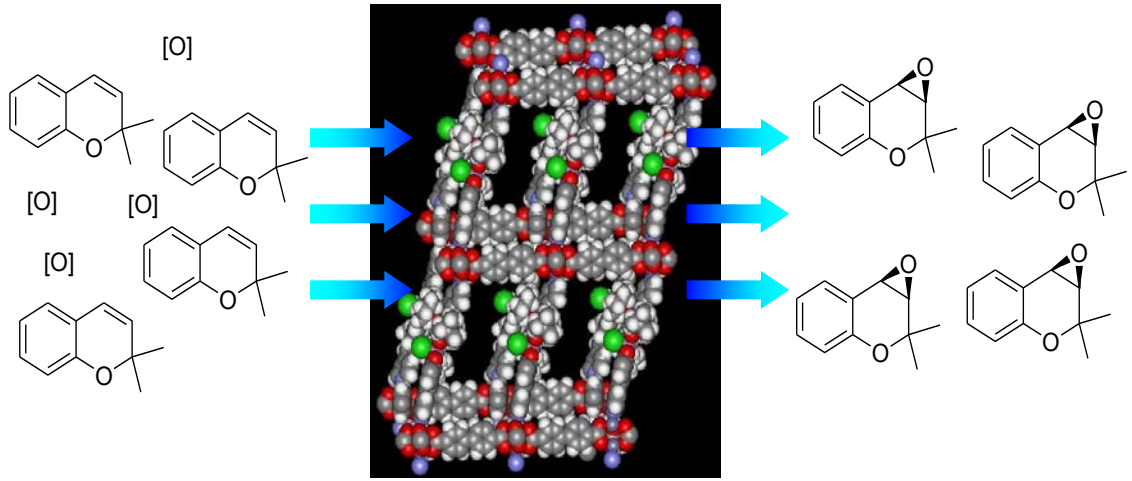
Metal-Organic Framework Materials for Energy Applications

Notre Dame, November, 2010



- U.S. Dept. of Energy
- AFOSR
- Northwestern NSEC
- DTRA

Acknowledgments

- Avi Shultz

- Prof. SonBinh Nguyen

- Dr. Andy Nelson

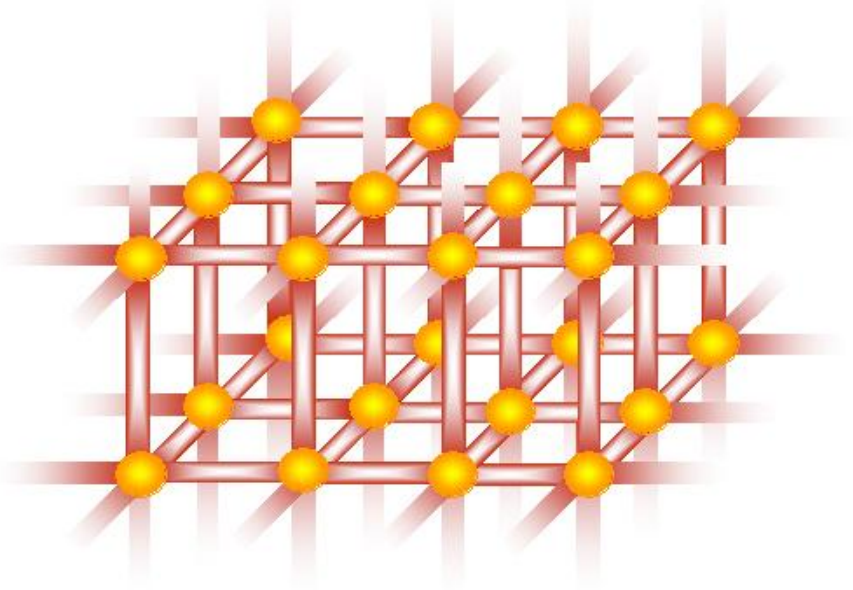
- Prof. Randall Snurr

Acknowledgments

- Research Prof. Omar Farha

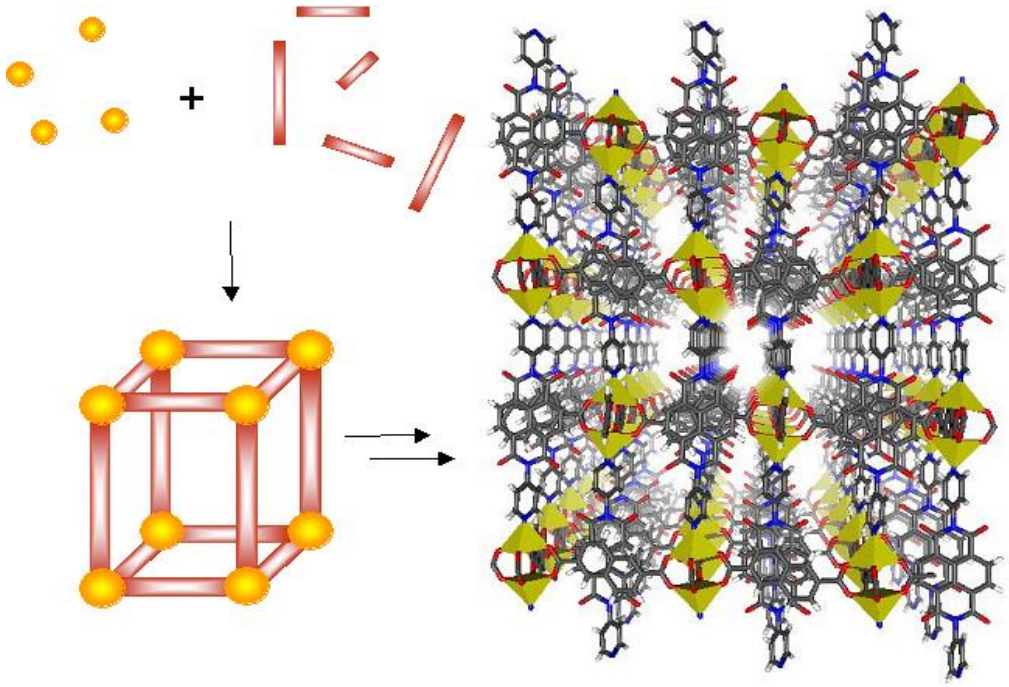
Metal-Organic Framework Materials for Energy Applications

- Hydrogen storage
- Chemical catalysis
- Carbon dioxide capture and storage
- Gas separations
- Light harvesting and energy conversion



Why Metal-Organic Frameworks?

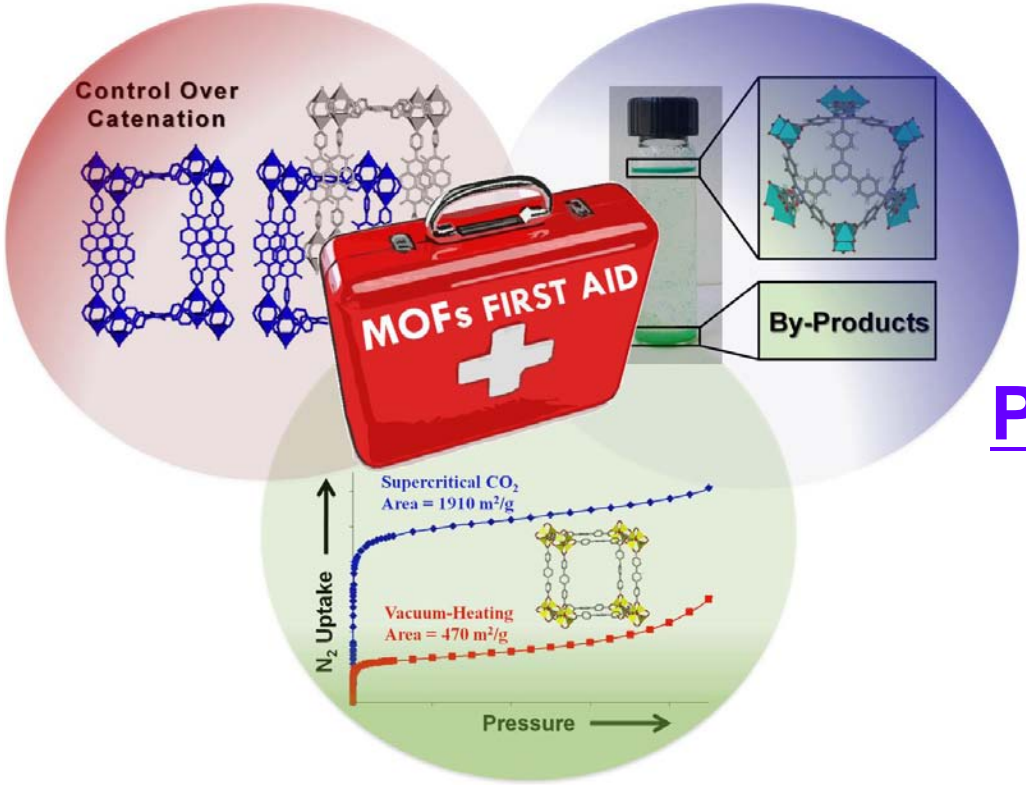
- Solvothermal synthesis ➔ simple, scalable materials assembly
- Broad channel and pore size tunability
- Complete uniformity of channels
- Amenable to experimental structural characterization



- Amenable to detailed explanative and predictive computational characterization
- Enormous internal surface areas: up to 5,200 m^2/g (e.g. Matzger)

Materials Challenges

Controlling catenation

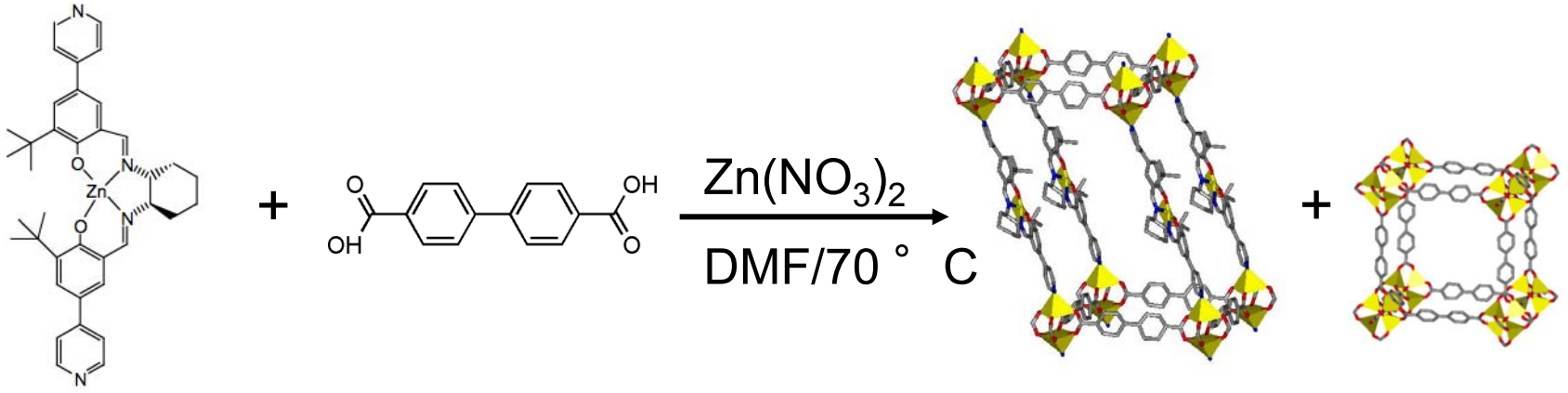


Purification

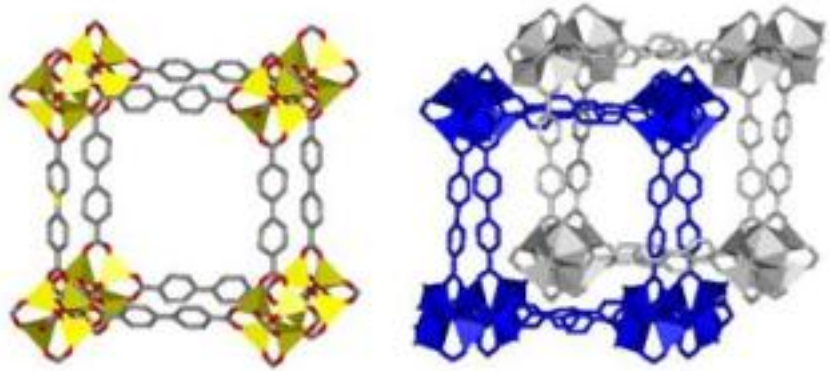
Retaining porosity

Problem: MOFs Are Often Obtained as Solid-state Mixtures

a) Paddlewheel from cubic



b) Catenated versus non-catenated:



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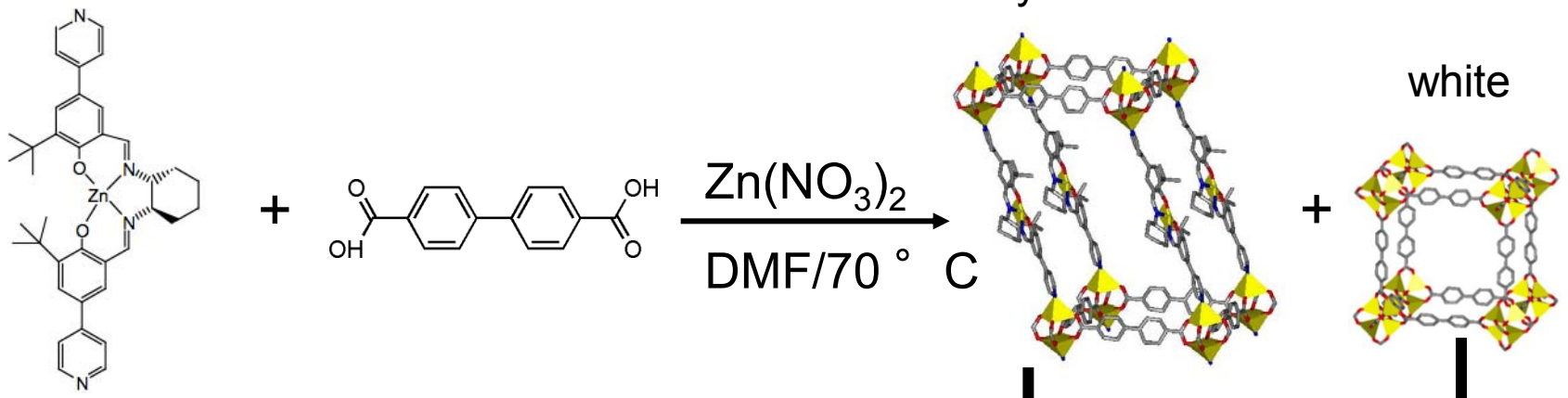
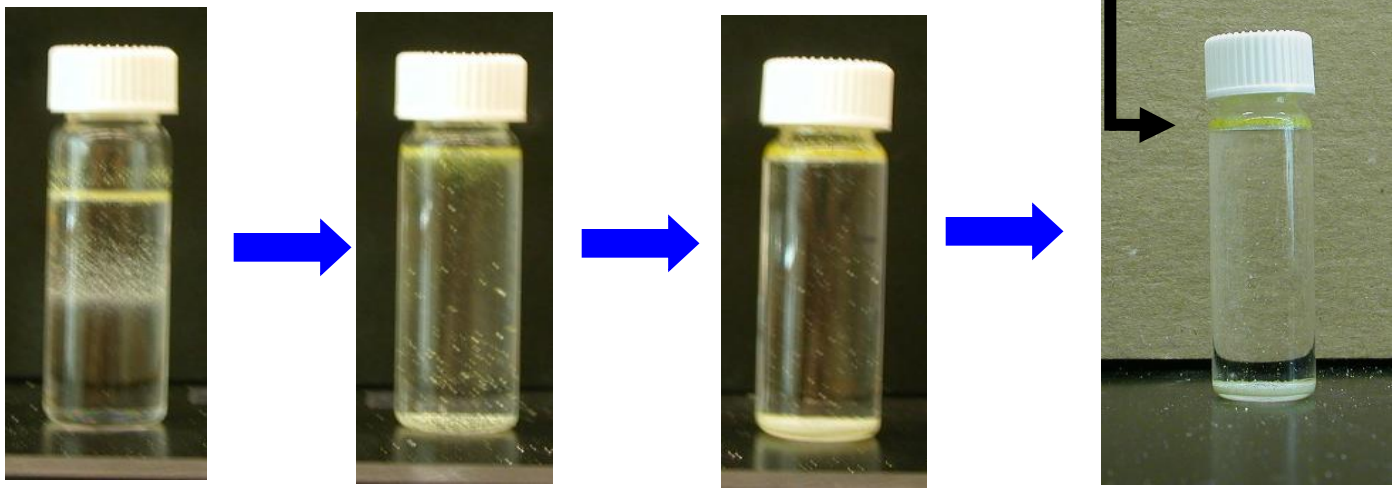
Solution: Density based separation using high-density solvents



