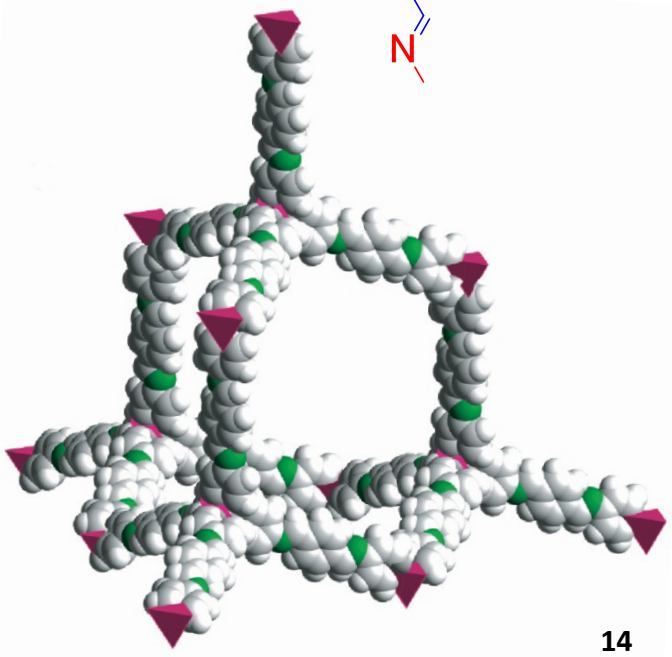
COF-300
JACS 2009

COF-300:

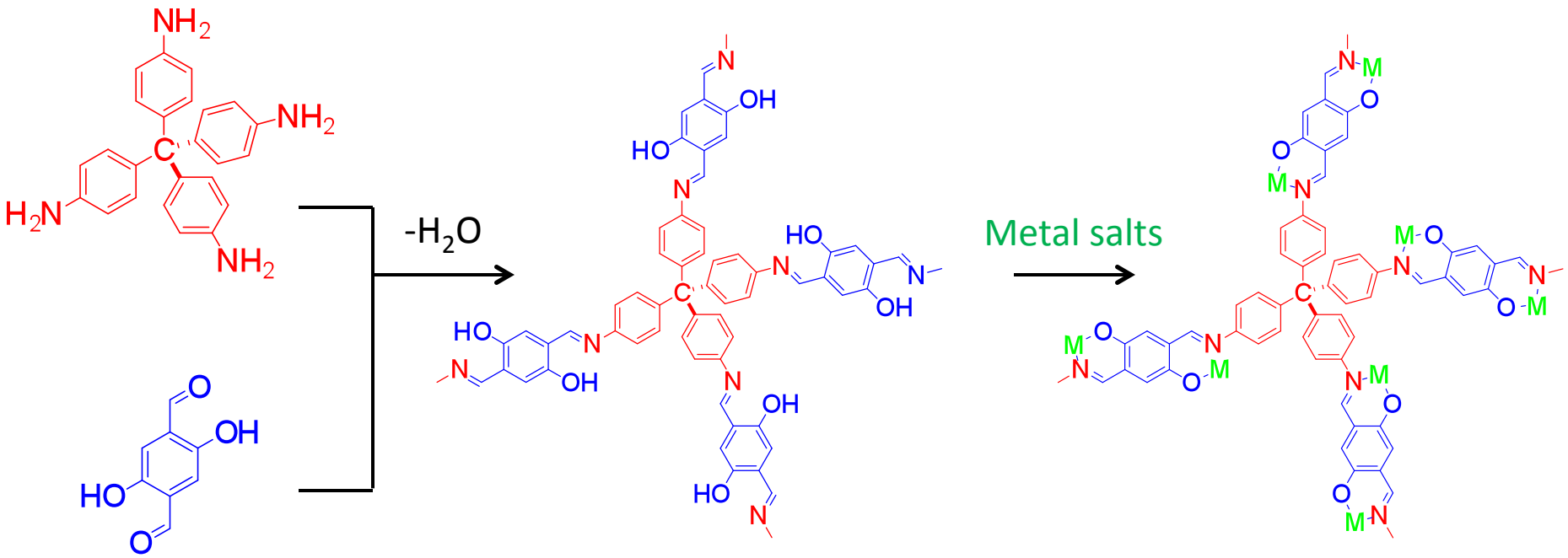
- Permanently porous
(BET SA = 1360 m^2/g, pore volume = 0.72 cm^3/g)
- 1.1 wt% H_2 uptake at 1 bar and 77 K
- However, no metal binding sites in the framework

