The Interplay between Experiment and Simulation for the Design of New Metal-Organic Frameworks

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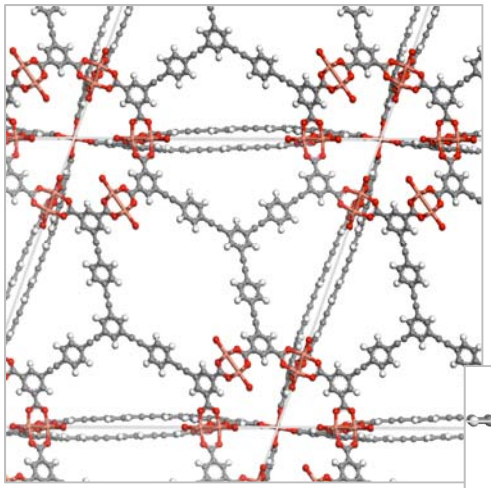
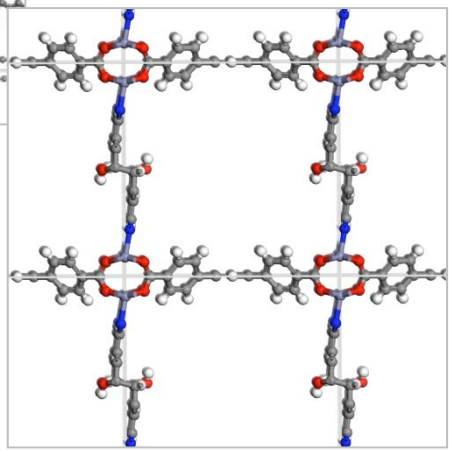
http://zeolites.cqe.northwestern.edu

Metal-Organic Frameworks

- "MOFs"
- Permanently porous, crystalline materials
- Metal or metal oxide nodes connected by organic "linker" molecules
- Large surface areas (up to 7000 m^2/g) and pore volumes
- Nodes and linkers can be tuned for desired purposes



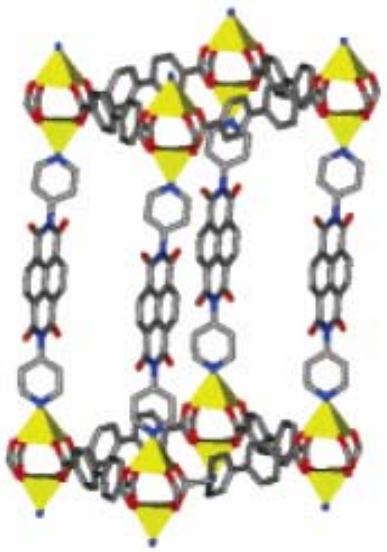
"NU-100"



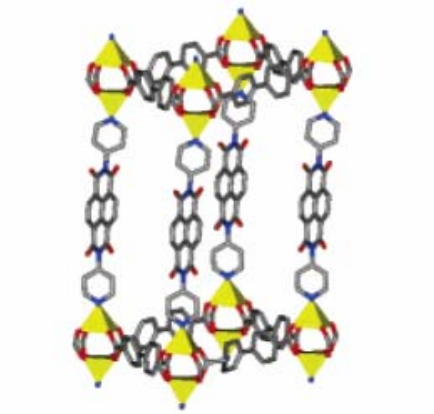
"DO-MOF"

Mulfort, Farha, Stern, Sarjeant, and Hupp, *J. Am. Chem. Soc.*, 2009.
Fahra, Yazaydin, Eryazici, Malliakas, Hauser, Kanatzidis, Nguyen, Snurr, and Hupp, *Nature Chem.*, 2010.

Molecular Tinker Toys



Materials Design



?

http://www.cottinginc.com/pressure-swing-adsorption.html

Can tune material properties via synthesis

- pore size
- linker functionality
- open-metal sites
- extraframework cations or anions

Can also modify MOFs after their synthesis

Outline

Molecular-level modeling is playing an important role in the development of new MOFs and in increasing our understanding of their properties.

→ Can we design new MOFs on the computer?

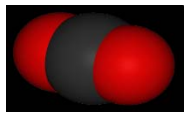
- Computer-aided design of new MOFs for
  - natural gas storage
  - hydrogen storage

- High-throughput screening of hypothetical MOFs for natural gas storage

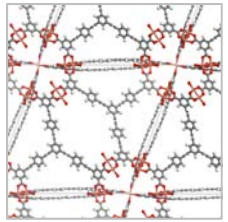
Molecular Simulation of Adsorption

Input

System specifications (T,P, fluids …)
Models for fluid and solid
Force field to describe interactions



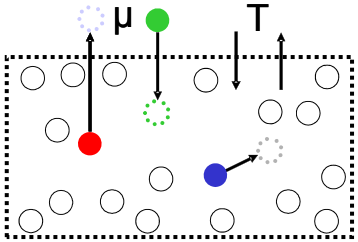
CO_2



MOF structure

Simulation methods based on statistical mechanics

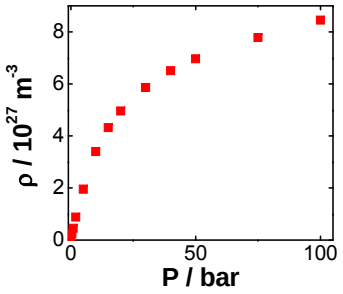
Grand canonical Monte Carlo (GCMC)
Molecular dynamics (MD)



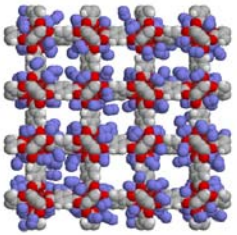
GCMC simulation

Output

Adsorption isotherms
Heats of adsorption
Adsorption selectivity for mixtures
Molecular-level structural information



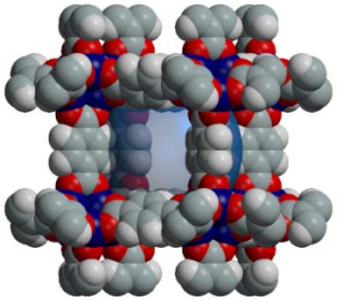
adsorption isotherm



molecular siting

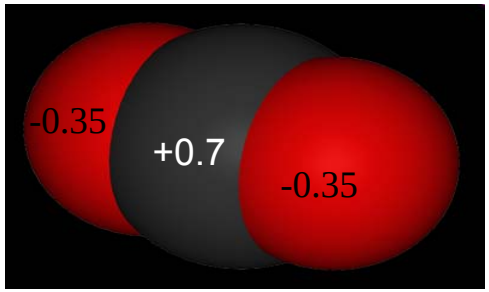
Simulation Model

- Atomistic representation of MOFs



- MOF atoms are held fixed at their crystallographic coordinates.
- Lennard-Jones parameters taken from the DREIDING force field.
- Charges on framework atoms from quantum chemical calculations.