Process of separation



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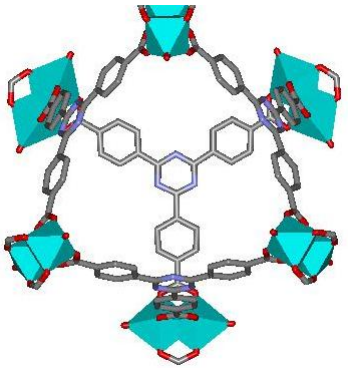
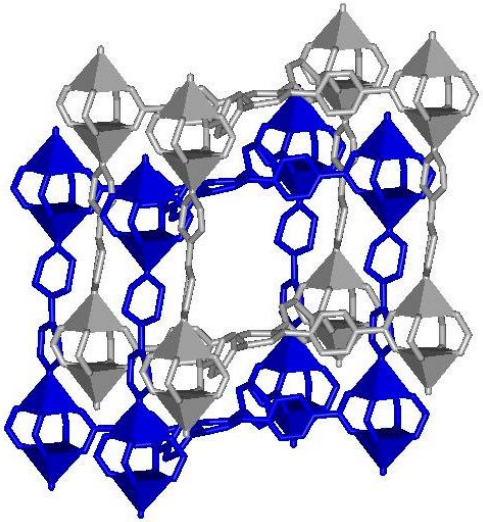
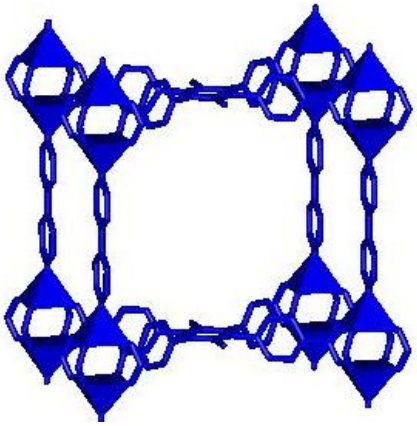
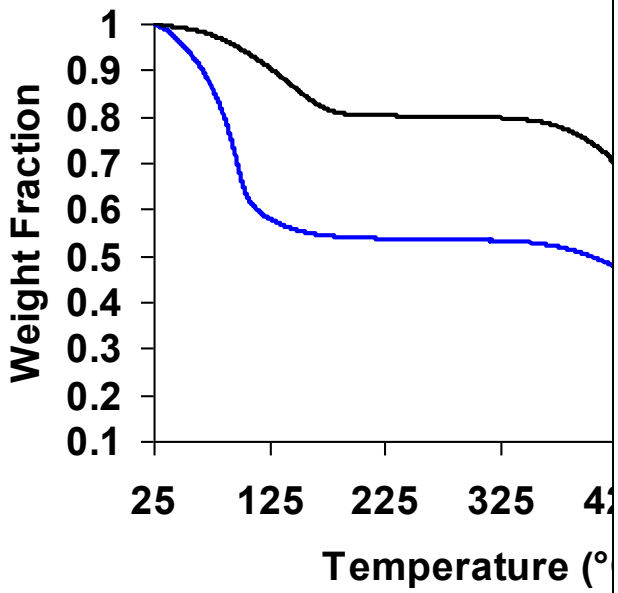


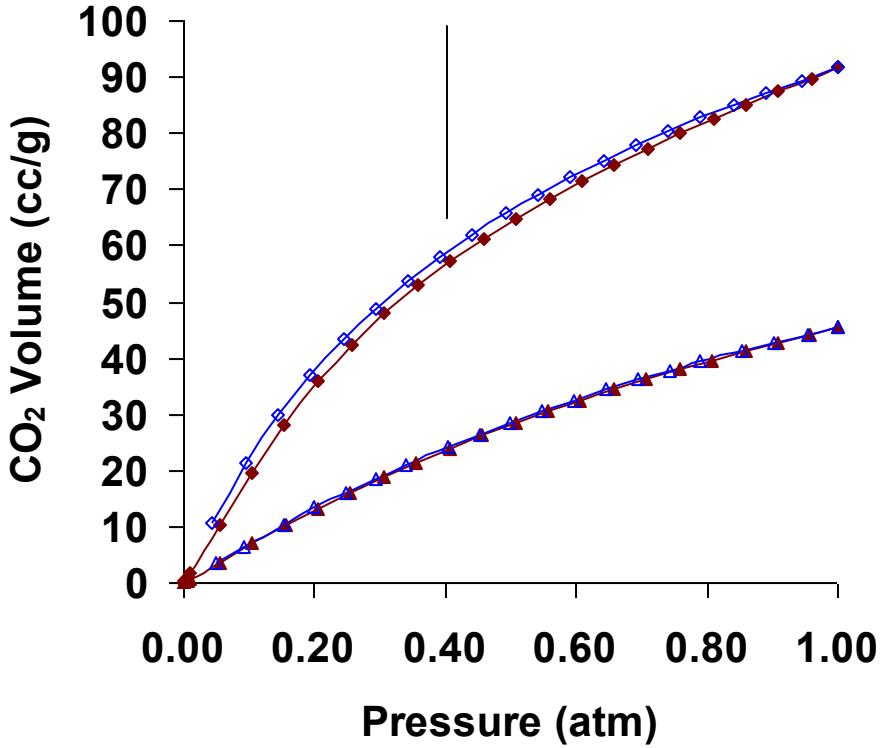
Differences in porosity and surface area



Vs.







Materials Challenges

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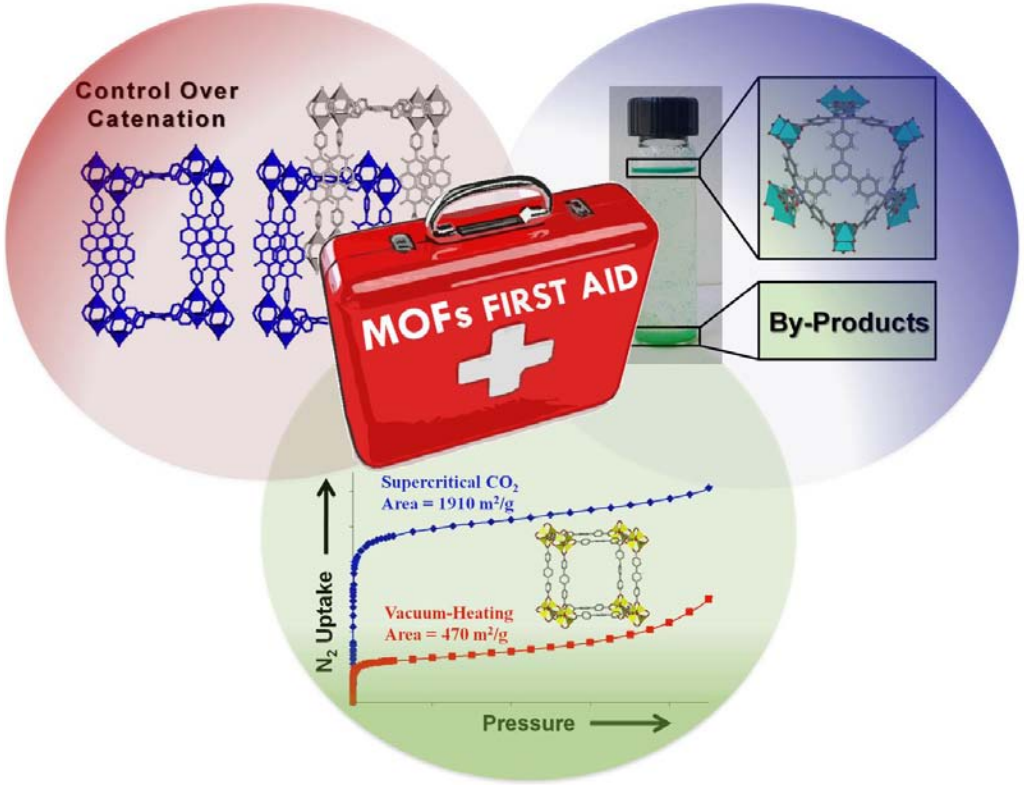
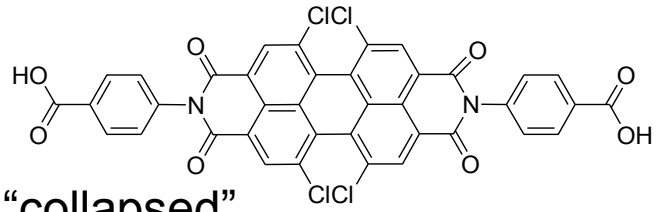


Purity

Retaining porosity

Case Study: Preventing Collapse of Cubic "TCIPDI" MOF

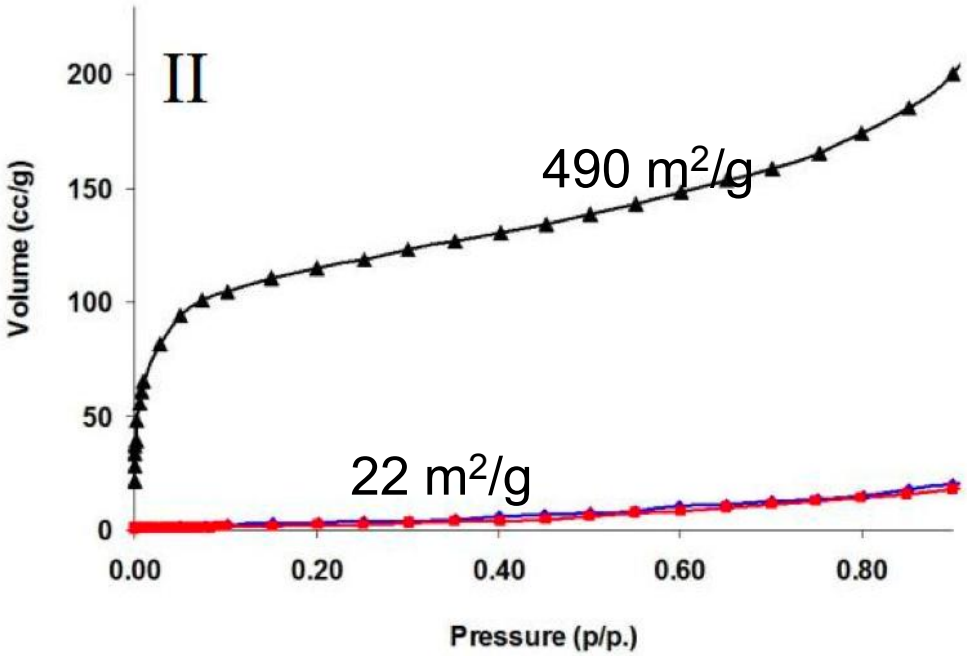


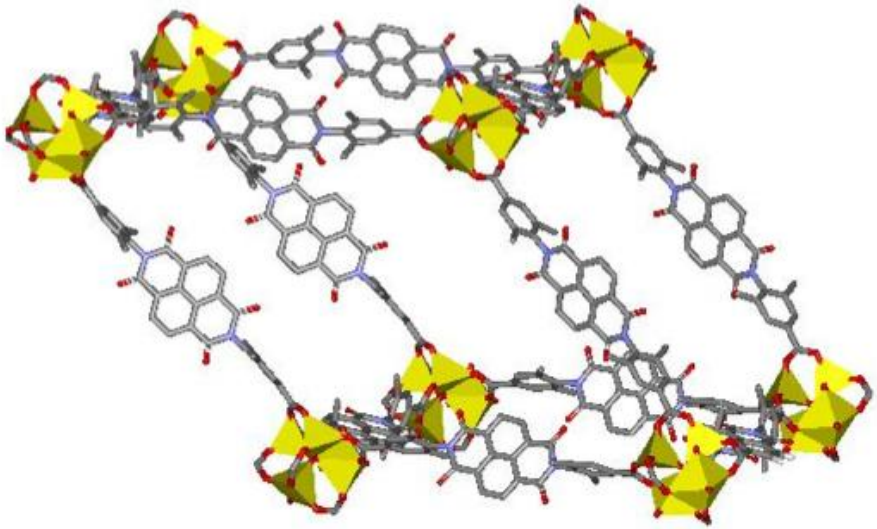
BET Surface Area:

Conventional evacuation ➔ 22 m^2/g ➔ completely "collapsed"

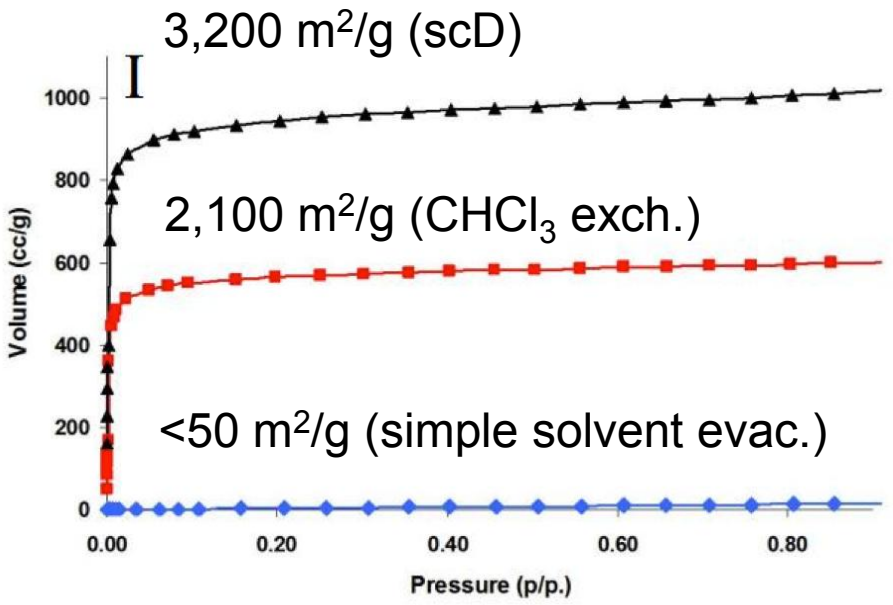
Supercritical CO_2 evacuation ➔ 490 m^2/g ➔ highly porous

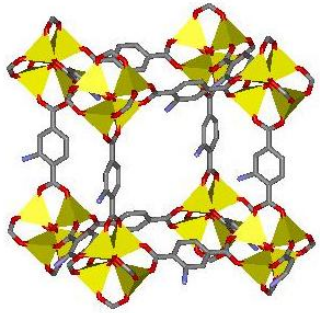
Nitrogen adsorption isotherms

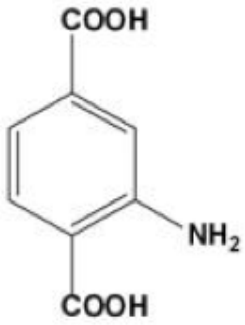


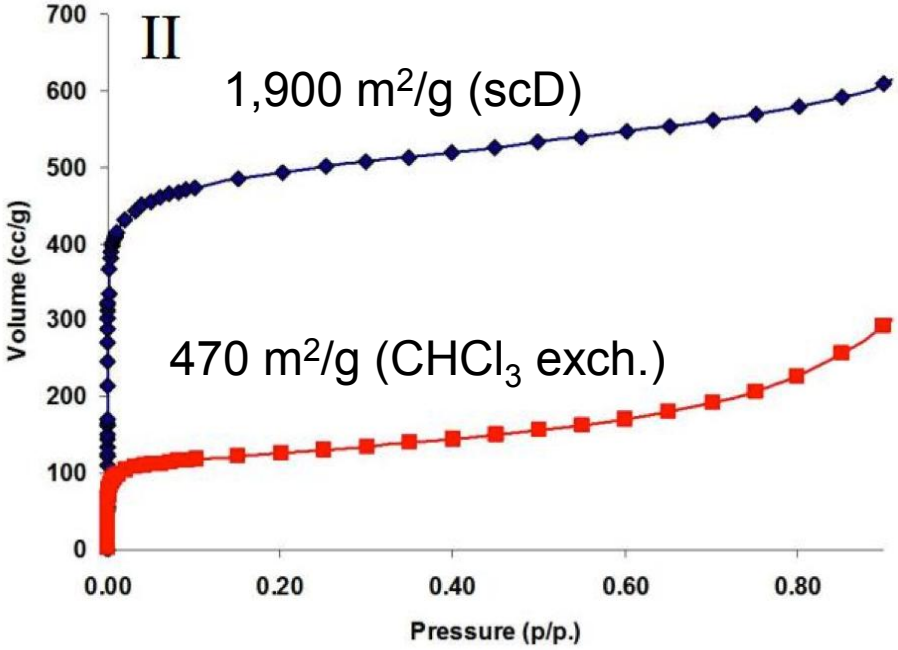


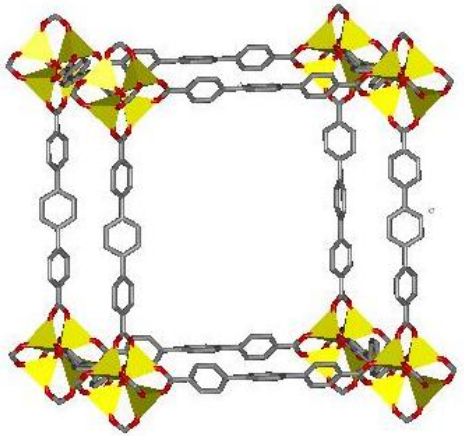
Other Examples with Supercritical CO_2…











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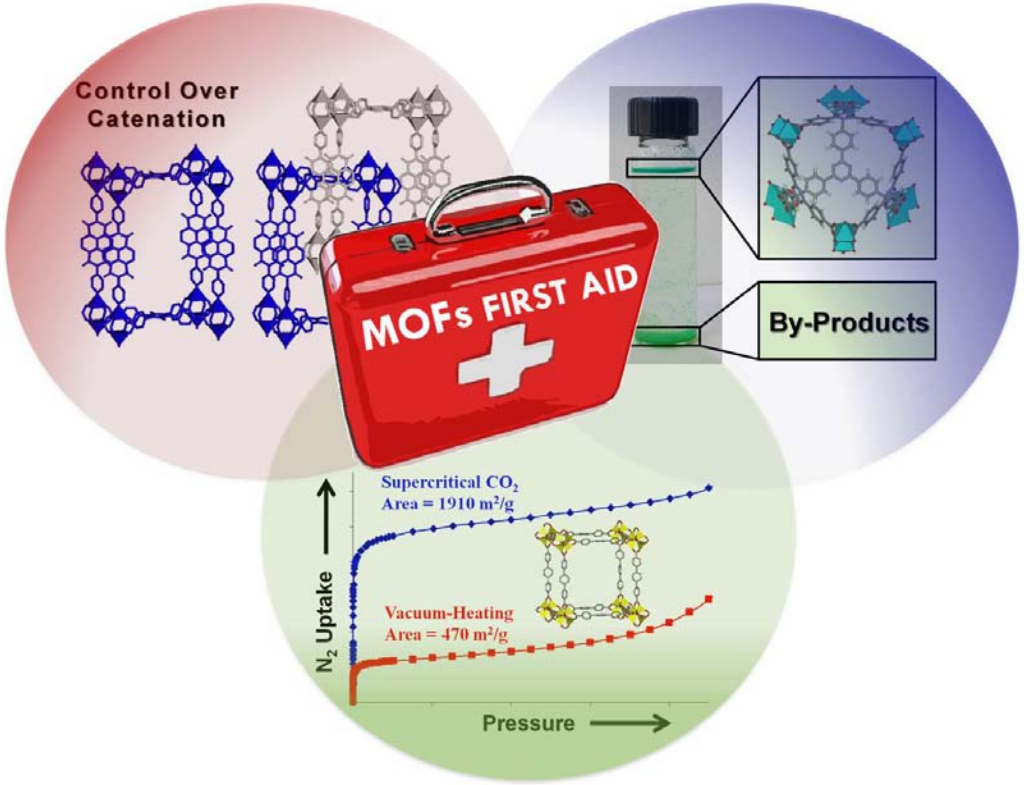
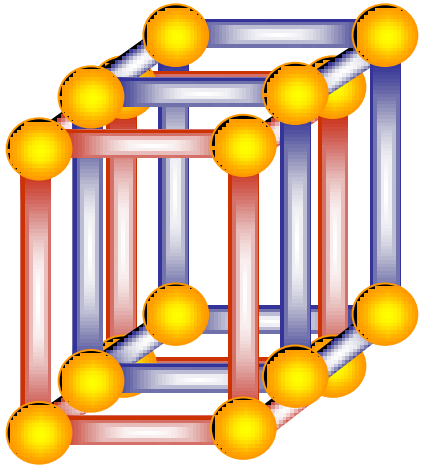