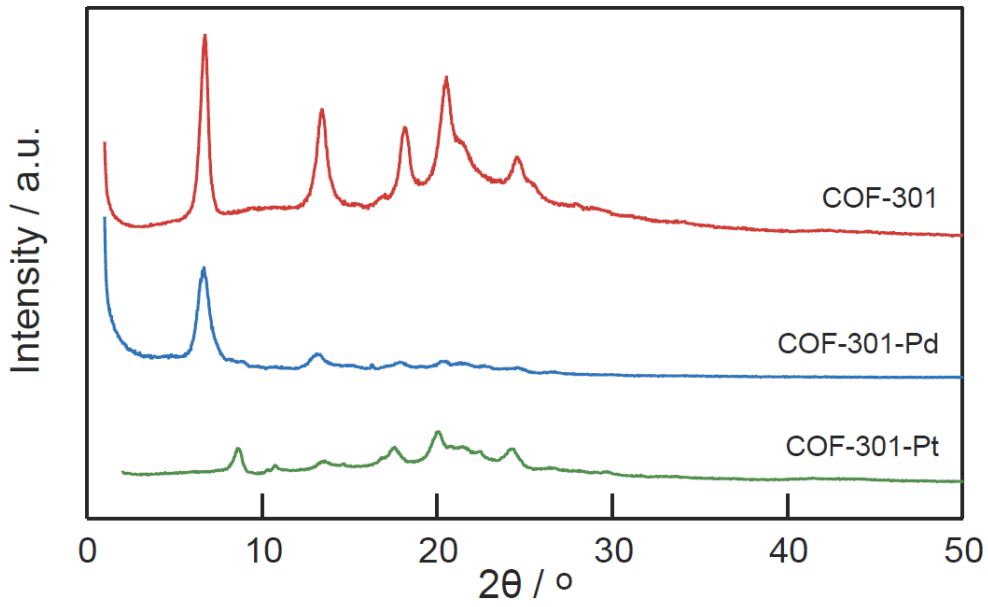
Use terephthaldehyde derivatives to introduce metal binding sites





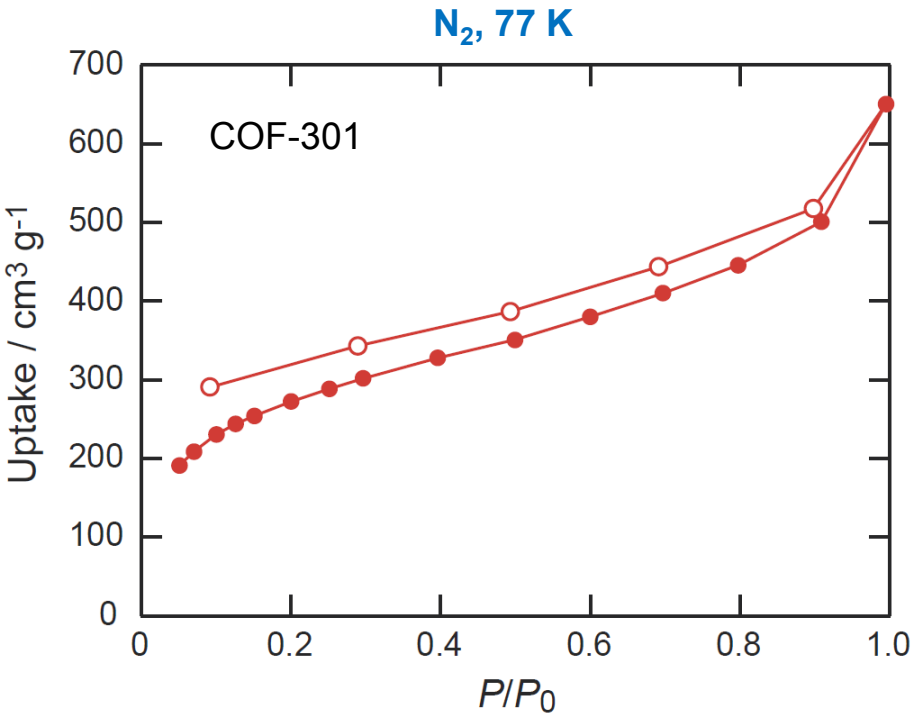
Synthesis of COF-301 and metalation

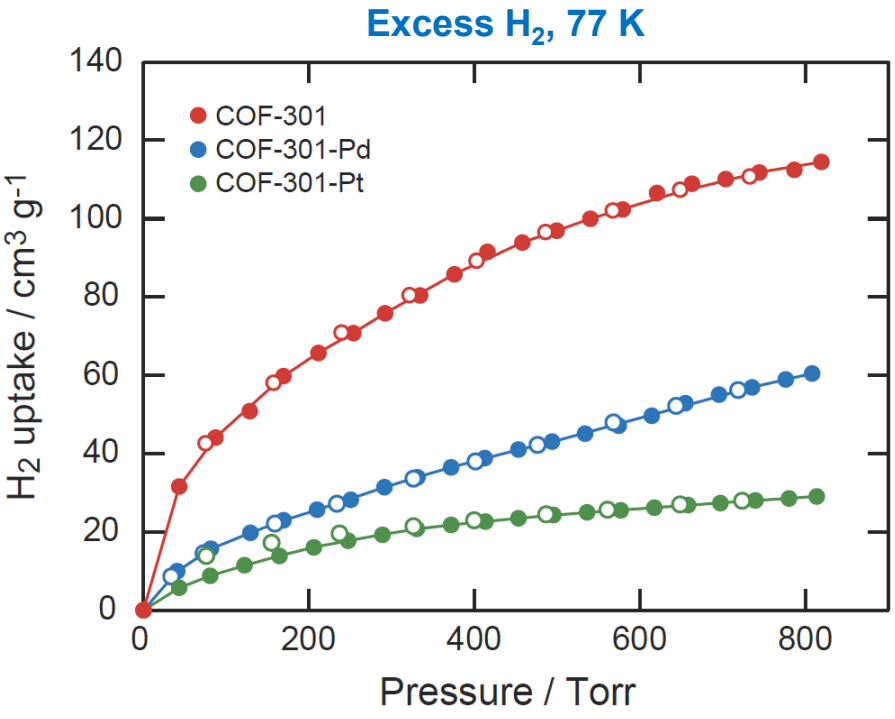




- Crystalline COF-301 was synthesized
- The formation of imine linkages in COF-301 was confirmed by FT-IR spectra
- Crystallinity remains after the metalation