- Atomistic representation of guest molecules
  - E.g. CO_2/CO_2 parameters taken from TraPPE force field that matches bulk vapor/liquid equilibria*
  - Lennard-Jones + Coulomb

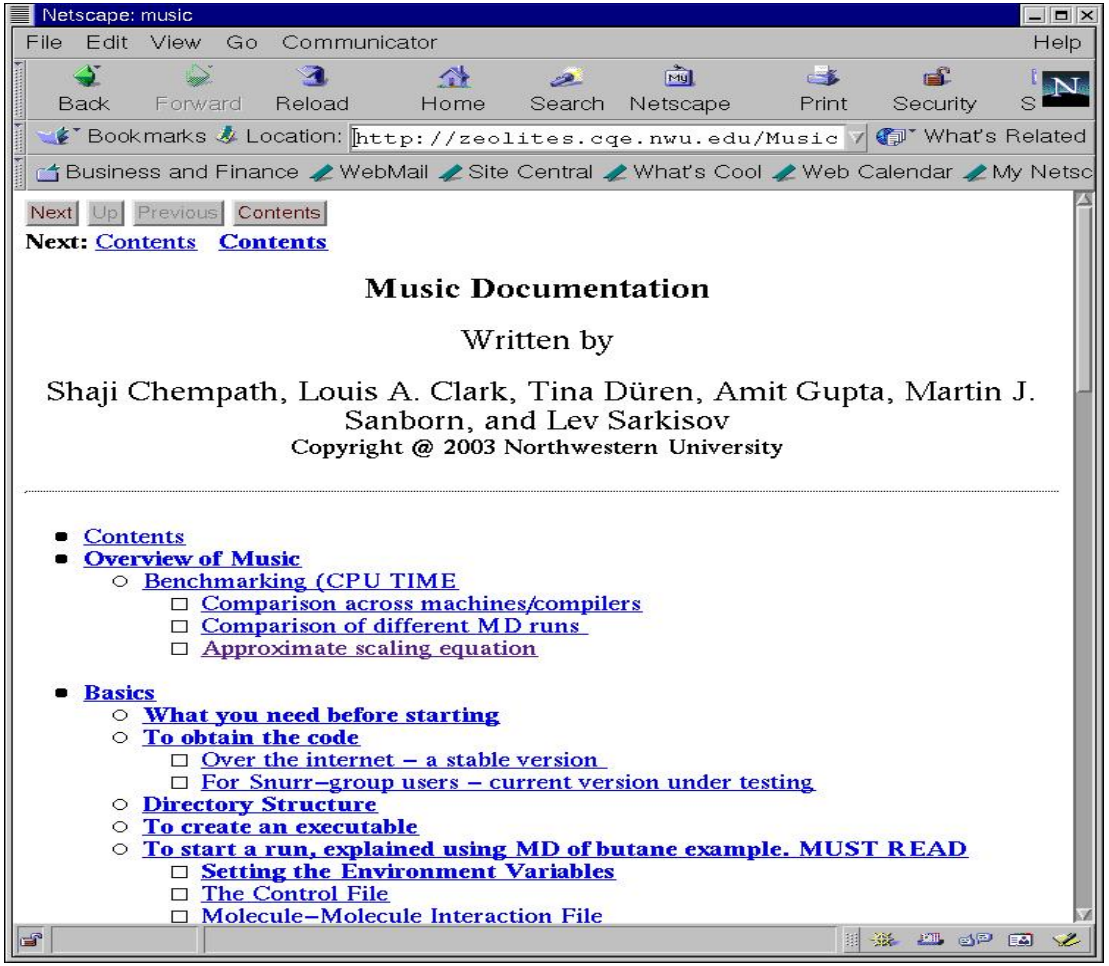


* Potoff, Siepmann, *AIChE J.*, 2001.

Molecular Simulation Code

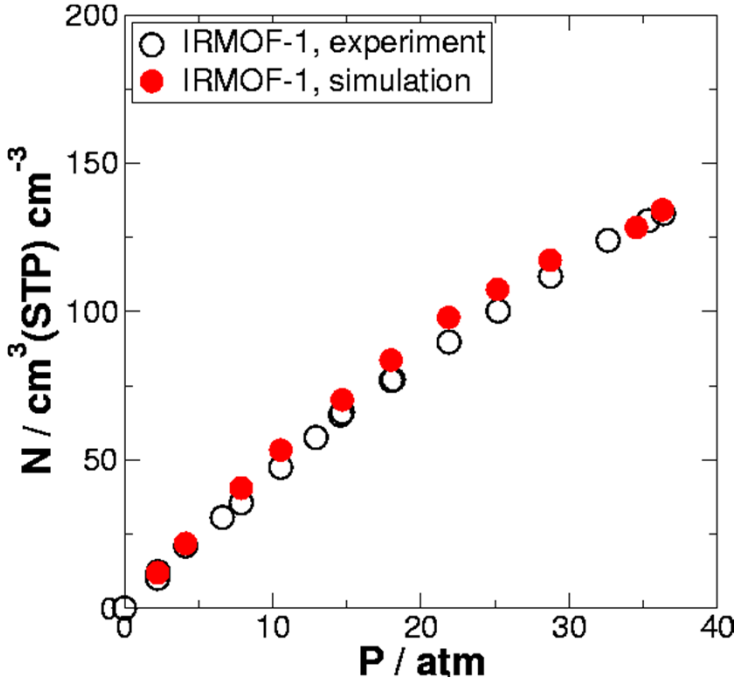
Music – **mu**ltipurpose **si**mulation **c**ode

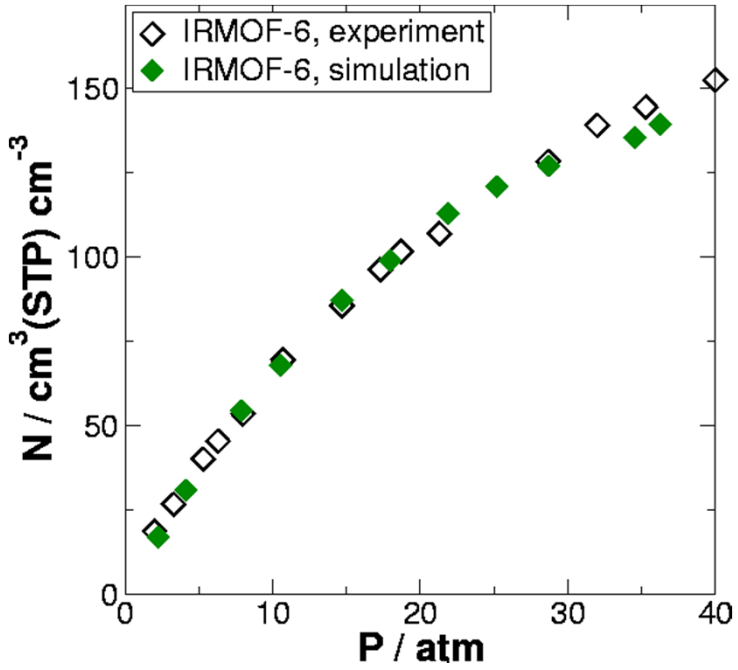
- Object-oriented F90 code
- Capable of GCMC, MD
- Publicly available from our web site

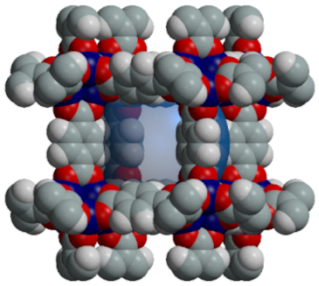


Gupta, Chempath, Sanborn, Clark, Snurr, *Molecular Simulation*, 2003.
Chempath, Düren, Sarkisov, Snurr, *Molecular Simulation*, 2013.