Purity

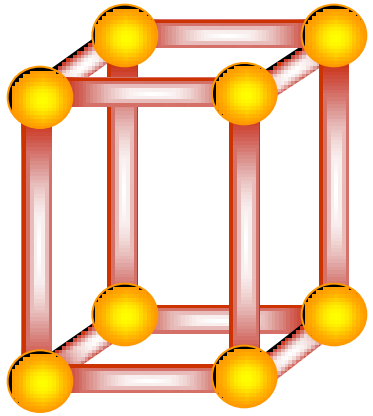
Retaining porosity

Catentated versus non-catenated MOFs

- *nearly all "paddle-wheel" MOFs are catenated*
- *but, for most applications, we desire non-catentated MOFS*



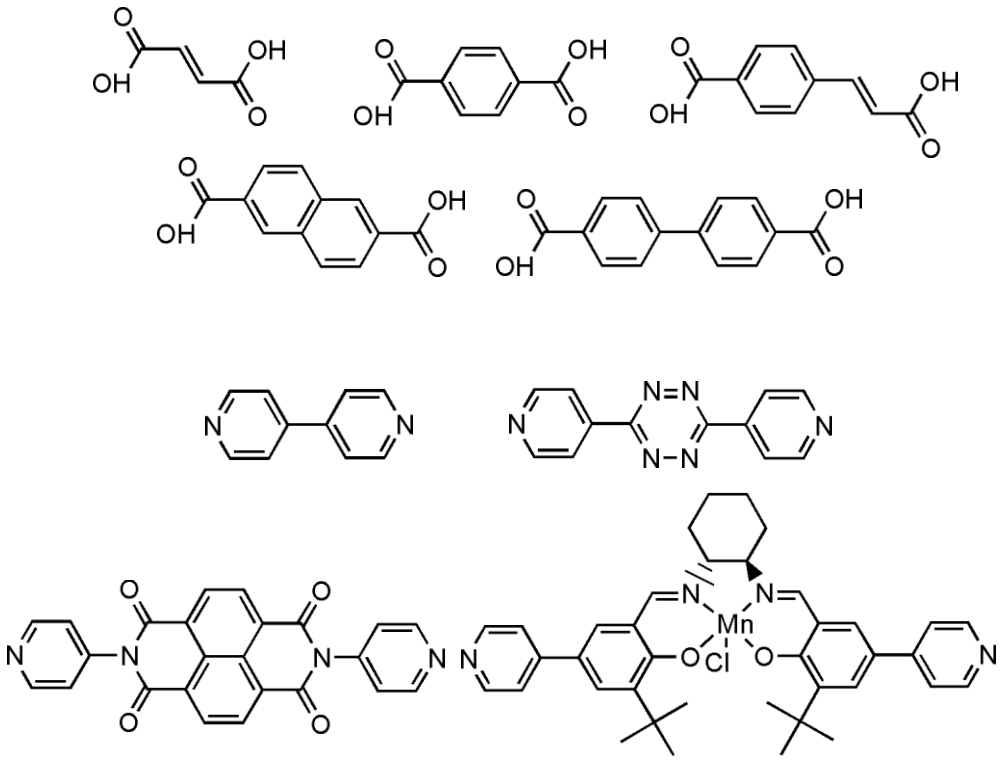
catenated

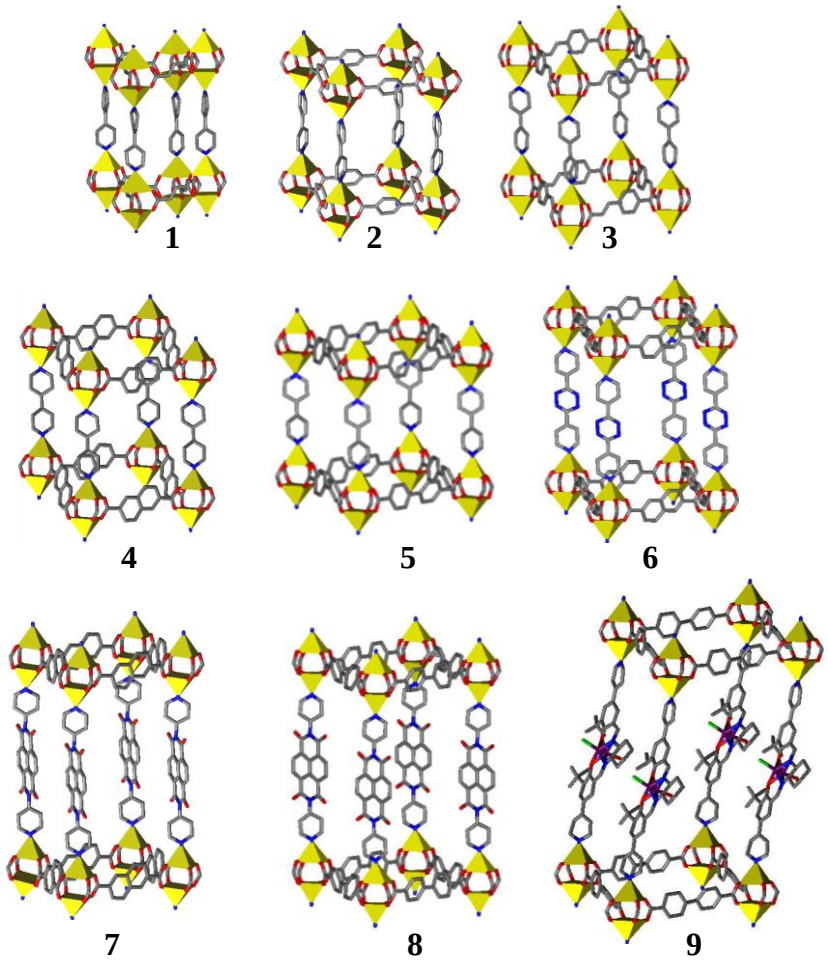


non-catenated

Examples of Catenated Paddlewheel MOFs

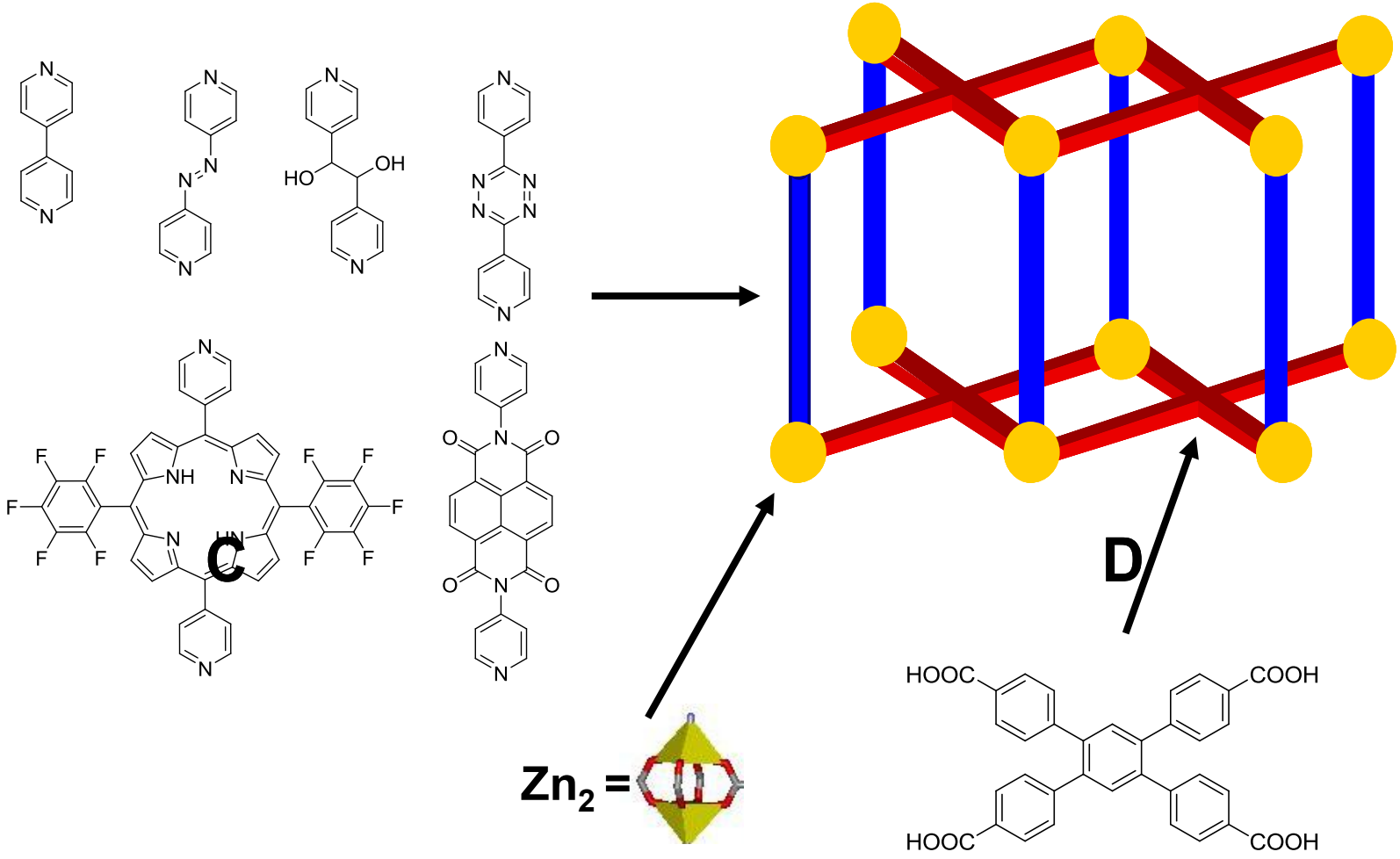
- $Zn_2(dicarboxylate)_2(dipyridyl)$





Ma, et al. Inorg. Chem., **2005**, 44, 4912-4914

Control over Catenation…



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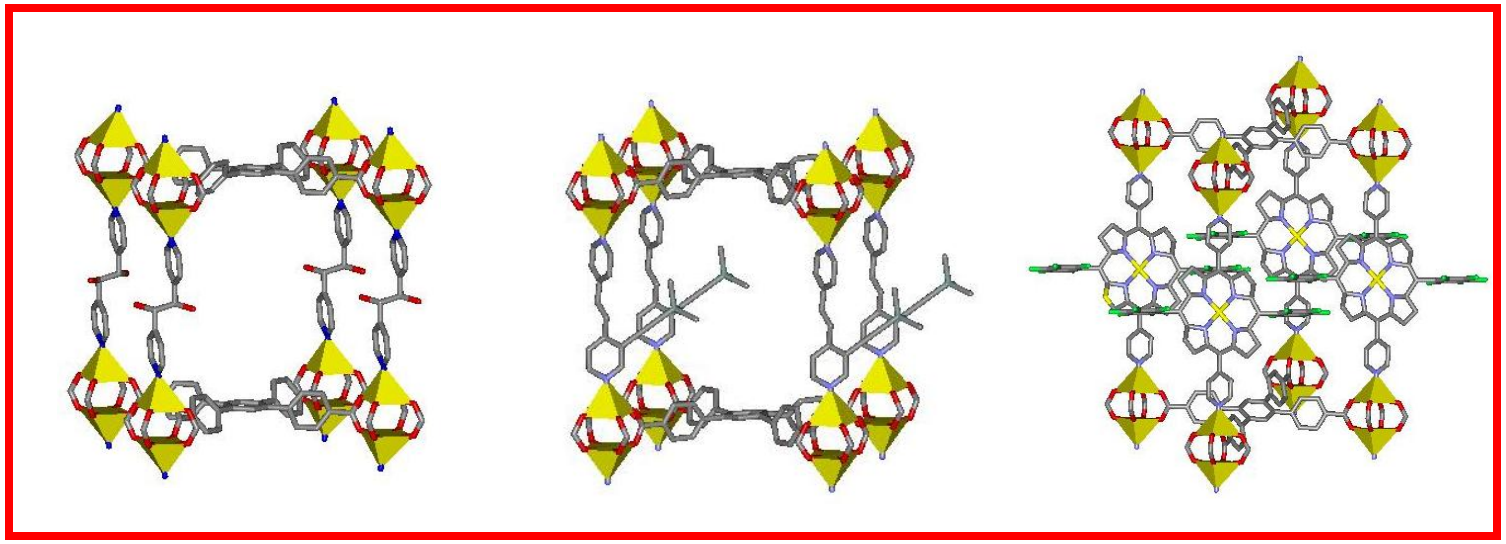
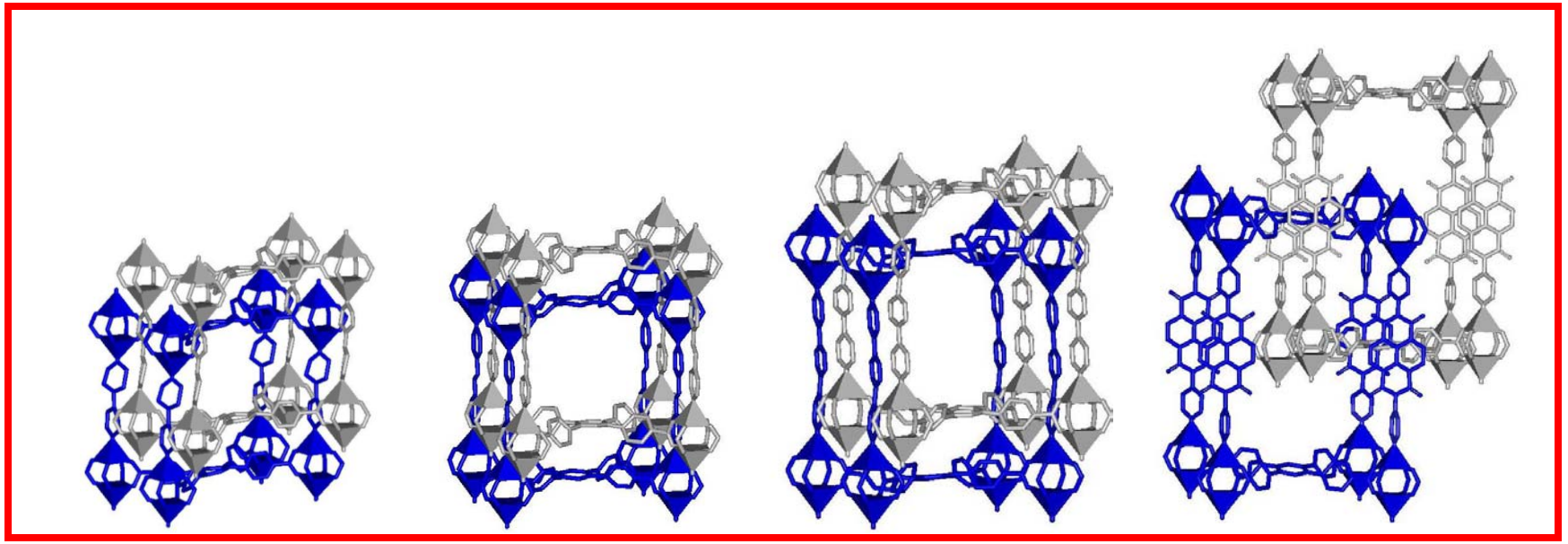
Mixed Results

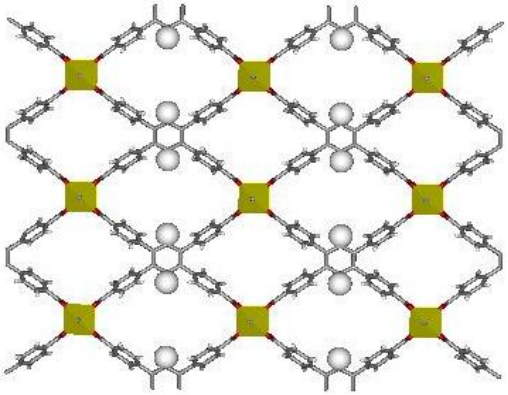
A)

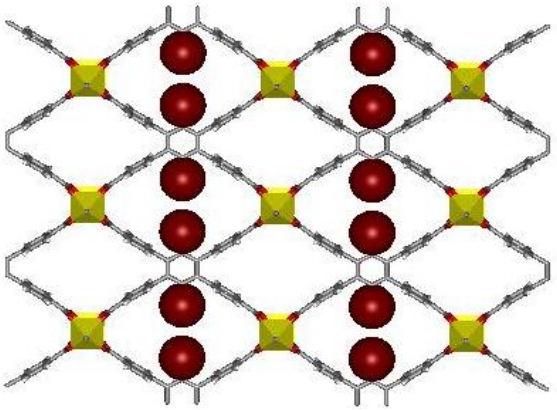


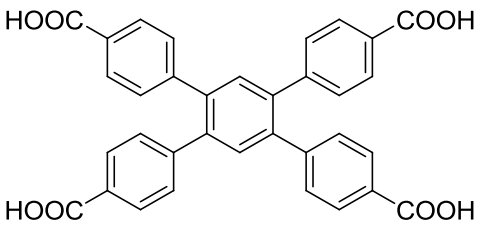
B)