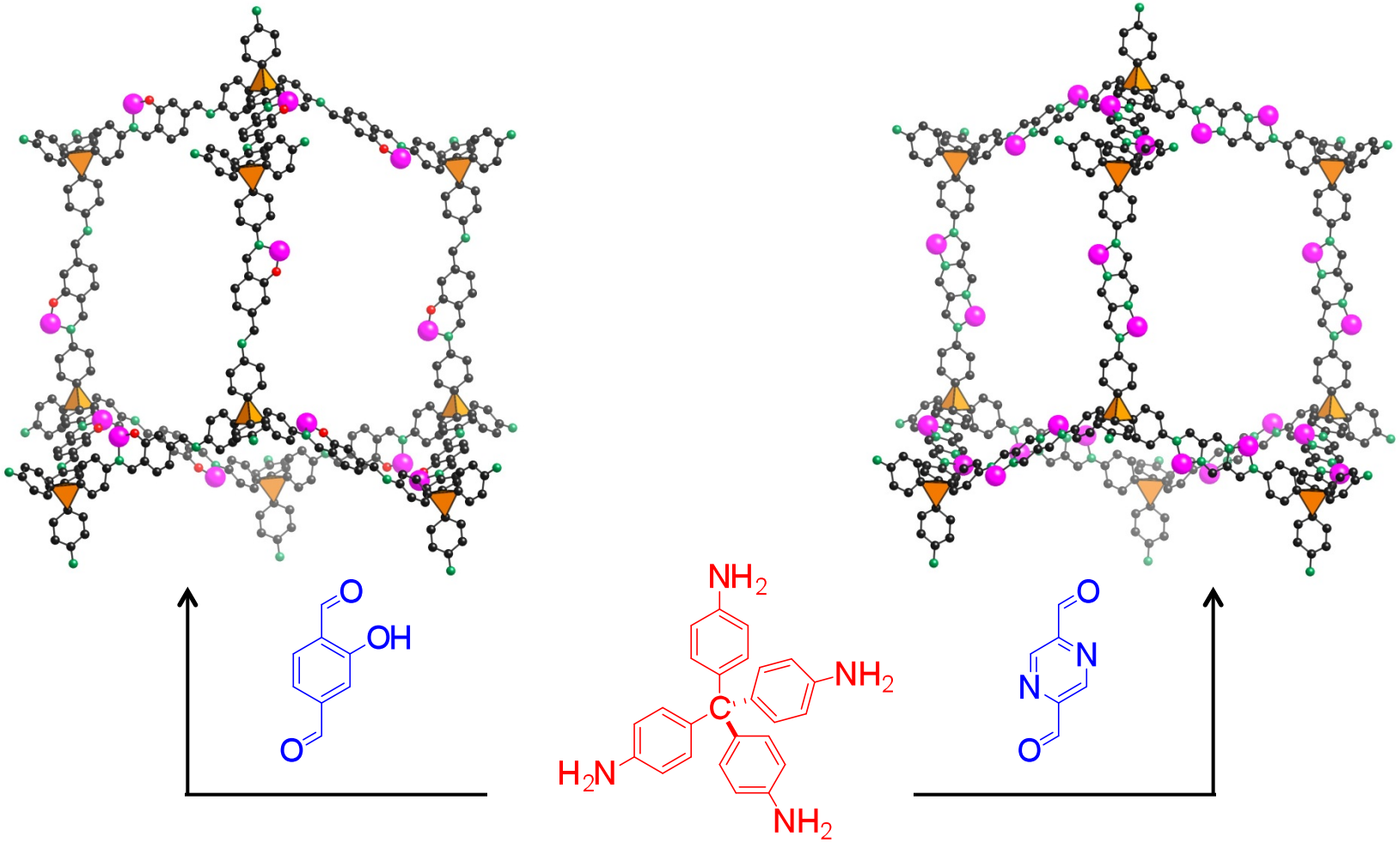
N_2 and H_2 uptake by COF-301 and metalated COFs





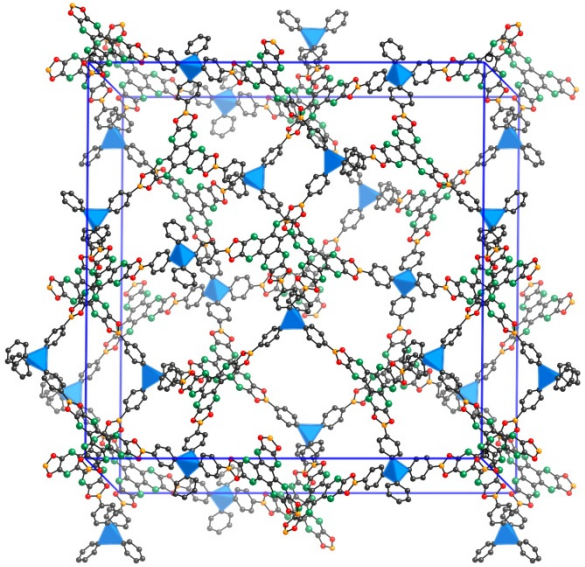
	Metal salt	BET SA (m^2/g)	H_2 uptake at 1 bar and 77 K (wt%)
COF-301	n/a	840	1.0
COF-301-Pd	$PdCl_2$	60	0.5
COF-301-Pt	$PtCl_2$	20	0.2

