DOE Hydrogen Program

HYDROGEN STORAGE IN METAL-ORGANIC FRAMEWORKS

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Project ID
ST12

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Overview

Timeline

Project start date: 5/1/2005
Project end date: 4/30/2009
Percent complete: 70%

Barriers

Barriers addressed

- ❑ Improved gravimetric and volumetric density of hydrogen uptake
- ❑ Hydrogen capacity and fast kinetics at 77 K
- ❑ Improved hydrogen binding energy
- ❑ Synthesic scale up of MOFs to cubic meters

Budget

- ❑ Total project funding
  - DOE share: $1.6 M
- ❑ Funding received in FY07: $375 K
- ❑ Funding for FY08: $400 K

Collaborating Partners

- ❑ Juergen Eckert (UCSB)
- ❑ Joe Hupp (NW)
- ❑ Randy Snurr (NW)
- ❑ Bill Goddard (Caltech)

Objectives (2007-08)

1. **Relationship between MOF structure and binding energy**
   - Low-pressure measurements at various temperatures

2. **High-pressure H_2 adsorption measurement at RT**
   - Impregnation of polymer and metal complex
   - Preparation of Li-doped MOFs

3. **Toward the practical use of MOFs**
   - Cycling and kinetics of H_2 charge/discharge
   - Effect of impurity in H_2 gas
   - Consideration of heat management

4. **Coordination with theory**
   - Prediction of H_2 uptake capacity

Milestones

June 2007	Impregnation with polymers and metal complexes Test interpenetrating MOFs with open metal sites
November 2007	Study of relationship between MOF structure and binding energy Begin Li-impregnation in MOFs
March 2008	Study effect of impurity in H_2 gas
August 2008	Li-impregnation by gas-phase adsorption Design and synthesis of novel MOFs for Li-doping
December 2008	H_2 adsorption in Li-doped MOFs at room temperature (3-4 wt% at 298 K and 100 bar)

Important Aspects of MOF Chemistry

- Design of composition (metal centers and organic links). Synthesis and structural characterization is well worked out.
- Control of structure, topology, interpenetration and porosity.
- Formulation of hypothesis and testing of hypothesis is quite feasible. This leads to definitive conclusions and allows for rapid identification of important parameters which impact hydrogen uptake.

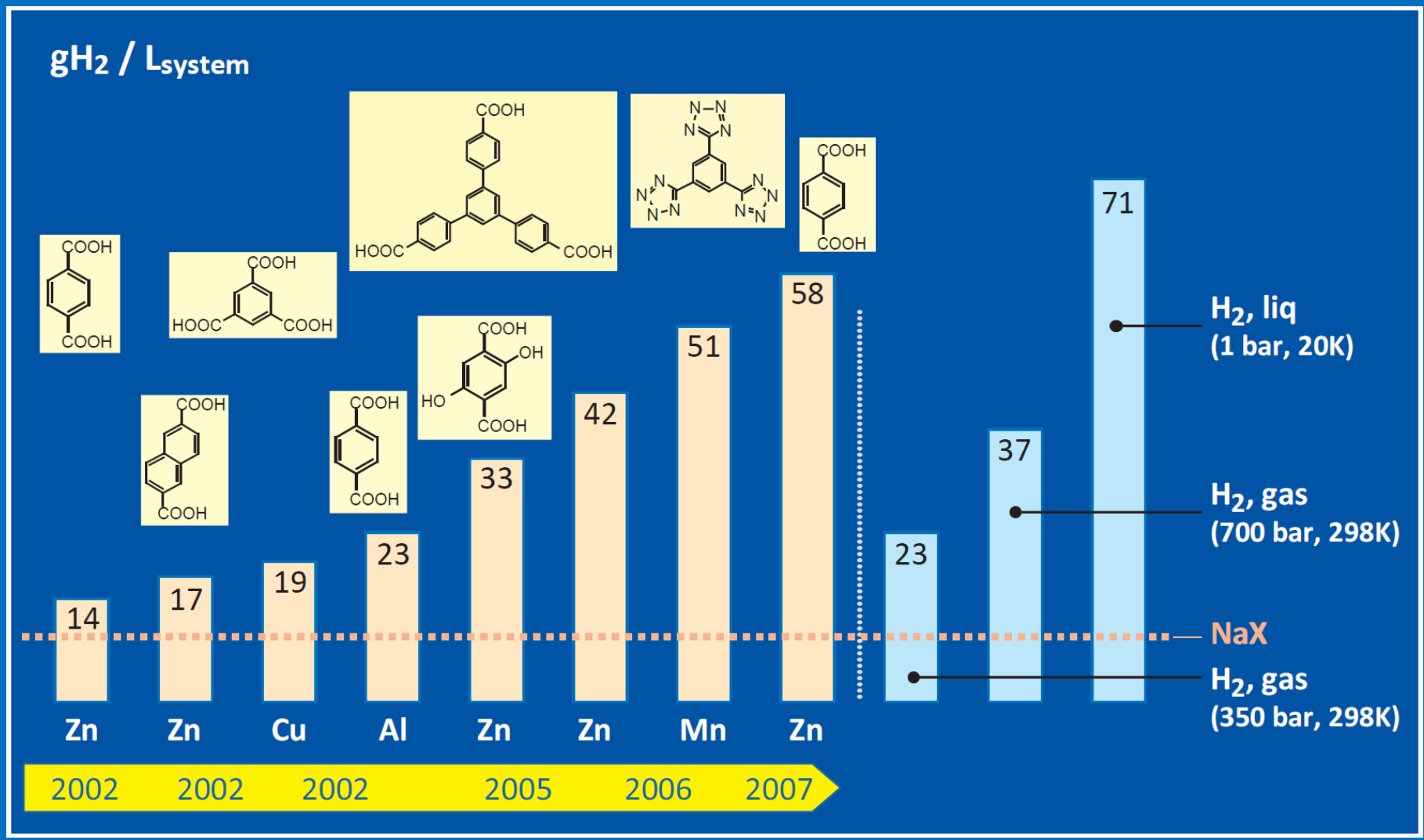
H_2 uptakes in representative MOFs

Using strategies to meet 2010 DOE targets

Compound	Chemical formula	Attribute	Low-pressure (77 K, 1 bar)		High-pressure (77 K)		ΔH
			mg g^{-1}	g L^{-1}	mg g^{-1}	g L^{-1}	kJ mol^{-1}
IRMOF-1	$Zn_4O(C_8H_4O_4)_3$	Non-functionalized	13.2	7.8	52.1	30.8	4.8
MOF-177	$Zn_4O(C_{27}H_{15}O_6)_2$	Non-functionalized	12.5	5.3	74.9	32.0	4.4
IRMOF-2	$Zn_4O(Br\text{-}C_8H_4O_4)_3$	Functionalized	12.1	7.9	-	-	-
IRMOF-3	$Zn_4O(NH_2\text{-}C_8H_4O_4)_3$	Functionalized	14.2	8.7	-	-	5.3
IRMOF-6	$Zn_4O(C_{10}H_8O_4)_3$	Functionalized	14.8	9.7	48.5	31.7	-
IRMOF-20	$Zn_4O(C_8H_2O_4S_2)_3$	Functionalized	13.5	6.9	66.7	34.1	-
IRMOF-11	$Zn_4O(C_{18}H_{12}O_4)_3$	Interpenetrating	16.2	12.3	35.2	26.7	9.1
IRMOF-13	$Zn_4O(C_{18}H_8O_4)_3$	Interpenetrating	17.3	13.0	-	-	-
MOF-199	$Cu_2(C_9H_3O_6)_{4/3}$	Open metal site	25.4	22.3	32.6	28.7	6.8
MOF-505	$Cu_2(C_{16}H_6O_8)$	Open metal site	24.7	22.9	42.0	38.9	6.5

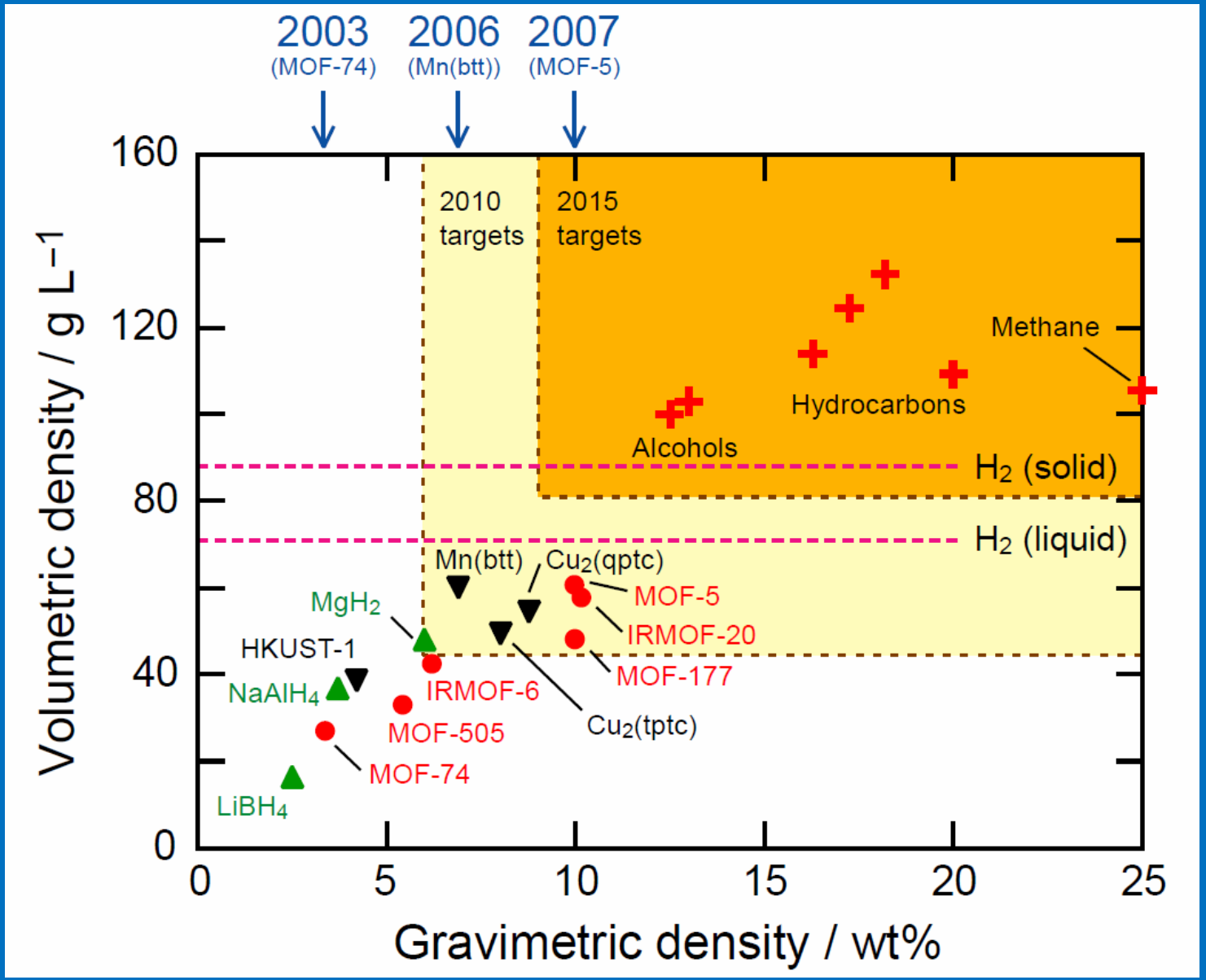
MOF

Hydrogen Storage Capacities (50 bar, 77K)



Stored hydrogen per mass and per volume

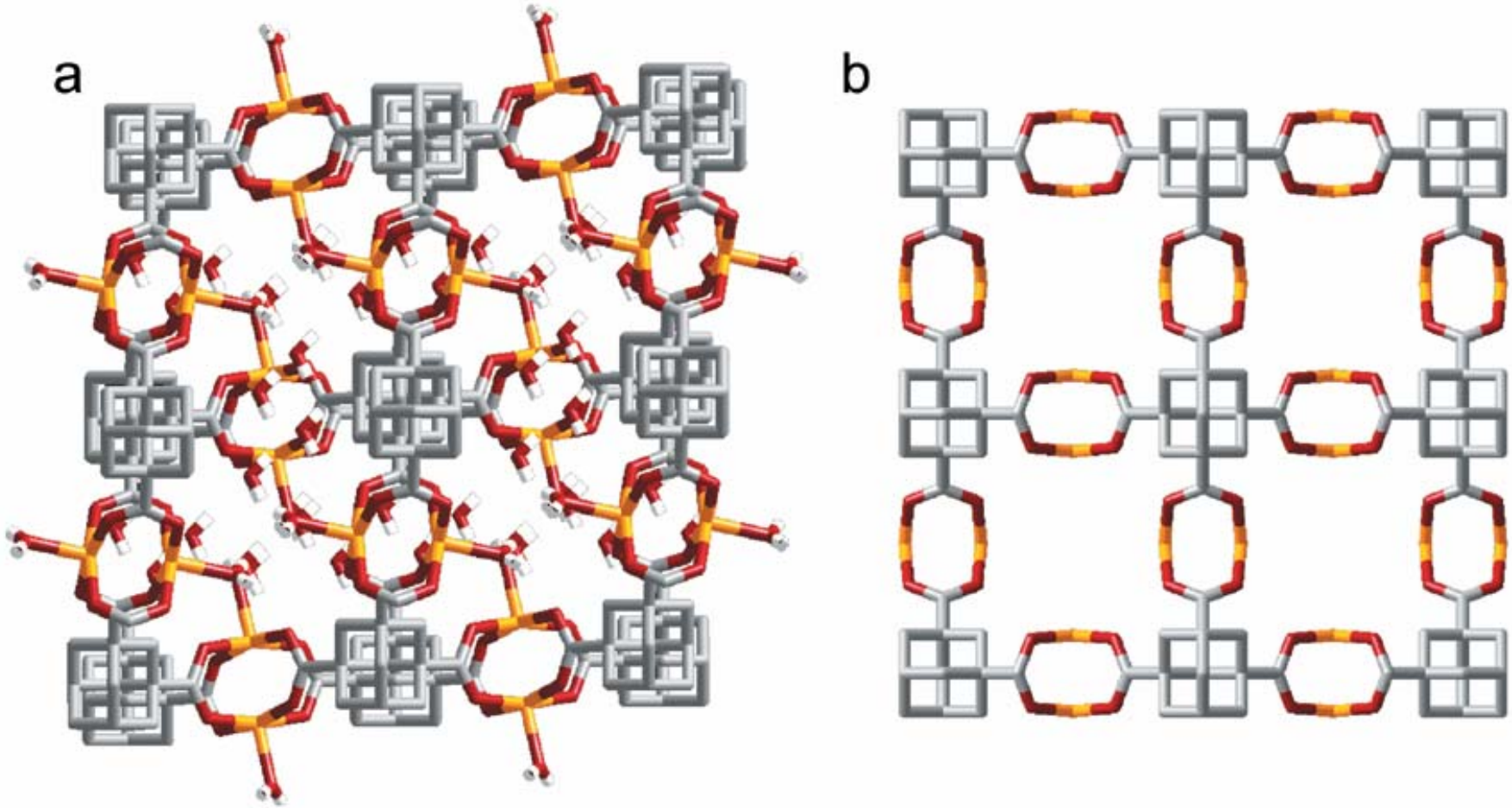
(only metal hydrides showing good recycling are included)



Room temperature hydrogen storage and the challenges addressed

- Stronger binding of hydrogen
  - Combination of interpenetration with open metal sites
  - Introduction of links containing B and N (as strong polarizing atoms)
  - Impregnation of MOF-177 with polymers
  - Impregnation of MOF-177 with transition metal complexes
  - Doping with Li
- Kinetics of uptake and release, multiple cycles, and impact of impurities on uptake of hydrogen
- Coordination with theory (close collaboration with Bill Goddard)
  - Concepts and prediction from theory for covalent-organic frameworks (COFs)
- Preliminary structures with potential for soft chemisorption
  - ZIF-100
  - ZIF-333

Open metal sites fully characterized in MOFs

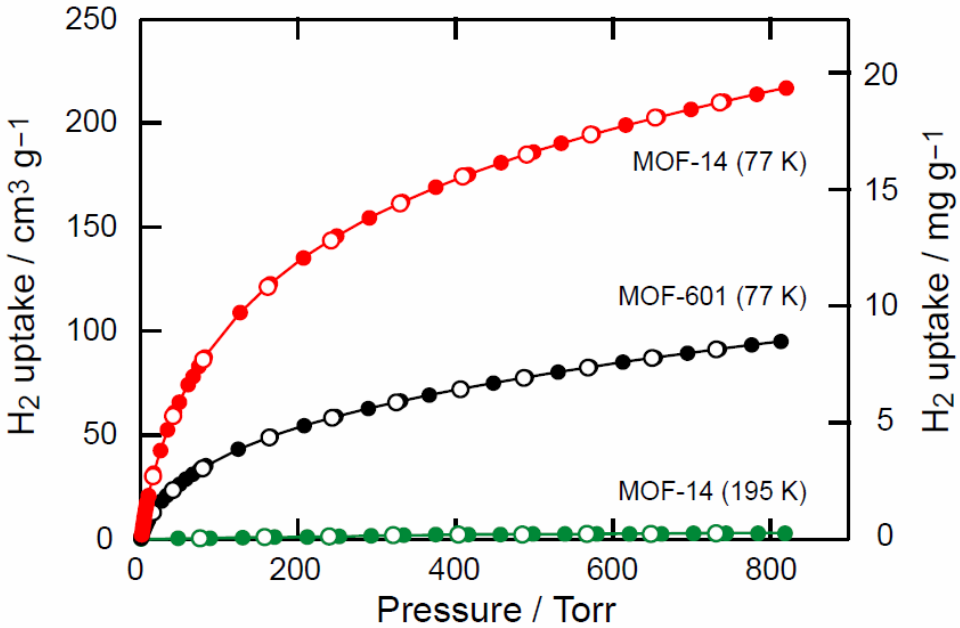


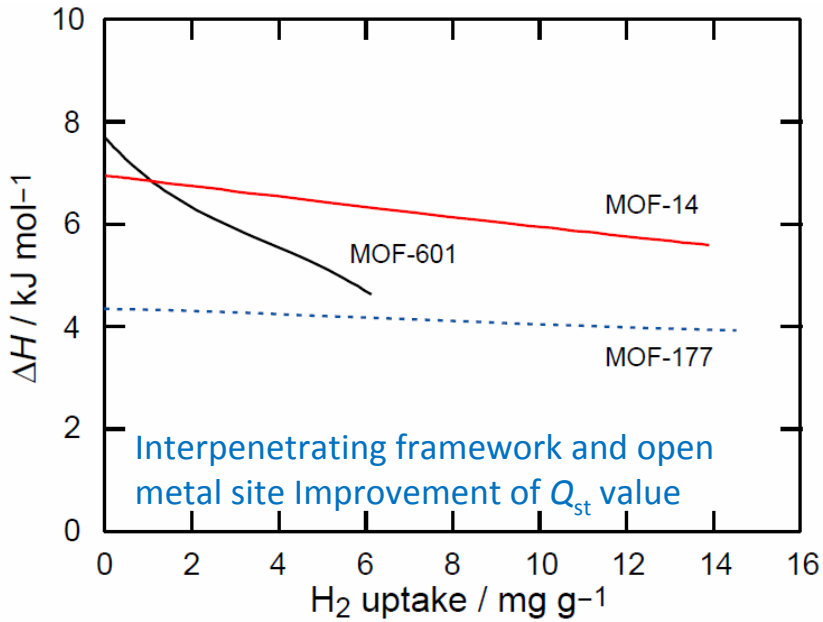
$Cu_2(ATC)\cdot 6H_2O$ $Cu_2(ATC)$

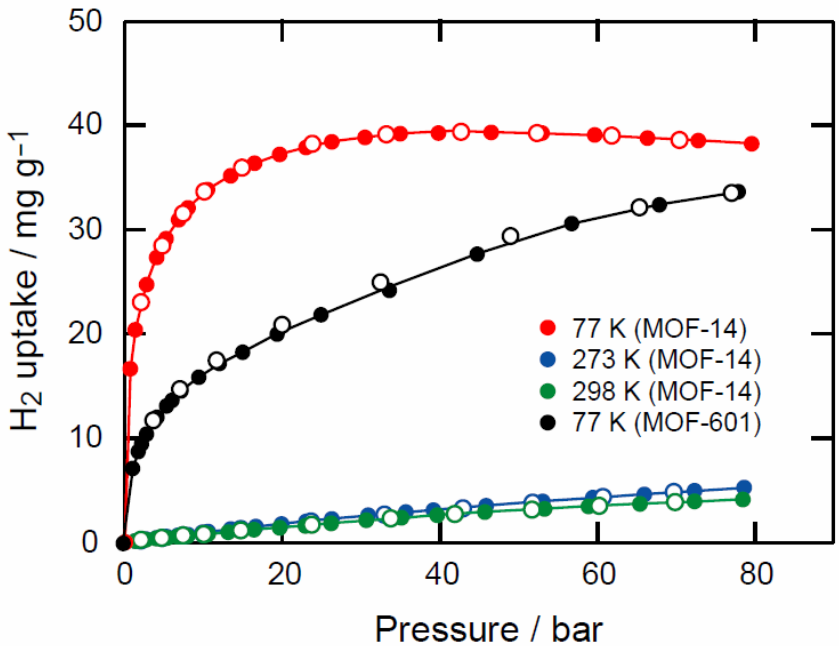
- H. Li and O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 2186.
- H. Li and O. M. Yaghi, *J. Am. Chem. Soc.* **1998**, *120*, 8571.
- B. Chen and O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 11559.