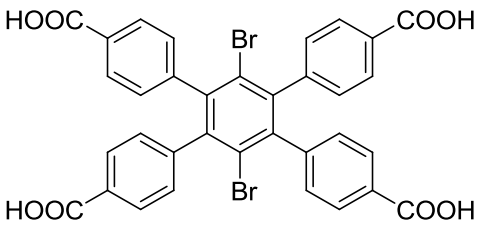


Redesigning the Tetratopic Strut

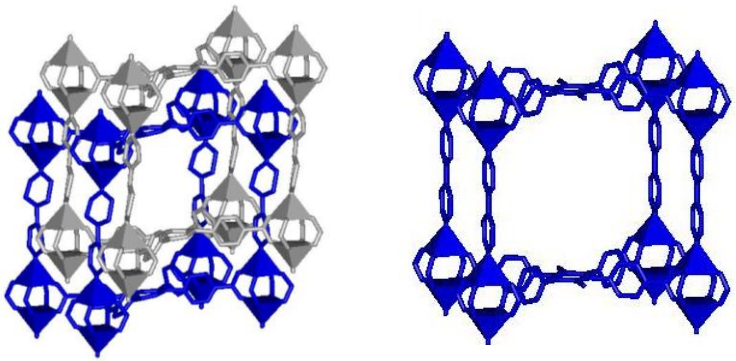


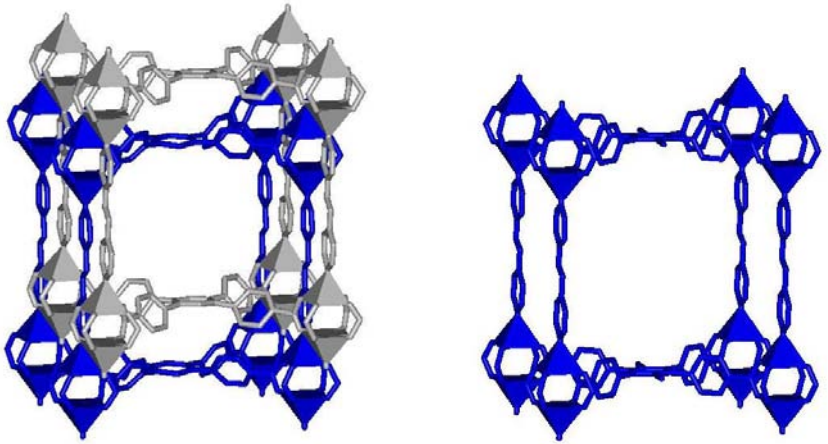


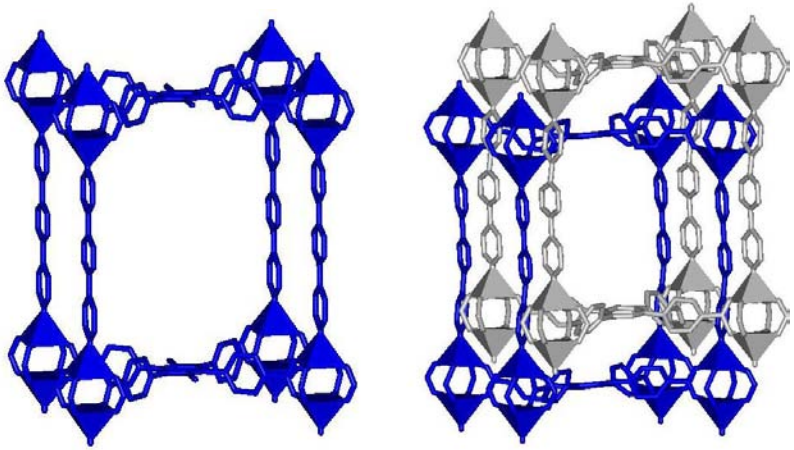


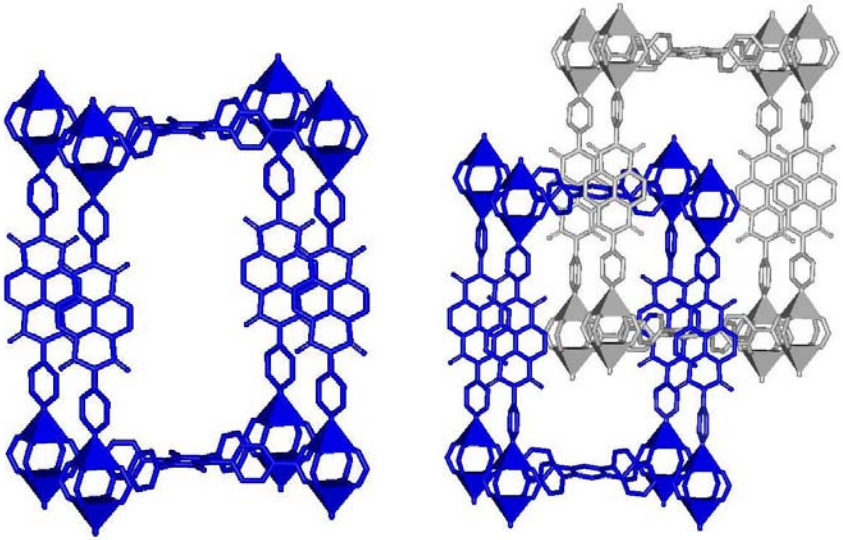


Control over Catenation



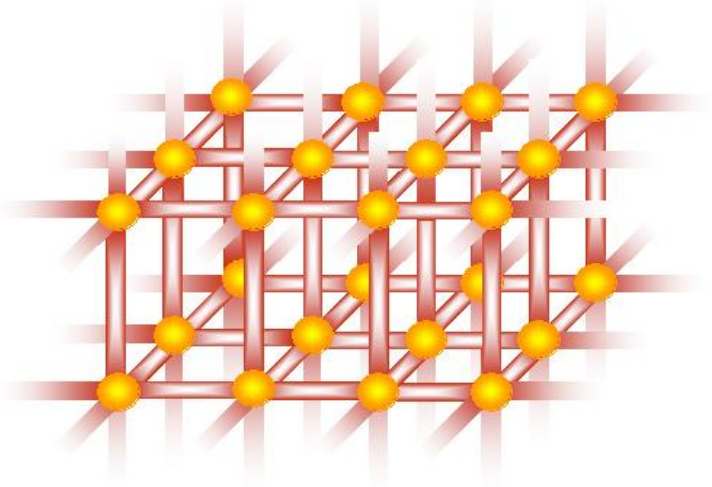






Metal-Organic Framework Materials for Energy Applications

- Hydrogen storage
- Catalysis
- Chemical sensing
- Gas separations
- Light harvesting…

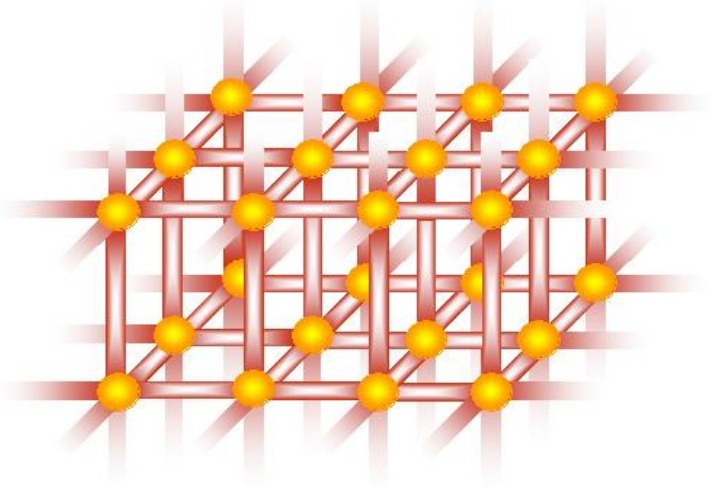


J. Am. Chem. Soc., **2007**, 129, 9604-9605.
Langmuir, **2009**; *Inorg. Chem.* **2008**

Metal-Organic Framework Materials for Energy Applications

Hydrogen storage. DOE-mandated goal:

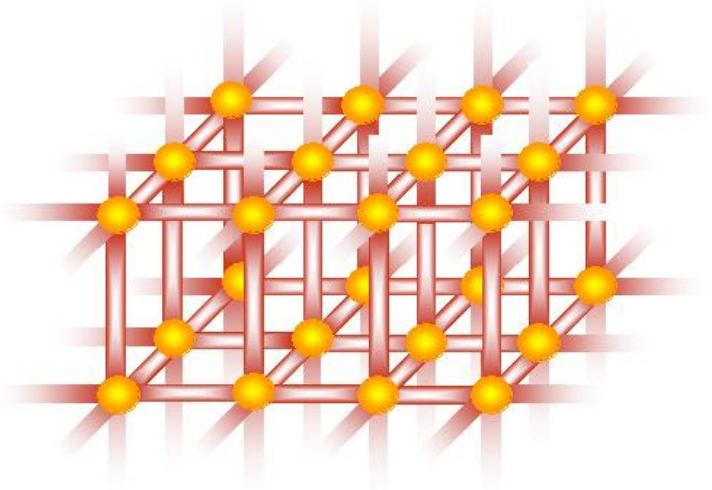
- 10 wt. percent
- 100 bar or less
- -30°C (243K)



Metal-Organic Framework Materials for Energy Applications

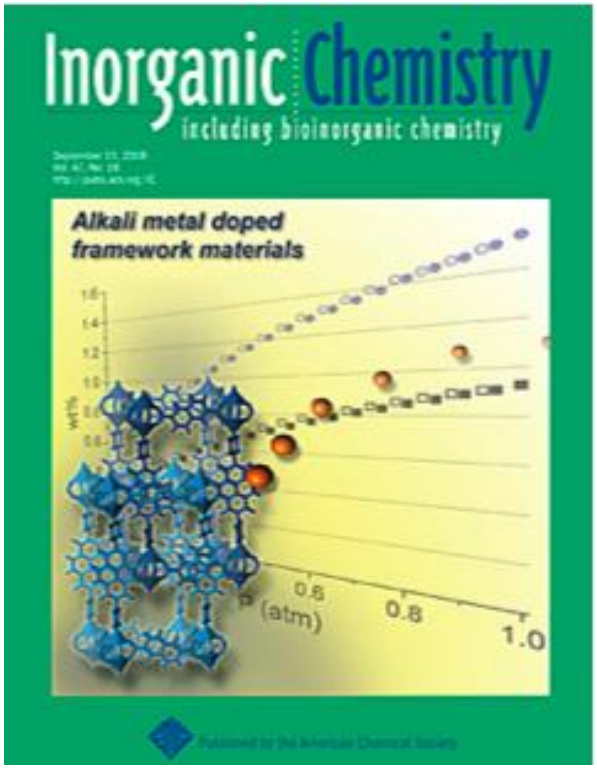
Hydrogen storage. DOE-mandated goal:

- ~~10 wt. percent~~ 5.5 %
- 100 bar or less
- -30°C (243K)



Goals → New Metal-Organic Frameworks Featuring:

- **High surface areas**
- Highly accessible H_2 binding sites
- Extraordinary heats of adsorption
- **High H_2 storage capacity** at ambient temperature



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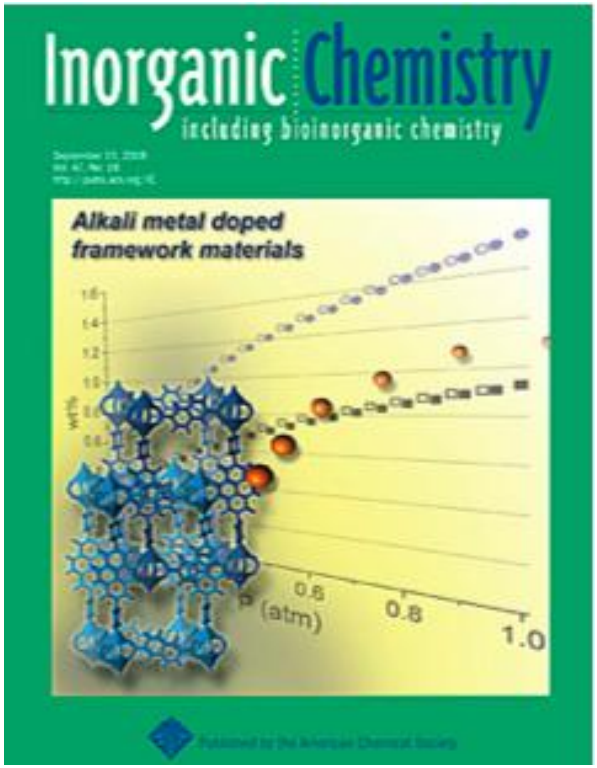
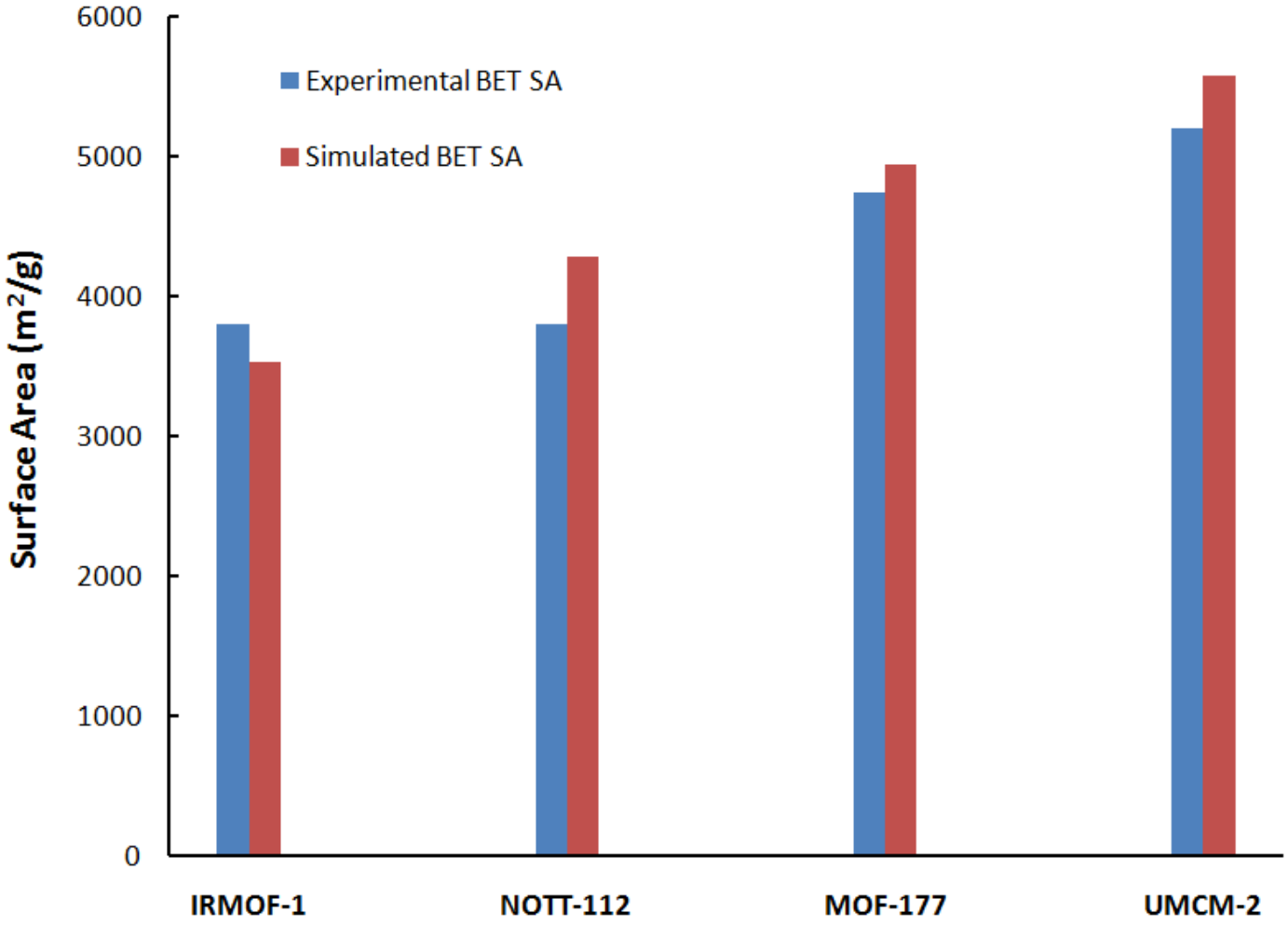


Materials Design via Computational Modeling

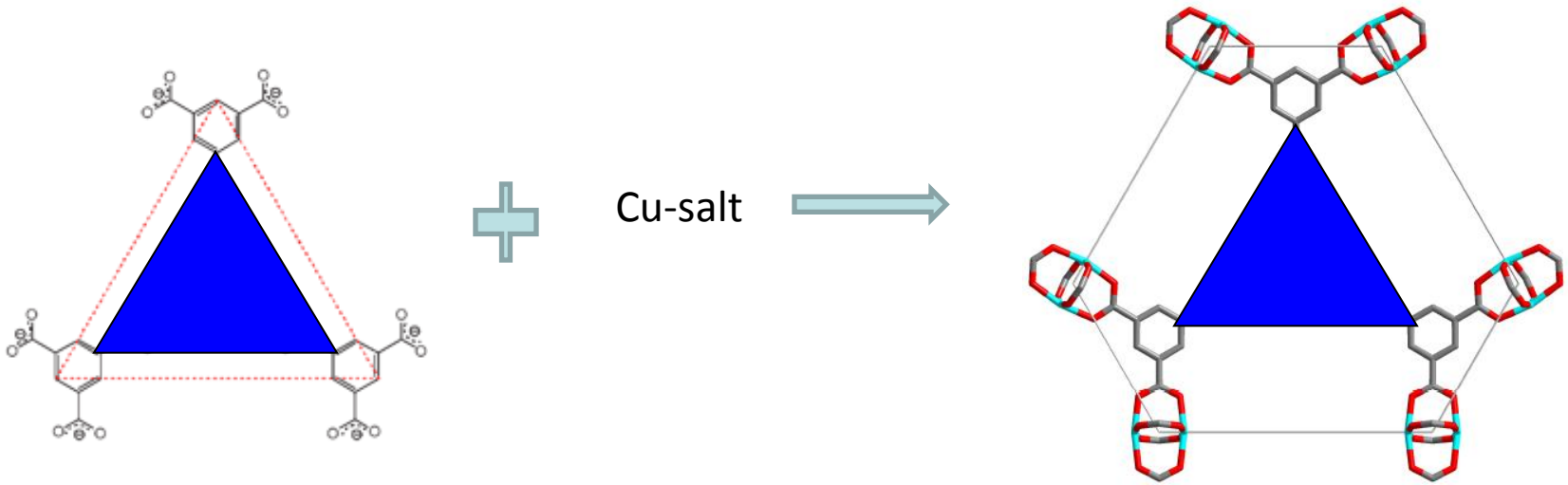
R. Q. Snurr and co-workers, Northwestern.