New COFs replete with metal binding sites

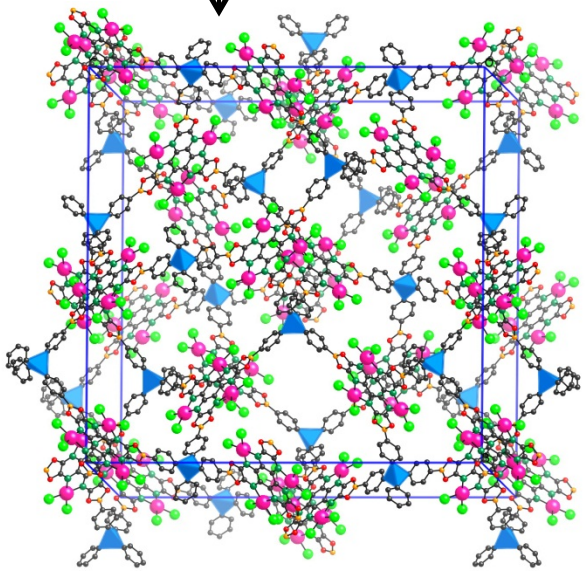


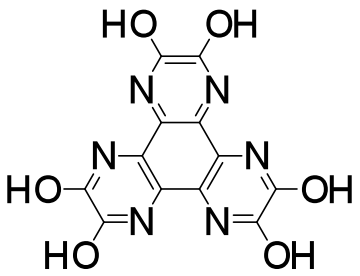
- All starting materials are in hand.
- Synthesis of these COFs has started.

Approach #1: Hexaazatriphenylene COFs



metalation





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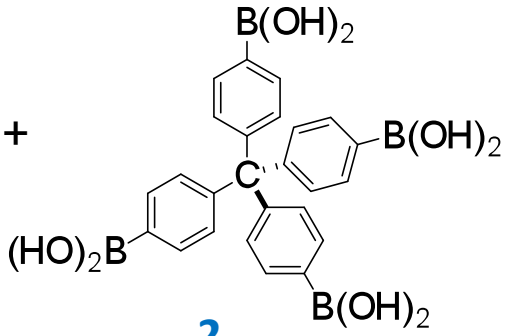

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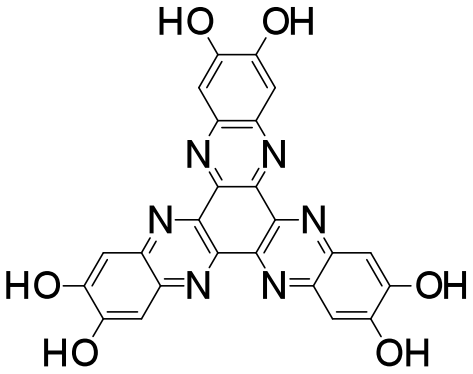

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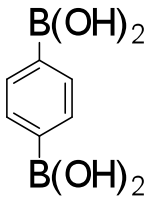

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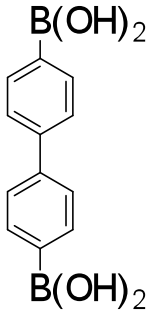
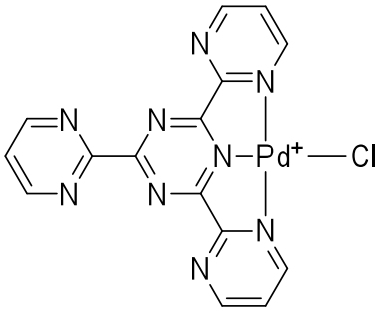


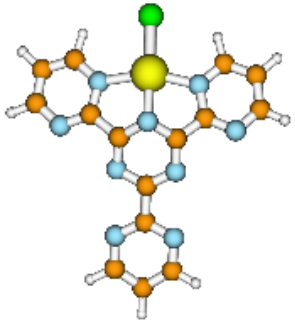
5

- Compound **3** was prepared.
- Studying COF synthesis condition of **3** with **2**, **4**, or **5**.