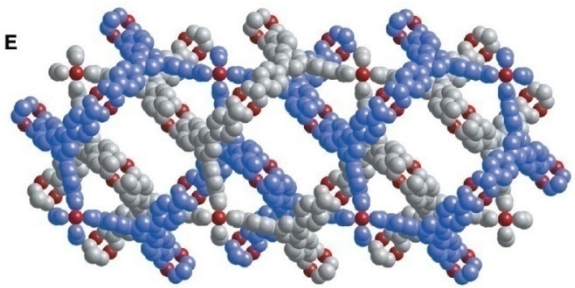
Combination of interpenetration with open metal sites

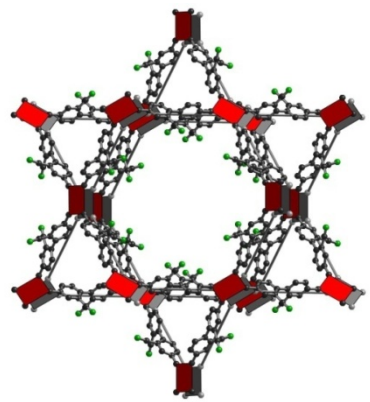
MOF structures combining interpenetration and open metal sites









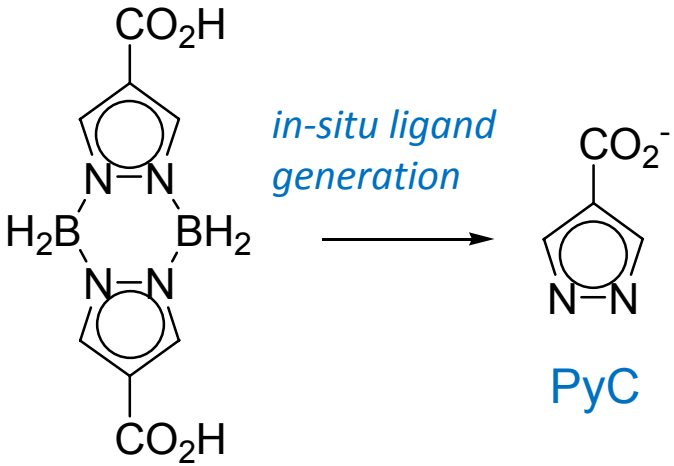


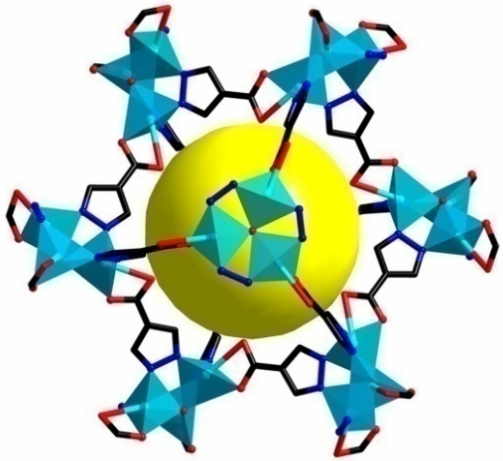
MOF-14
SA = 2000 $m^2 g^{-1}$
V_p = 0.71 $cm^3 g^{-1}$

MOF-601
SA = 1520 $m^2 g^{-1}$
V_p = 0.47 $cm^3 g^{-1}$

Introduction of links containing B and N
(as strong polarizing atoms)

MOF-324 and 326



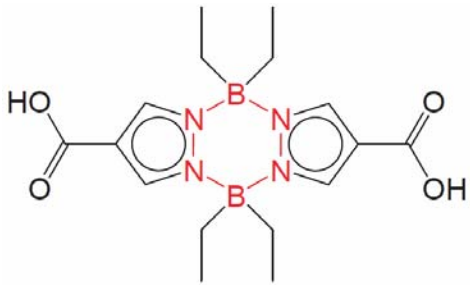


MOF-324

$Zn_3(OH)[(PyC)_2(HPyC)]$

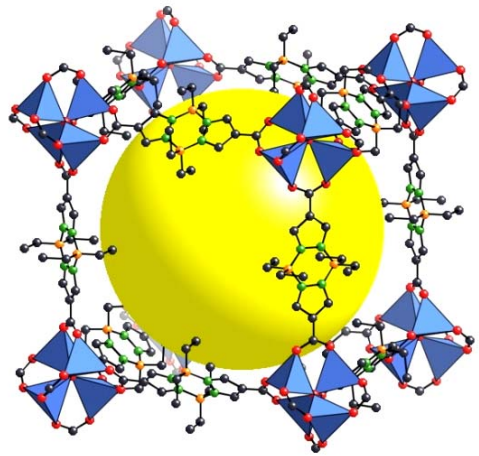
Pα-3, *a* = 20.123 Å
Pore diameter = 7.6 Å

MOF-5 type structure



Et-PzDC

+ $Zn(NO_3)_2$



MOF-326

$Zn_4O(Et\text{-}PzDC)_3$

Fm-3*m*
a = 33.410 Å
V = 37294 Å^3

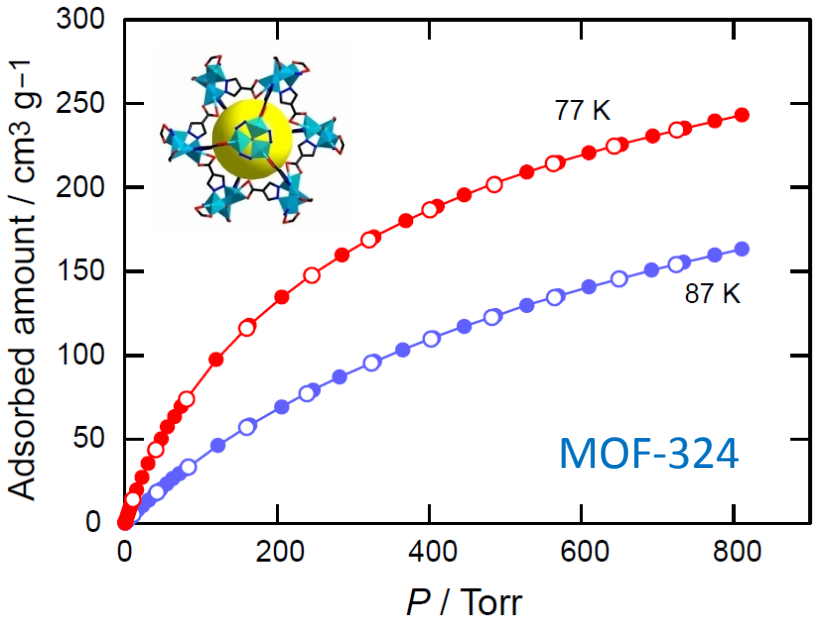
❑ Stable compounds

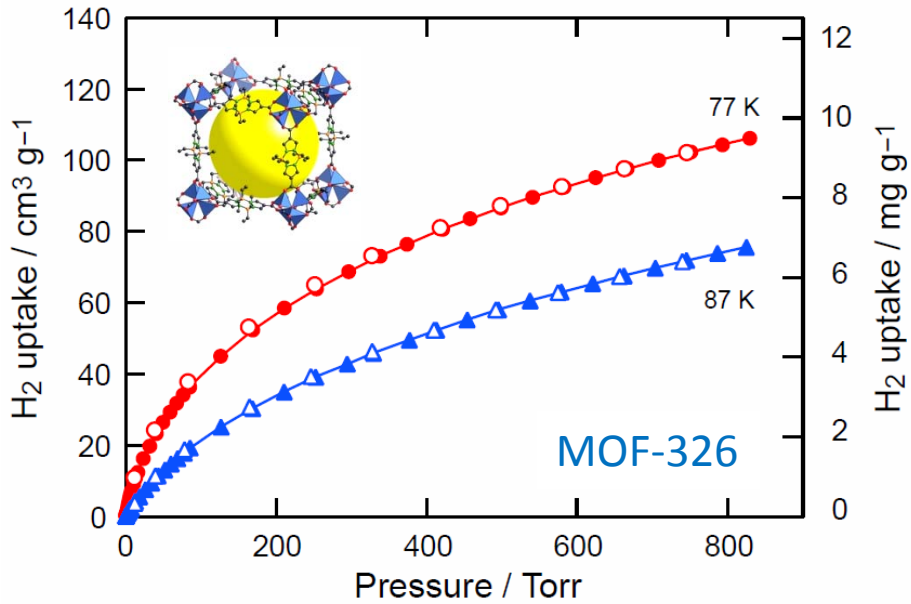
- Strong B–N bonds (450 kJ/mol)
- Stable in aqueous, basic media

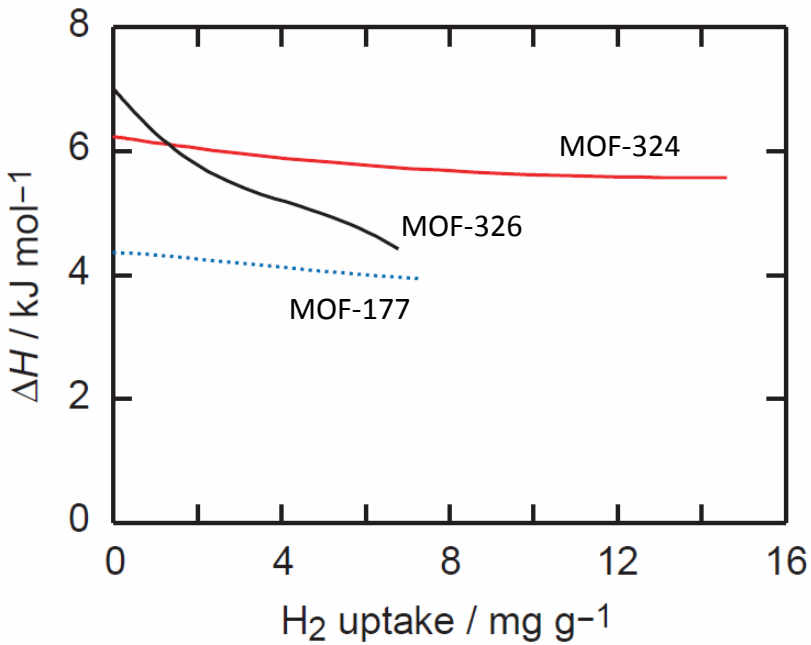
❑ Charged compound

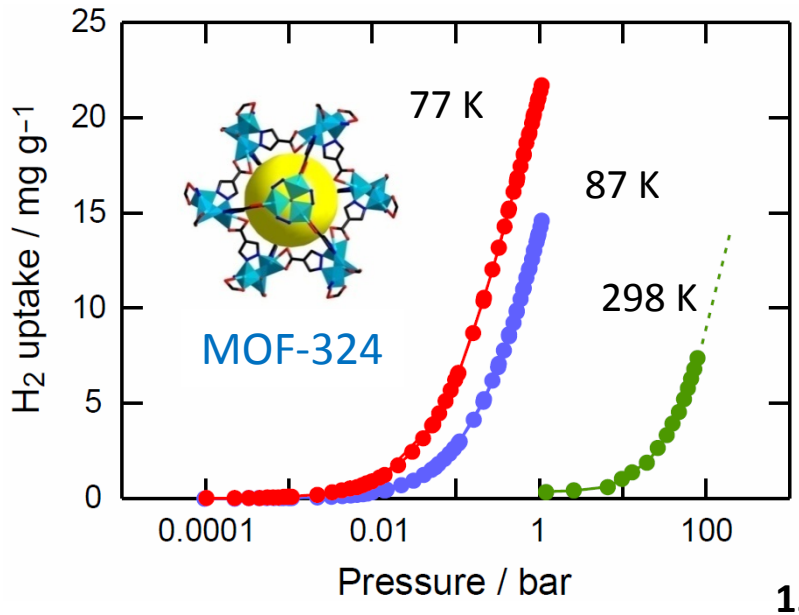
- B: negative charge
- N: positive charge

H_2 isotherms for MOF-324 and 326



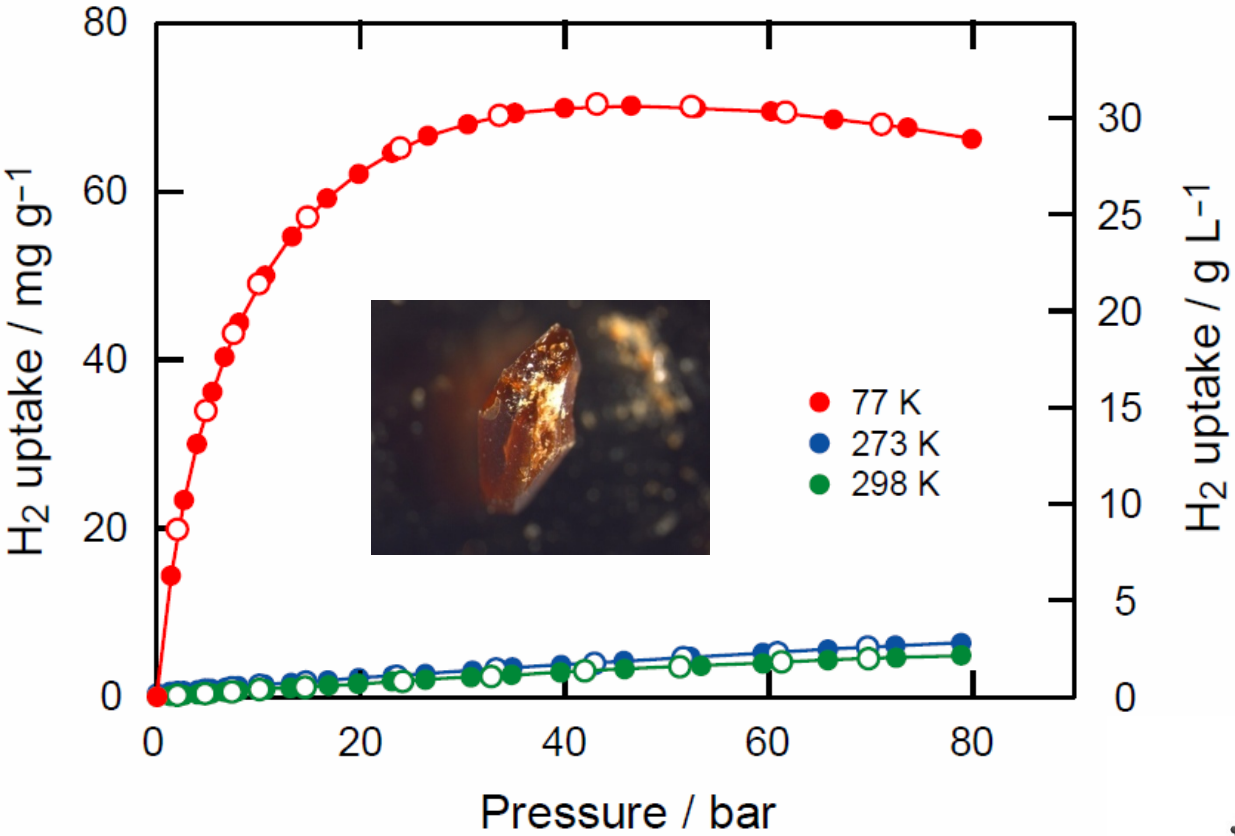


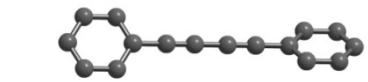




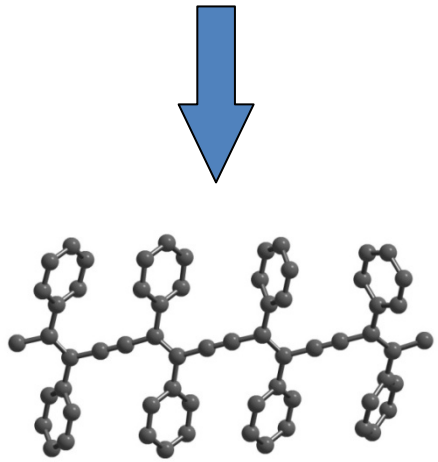
- Impregnation of MOF-177 with polymers
- Doping with lithium