Literature: High Surface Area MOFs



R. Q. Snurr and co-workers, Northwestern.

Target Coordination and Topology



Why this topology:

(a) high stability under ambient conditions

(b) unsaturated coordination sites (Cu(II) sites)

(c) impossibility of forming interpenetrated multi-network structures.

cf. M. Schroder, et al. and H-C. Zhou, et al.

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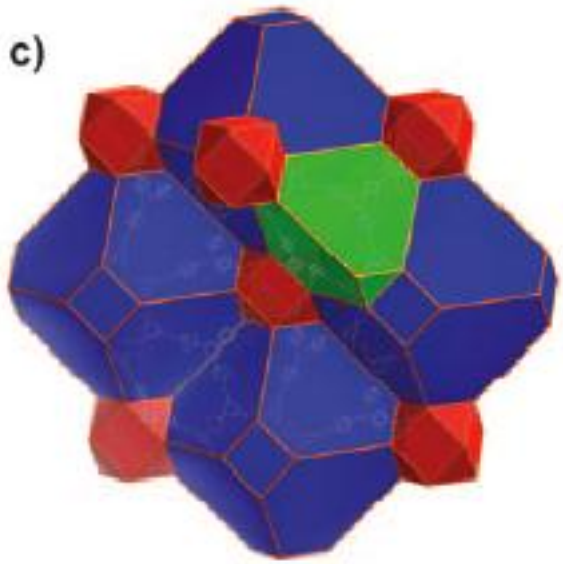

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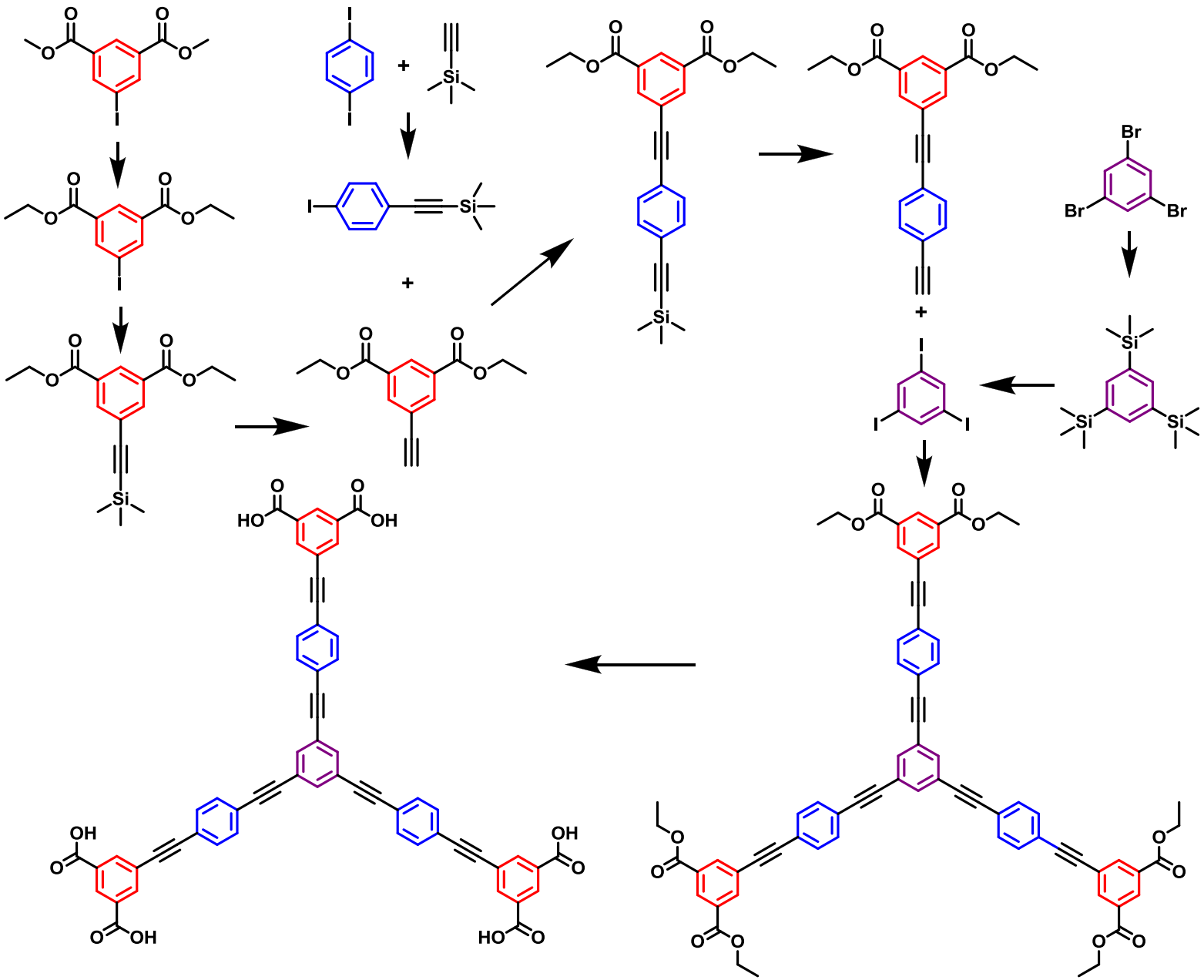
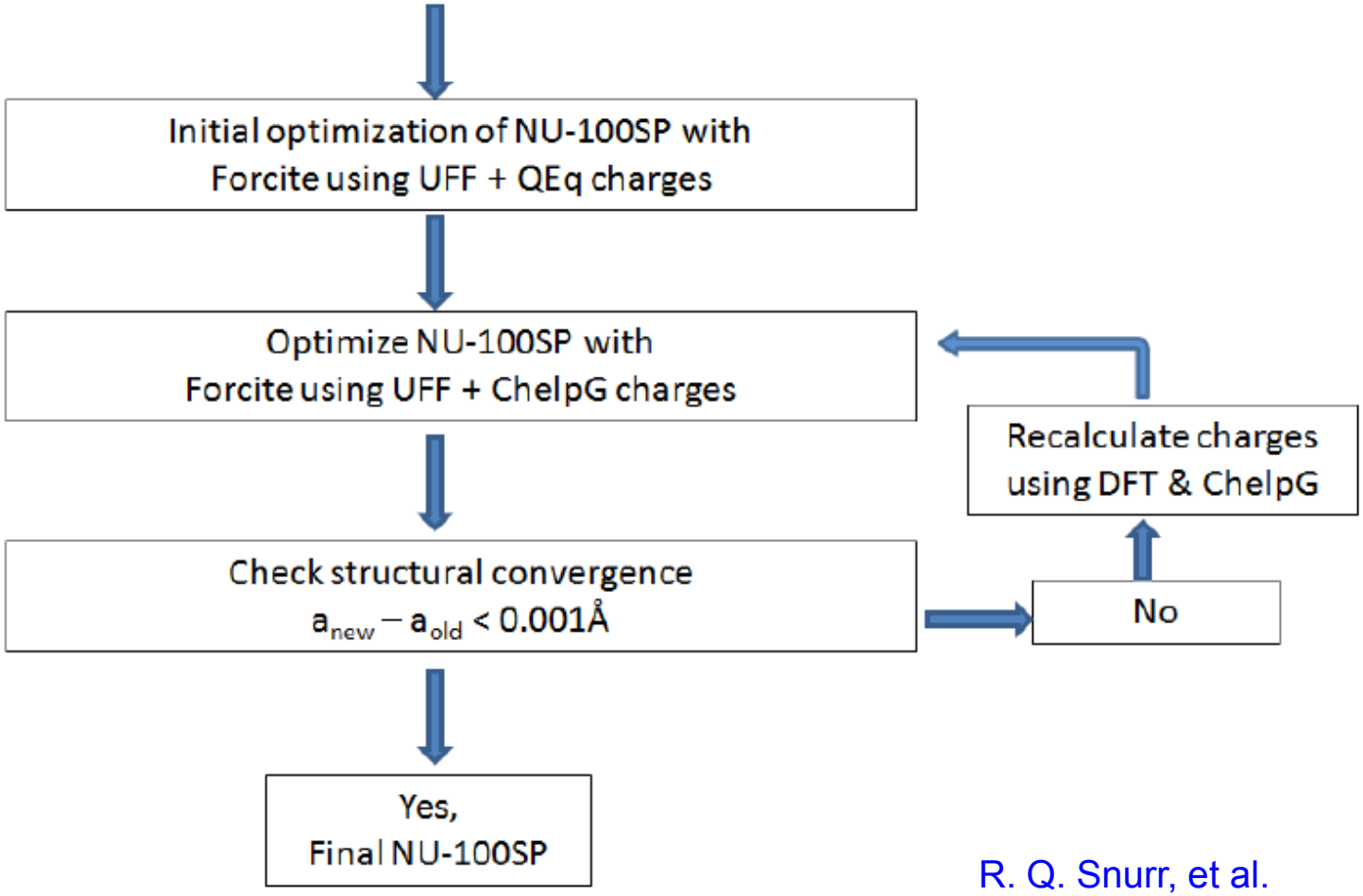
New Hexatopic Strut → 3,24 Net Expected



Structure Prediction

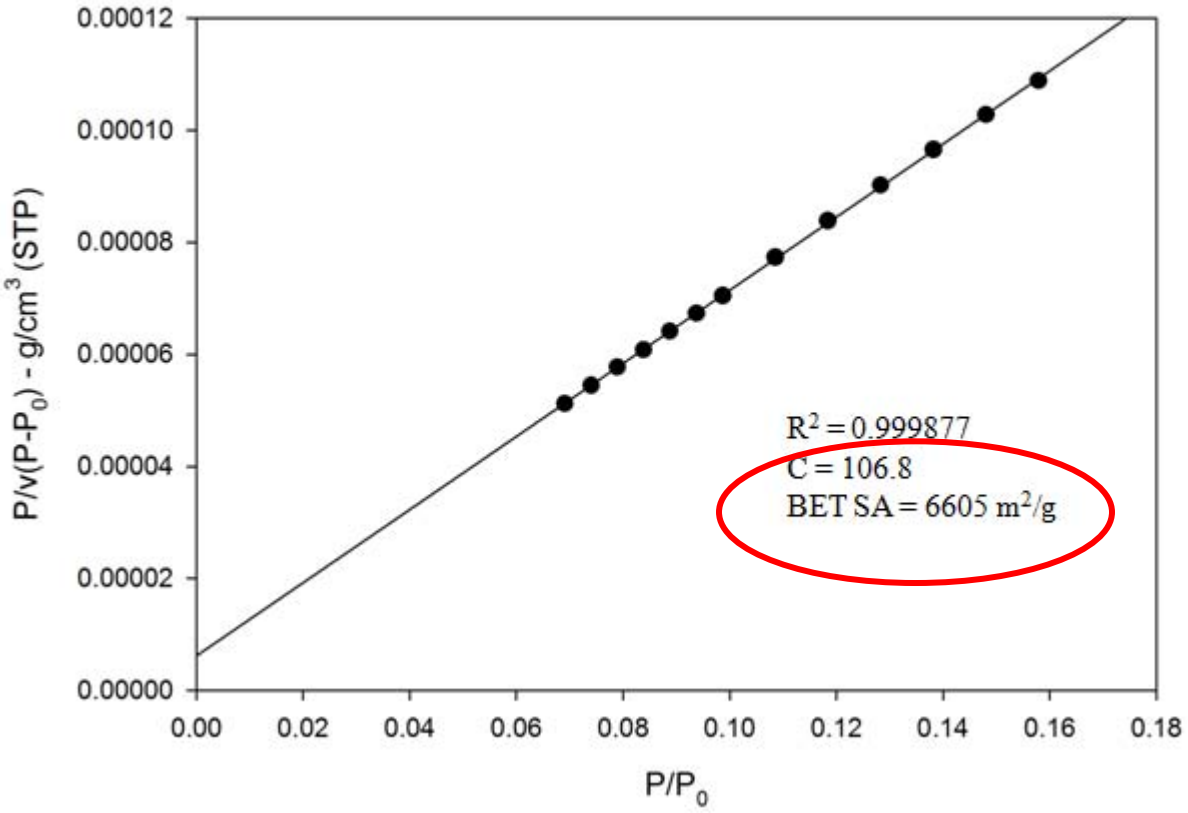
Combine new strut with Cu-paddlewheels in Fm-3m space group



R. Q. Snurr, et al.

Predicted Surface Area of NU-100

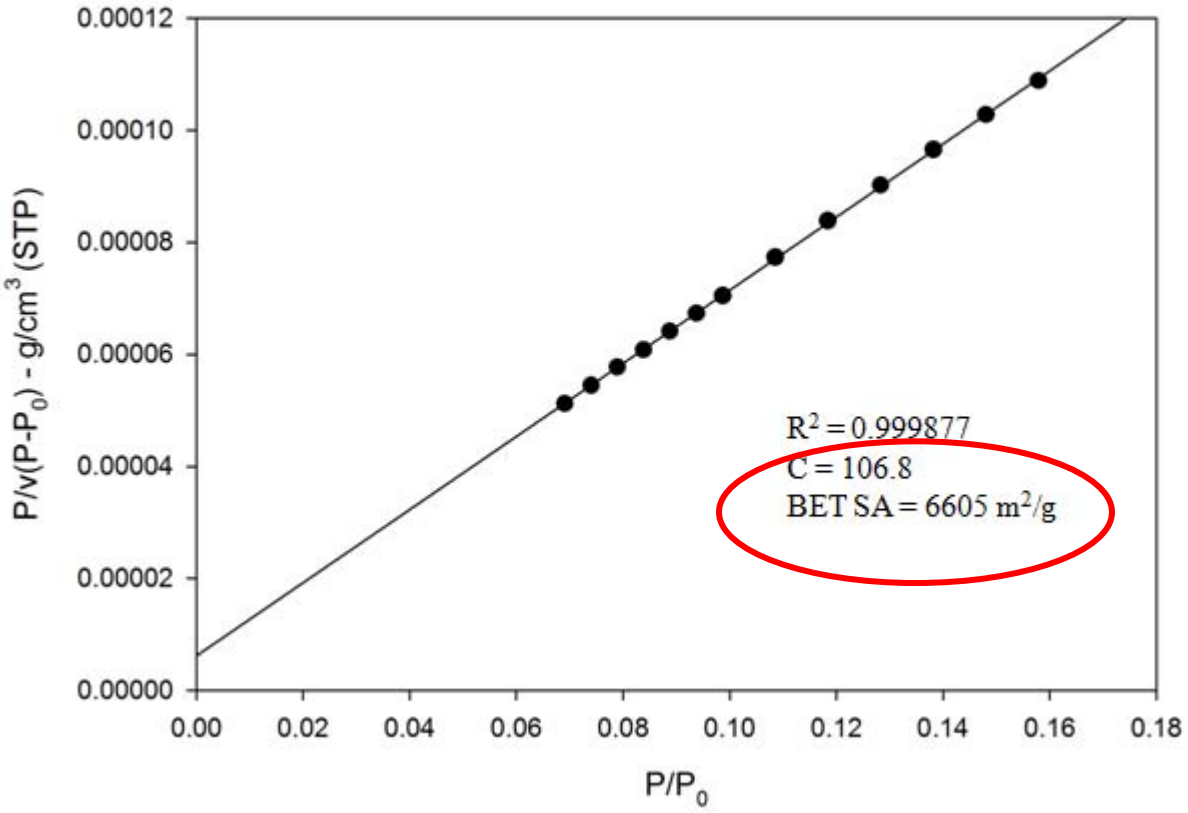
Simulated Structure → Simulated N_2 isotherm → BET Model



Applicability of the BET method to MOFs: Y. S. Bae, O. Yazaydin, R. Q. Snurr, "Evaluation of the BET Method for Determining Surface Areas for MOFs and Zeolites that Contain Ultramicropores," *Langmuir* **2010**, *26*, 5475-5483.

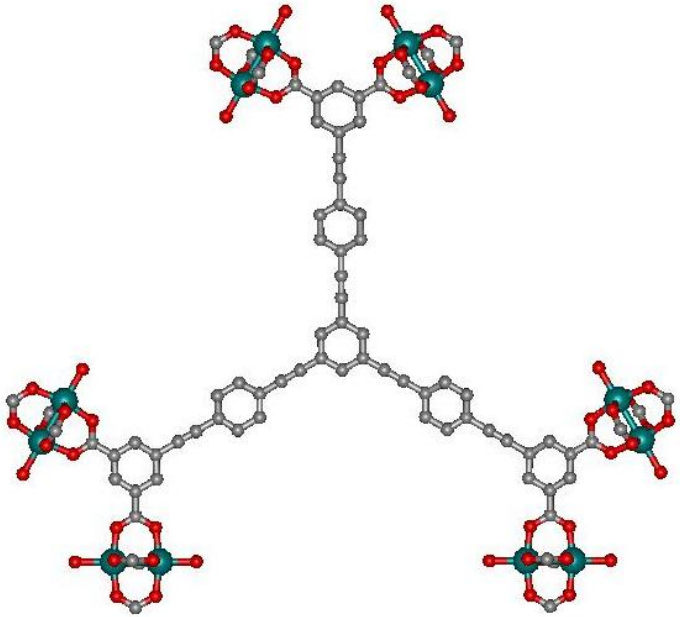
Predicted Surface Area of NU-100

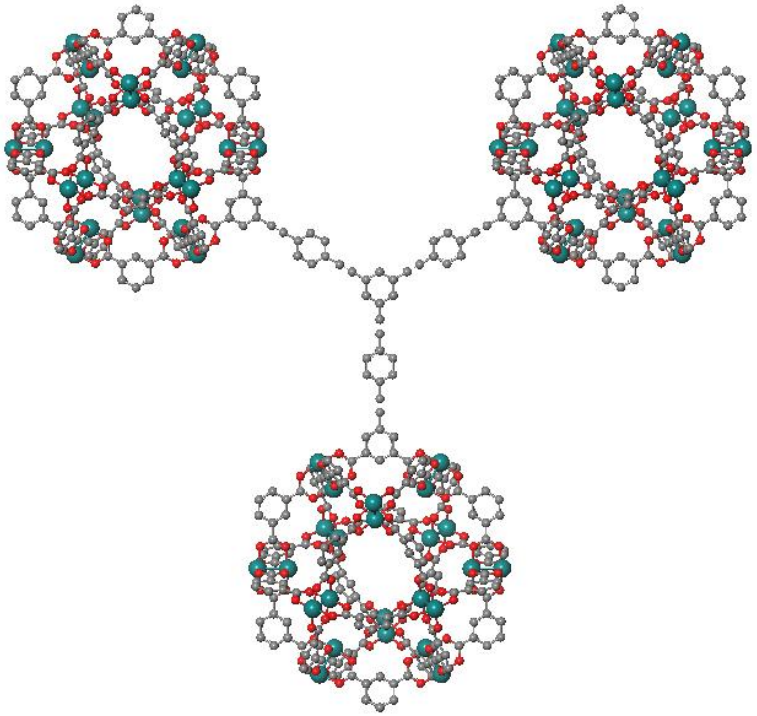
Simulated Structure → Simulated N_2 isotherm → BET Model



Applicability of the BET method to MOFs: K. S. Walton, R. Q. Snurr, "Applicability of the BET Method for Determining Surface Areas of Microporous Metal-Organic Frameworks," *J.Am.Chem.Soc.* **2007**, *129*, 8552-8556.