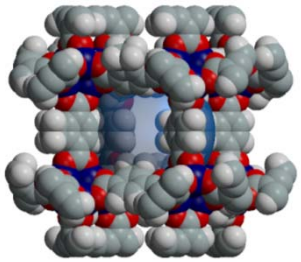
Predicted CH_4 Adsorption Isotherms







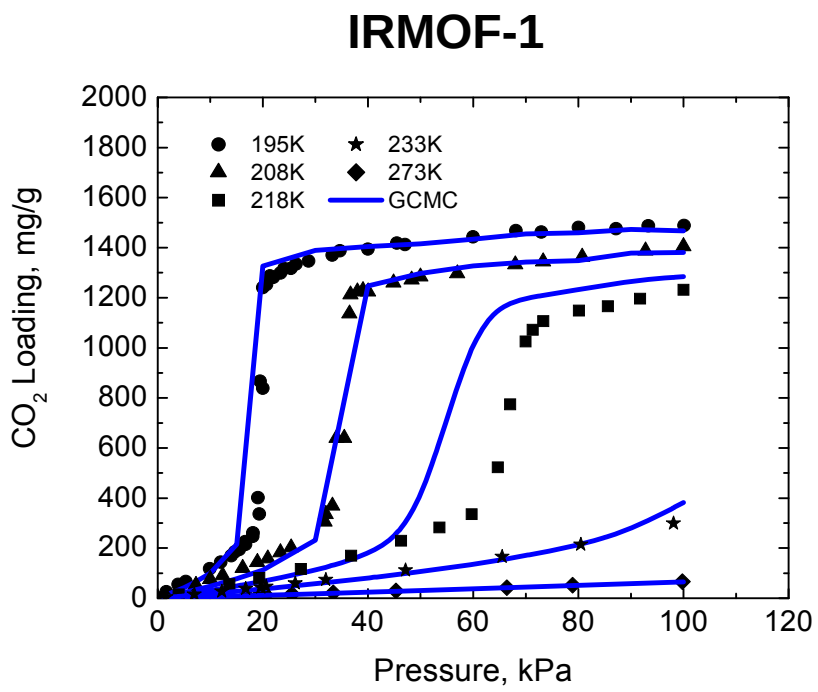
IRMOF-1



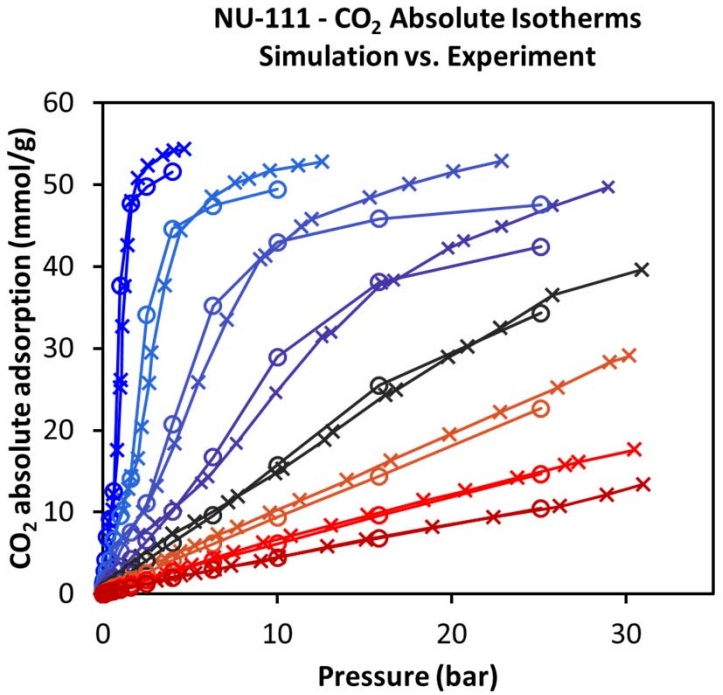
IRMOF-6

Düren, Sarkisov, Yaghi, Snurr, *Langmuir*, 2004.

CO_2 Adsorption in MOFs



Walton, Millward, Dubbeldam, Frost, Low, Yaghi, Snurr, *J. Am. Chem. Soc*., 2008.



Peng, Srinivasa, Wilmer, Eryazici, Snurr, Hupp, Yildirim, Farha, *Chem. Commun*., 2013.

Working Hypothesis

Molecular modeling can predict adsorption of small molecules in rigid MOFs that do not have strongly-interacting functional groups in good agreement with experiment.

Challenges:

- Flexible MOFs
- MOFs with interesting functional groups

Outline

Molecular-level modeling is playing an important role in the development of new MOFs and in increasing our understanding of their properties.

→ Can we design new MOFs on the computer?

- Computer-aided design of new MOFs for
  - natural gas storage
  - hydrogen storage

- High-throughput screening of hypothetical MOFs for natural gas storage

Storage of Natural Gas

Compressed Natural Gas

- rather heavy pressure vessels
- storage at pressure > 207 bar requires expensive multistage compression
- energy density is lower than in gasoline

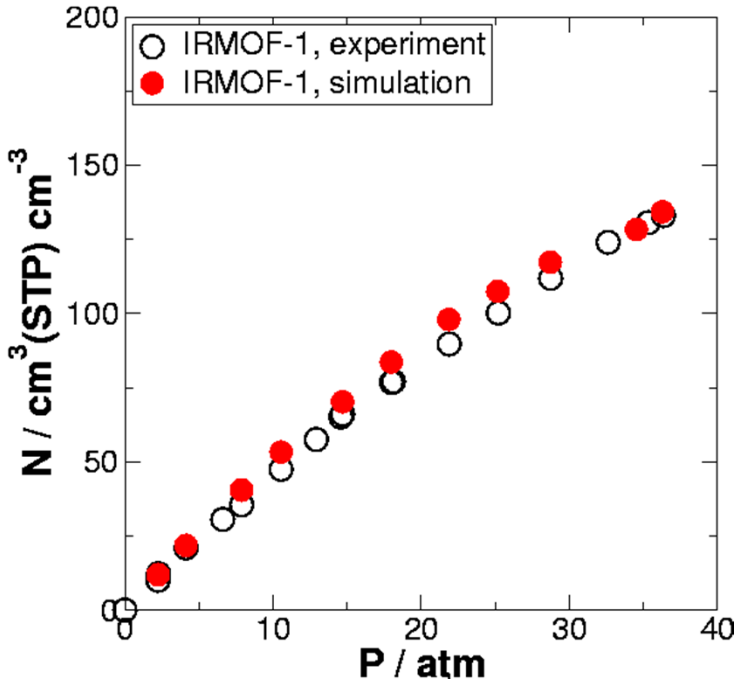
Alternative: Adsorbed Natural Gas

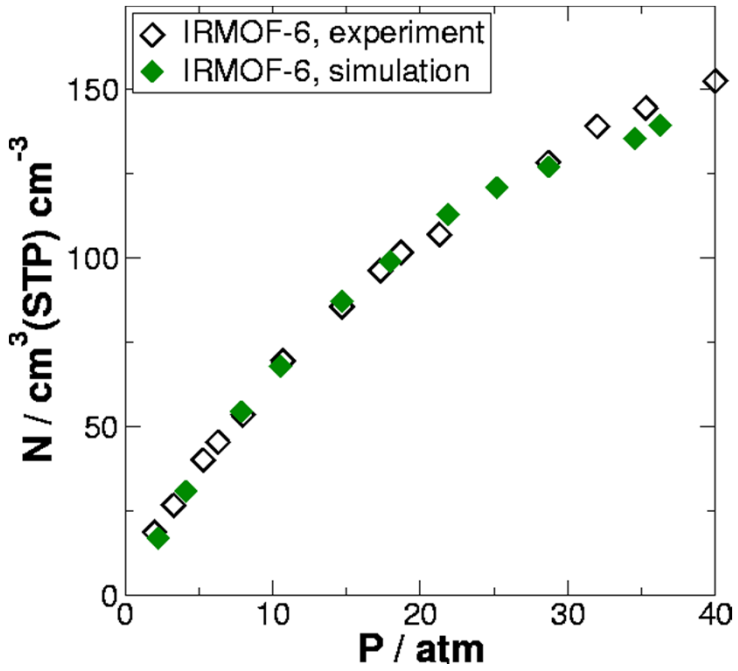
- storage by physical adsorption at lower pressure
- less expensive compression
- lower cost of storage vessels

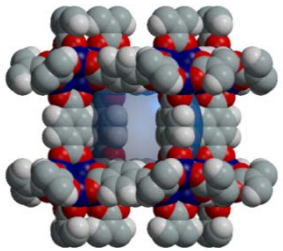
DOE target: 180 cm^3(STP) / cm^3 at 35 bar

ARPA-E target: ~300 cm^3(STP) / cm^3

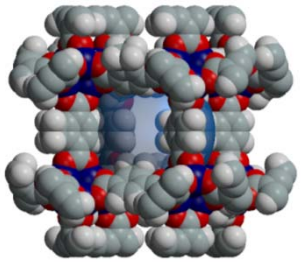
Predicted CH_4 Adsorption Isotherms







IRMOF-1



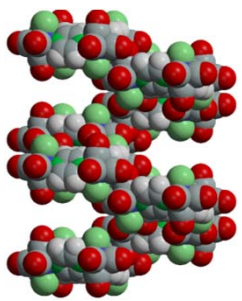
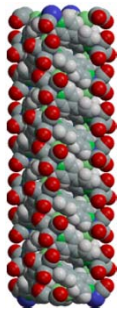
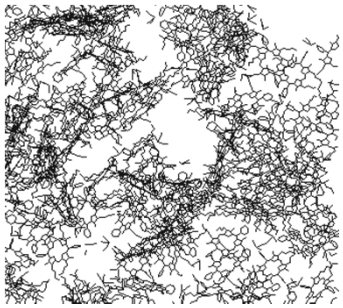
IRMOF-6

Why is the methane uptake so high?