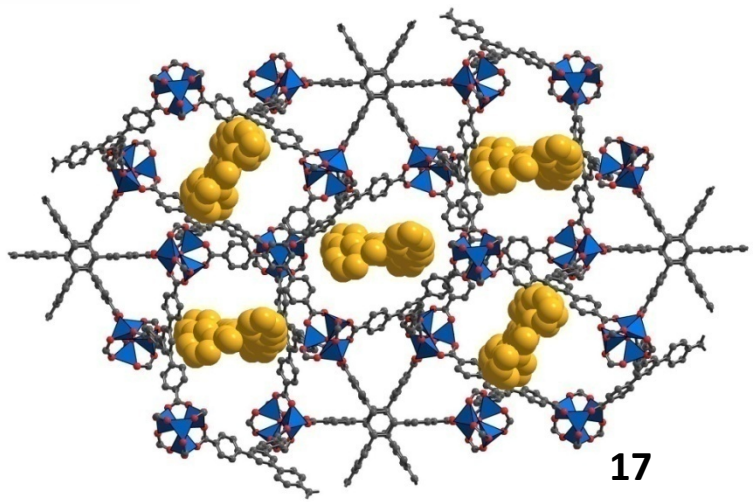
Polymer impregnation in MOF-177





1,4-Diphenylbutadiyne





Langmuir SA = 4050 $m^2\ g^{-1}$

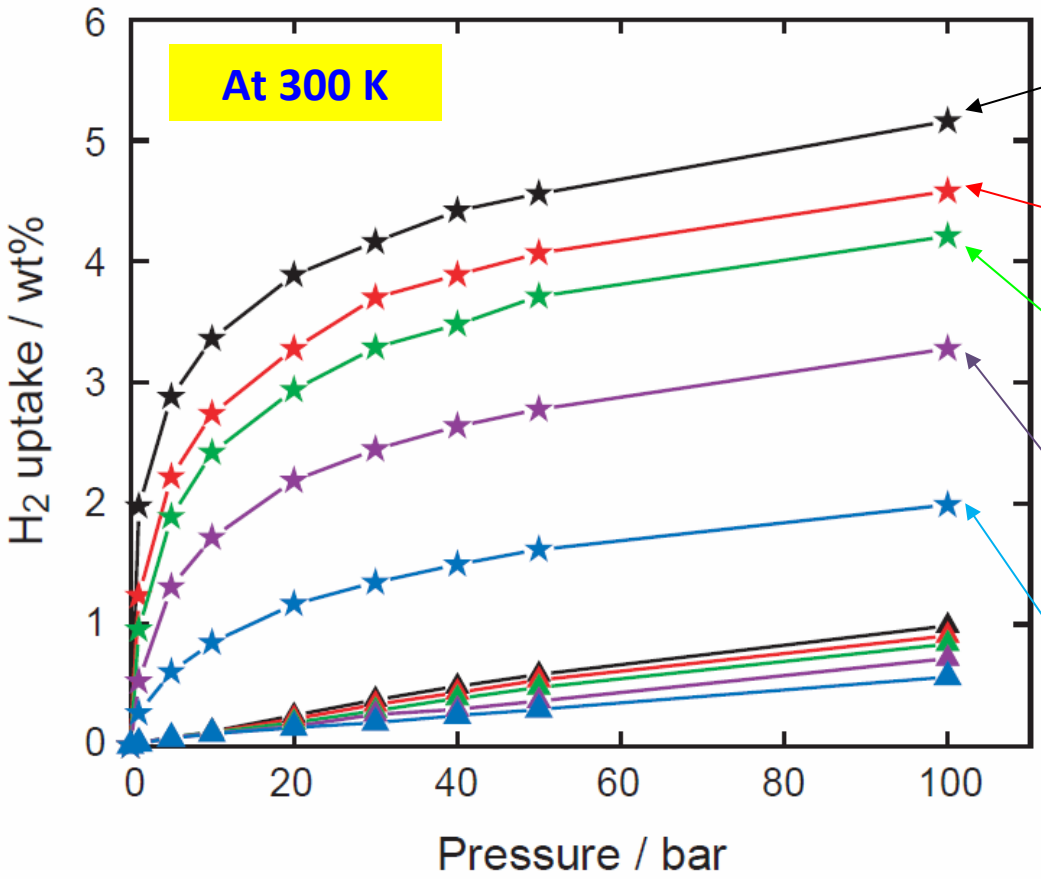
V_p = 1.7 $cm^3\ g^{-1}$

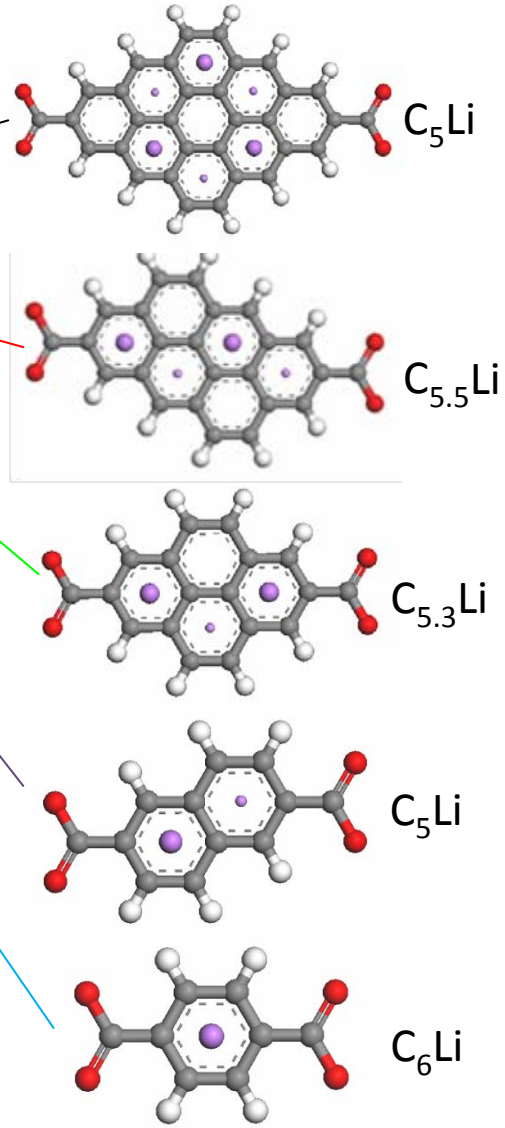
d_{bulk} = 0.44 g cm^{-3}

RT H_2 uptake is not improved.

High room temperature H_2 uptake (5 wt%) in Li-doped Zn-MOF systems

Predictions (Han and Goddard, Caltech)

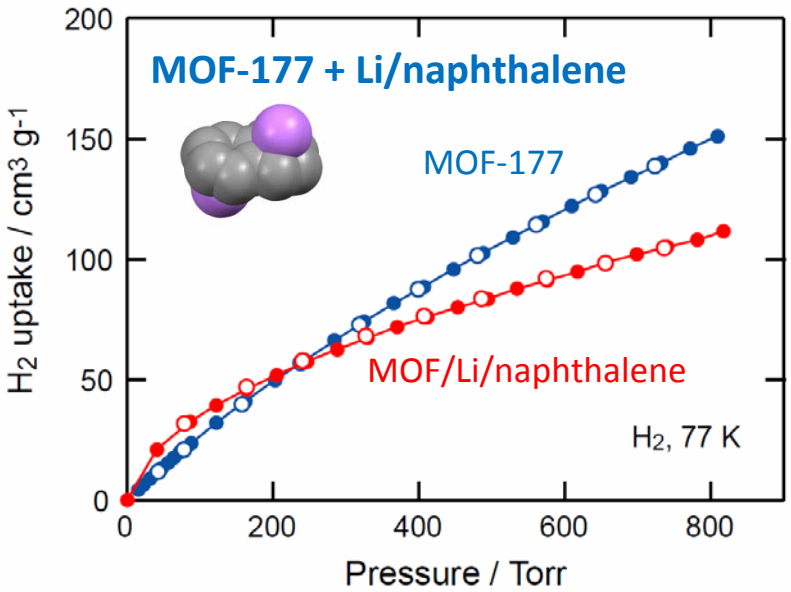




Triangle: pure MOFs, Star: Li-doped MOFs

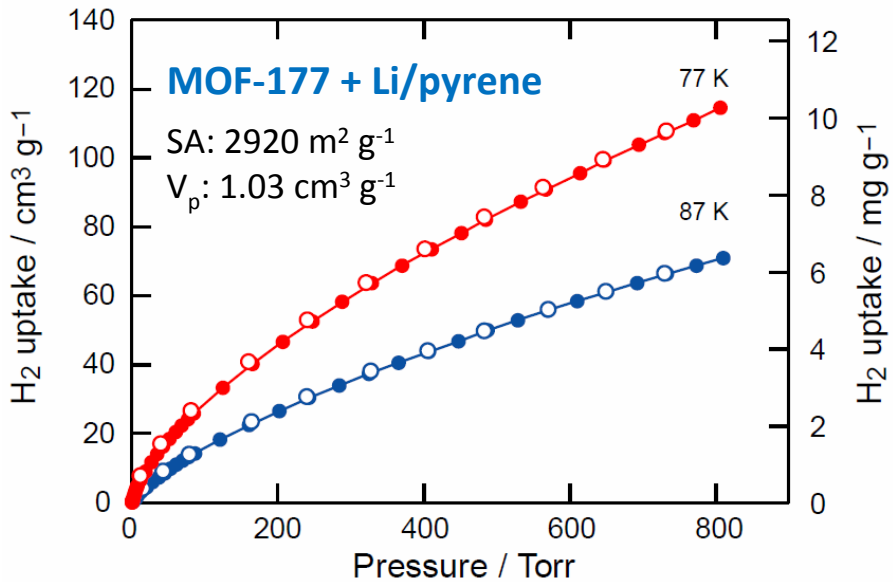
Blue: MOF6, Purple: MOF10, Green: MOF16, Red: MOF22, Black: MOF30

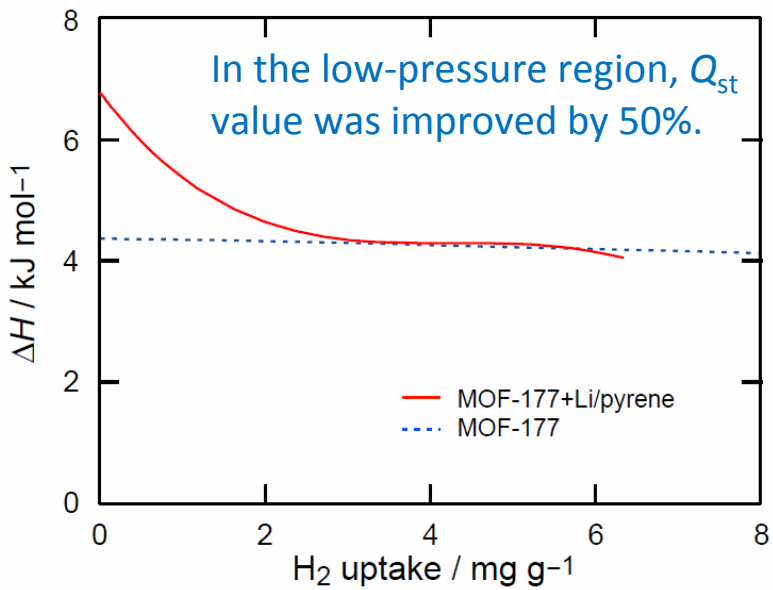
Possibility of Lithium transfer by Li/hydrocarbon complexes



- Li/naphthalene complex was formed in THF
- The complex was immobilized in the pore of MOF-177 (No lithium transfer)
- Naphthalene was not removed by either washing or heating

MOF-177: 5250 m^2/g
MOF/Li/naphthalene:1820 m^2/g





What's next?

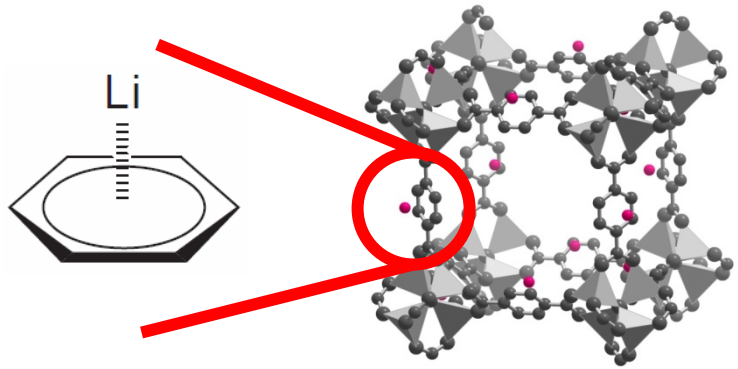
Make an ion pair in MOF frameworks by metal impregnation (e.g. Li, K, Na, Cs)

- Bond dissociation enthalpy (experimental data)

  102 kJ mol^{-1} for $Li^+(acetone)_3$; **101 kJ mol^{-1}** for $Li^+(THF)_3$ *JPC A 2000*

- Predicted adsorption enthalpy of H_2 in Li/MOFs: **17 kJ mol^{-1}** *JACS 2007*

Gas-phase adsorption will be attempted rather than conventional liquid-phase adsorption to prepare Li-MOF complexes



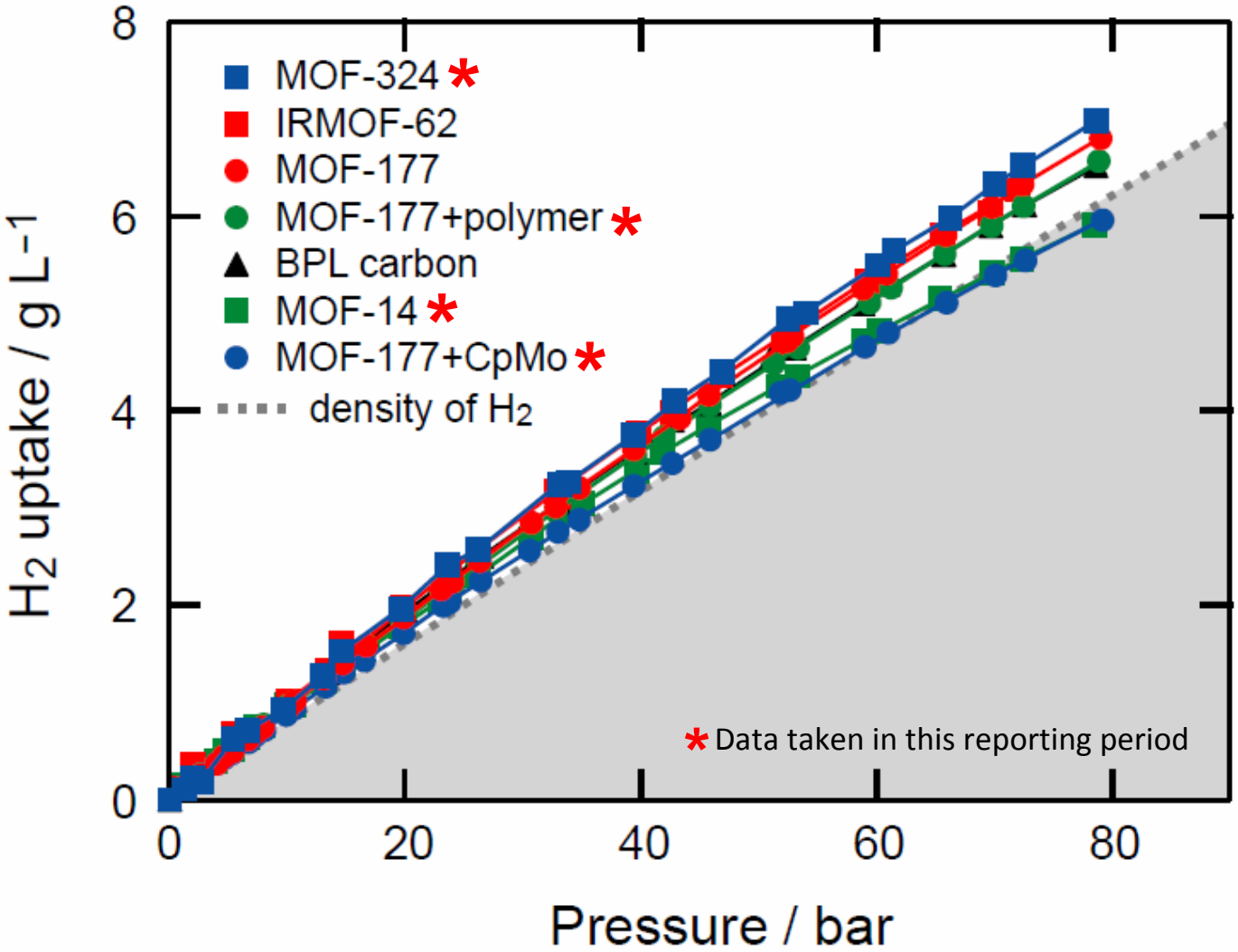
Proof-of-concept

- Li-benzene and Li-dibenzene complexes were synthesized and their IR spectra were measured (*JACS* 1988).
- Simulated IR spectrum for Li-benzene complex based on the DFT calculation shows similar IR profile comparing to the experimental data. *(Han and Goddard, Caltech)*

Li-hydrocarbon complexes should be experimentally accessible.

Summary of high-pressure hydrogen adsorption measurements at room temperature

Volumetric total uptake at 298 K



Better volumetric H_2 density compared to compressed H_2

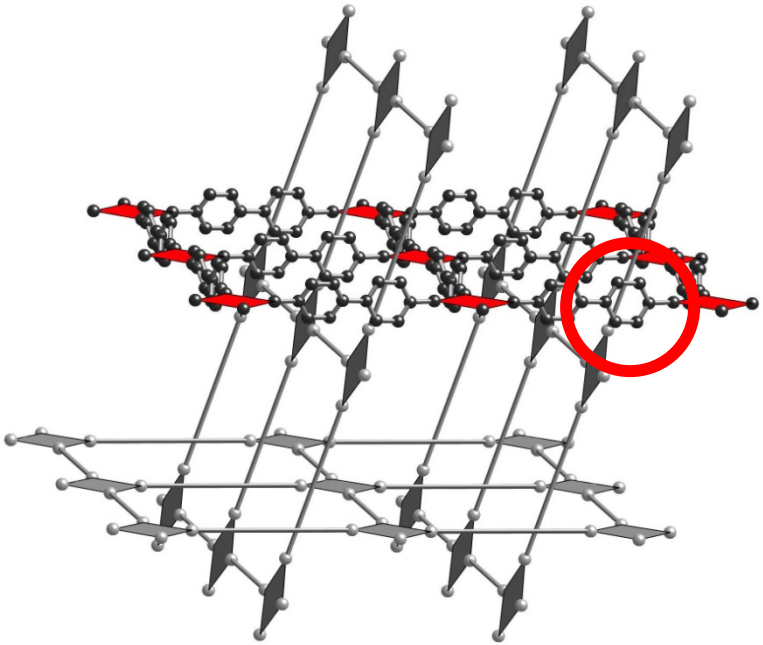
Toward the practical use of MOFs

- Cycling uptake and release
  - Excellent durability
  - Fast H_2 charge rate (< 3 min)
  - At least 4 wt% of H_2 should be deliverable
- Impact of impurities
  - Contaminated water could be adsorbed in MOF-177
- Heat management
  - 10^4 kJ of heat can be released if 4 kg of H_2 is charged in aluminum cylinder with MOF ($\Delta T \sim 70\ ^\circ C$)

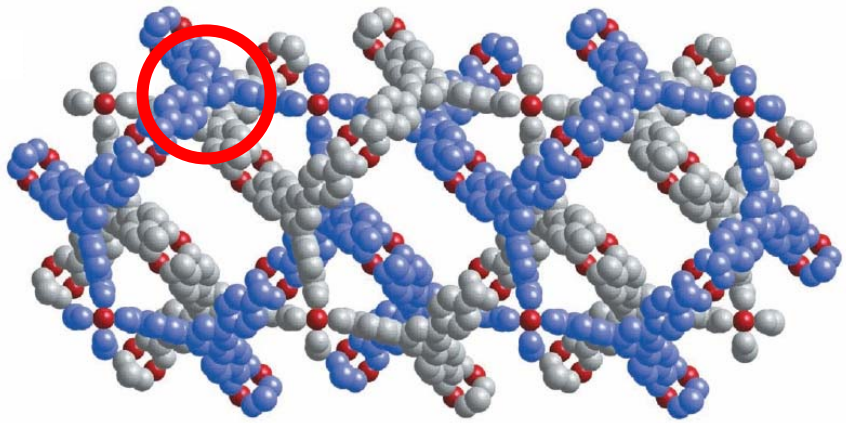
Progress in making materials suitable for soft chemisorption

Approach 1: Metal ions in π-π gaps in interpenetrating structure

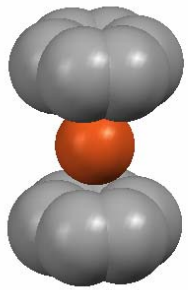
- In several MOFs, two benzene rings face each other across a short distance.
- After metal impregnation, greater polarization is expected.