What we find: NU-100

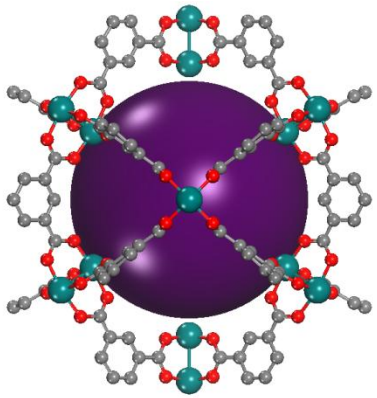




What we find: NU-100

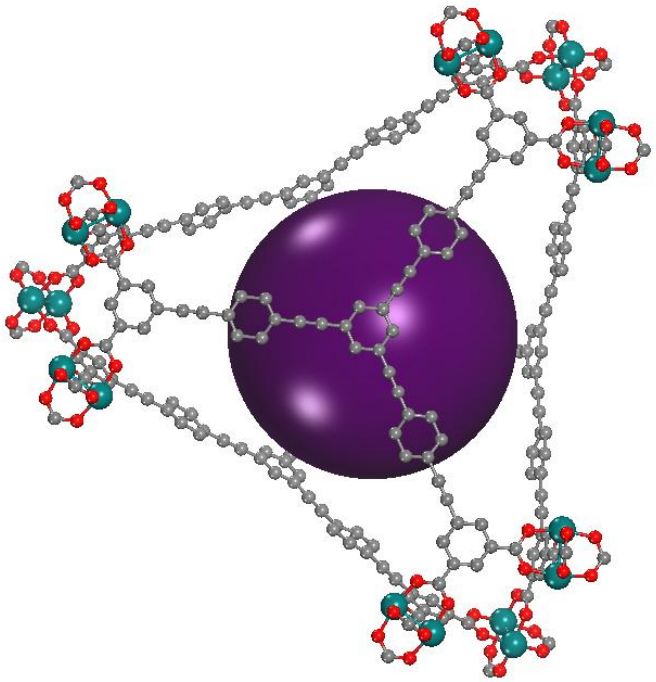
cubaoctahedral

≈14 Å



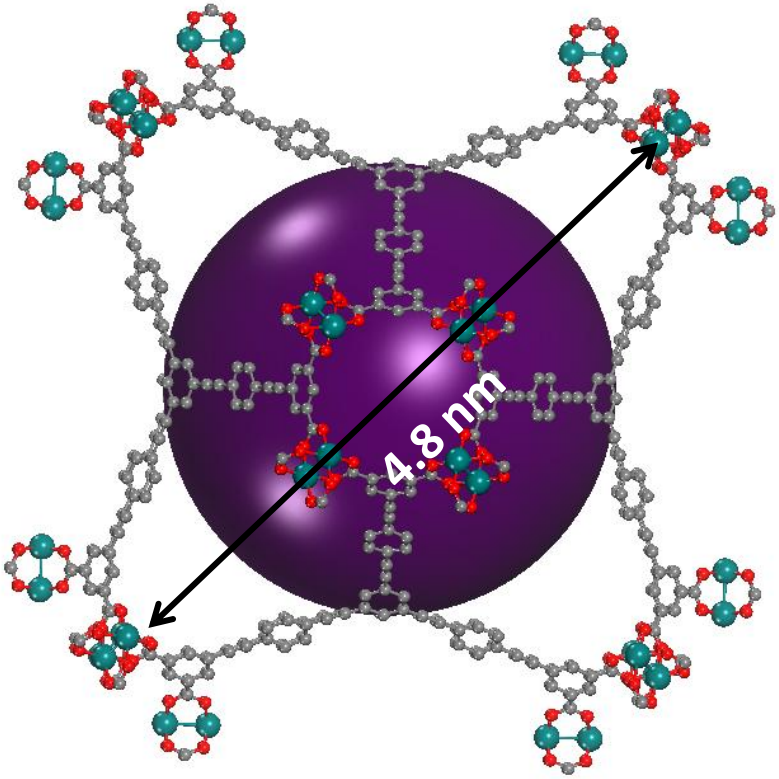
truncated tetrahedral

≈15 Å

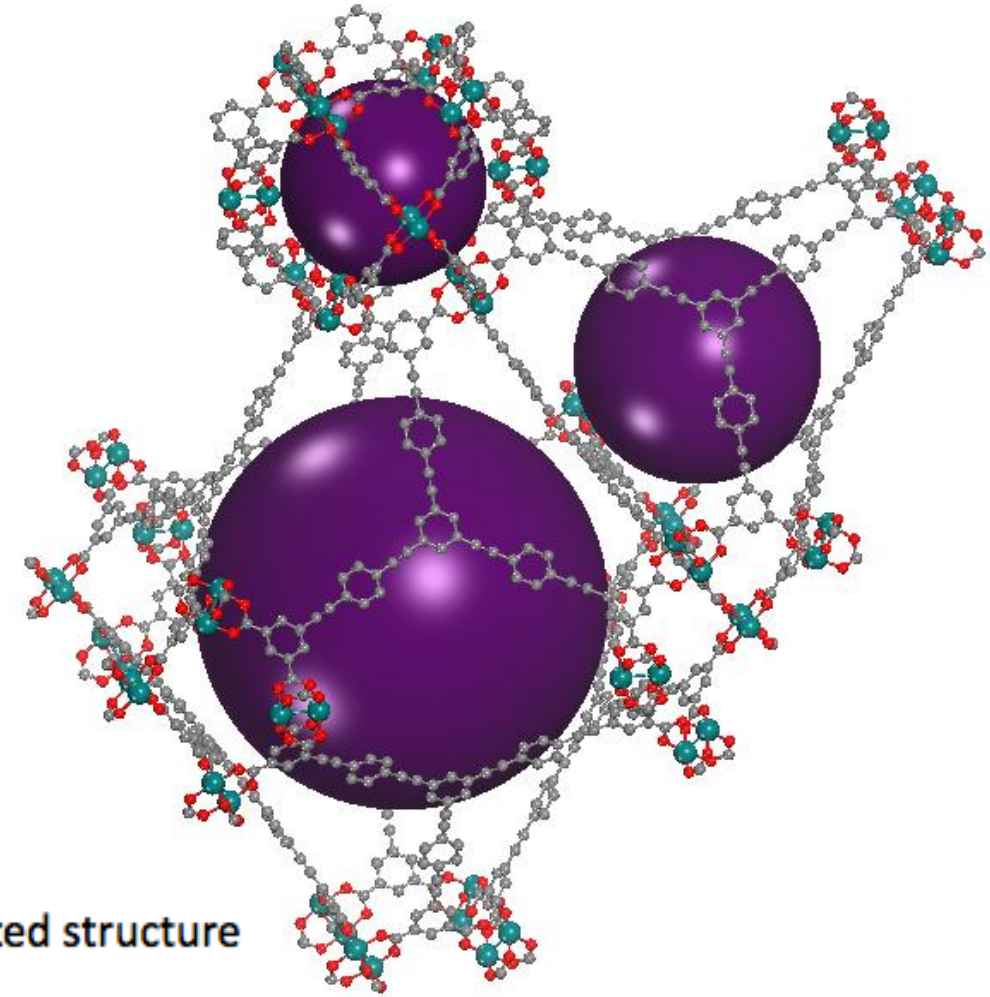


truncated octahedron

≈28 Å



What we find: NU-100



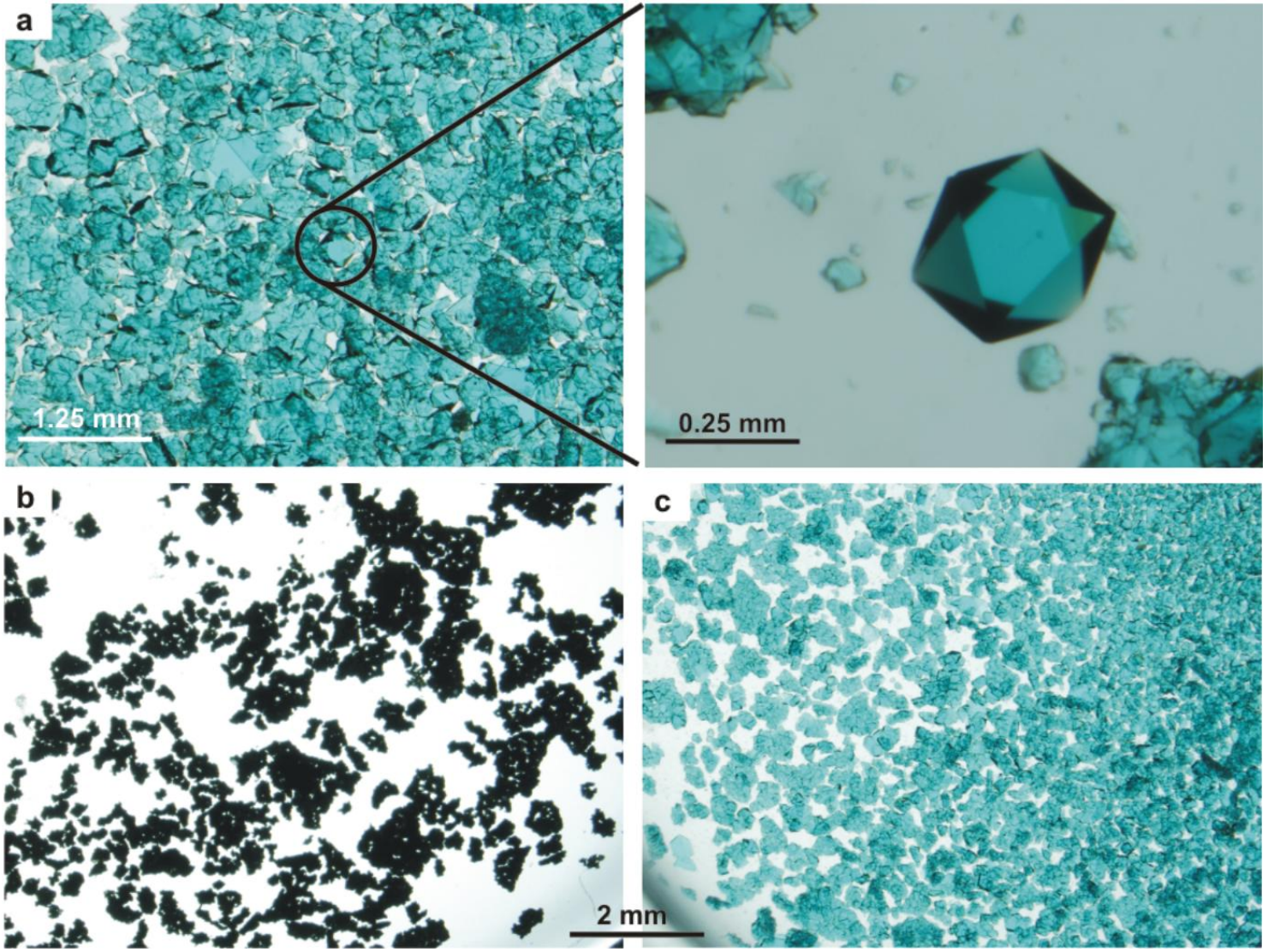
Matched with predicted structure

a=b=c=59.872002 Å

a=b=c=59.539389 Å

MOF Activation: Can We Use This New Material?

- Heating at 100° C under vacuum → Failed
- Solvent exchange, then room temperature evacuation → Failed
  - -ethanol
  - -acetone
  - -chloroform
- Modified supercritical drying → success