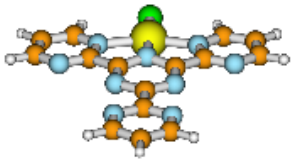
Proposed target structure #1

TPymT-COF-PdCl

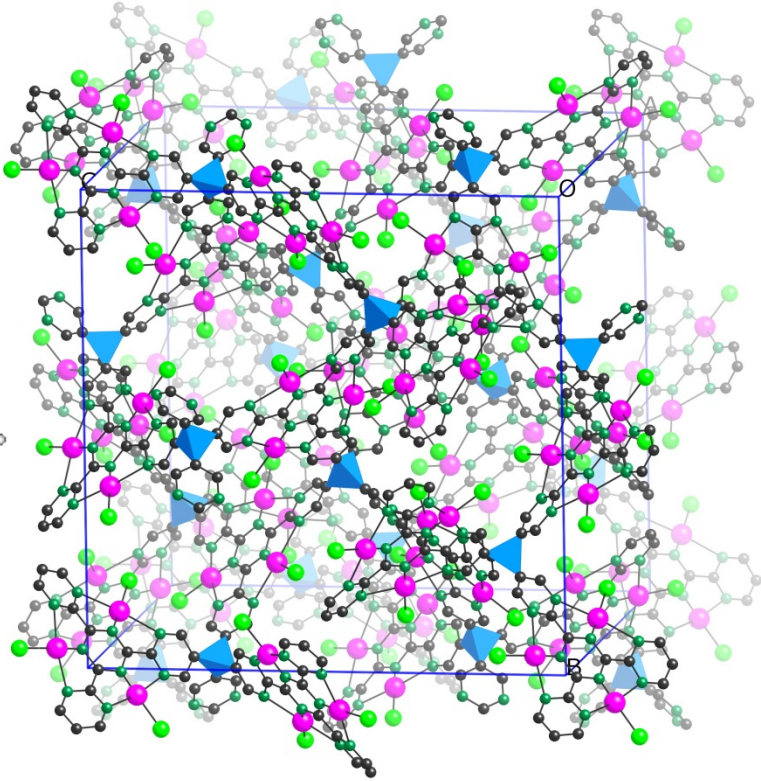




View 1



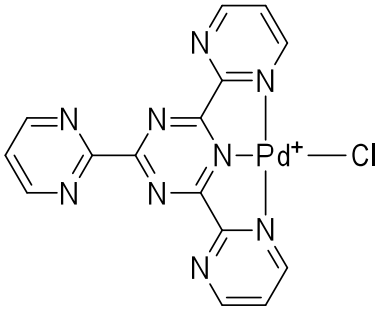
View 2

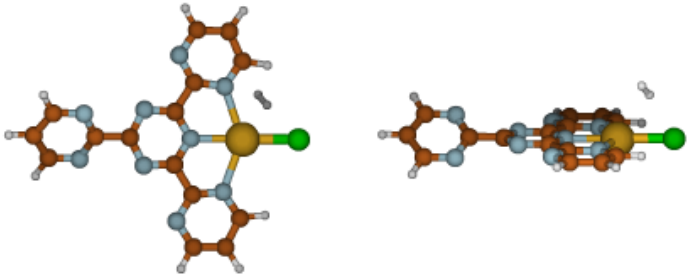


TPymT-COF-PdCl

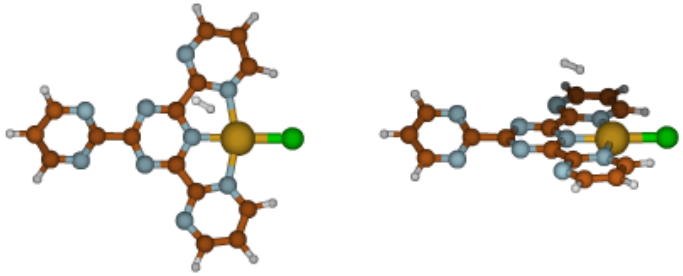
H-H

TPymT-PdCl





Configuration 1



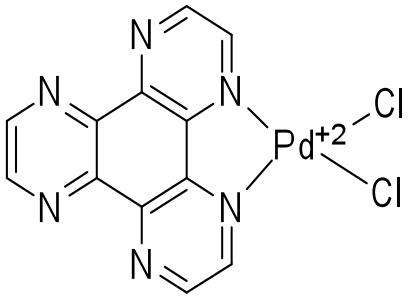
Configuration 2

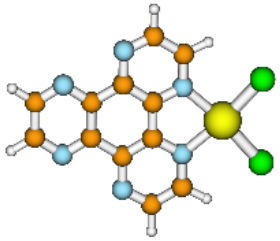
TPymT-PdCl-H_2

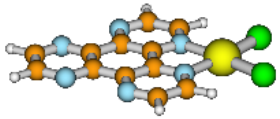
The calculation of the isotherm is underway.