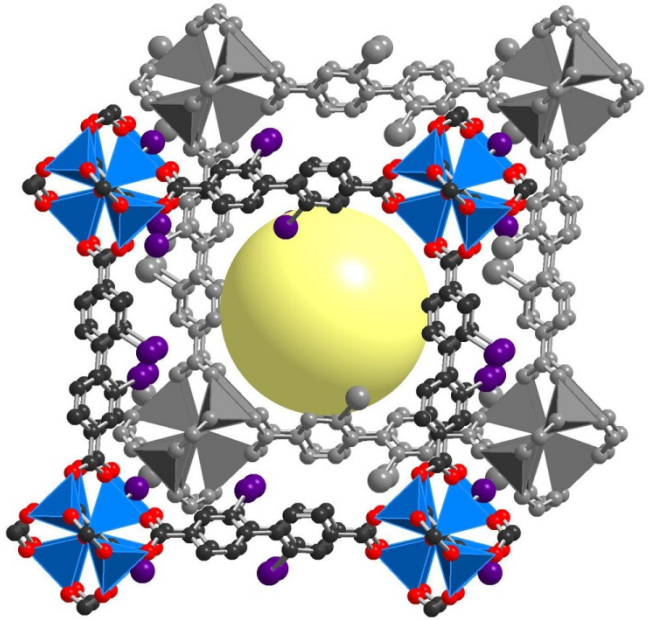
MOF-118



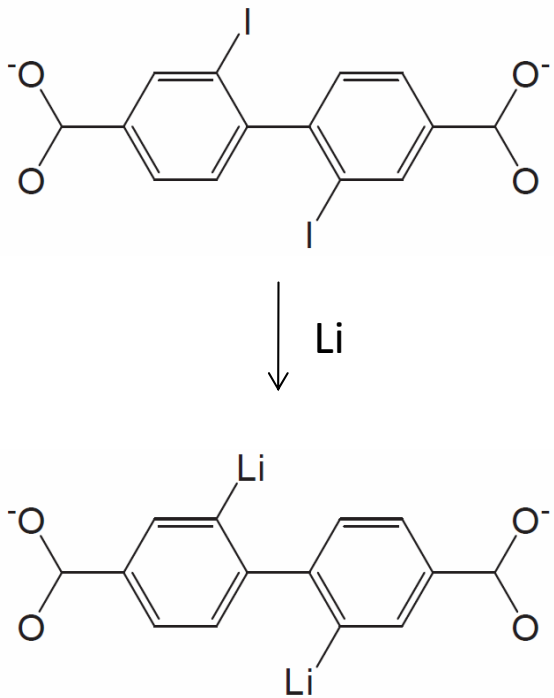
MOF-14



Approach 2: Post-synthesis modification of MOFs (e.g. potential halogen-lithium exchange)



IRMOF-19



IRMOF-19
d = 1.147 g cm^{-3}

Li-IRMOF-19
d = 0.676 g cm^{-3}

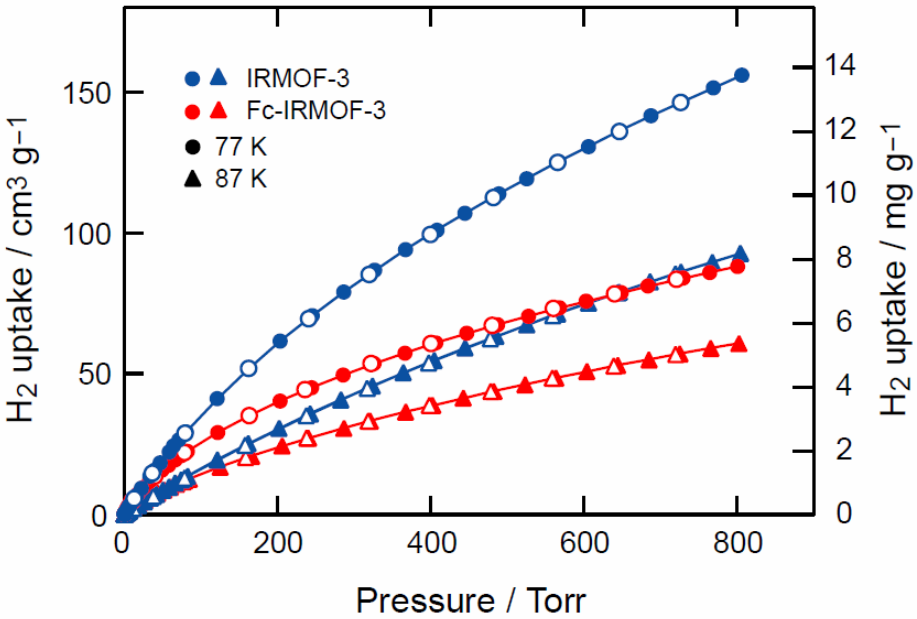
R-3*m*
a = 23.8130 Å, c = 31.0160 Å
V = 15231.6 Å^3

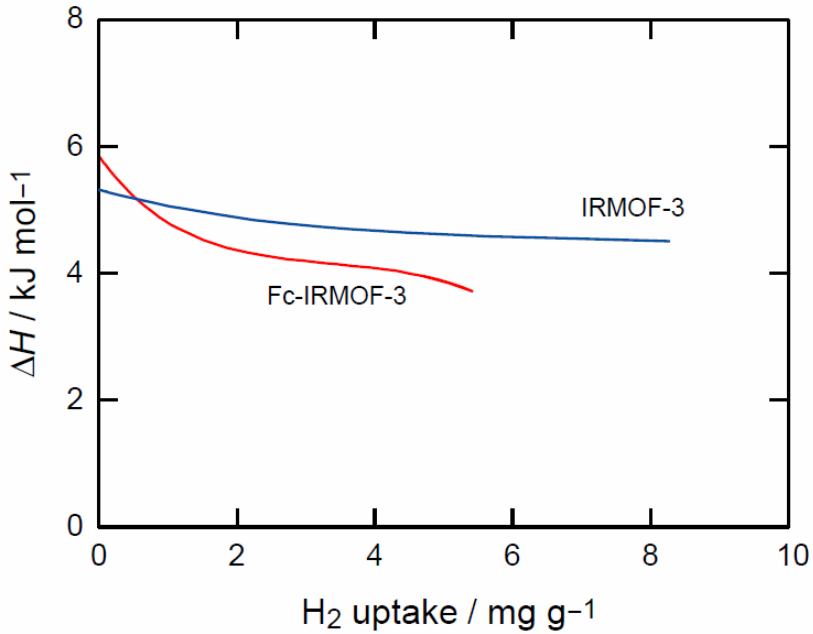
- MOF-5 type topology
- Doubly interpenetrated framework

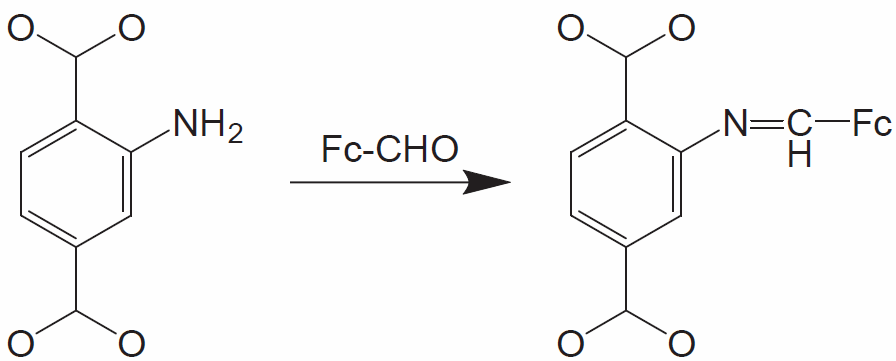
If each Li in the link can capture 3 H_2 molecules, 4-5 wt% of H_2 uptake at RT is expected.

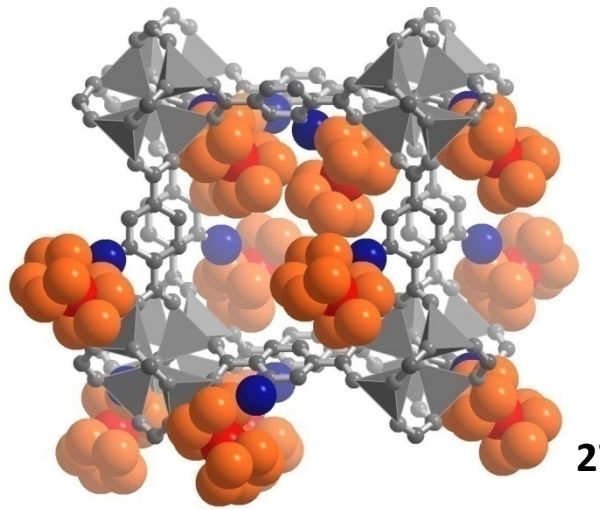
Approach 3: Post-synthesis modification with metal-complexes capable of soft-chemisorption

Proof-of-concept: Ferrocene-derivatives of IRMOF-3 successfully made

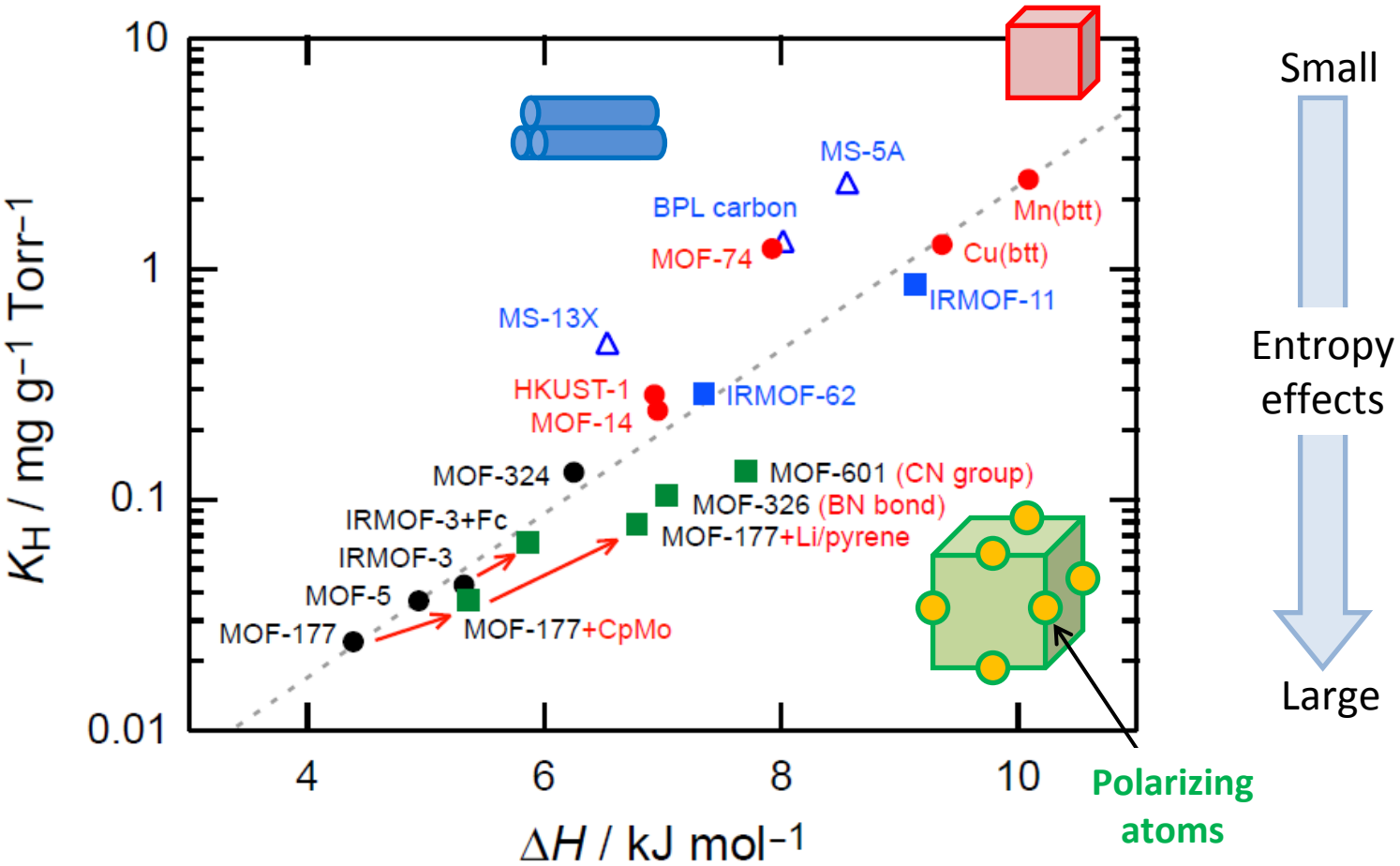








ΔH *vs.* Henry's constant



- In general, ΔH is proportional to log(K_H).
- Polarizing atoms enhance the adsorption enthalpy of H_2.
- If effect of entropy is small, greater K_H is expected.
- As long as maximum H_2 uptake is the same, smaller K_H but greater ΔH is preferable to increase deliverable H_2.

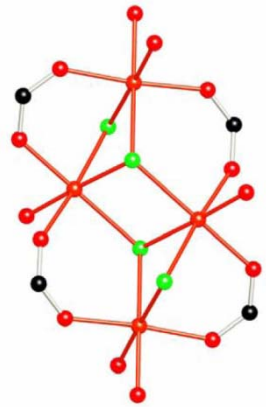
Approach 4: Use inorganic SBUs with transition metals Predicted to have higher adsorptive energy

Metal	Sc	Ti	V	Cr	Mn
E_b (kJ mol^{-1})	21.9	34.6	46.5	10.4	8.4
d (Å)	2.35	2.07	1.93	2.32	2.42

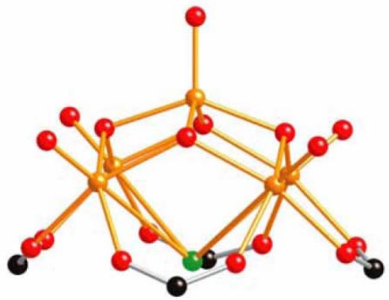
Sun *et al.*, *JACS* 2007

Reticular synthesis of novel materials combining all attributes deemed favorable to hydrogen storage

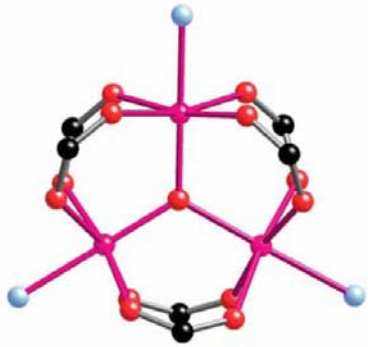
- Highly porous with little dead volume
- Smaller pore diameter (< 10 Å)
- Unsaturated metal surface
- Large density of strong binding sites



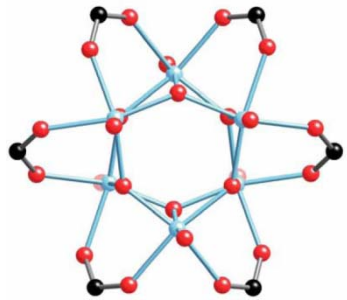
$V_4(CO_2)_4Cl_4(\mathbf{L})_6$



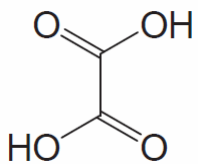
$V_5O_5(CO_2)_4Cl(\mathbf{L})_4$

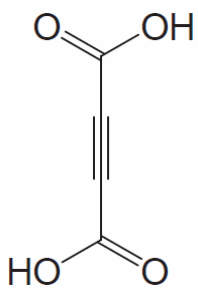


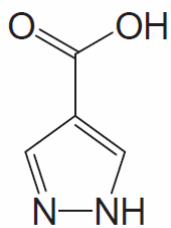
$M_3O(CO_2)_6(\mathbf{L})_3$
(M = V, Mn, Cr)