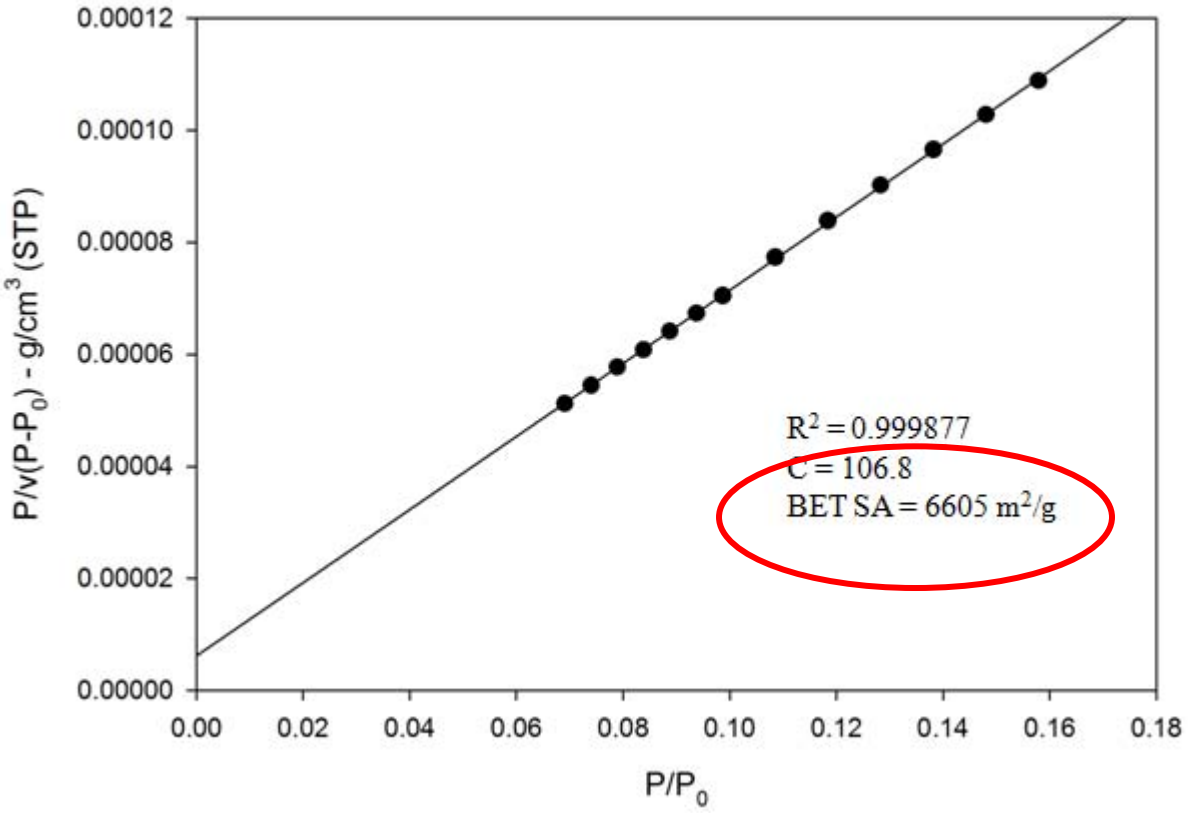


Conventional and Solvent Exchange Activation

Supercritical CO_2 Activation

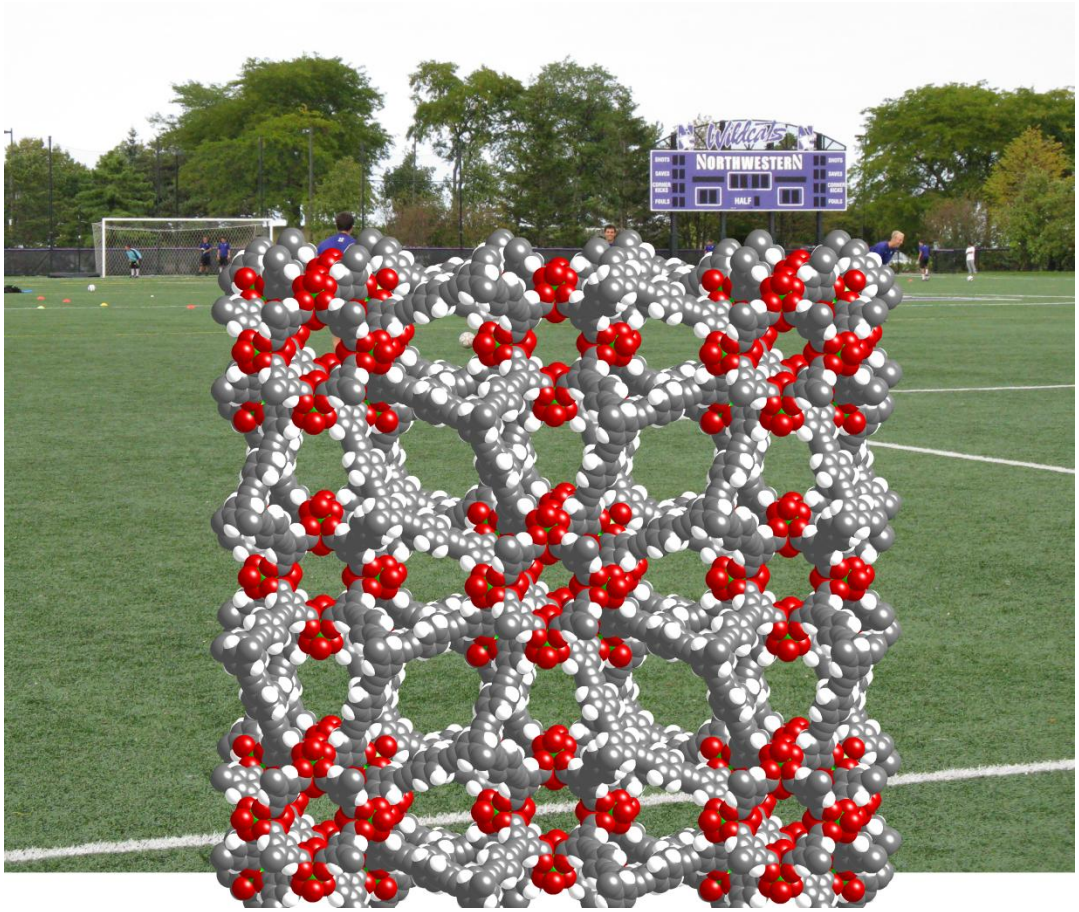
Predicted Surface Area of NU-100

Simulated Structure → Simulated N_2 isotherm → BET Model

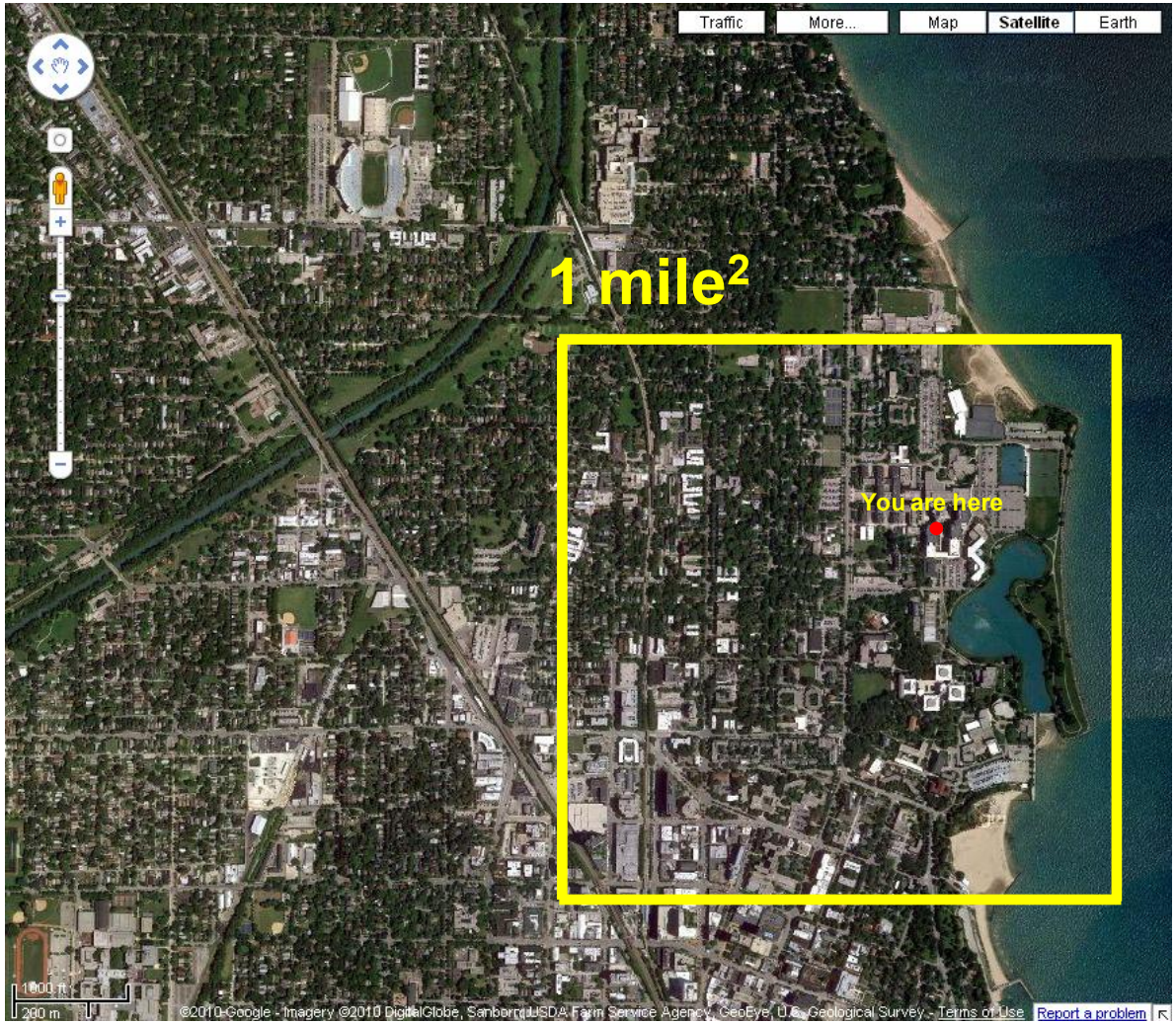


Experimental BET Surface Area → 6,200 m^2/g

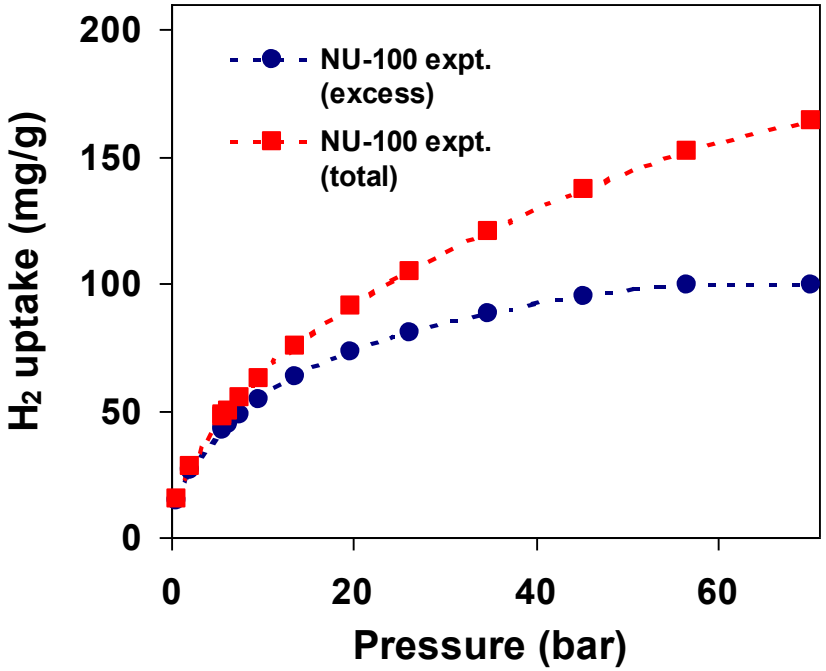
One gram of NU-100 has the same surface area as a soccer field



One pound of **NU-100** has a surface area of one square mile



NU-100. State-of-the-Art for



99.5 mg / g excess (56 bar)

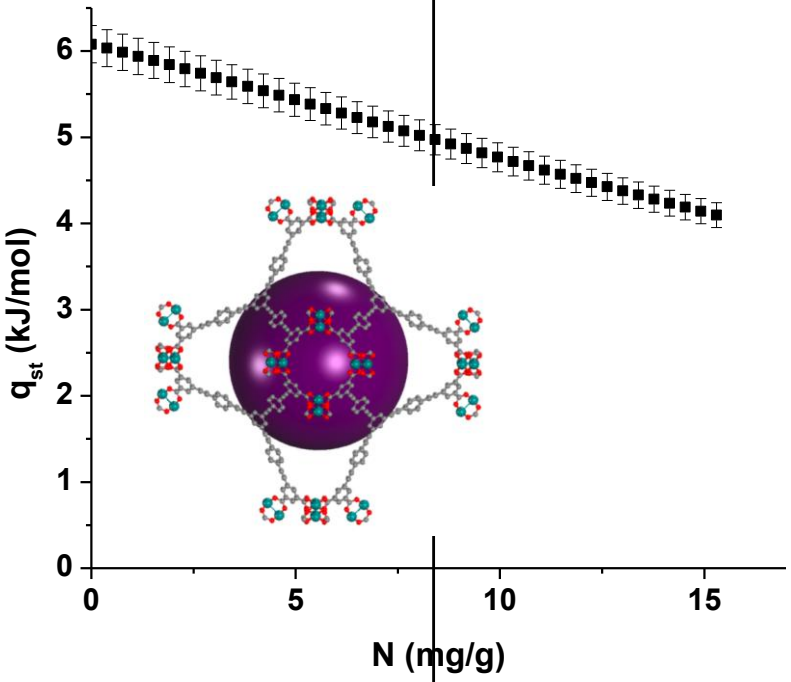
164 mg / g total

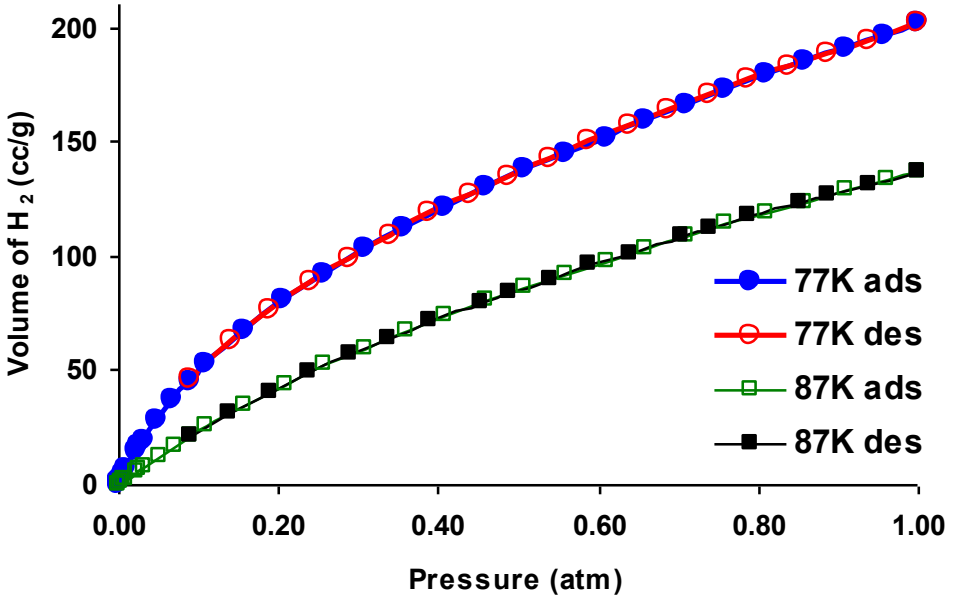
14.3 wt% total

45 g/L total

Farha, et al., *Nature Chemistry*, 2010.

NU-100. Ineffective at ambient temperature: Binding is too weak





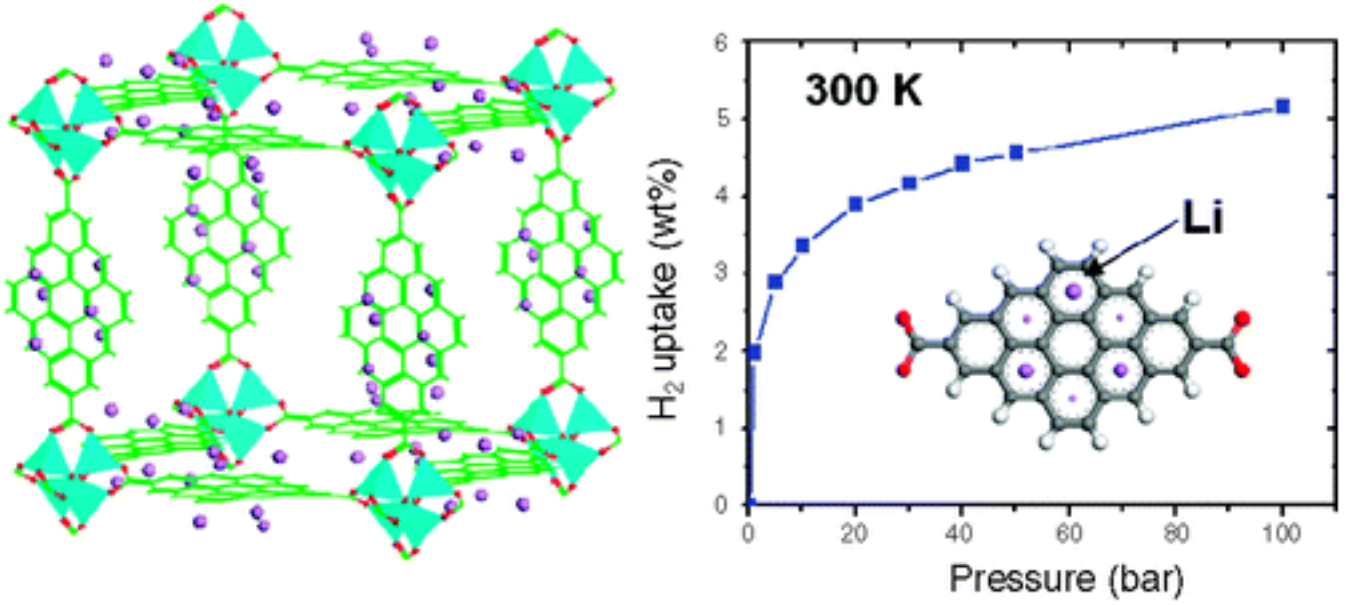
Farha, et al., *Nature Ch*

Goal: Enhance H_2 uptake via frame-work reduction and cation doping

- Enhanced London dispersion interactions due to enhanced strut polarizability?
- Adsorption of polarizable molecules due to electric field enhancement?
- Enhanced molecular adsorption due to charge/quadrupole interactions?

The major technical and scientific challenge in this area is to increase the heat of adsorption of H_2 to ca. 15-25 kJ/mol (to enable high loading at ambient temperature)

A Computational Example: >5 wt. % at 300K!



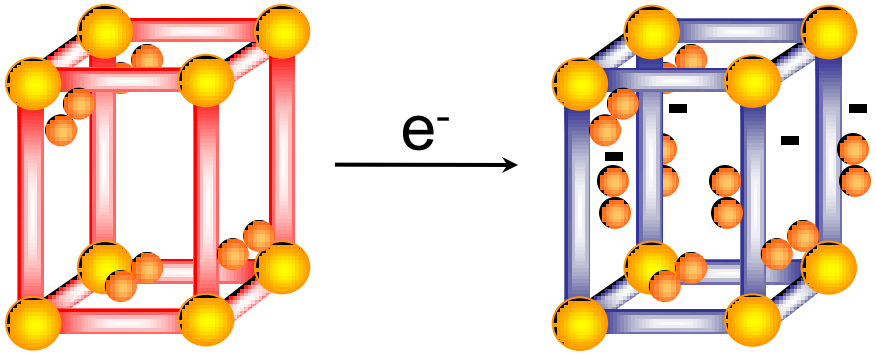
S. Han and W. A. Goddard III *J. Am. Chem. Soc., 2007, 129, 8422–8423*

(Mulfort, et al. Inorg. Chem. 2005)

Framework reduction and cation doping

Exploit organic struts within frameworks to introduce charge: enhance H_2 binding and uptake

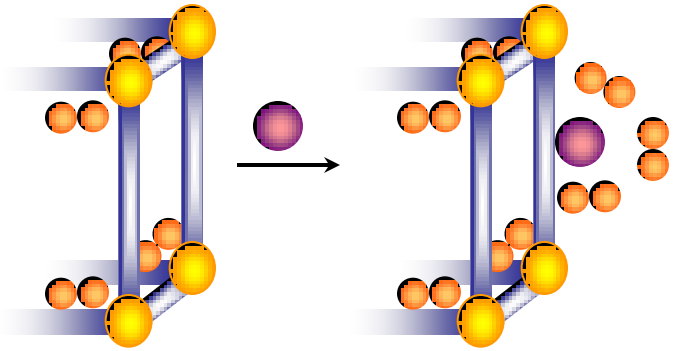
Chemically reduce struts



induced dipole – induced dipole

(strut) – (H_2)

Charge compensating cations

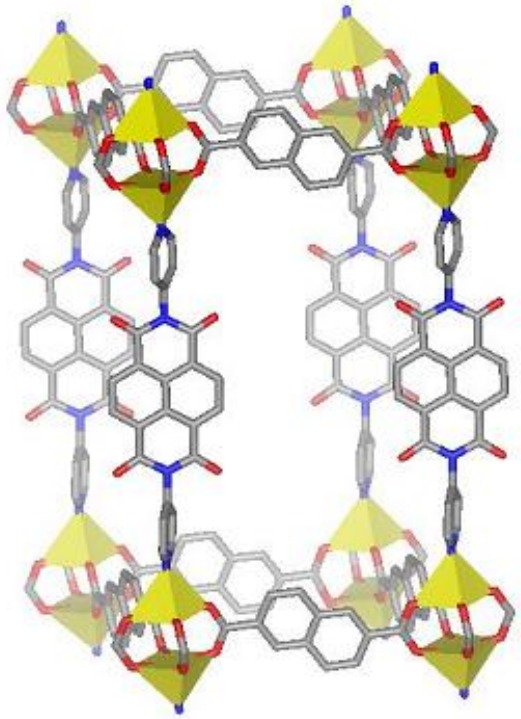


charge – quadrupole

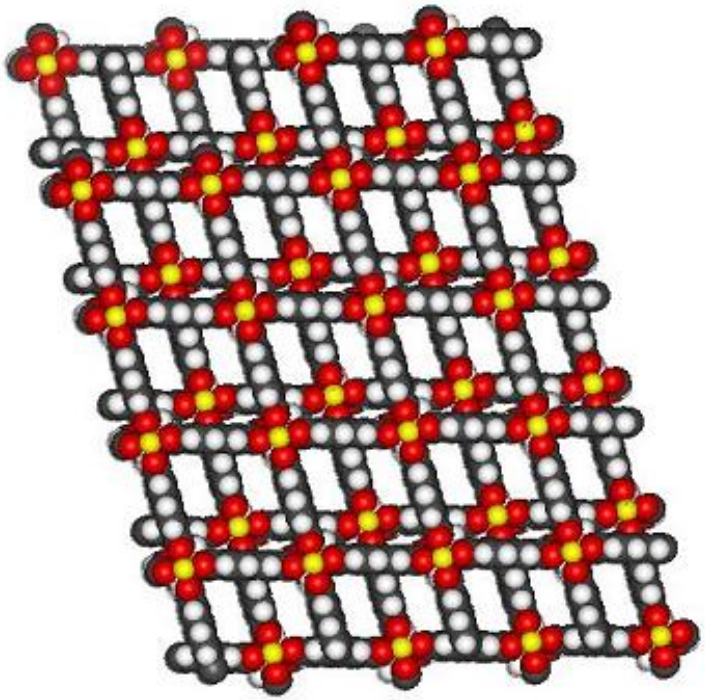
(cation) – (H_2)