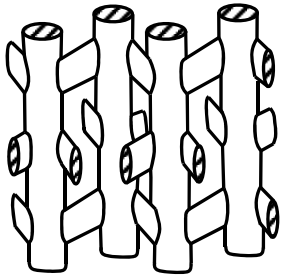
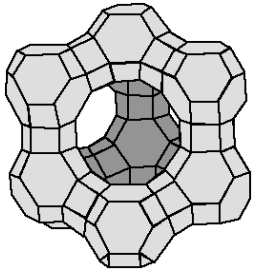
Düren, Sarkisov, Yaghi, Snurr, *Langmuir*, 2004.

Comparison with Other Adsorbents

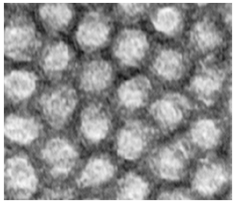
- Molecular squares
  - pyrazine squares
  - bipyridine squares
  - porphyrin squares

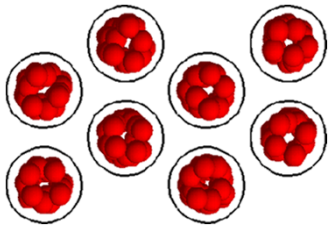
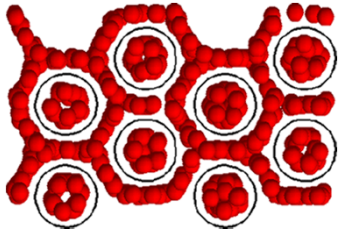
- Zeolites
  - silicalite
  - faujasite

- MCM-41



- Carbon nanotubes (CNT)
  - with and without
  - interstitial adsorption

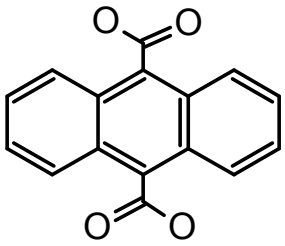
Methane Storage

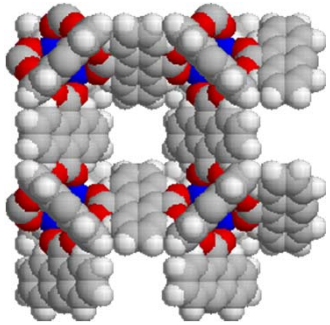
- Optimal material for CH_4 storage should have
  - large accessible surface area
  - high free volume (large capacity)
  - high heat of adsorption
  - narrow pore size distribution
  - low crystalline density (if high storage per gram is important)
- GCMC simulations can reveal the complex interplay of properties responsible for CH_4 adsorption.
- Using these insights, GCMC simulations can be used to screen new candidate materials before their synthesis…

Düren, Sarkisov, Yaghi, Snurr, *Langmuir*, 2004

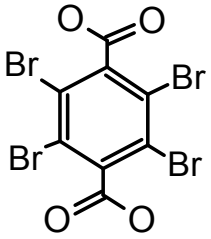
Rational Design of New IRMOFs

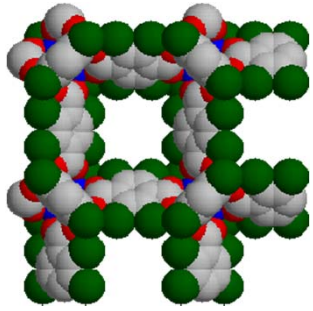
IRMOF-Anthracene

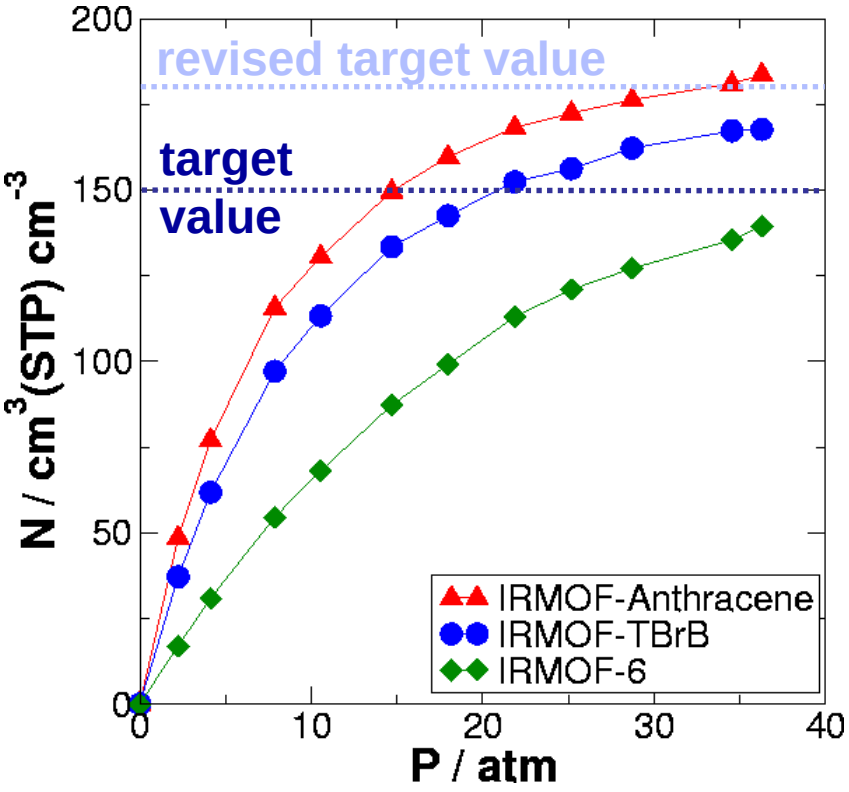




IRMOF-TBrB

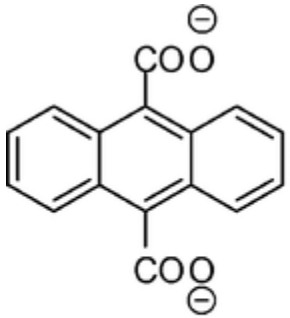




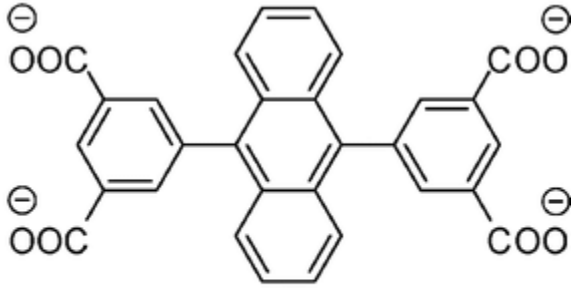


at 35 bar	IRMOF-6	IRMOF-TBrB	IRMOF-Anthracene
N / cm^3(STP) cm^{-3}	135.5	167.2	181.0