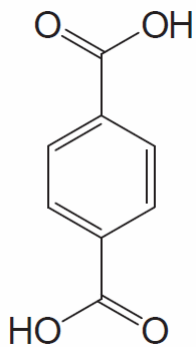


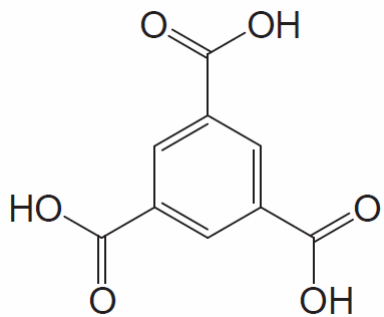
$Ti_6(CO_2)_6(\mathbf{L})_6$







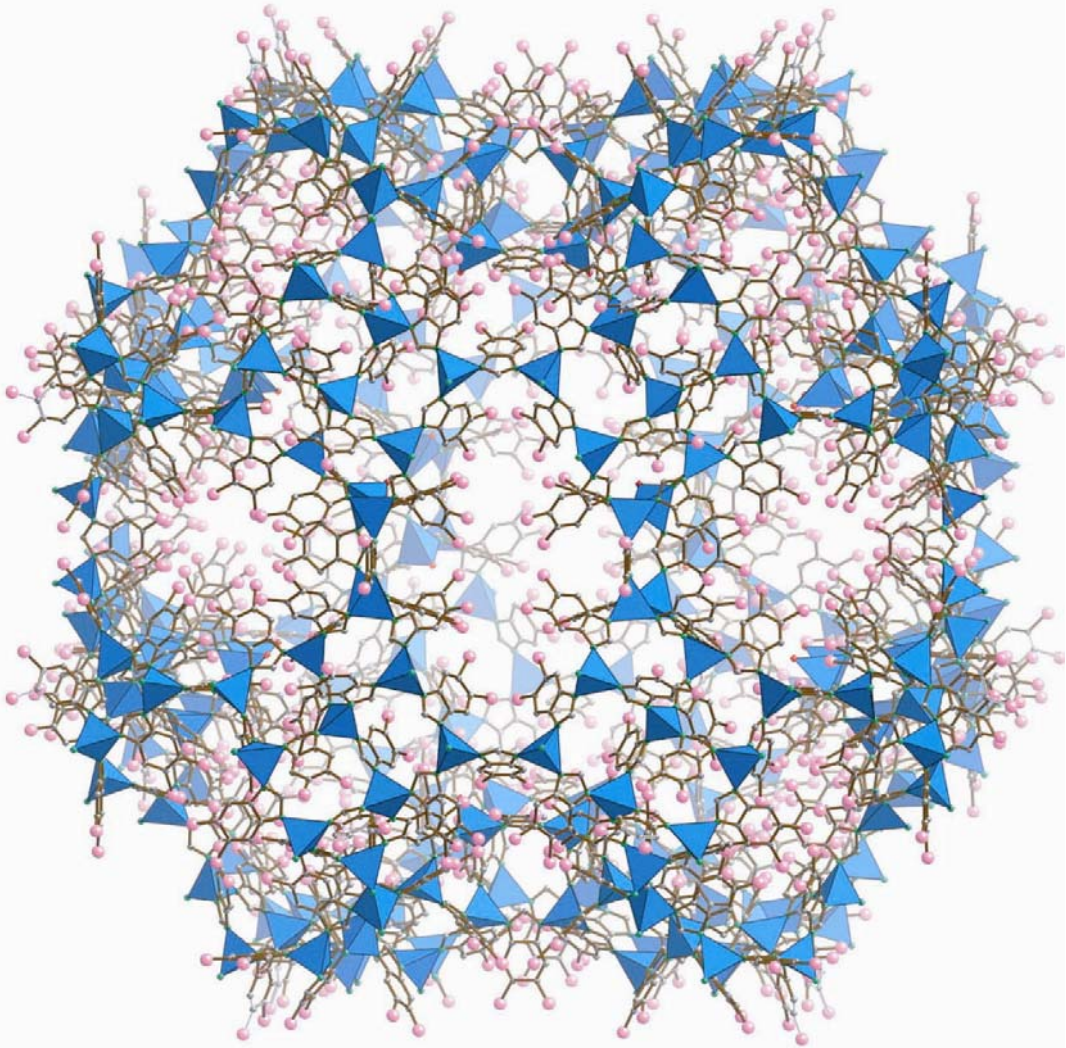




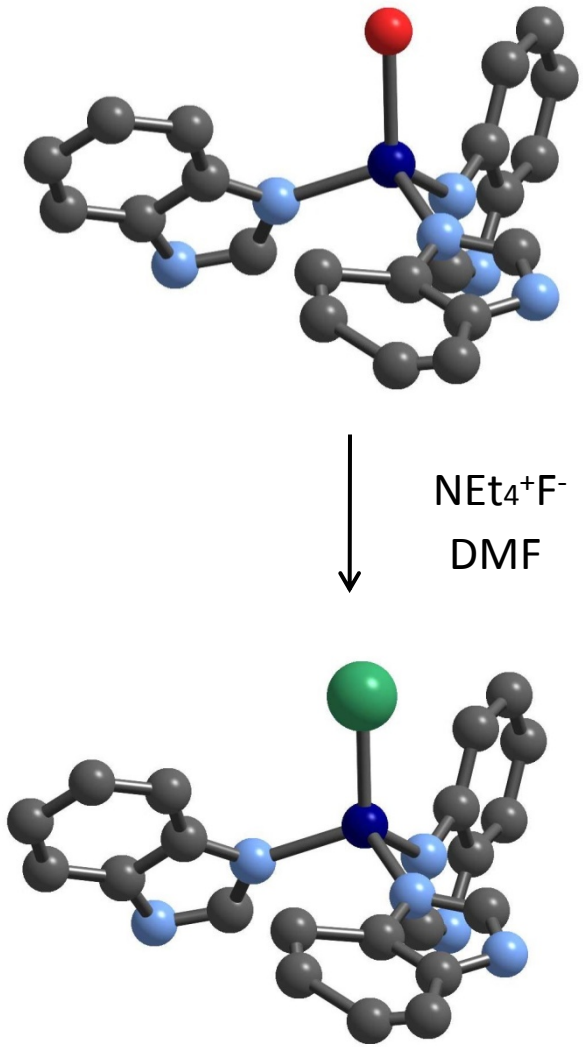
Preliminary structures with potential for soft chemisorption

The case of zeolitic imidazolate frameworks

Approach 5: Zeolitic imidazolate frameworks
High density of proximal Lewis acid-base sites (case 1)

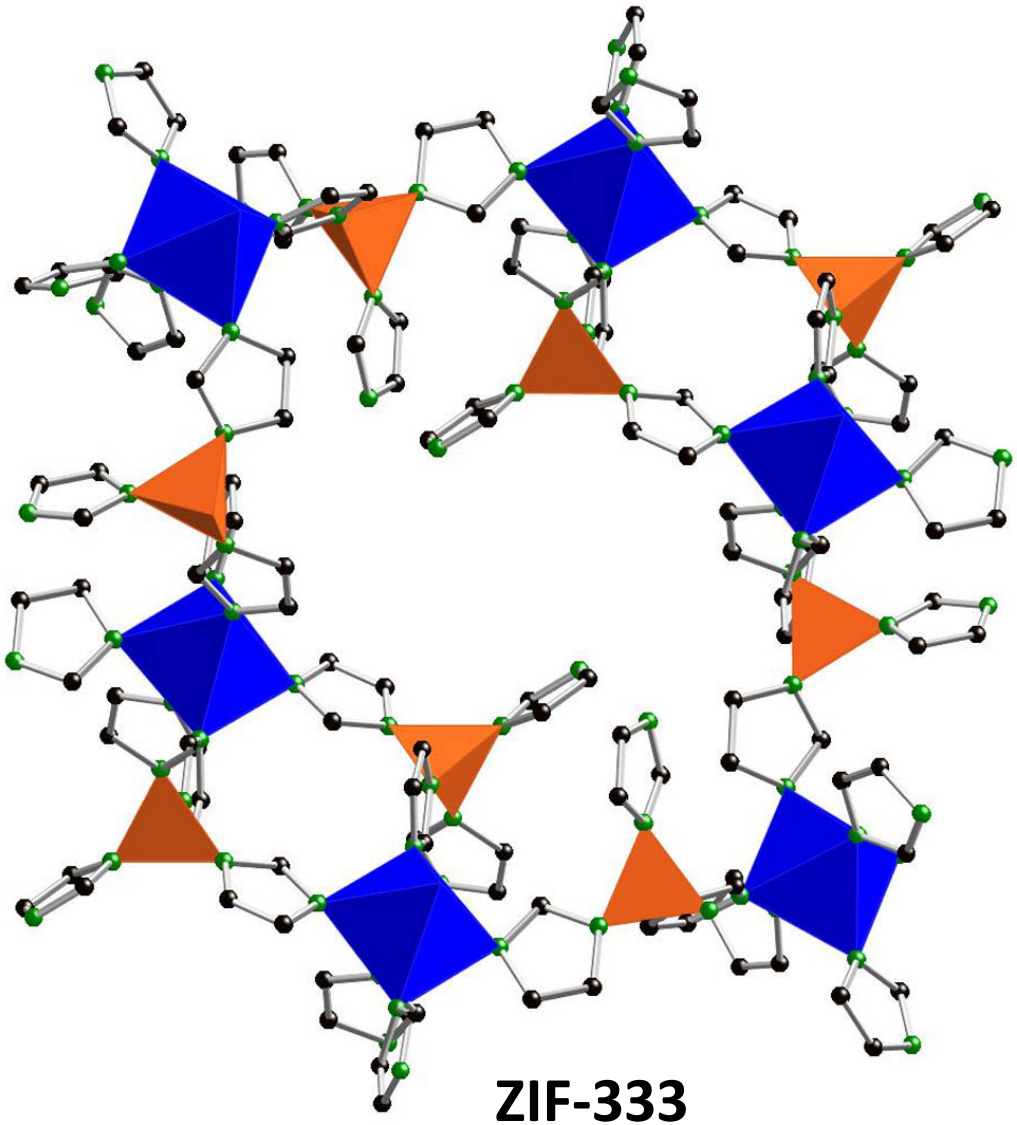


ZIF-100



Zn atoms are capped by OH^-, which were replaced by fluorine group

Approach 5: Proximal Boron and Nickel sites linked by imidazolate within ZIF-333 (case 2)

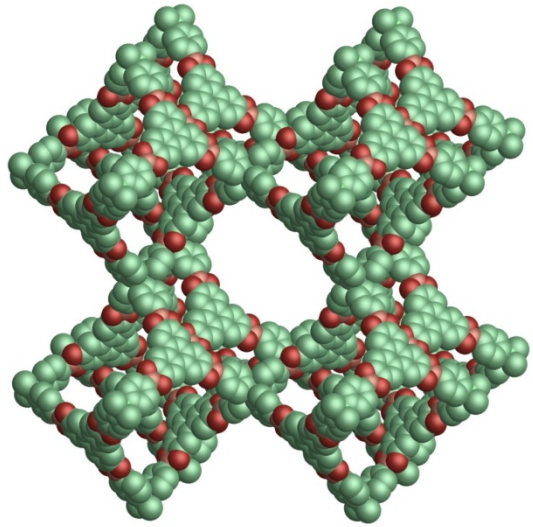


ZIF-333

Predictions for covalent-organic frameworks

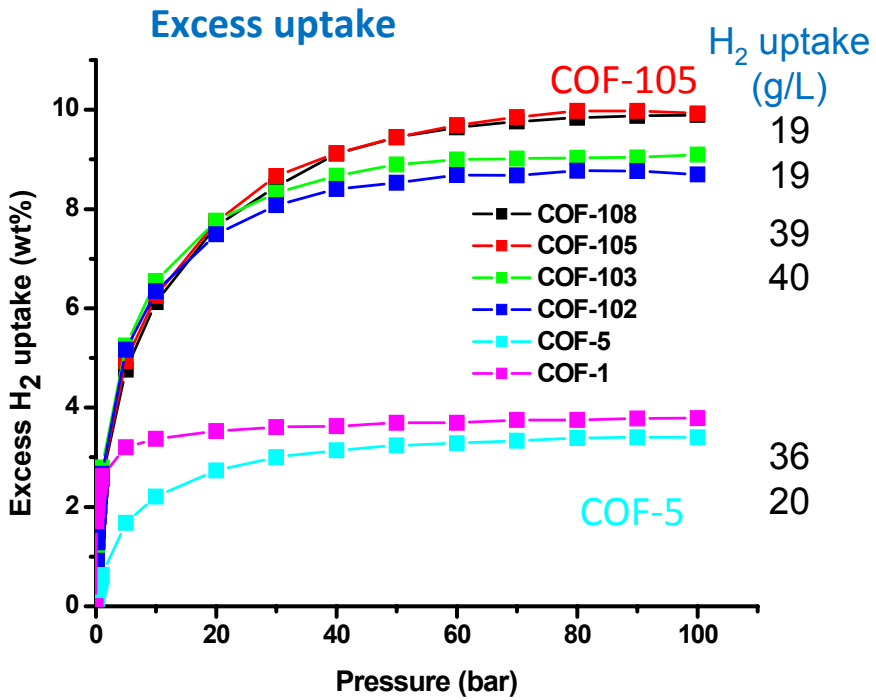
Gravimetric excess and total H_2 uptake of COFs at 77 K

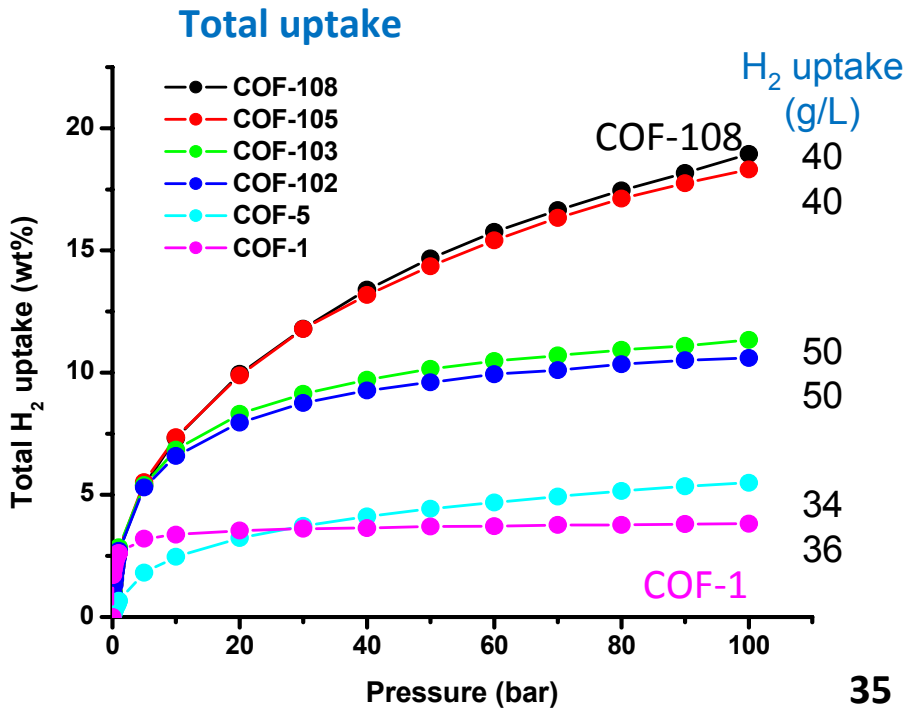
COF-105 will have the highest uptake (excess 10% and total 20%)



Structure of COF-108 with **bor** blueprint
d = 0.17 g/cm^3, S.A. = 4,700 m^2/g, *Science* **2007**

Goddard's calculations





Summary

Relevance: For room temperature hydrogen storage, a systematic survey was pursued 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:

- Impregnation of MOF-177 with polymers and metal complexes
- Considered relationship between Q_{st} values and pore structures
- Began metal-doping experiments
- Demonstrated the stability and durability of MOF-177

Technology transfer/collaborations: Active relationship with collaboration partners and BASF. Beginning new collaboration with Goddard theory group.

Proposed future research:

- Employ light weight metals to create strong binding sites.
- Implement the concept of “soft chemisorption”.
- Material design based on theoretical prediction.

Current Group Members

Dr. C. Knobler

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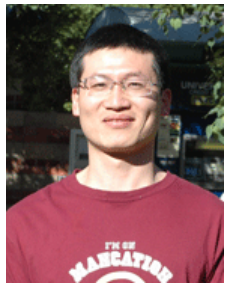
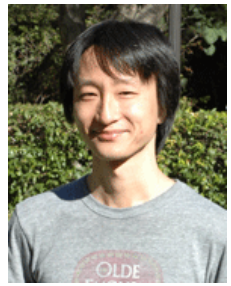
Dr. A. Côté