Proposed target structure #2

HAT-COF-$PdCl_2$

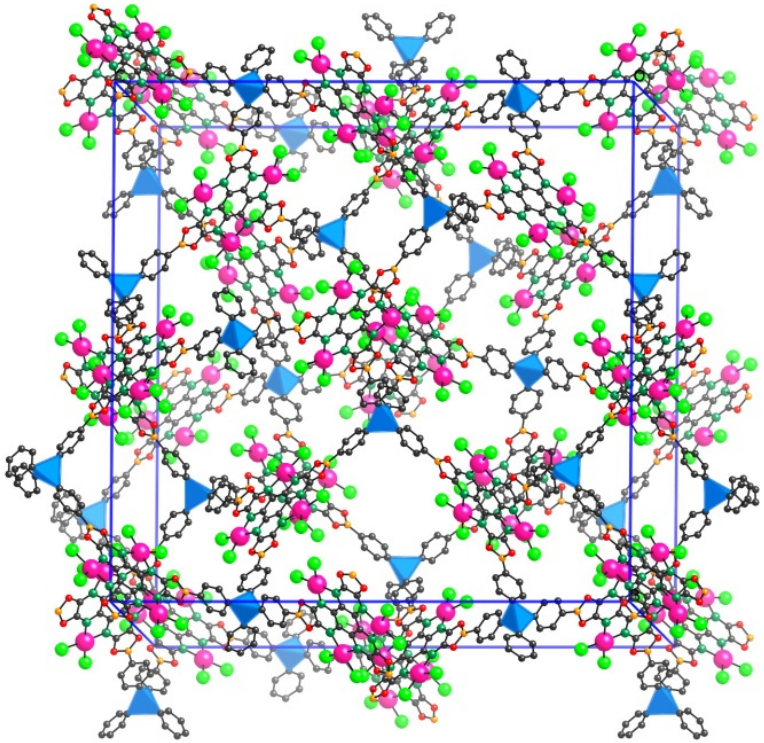






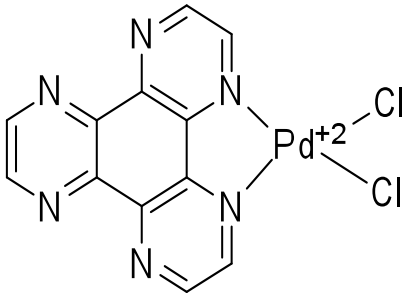
View 1 View 2

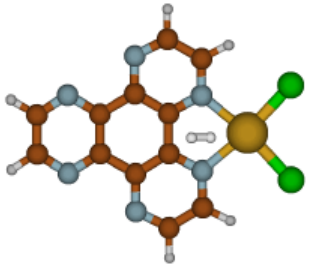
$HAT\text{-}PdCl_2$

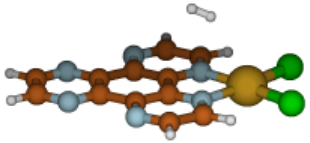


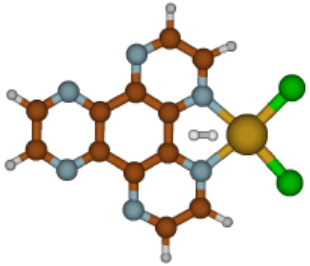
$HAT\text{-}COF\text{-}PdCl_2$

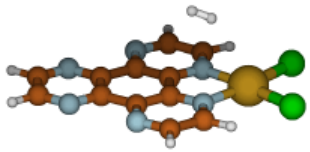
H-H











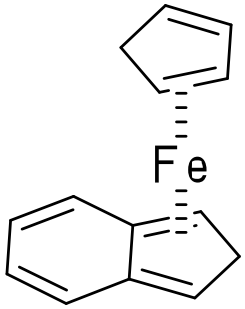
Configuration 1 Configuration 2

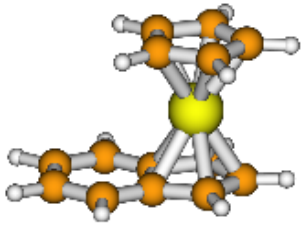
$HAT\text{-}PdCl_2\text{-}H_2$

The calculation of the isotherm is underway.