PCN-14



adc^{2-}



$adip^{4-}$

- PCN-13
- Limited methane uptake

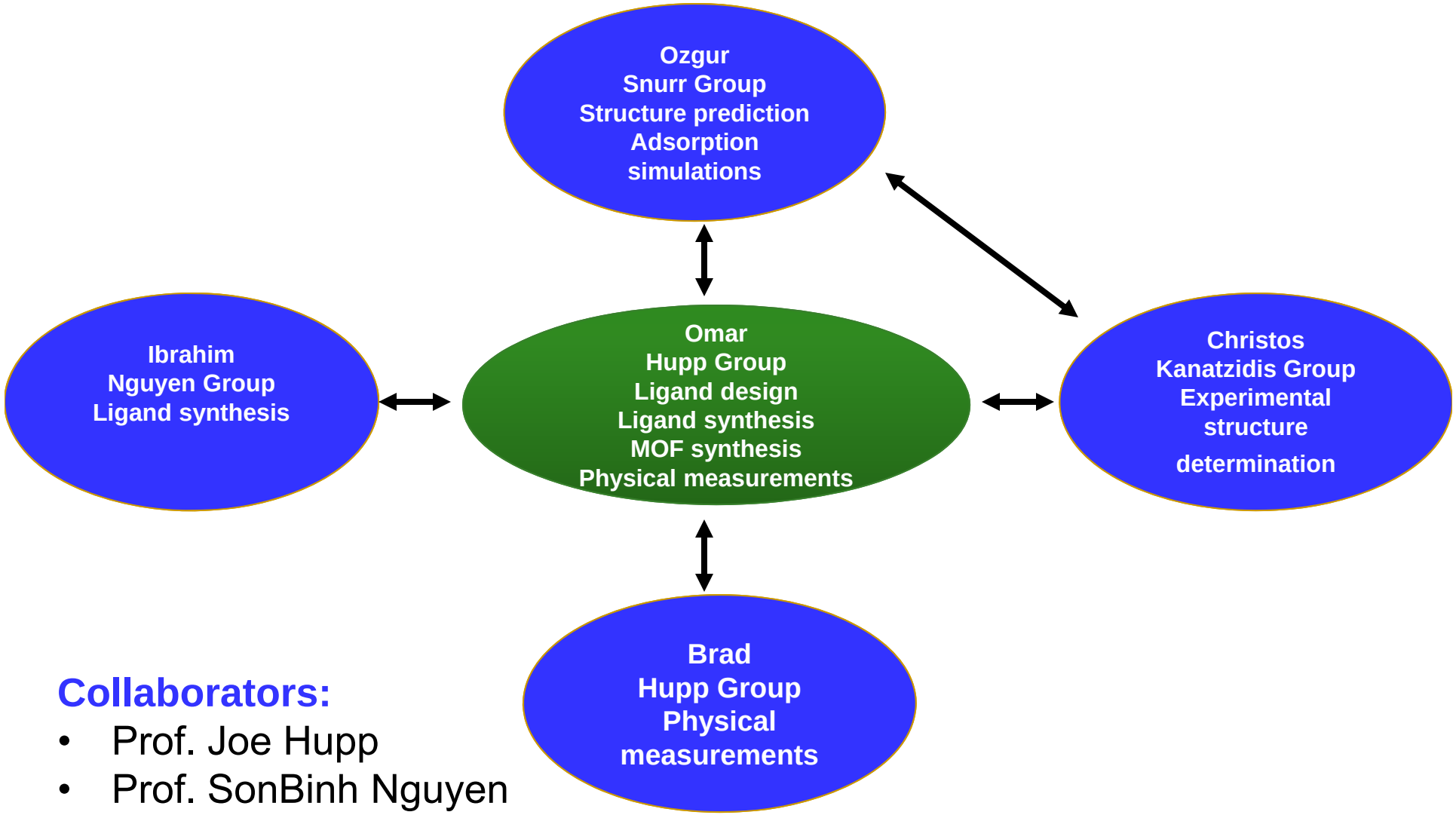
- PCN-14
- Record methane uptake

Ma, Sun, Simmons, Collier, Yuan, Zhou, *J. Am. Chem. Soc.,* 2008

From Modeling to Reality

Farha, Yazaydin, Eryazici, Malliakas, Hauser, Kanatzidis, Nguyen, Snurr, Hupp, *Nature Chem.,* 2010.

High Surface Area MOFs: Team Approach



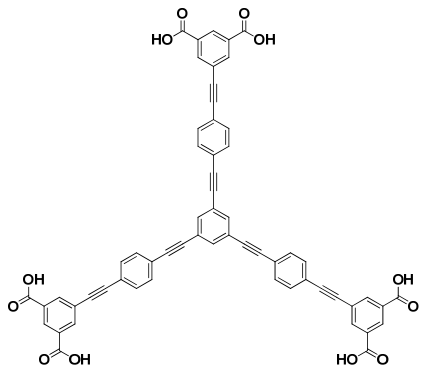
Collaborators:

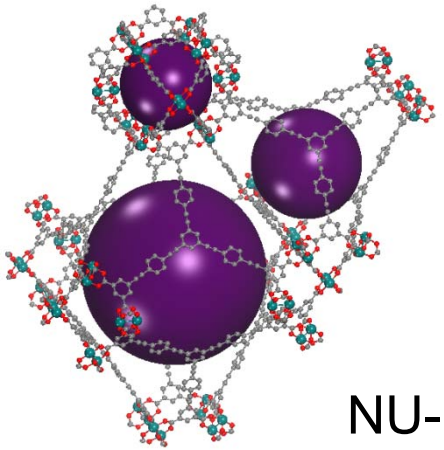
- Prof. Joe Hupp
- Prof. SonBinh Nguyen
- Prof. Mercouri Kanatzidis
- **Prof. Omar Farha**