Dr. C. Doonan

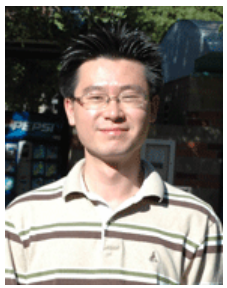
Dr. H. El-Kaderi

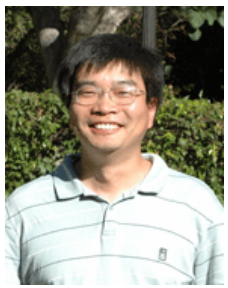

Dr. Q. Fang

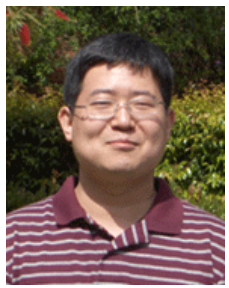

Dr. H. Furukawa

Dr. Y. Go

Dr. H. Hayashi

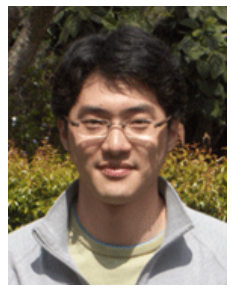

Dr. S. Kim


Dr. Z. Lu


Dr. K. Park

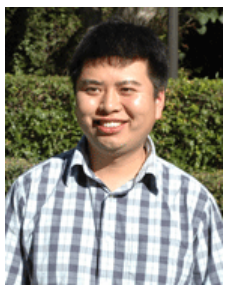
Dr. D. Tranchemontagne

D. Britt


E. Choi

L. Dudek

J. Hunt

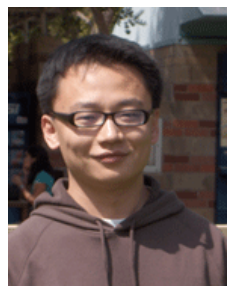

Q. Li

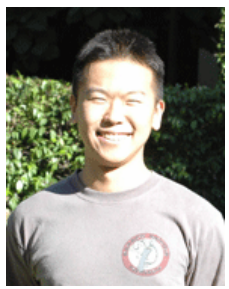
G. Liu

W. Morris

A. Phan

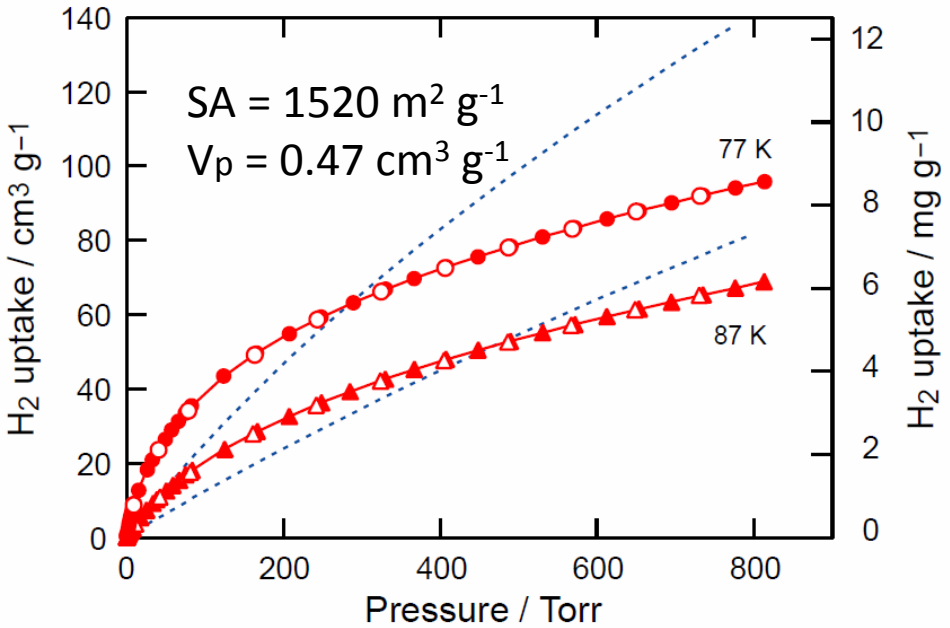
F. Uribe-Romo

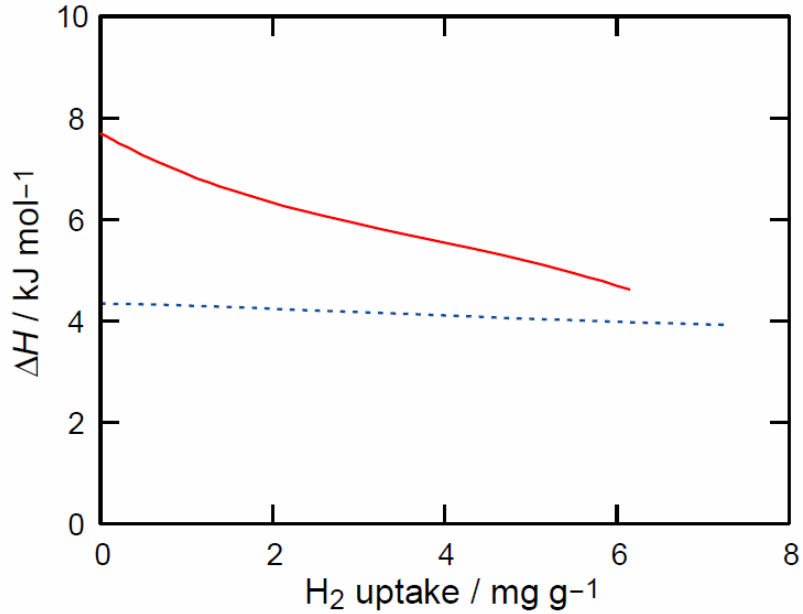

B. Wang

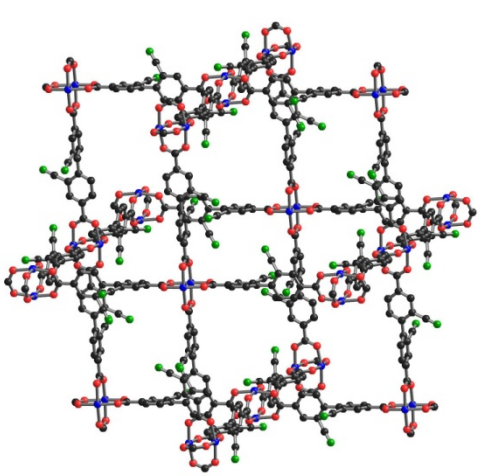

C. Lee

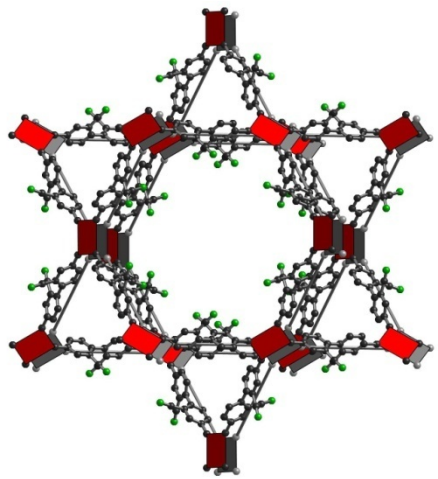
Additional Slides
(For Supporting Information)

MOF-601: A MOF structure combining interpenetration and open metal sites





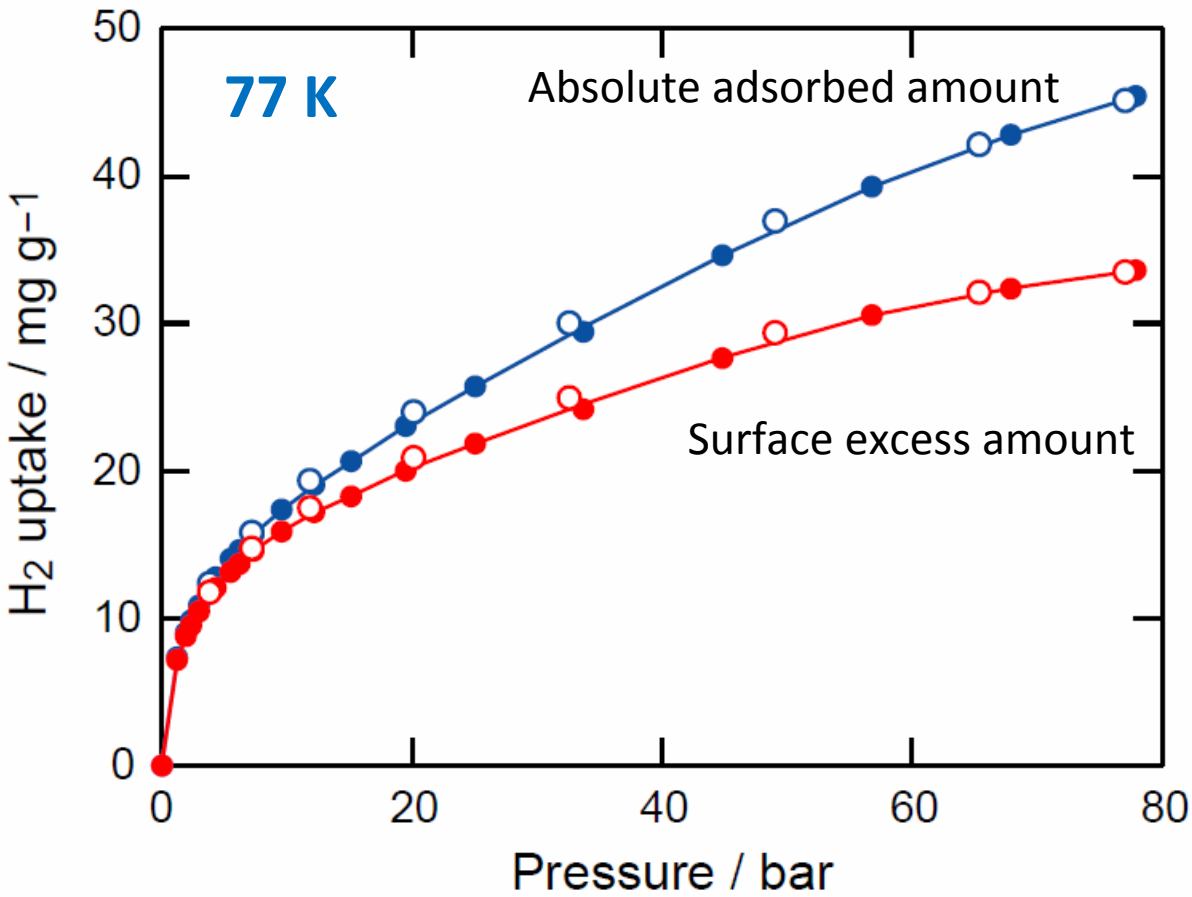




R-3*m*
a = 43.9991 Å, *c* = 12.2585 Å
V = 20552.1 Å^3

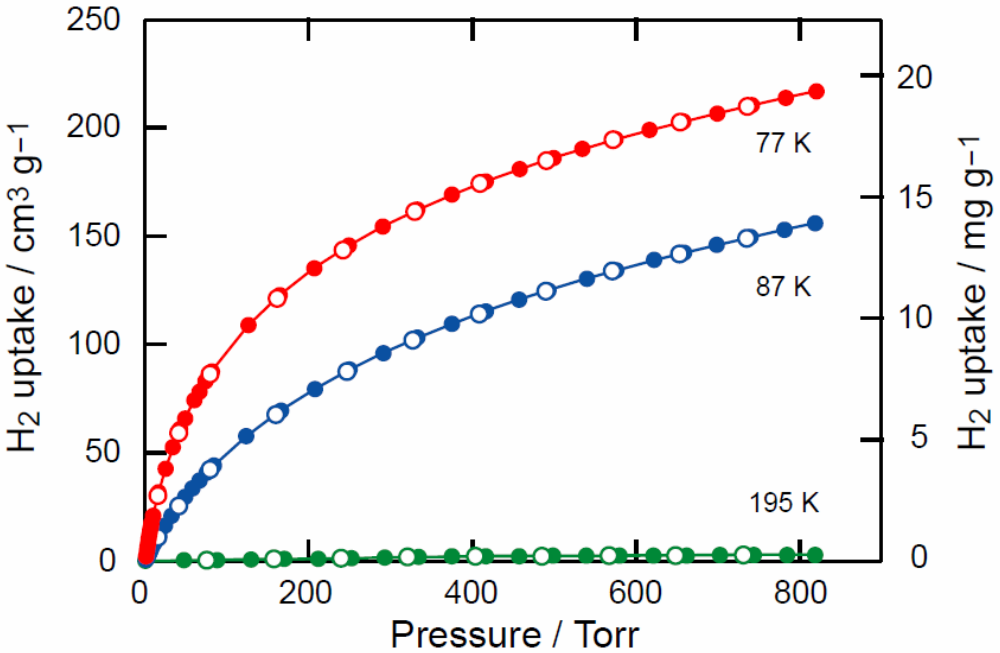
Cu paddlewheel and CN group
Interpenetrated **nbo** net

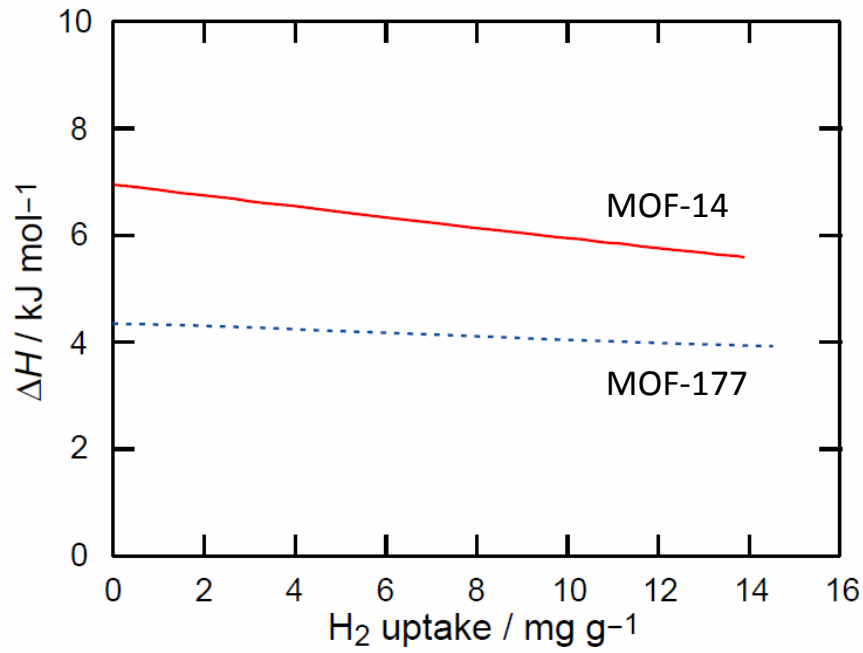
MOF-601 (high-pressure) hydrogen uptake is unexceptional



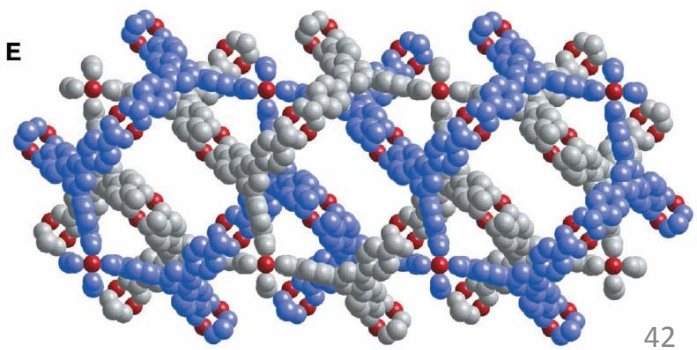
MOF-14: Another MOF combining interpenetration with open metal sites

Interpenetrating framework and open metal site
Improvement of Q_{st} value



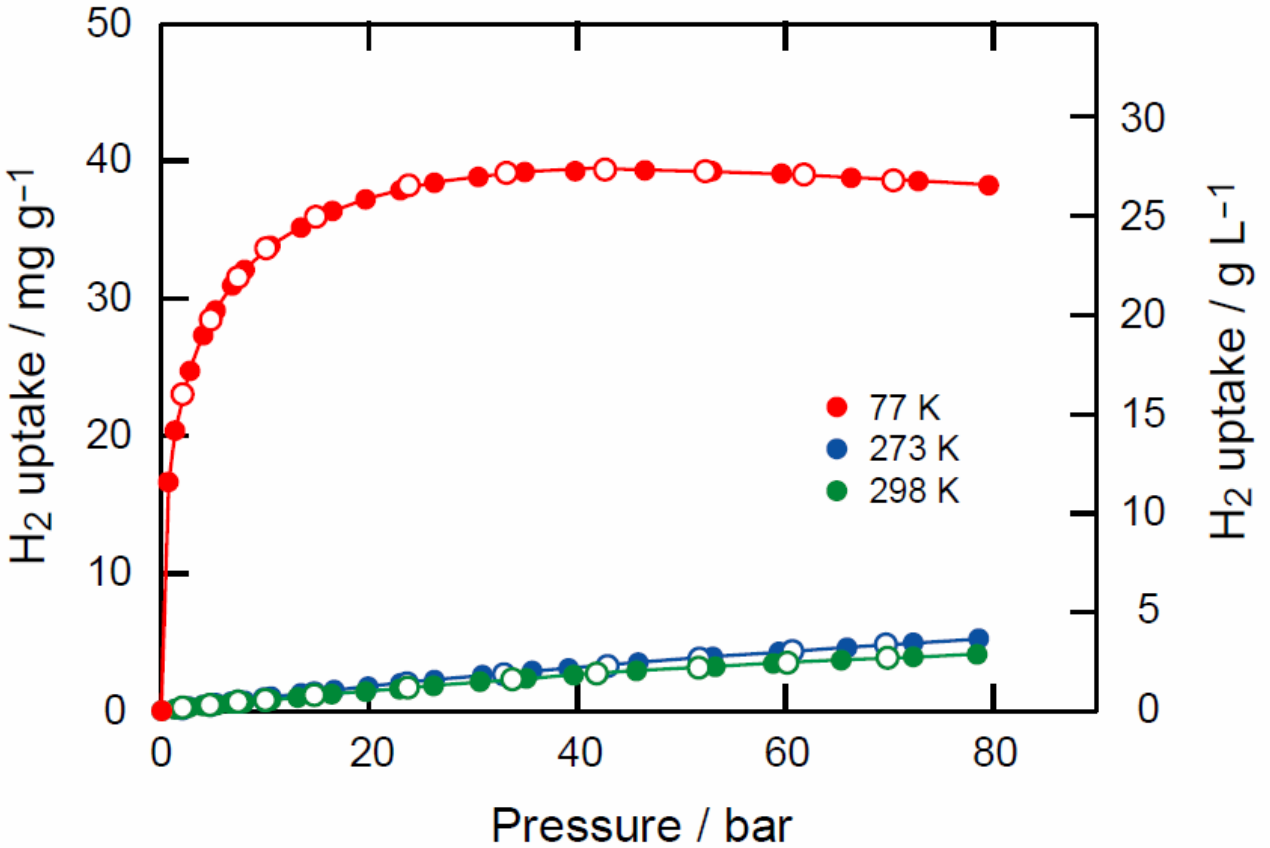


MOF-14
SA = 2000 $m^2\ g^{-1}$
V_p = 0.71 $cm^3\ g^{-1}$
d = 0.721 g cm^{-3}

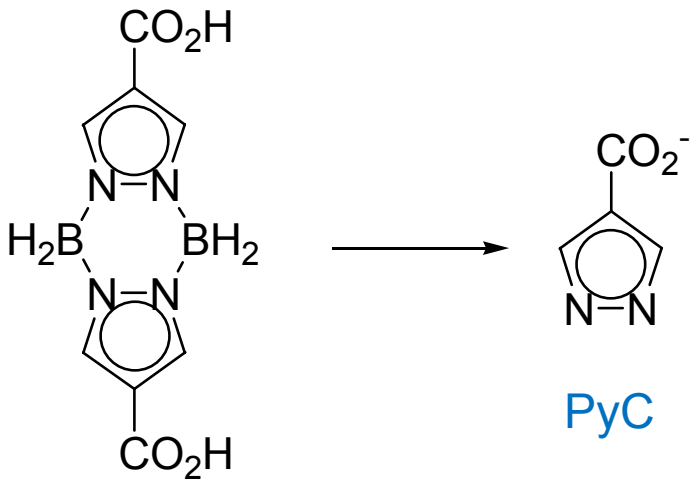


MOF-14 (high-pressure)

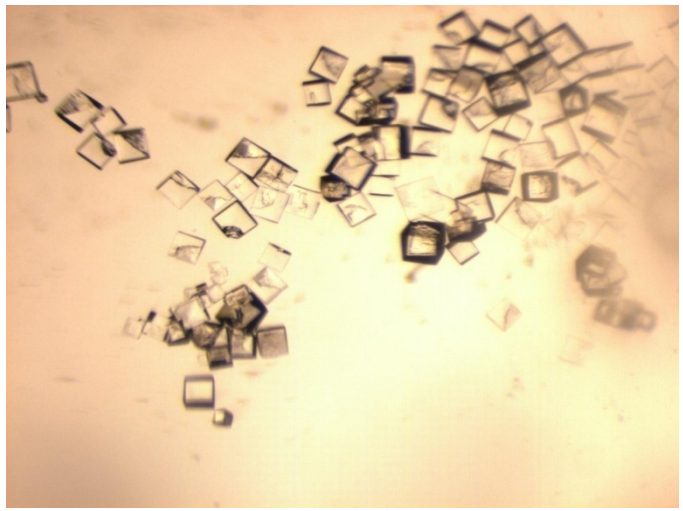
At 77 K: 3.9 wt% (surface excess), 5.5 wt% (total uptake, 70 bar)
RT: open metal sites and interpenetration is not enough