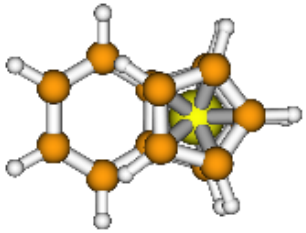
Proposed target structure #3

CpFe-COF



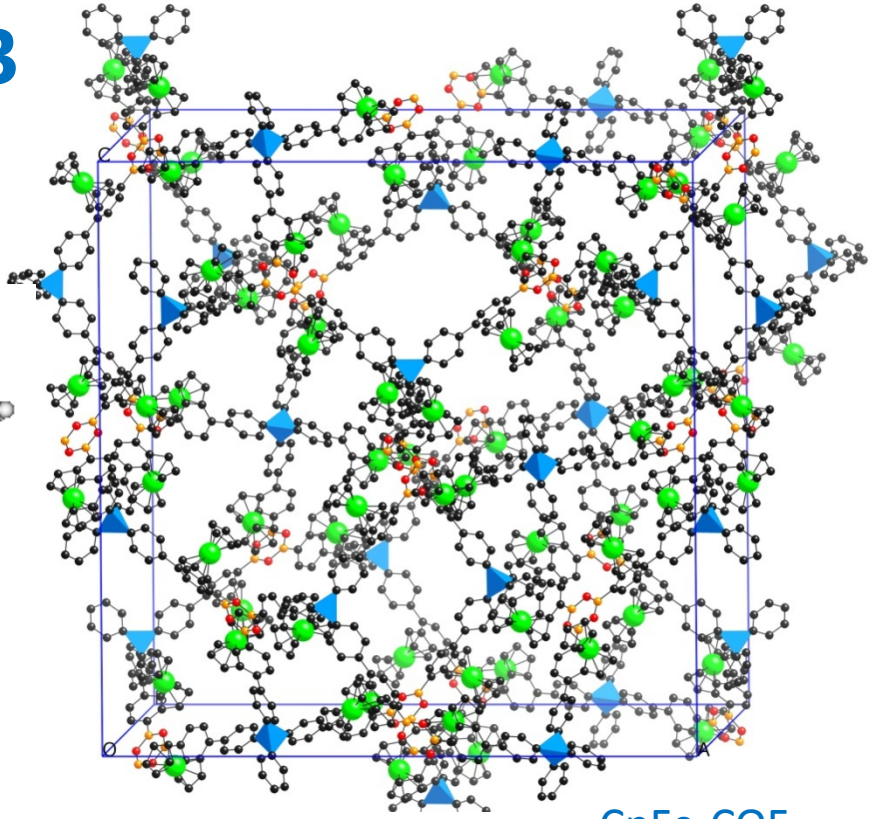


View 1



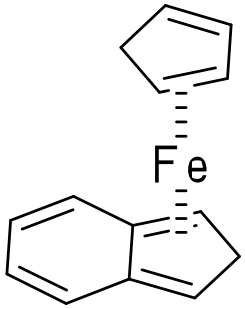
View 2

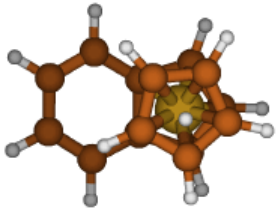
CpFe

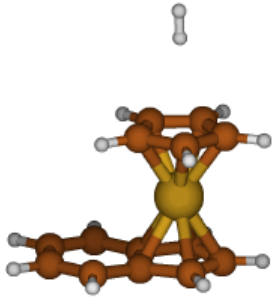


CpFe-COF

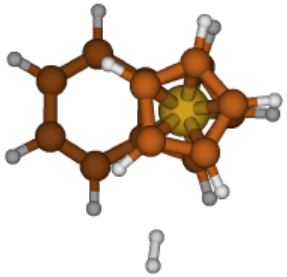
H-H

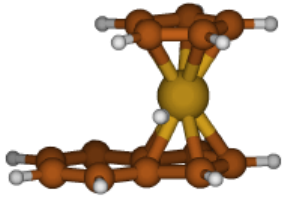






Configuration 3



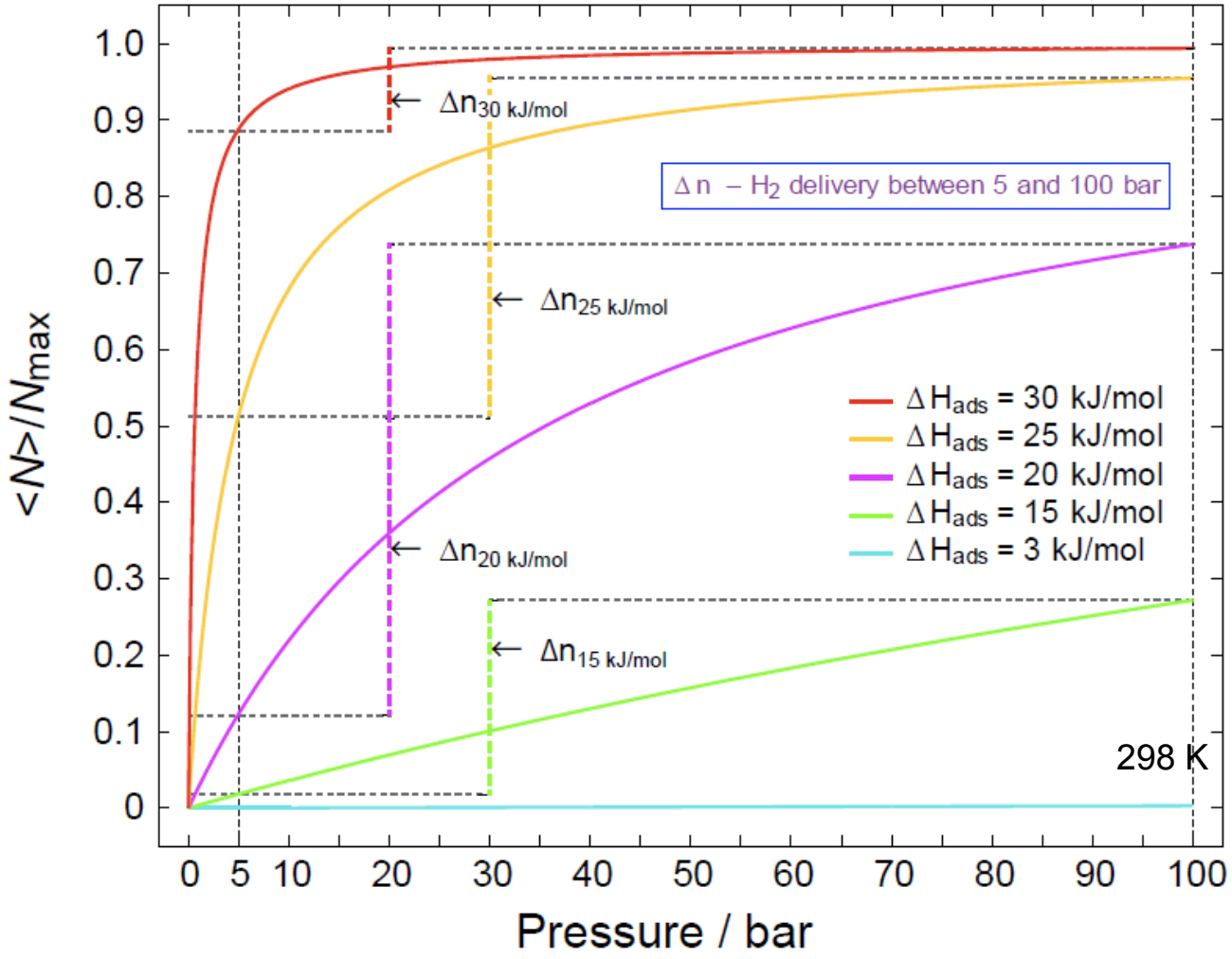


Configuration 5

$CpFe\text{-}H_2$

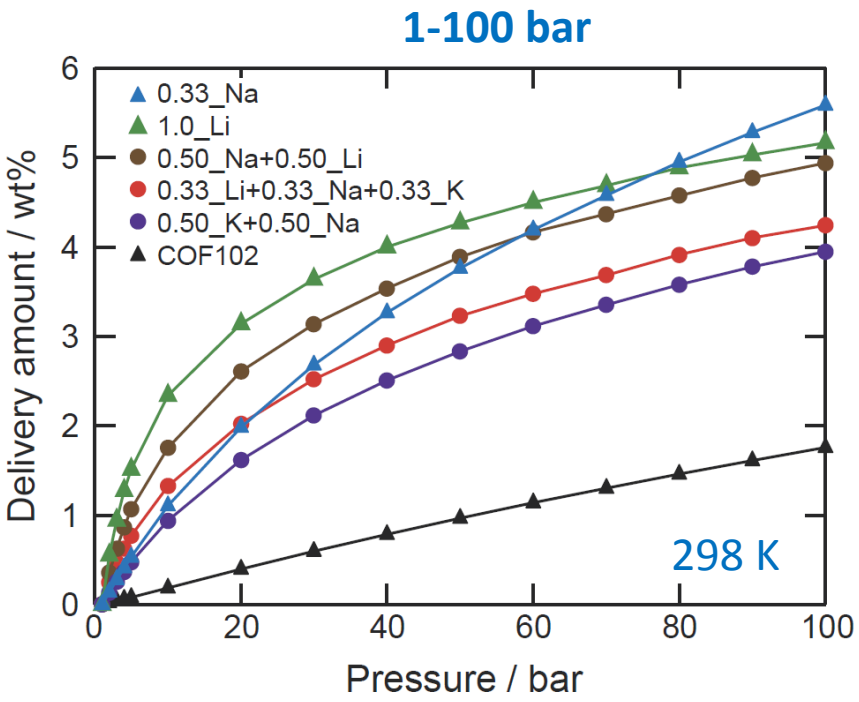
The calculation of the isotherm is underway.

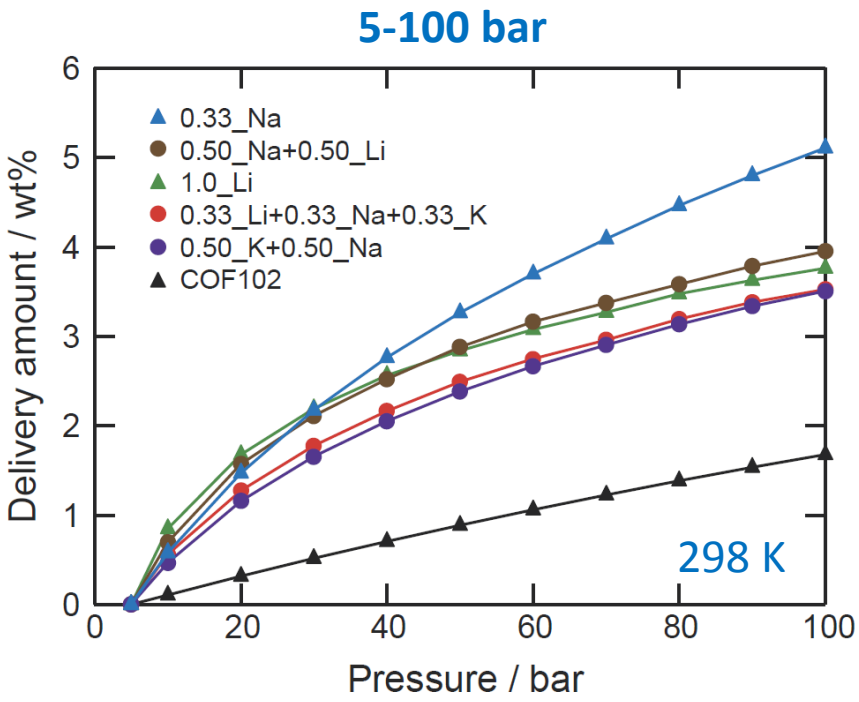
Ideal ΔH for maximized delivery amount of H_2



- Langmuir model was used for the generalization.
- ΔH = 20 kJ/mol is the optimal value to maximize the delivery amount between 5 and 100 bar.

Approach #2: Optimization of metal loading





- Simulated data indicate that delivery amount of H_2 (total, 298 K) can be maximized by either partial metalation or mixed metal impregnation.
- Implement calculations on other COFs (e.g. COF-301, COF-42) to optimize delivery amount of H_2.
- Study the effects of mixed metal impregnation to control the Q_{st} profile.
- Based on the prediction, metalation experiments will be performed.

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:

- Synthesized new COFs through hydrazone and imine condensation
- Began metalation experiments of COFs
- Began synthesis of mixed-metal ZIFs for improved adsorption enthalpy
- Found linkers with optimal binding energy for H_2 storage (20 kJ/mol)
- Designed new architectures with these linkers and began simulation calculations of H_2 uptake

Technology transfer/collaborations: Active relationship with collaboration partners (organic synthesis and material design) and BASF (verification of the data).

Proposed future research:

- Prepare COFs with metal binding sites and optimize the activation condition
- Employ metals to create strong binding sites and experimentally evaluate the Q_{st}
- Predict H_2 isotherms for modeled compounds with metals
- Study plausible route to synthesize the modeled compounds based on the thermodynamics
- Calculate the diffusion coefficient to estimate the kinetic factor with new force field