Computational Design of a High Surface Area MOF

Known MOF topology from literature

+

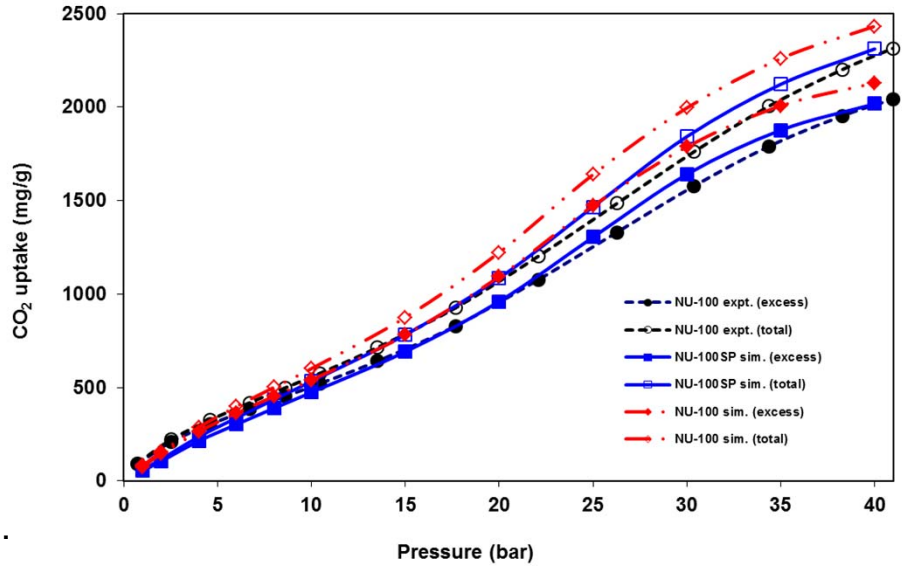




NU-100

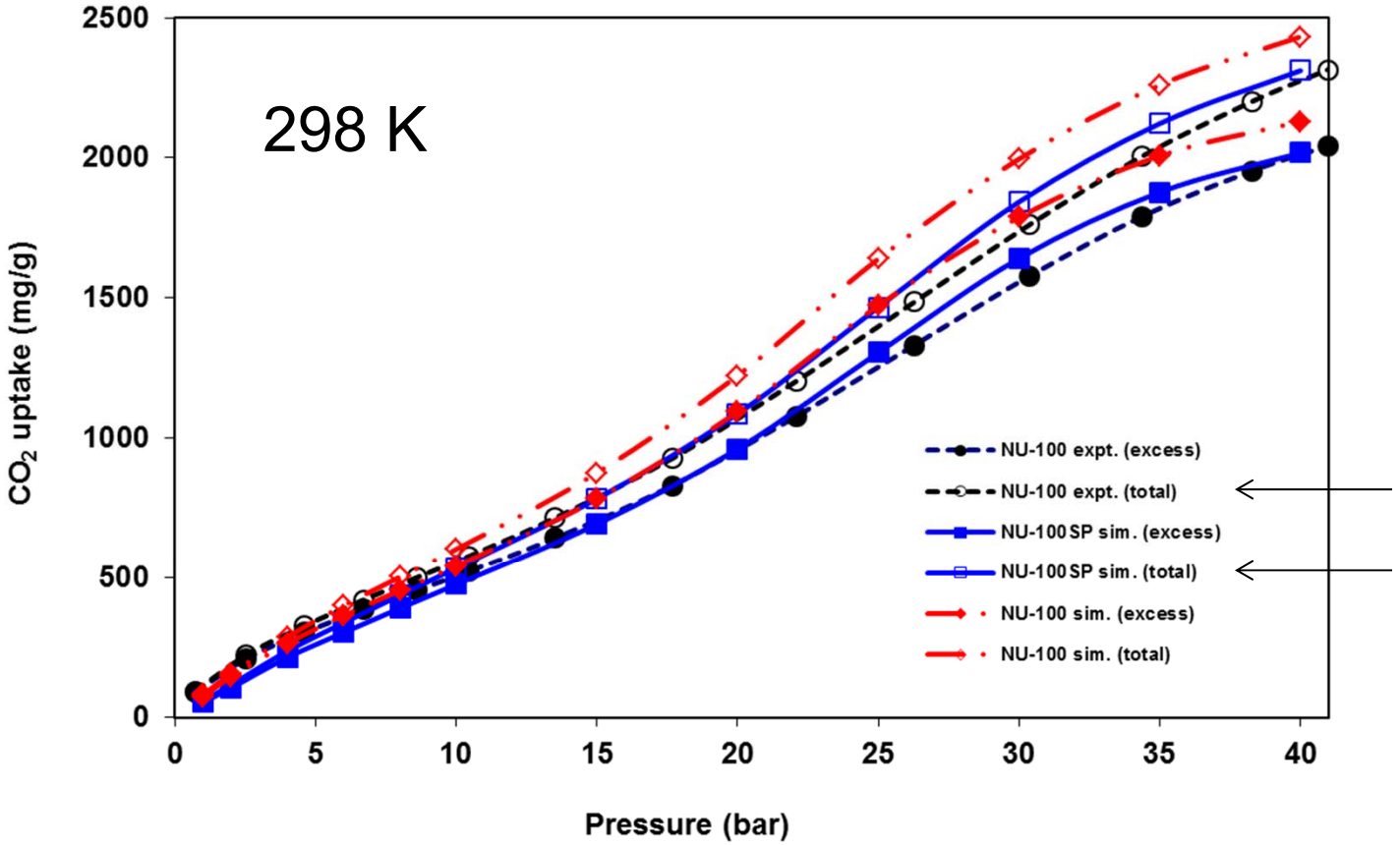
M. Schroder et al. and
H-C. Zhou et al. and
Zawarotko et al.

This new MOF was constructed and evaluated on the computer before synthesis.

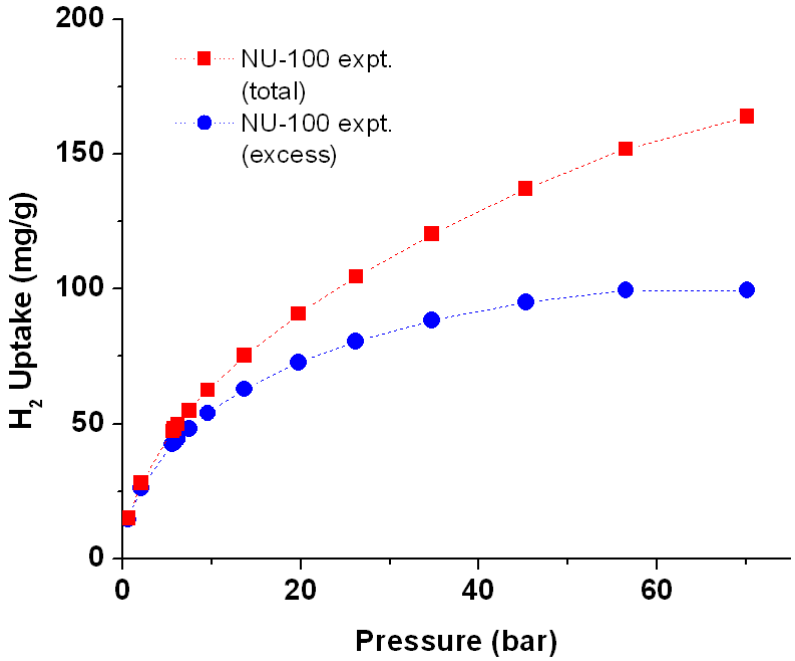


Farha, Yazaydin, Eryazici, Malliakas, Hauser, Kanatzidis, Nguyen, Snurr, Hupp, *Nature Chem.,* 2010.

CO_2 Adsorption



Hydrogen Storage



DOE targets at 100 bar and ambient temperature:

5.5 wt%

40 g/L

Hydrogen uptake at 77 K

Excess 99.5 mg / g

9 wt%

28 g/L

Total 164 mg / g

14 wt%

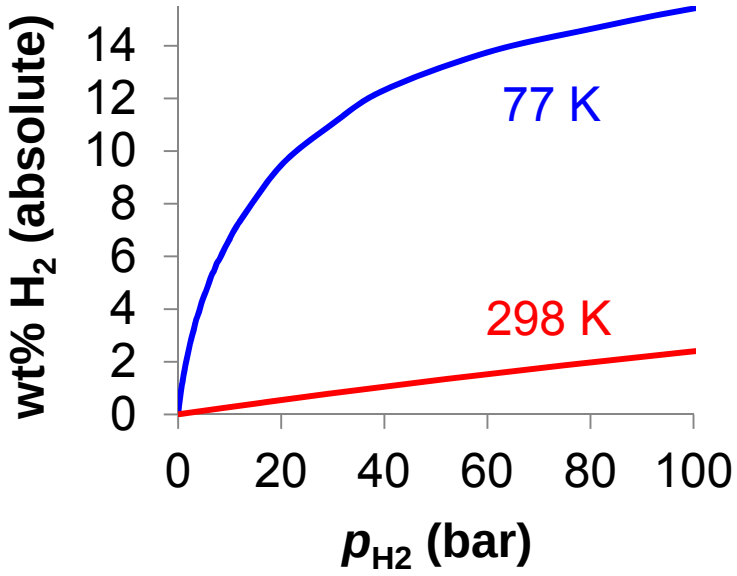
45 g/L

These excess values are the highest reported to date at 77 K.

Room Temperature Storage?

Enthalpy of adsorption for H_2 in NU-100 is ~ 6 kJ/mol: weak physisorption.