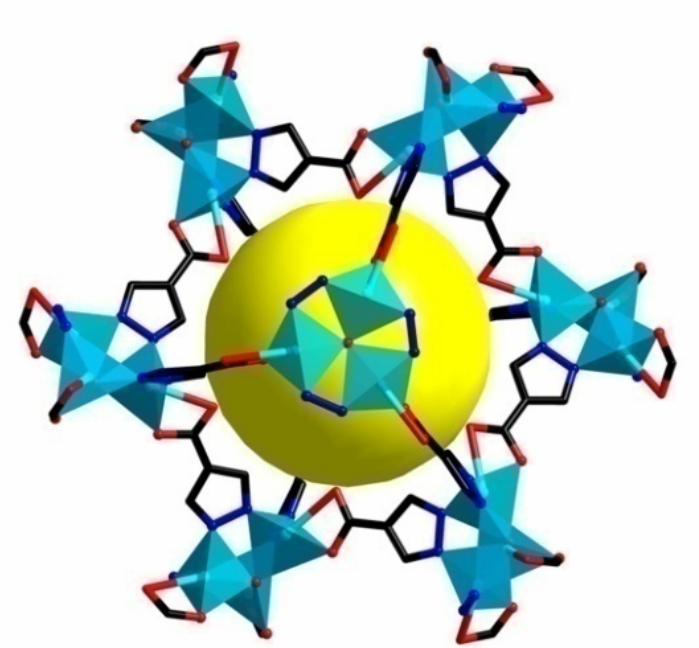


MOF-324



in-situ ligand generation





$Zn_3(OH)[(PyC)_2(HPyC))]$

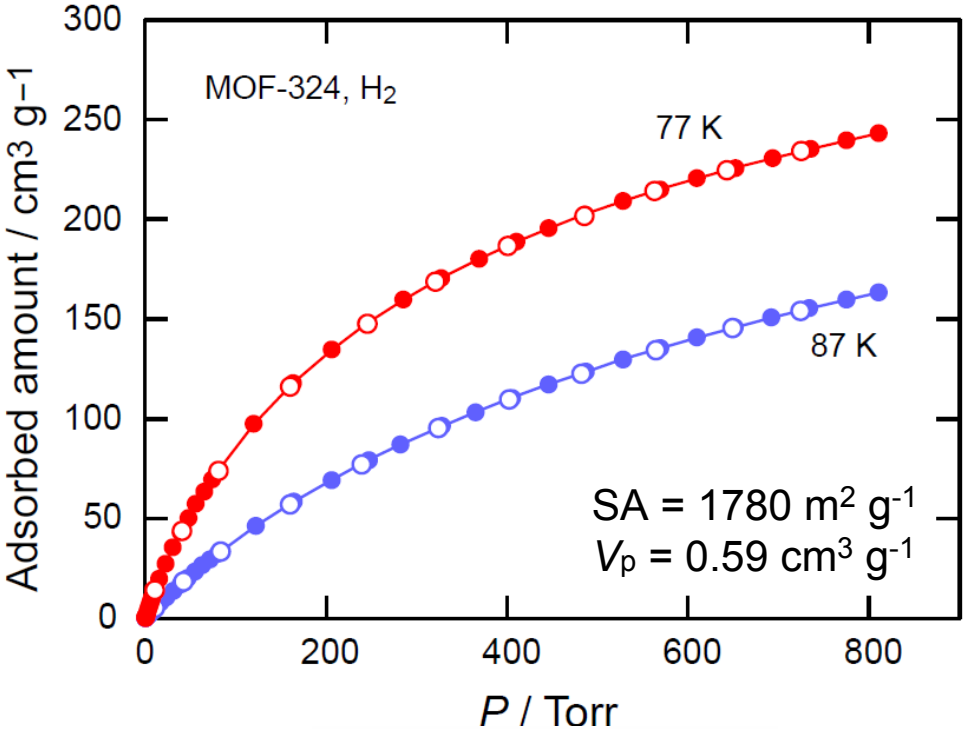
Pa-3, *a* = 20.123 Å

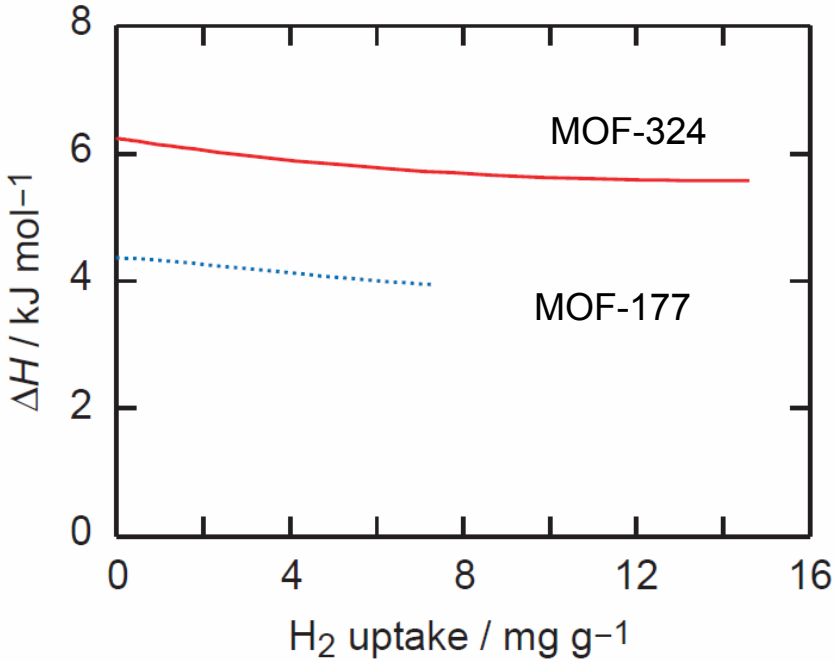
Pore diameter = 7.6 Å

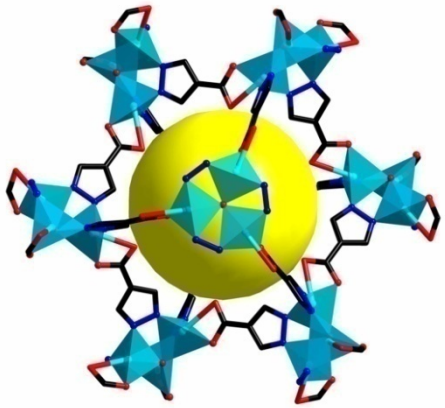
MOF-5 type structure

MOF-324

Smaller pore diameter improve H_2 uptake in the low-pressure region





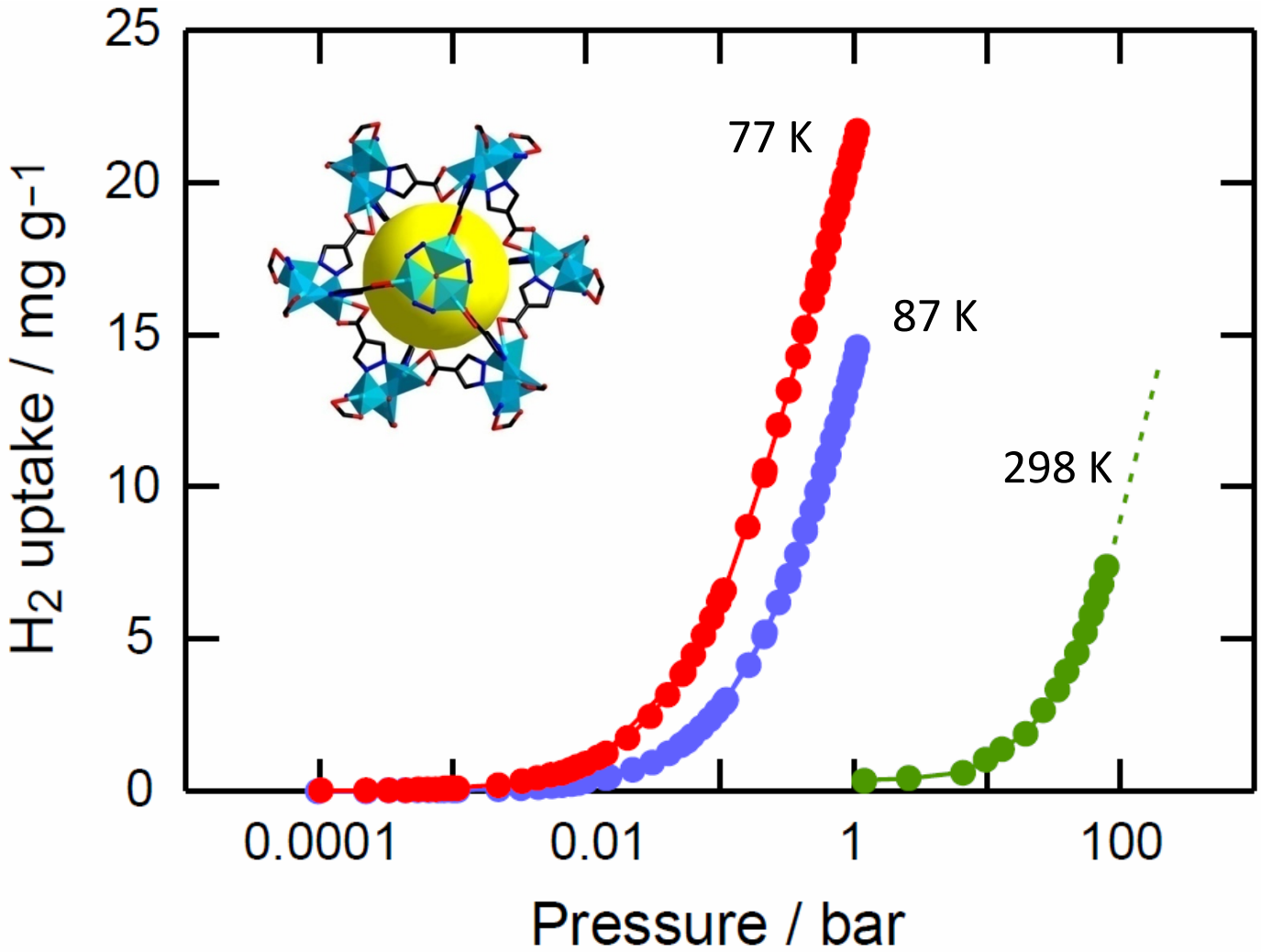


<u>High-pressure H_2 uptake</u>

Excess uptake: 3.3 wt% at 77 K

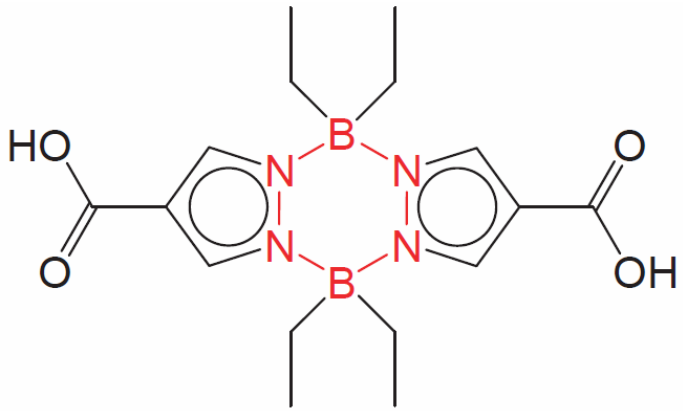
Total uptake: 4.6 wt% at 77K

MOF-324



H_2 uptake at RT and 100 bar seems to be lower than that at 87 K and 1 bar. Adsorbent-adsorbate interaction needs to be improved.

MOF-326

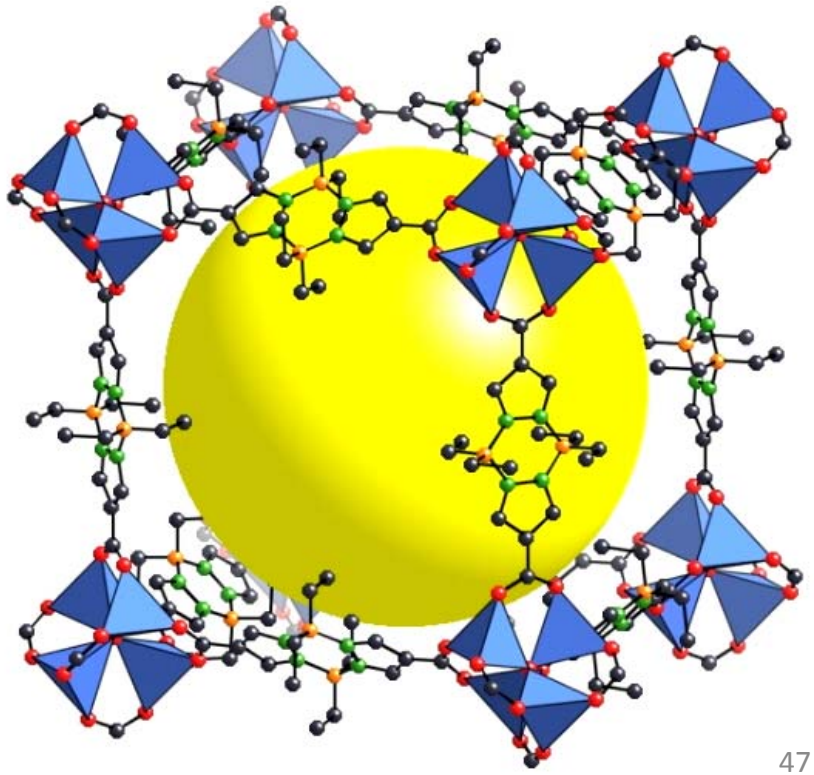


Et-PzDC

+ $Zn(NO_3)_2$

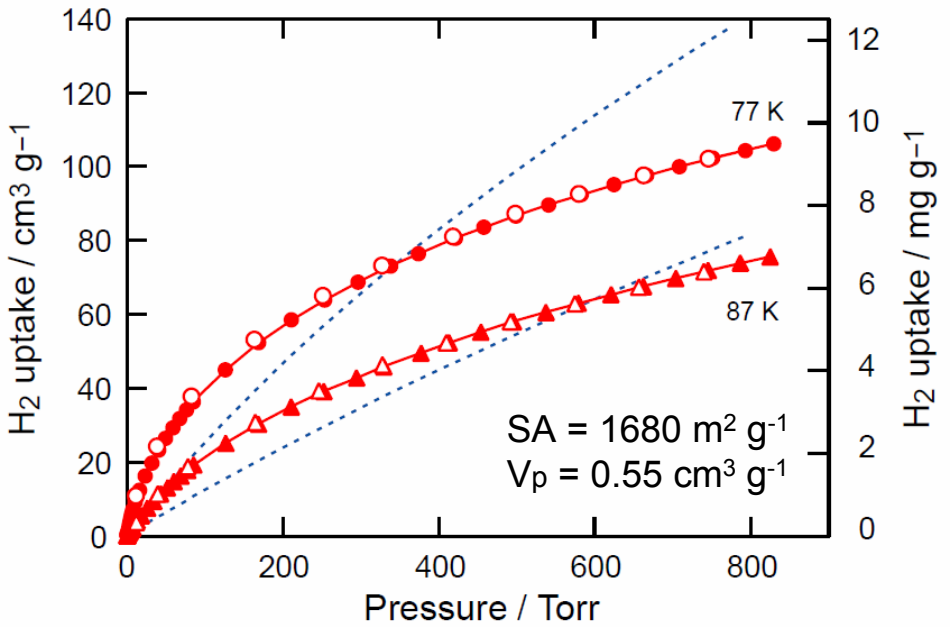
$Zn_4O(Et\text{-}PzDC)_3$

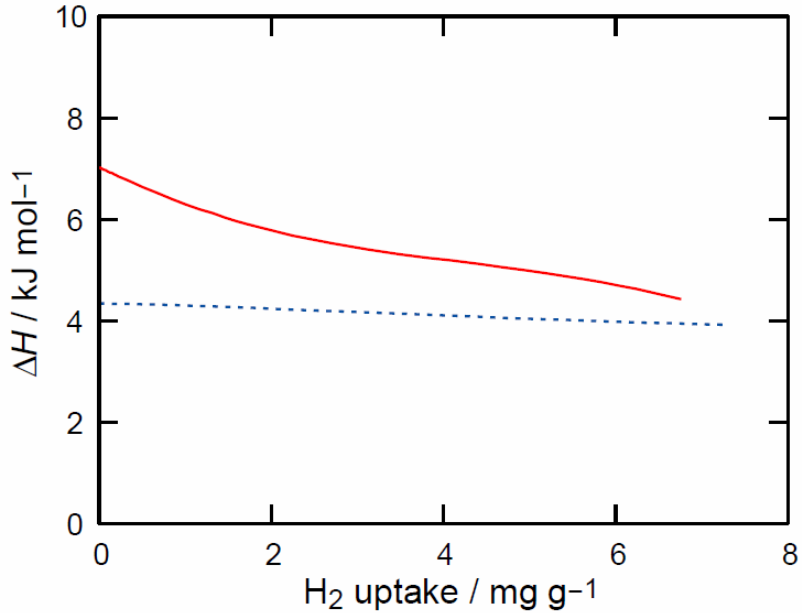
Fm-3*m*
a = 33.410 Å
V = 37294 Å^3

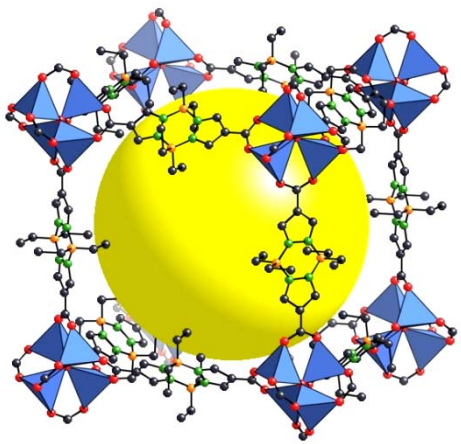


- Stable compounds
  - Strong B–N bonds (450kJ/mol)
  - Stable in aqueous, basic media
- Charged compound
  - B: negative charge
  - N: positive charge