Framework Reduction and Cation Doping

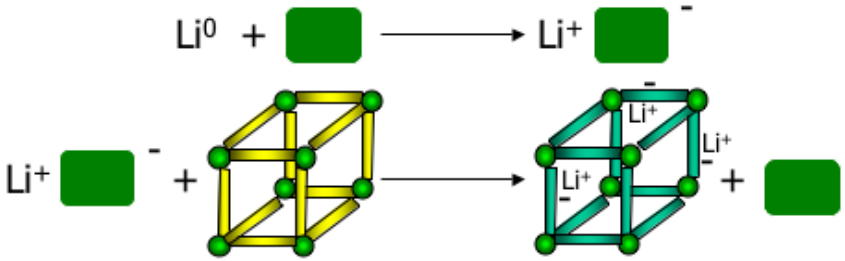
a reducible-framework material



A



B

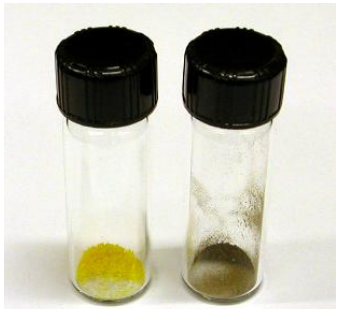


(One of two identical networks shown)

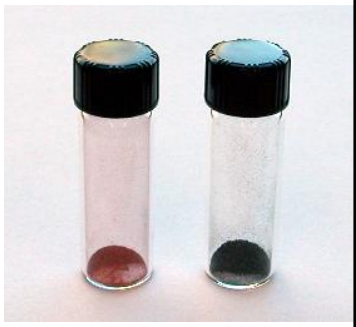
Observing Framework Reduction

- ✓ Solid state color changes mimic solution

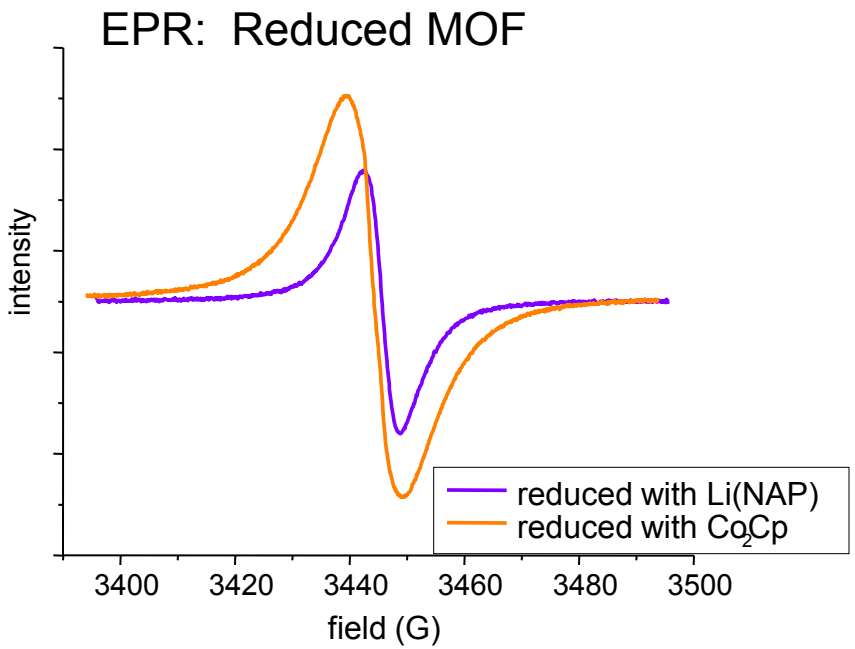
$Zn_2(NDC)_2(diPyNI)$ + Li(NAP)



$Zn_2(NDC)_2(diPyPI\text{-}Cl_4)$ + $CoCp_2$

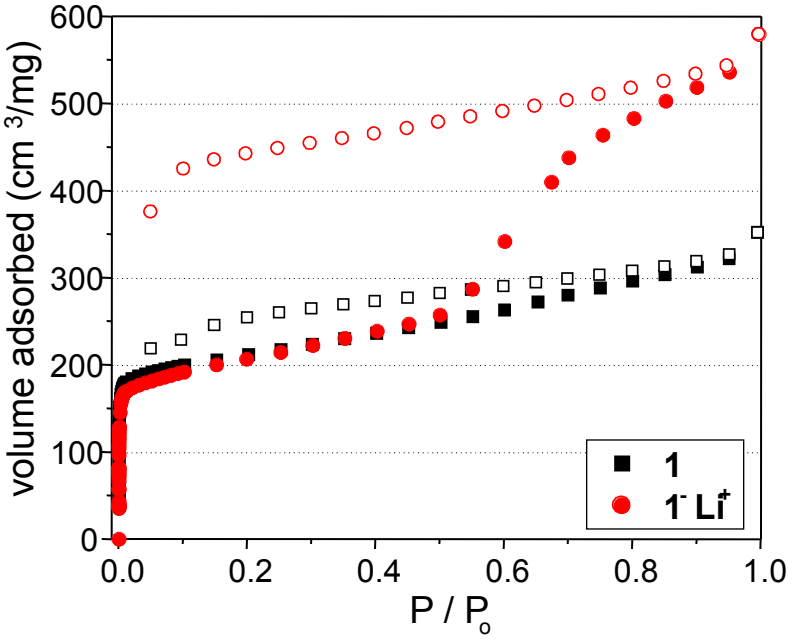


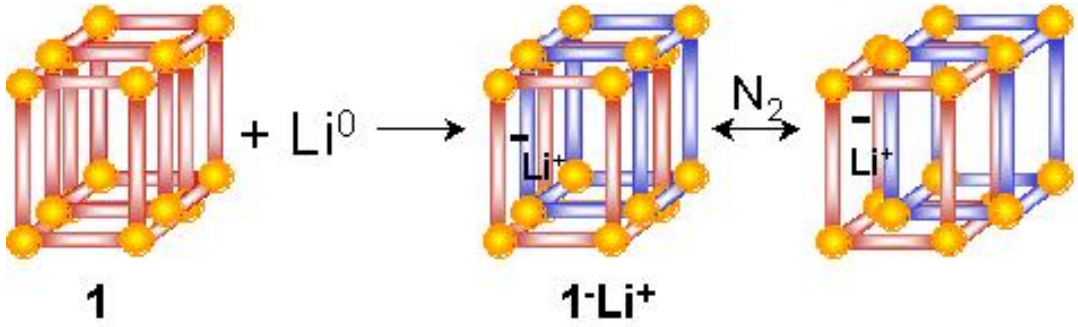
- ✓ Solid state EPR verifies presence of radicals



Consequences of Framework Reduction…

- $Zn_2(NDC)_2(diPyNI)$ is reduced upon exposure to Li^0 in DMF
- N_2 adsorption displays striking hysteresis w/5% lithium doping
- *Interpretation:* nitrogen loading dependent conversion between interwoven and interpenetrated forms of the MOF structure

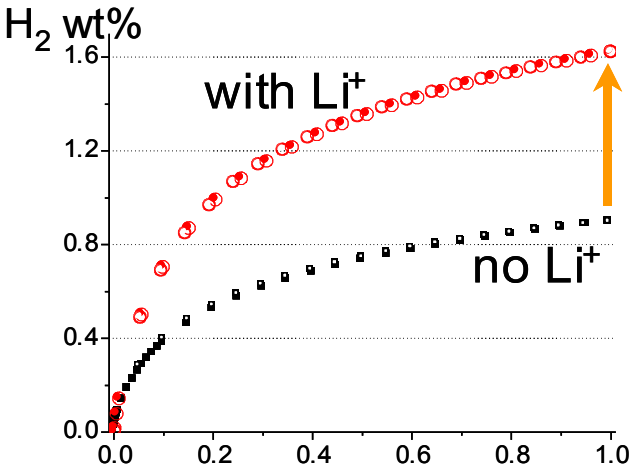


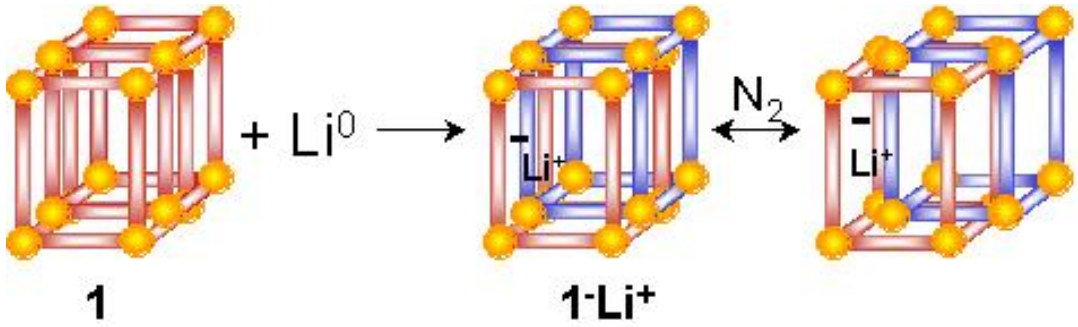


Consequences of Framework Reduction…

Hydrogen Adsorption

- $Zn_2(NDC)_2(diPyNI)$ is reduced upon exposure to Li^0 in DMF
- H_2 uptake is nearly doubled w/ Li^+ doping

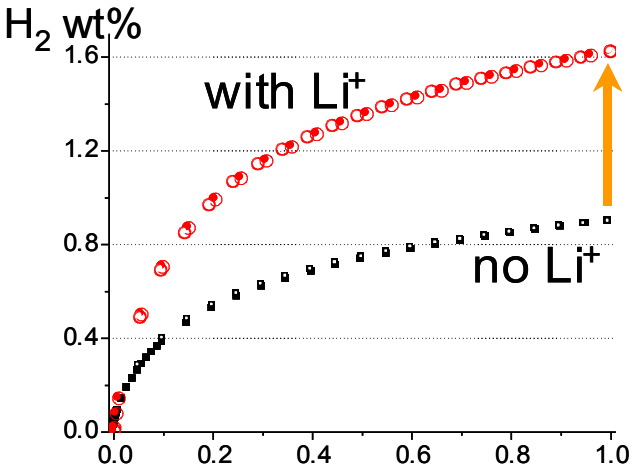


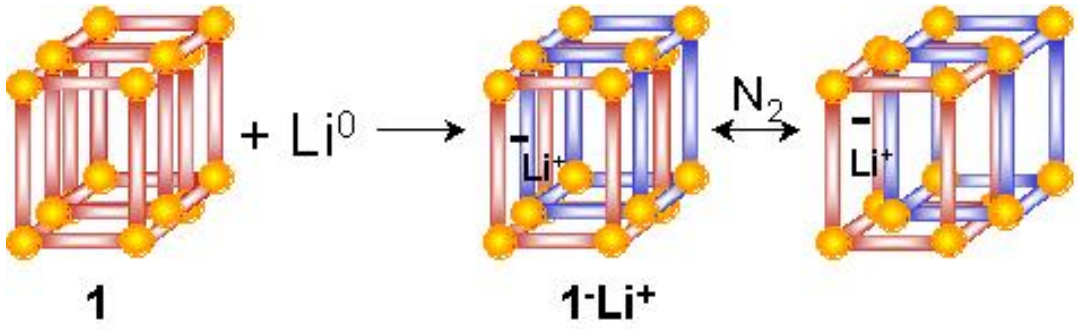


Consequences of Framework Reduction…

Hydrogen Adsorption

- $Zn_2(NDC)_2(diPyNI)$ is reduced upon exposure to Li^0 in DMF
- H_2 uptake is nearly doubled w/ Li^+ doping ➔ 48 H_2 molecules per Li^+ !

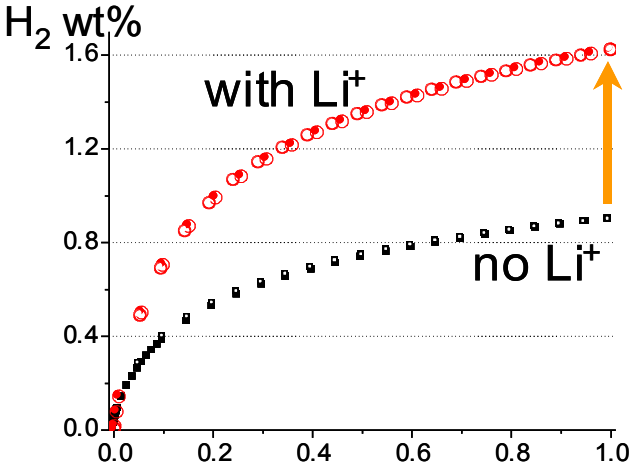


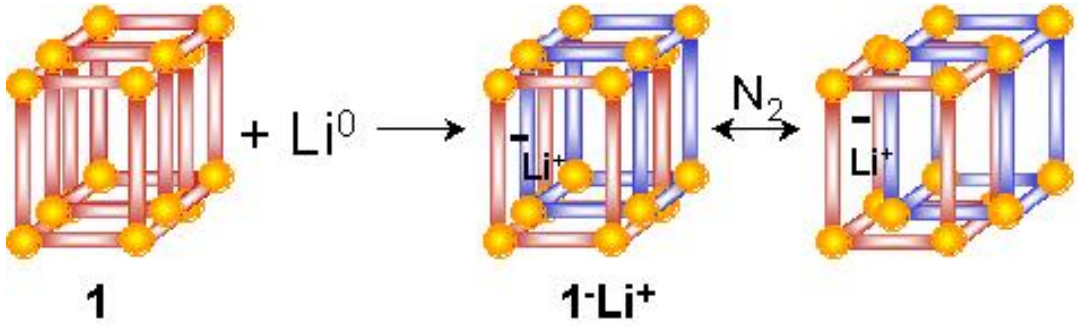


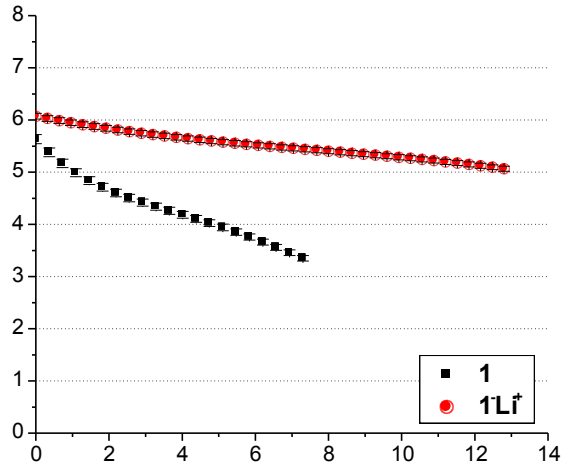
Consequences of Framework Reduction…

Hydrogen Adsorption

- $Zn_2(NDC)_2(diPyNI)$ is reduced upon exposure to Li^0 in DMF
- H_2 uptake is nearly doubled w/ Li^+ doping ➔ 48 H_2 molecules per Li^+ !
- Heat of adsorption only very slightly increases





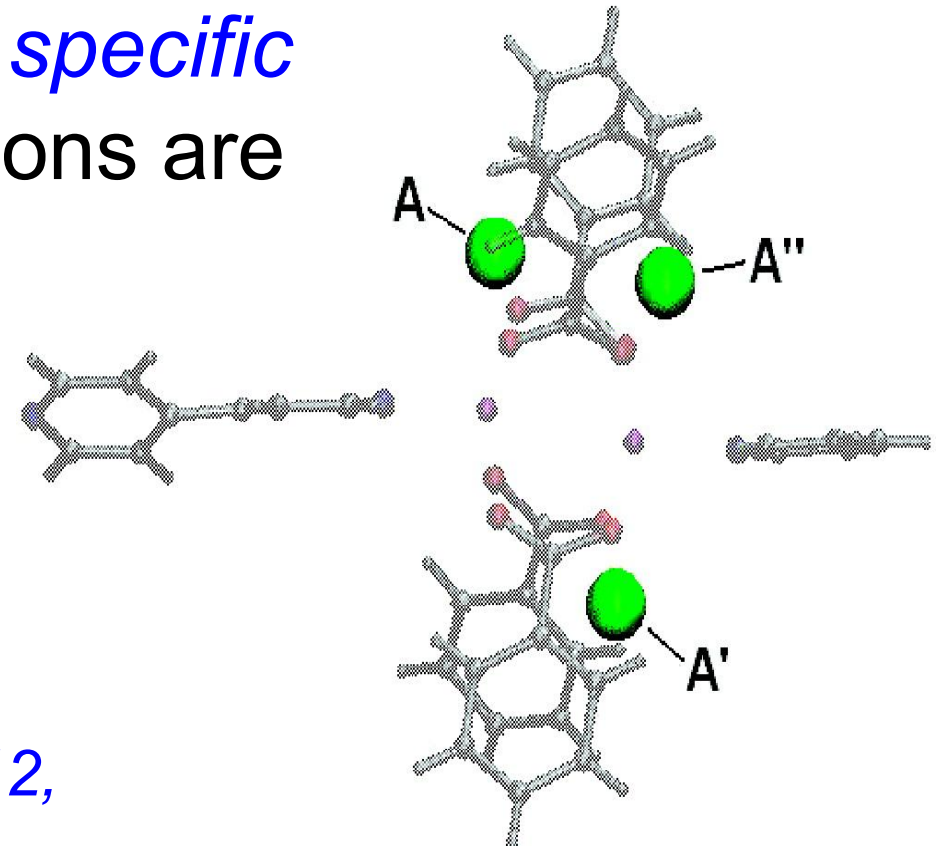


Goal: Enhance H_2 uptake via framework reduction and cation doping

- Enhanced London dispersion interactions due to enhanced strut polarizability?
- Adsorption of polarizable molecules due to electric field enhancement?
- Enhanced molecular adsorption due to charge/quadrupole interactions?
- Enhanced adsorption due to ion-induced displacement of catenated frameworks

Problem:

Ions are sited around catenated paddlewheel nodes ➔ desired *specific* cation/H_2 interactions are precluded



Dalach, Frost, Snurr, Ellis, J. Phys. Chem. C ***2008,*** *112, 9278-9284.*

Acknowledgments