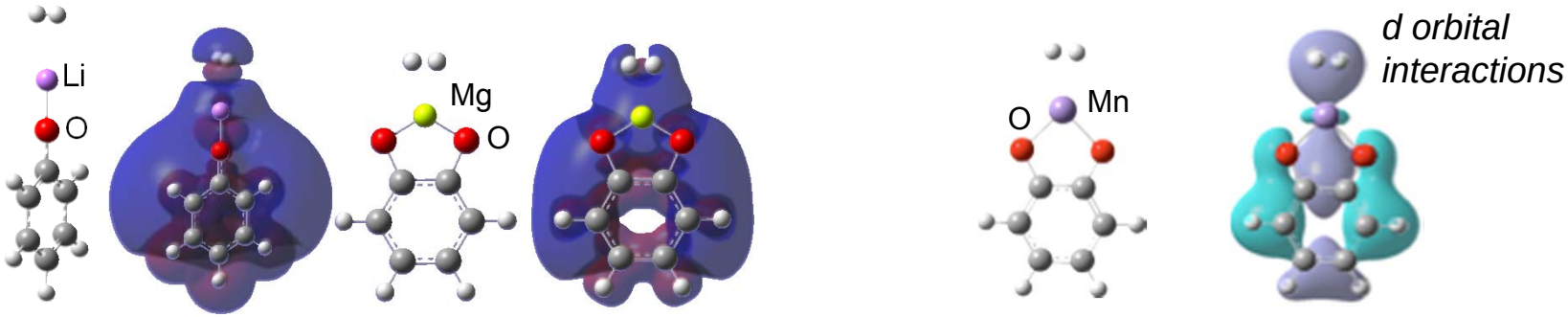
For room temperature storage, we need ~20 kJ/mol.



Improved Adsorption Enthalpies

Computational exploration of metal-alkoxides

- Li-alkoxide MOFs do not meet DOE hydrogen storage targets.
- Divalent cations have larger electric fields than Li.
- Transition metals can interact strongly with hydrogen.



Getman, Miller, Wang, Snurr, *J. Phys. Chem. C*, 2011.
Brand, Colon, Getman, Snurr, *Micropor. Mesopor. Mater.*, 2013.

Outline

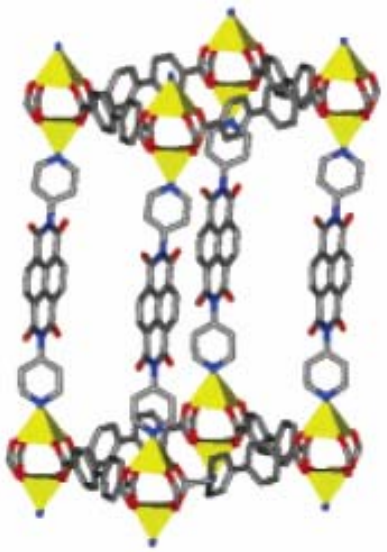
Molecular-level modeling is playing an important role in the development of new MOFs and in increasing our understanding of their properties.

→ Can we design new MOFs on the computer?

- Computer-aided design of new MOFs for
  - natural gas storage
  - hydrogen storage

- High-throughput screening of hypothetical MOFs for natural gas storage

Molecular Tinker Toys

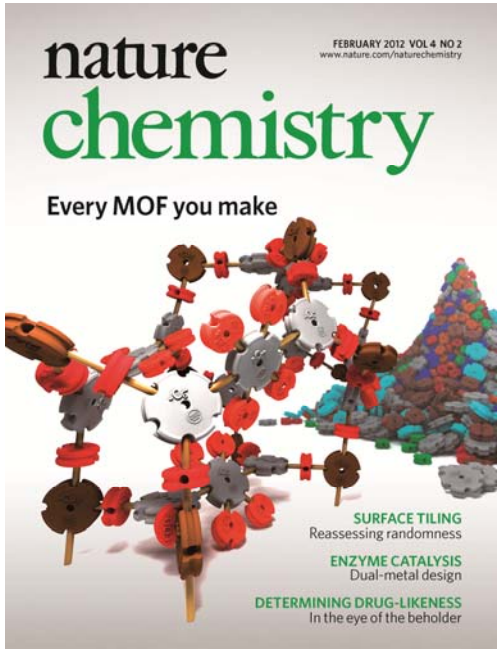


How can we more rapidly find the best MOFs for a given application?