H_2 isotherms for MOF-326



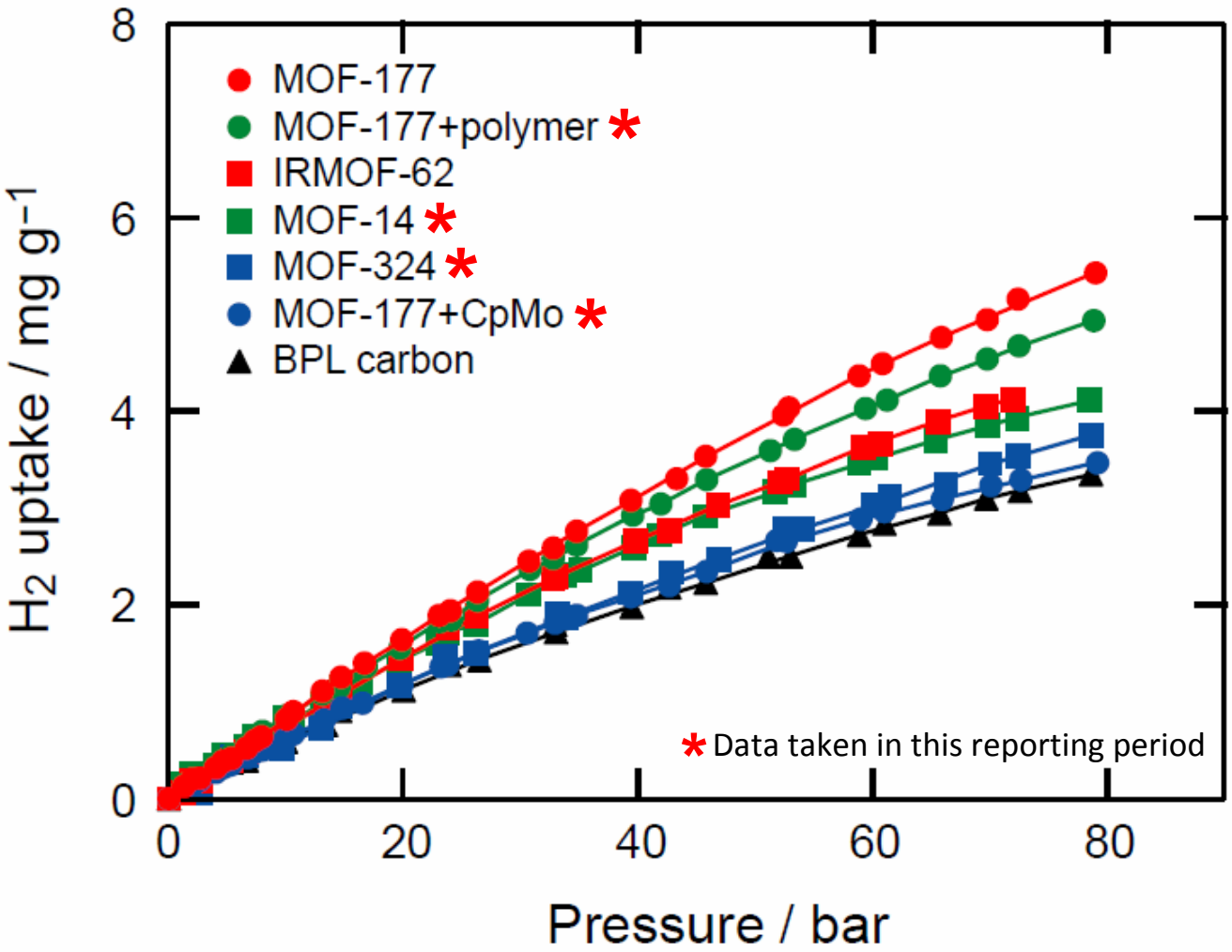




- MOF-5 type structure
- B-N bond
- **Improvement of Q_{st} value**

Gravimetric excess uptake at 298 K

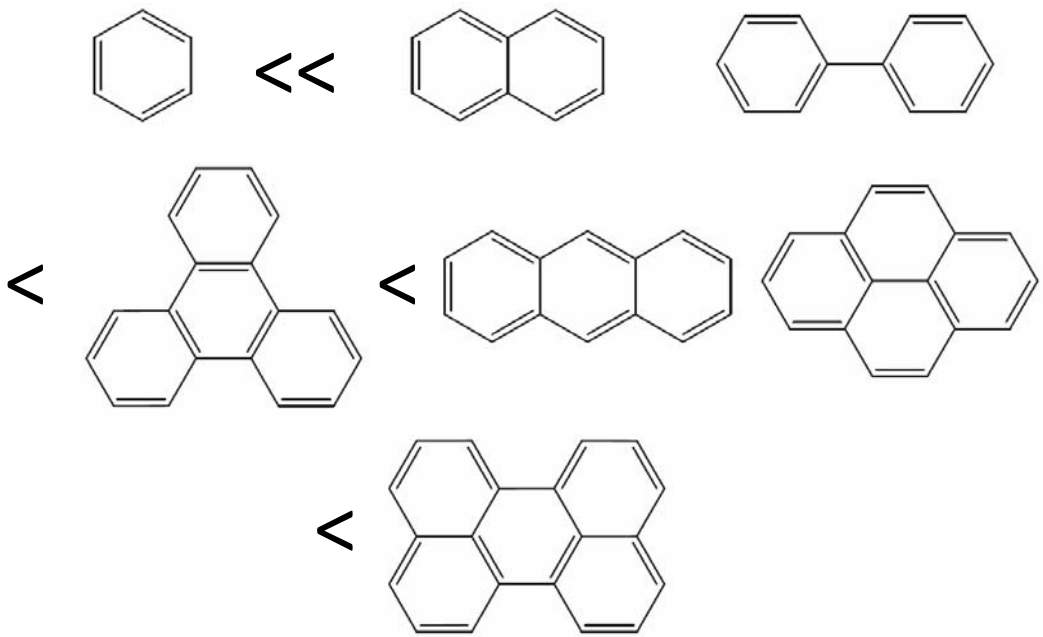
- High surface area is necessary even at RT
- Gravimetric uptake is too low to meet the target



How to make ion pair?

- Metal should be positively charged
- Anion of hydrocarbon should also be formed
- Large fused aromatic cycle is preferable
- RT H_2 uptake can be proportional to Li density in MOFs
- Dianion or trianion is better for high performance

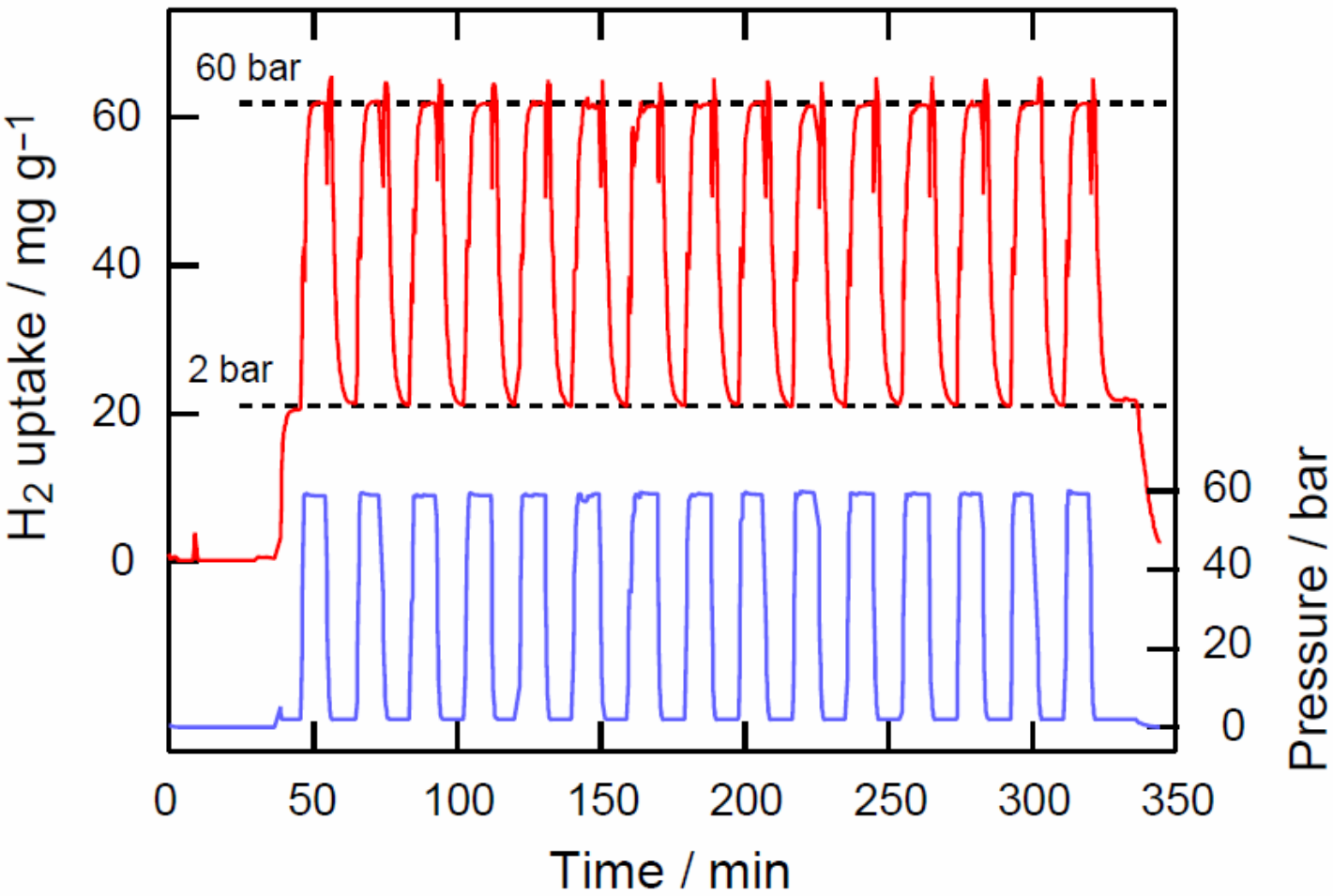
Ease of reduction



Oxidation potential

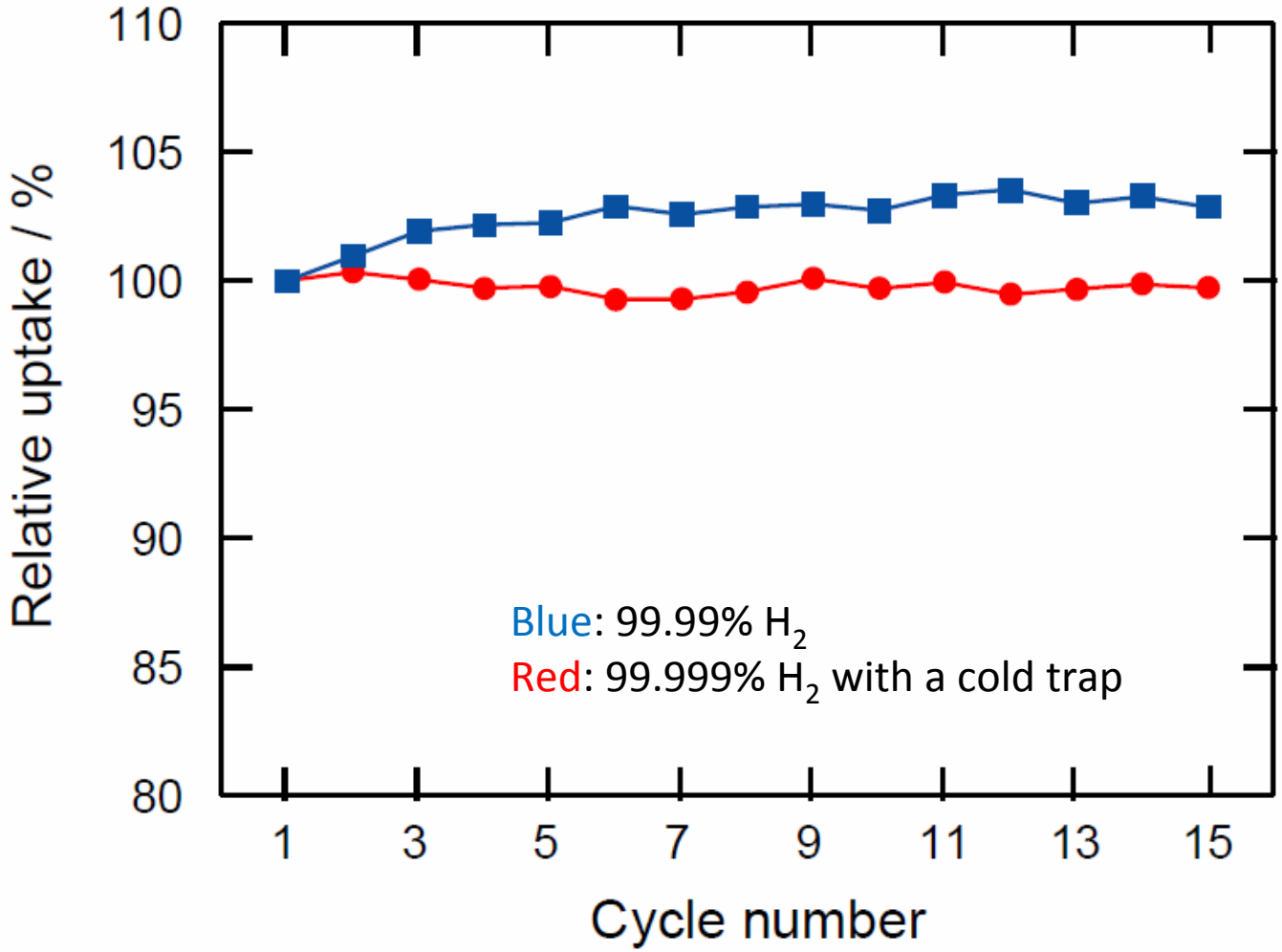
	E^0 *vs.* SHE
Li^+/Li	-3.05 V
Rb^+/Rb	-2.98 V
K^+/K	-2.93 V
Cs^+/Cs	-2.92 V
Ca^{2+}/Ca	-2.84 V
Na^+/Na	-2.71 V
Mg^{2+}/Mg	-2.36 V

Cycle performance for MOF-177 at 77 K



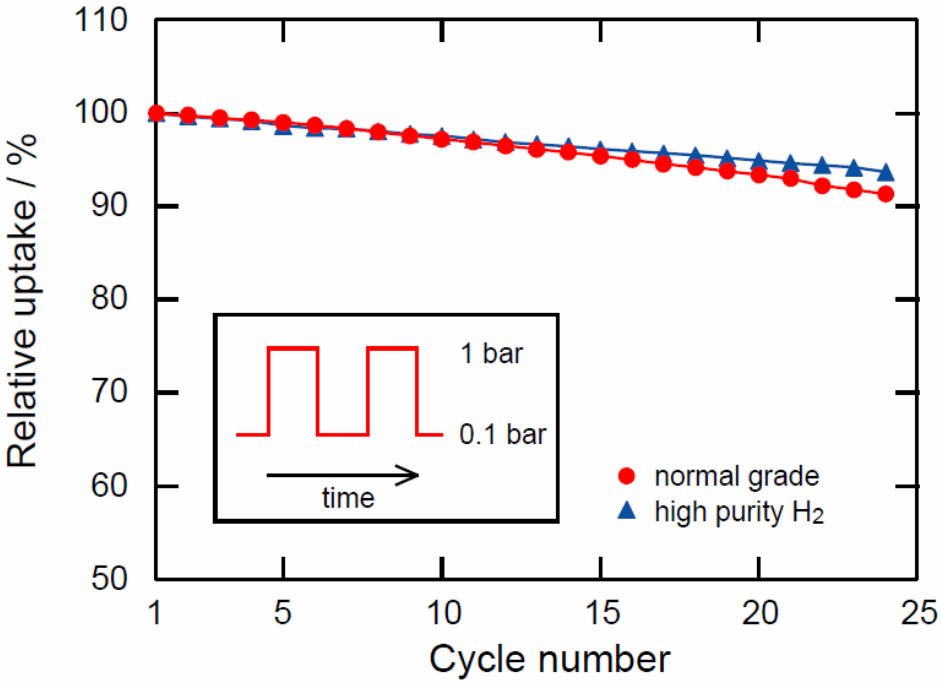
- Excellent durability
- Fast H_2 charge rate (< 3 min)
- At least 4 wt% of H_2 should be deliverable

Effect of impurity in H_2 gas (High-P)



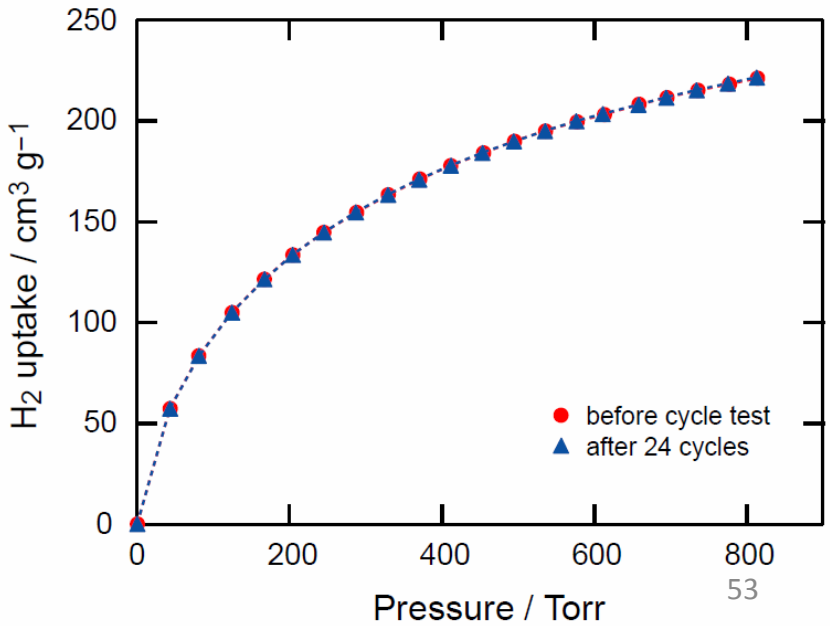
Contaminated water could be adsorbed in MOF-177

Cycle performance for HKUST at 77 K



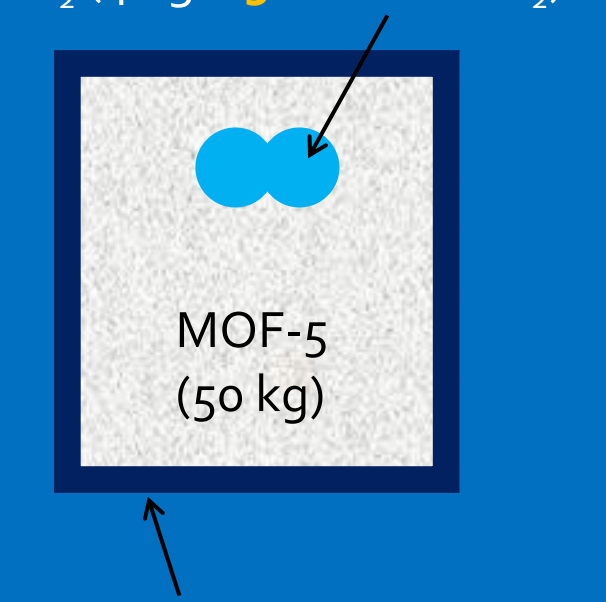
Cycle performance test for HKUST
- Volumetric
- Low-pressure (0.1 to 1 bar)
- Cold trap was not applied for both cases

After cycle performance test, H_2 isotherm for regenerated material was measured.
No change was observed by the sample for the low-purity H_2 test.



Heat formation in MOFs

Outstanding challenge: Since the adsorption process is exothermic, heat is released when H_2 molecules are adsorbed in MOFs



If H_2 is charged in the cylinder *instantaneously* and ΔH = 5 kJ mol^{-1}

⬇

Heat formation: 10000 kJ

⬇

$\Delta T \sim 70$ °C*

*ΔH [kJ/mol] = C_v [J/K·mol] x ΔT [K], Specific heat capacity (C_v) for H_2, Al, and MOF-5 is 20.7, 24.2, and 10^4 J/K·mol

To avoid significant temperature change, (1) the system can be constructed by assembly of small cylinders that contain heat releasing attachments, or (2) coolant needs to be provided at the fuel station.