Virtual High-Throughput Screening

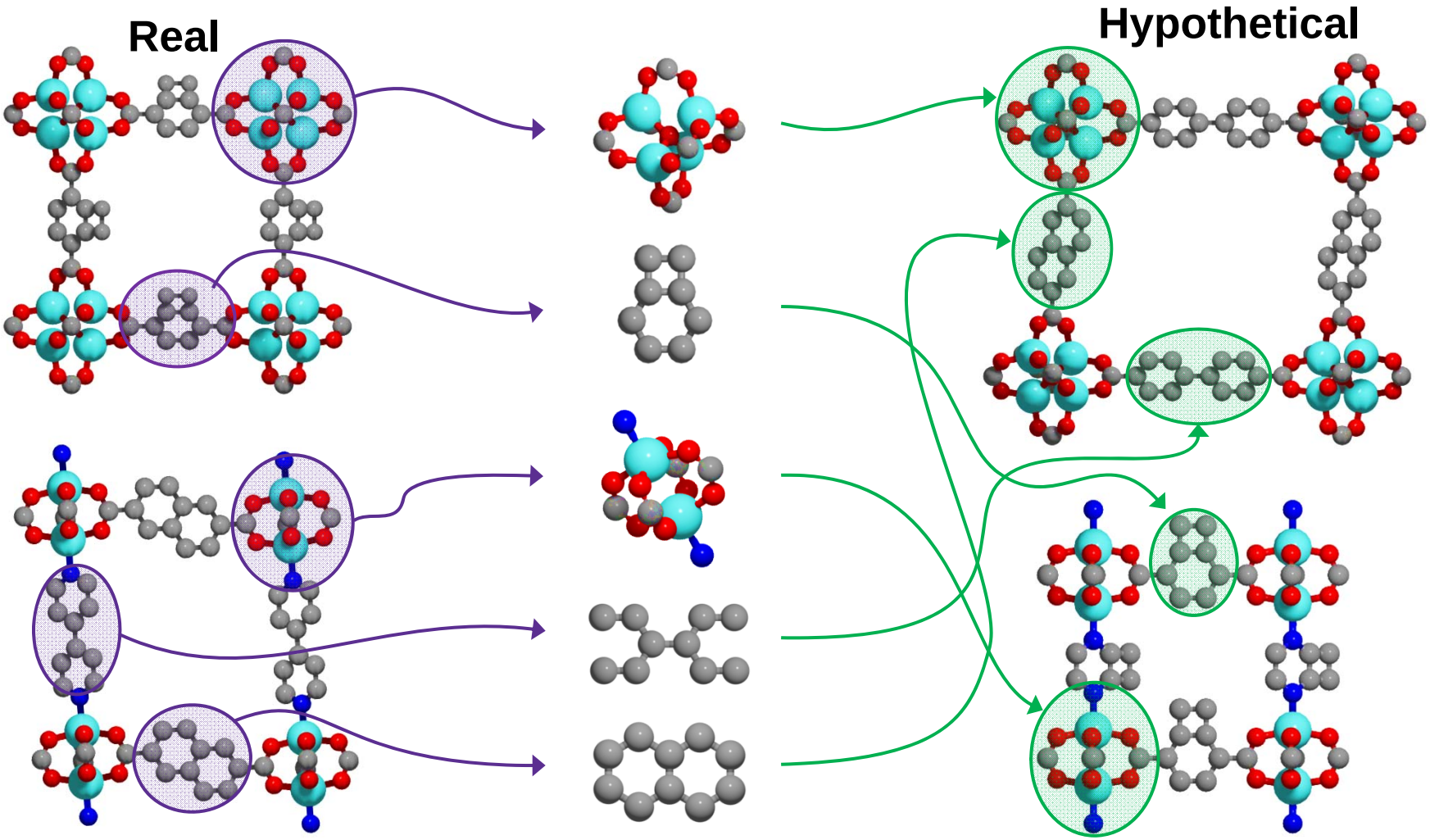
Crystal generator for hypothetical MOFs

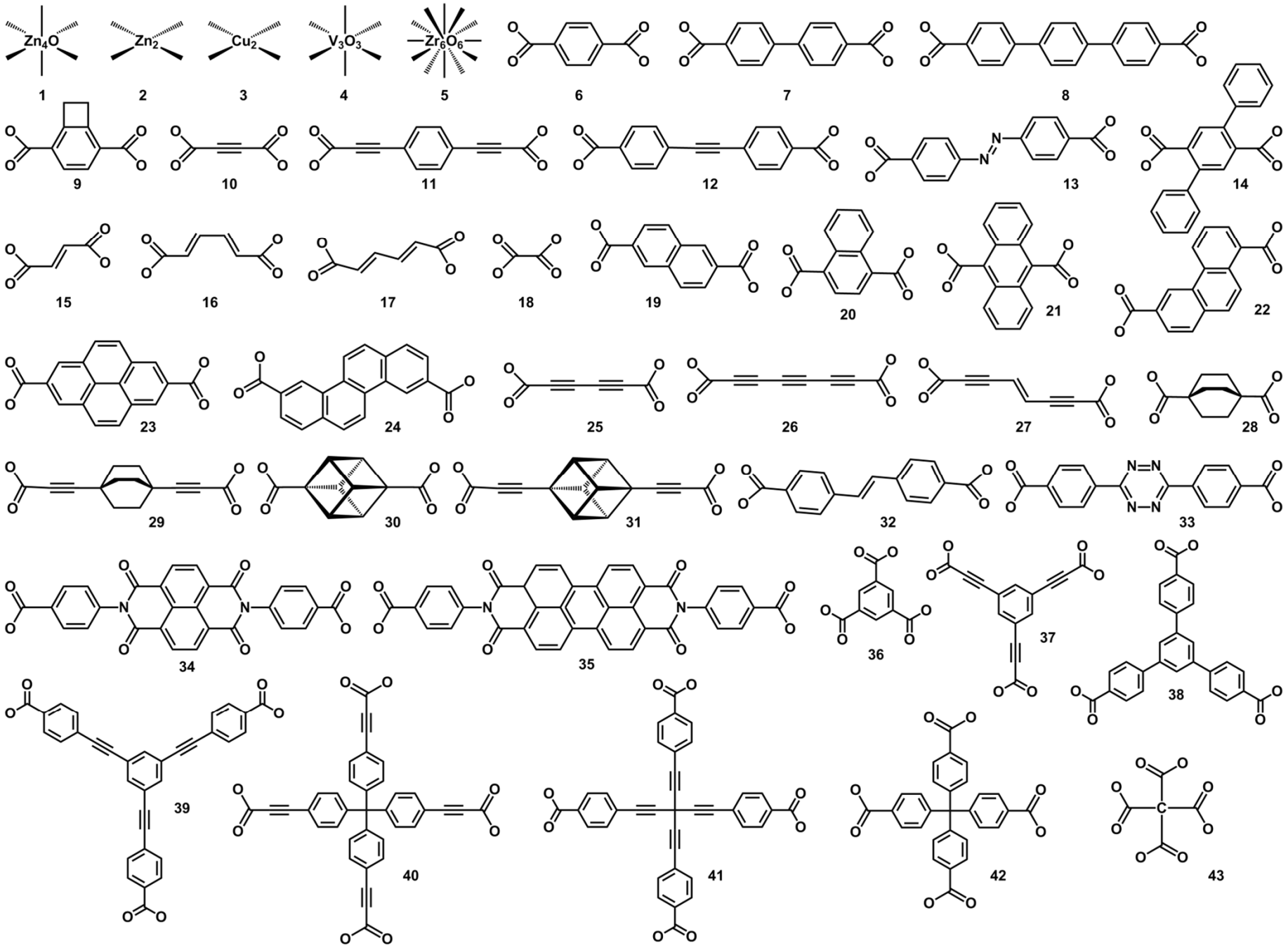
- Systematically generates MOF structures from a library of building blocks
- Created a large database of hypothetical MOFs (over 137,000 entries and growing)
- Designed for high-throughput screening of physical properties



Wilmer, Leaf, Lee, Farha, Hauser, Hupp, Snurr, *Nature Chem.*, 2012.

Virtual High-Throughput Screening




Zn4O
Zn2
Cu2
V3O3
Zr6O6
1
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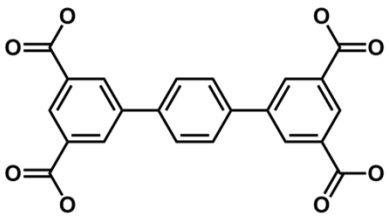
Continued…



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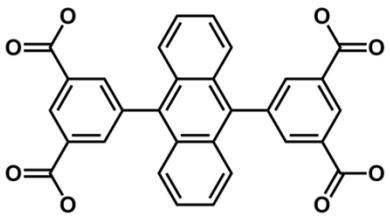

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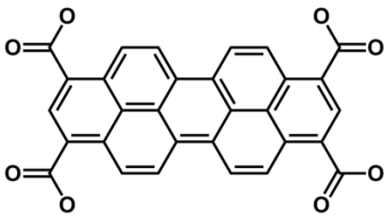

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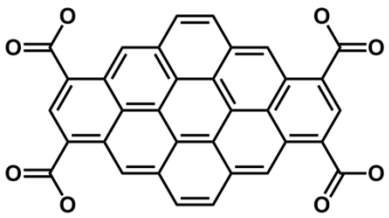

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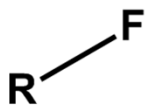
+ functional groups…



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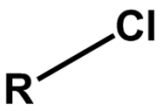

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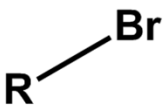

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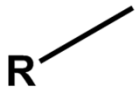

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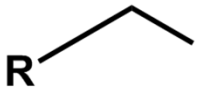

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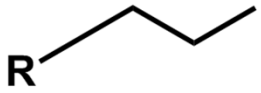

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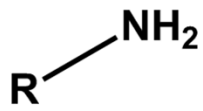

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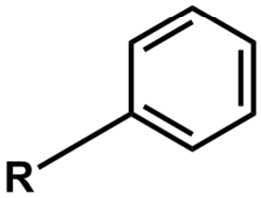

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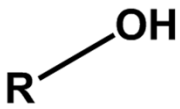

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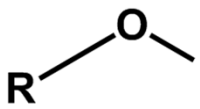

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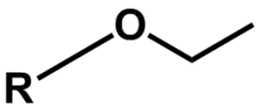

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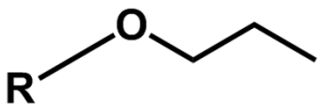


60

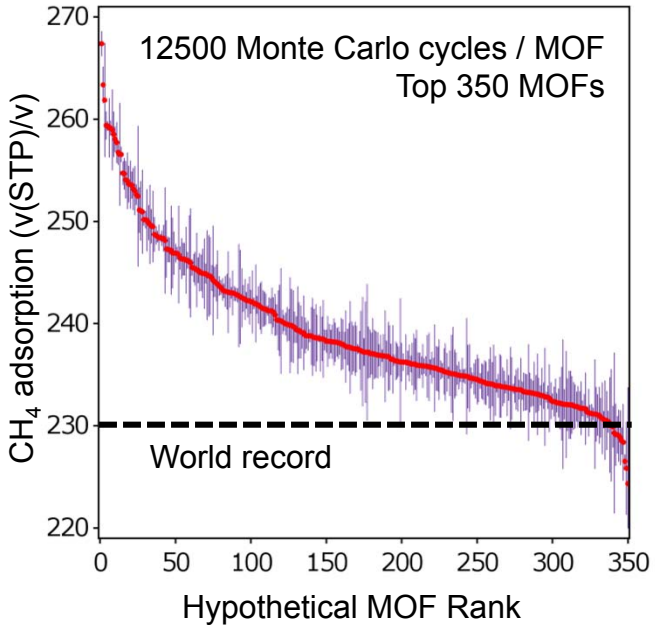
Database of Hypothetical MOFs

Restricting ourselves to MOFs with

- one type of node and
- one or two types of linkers

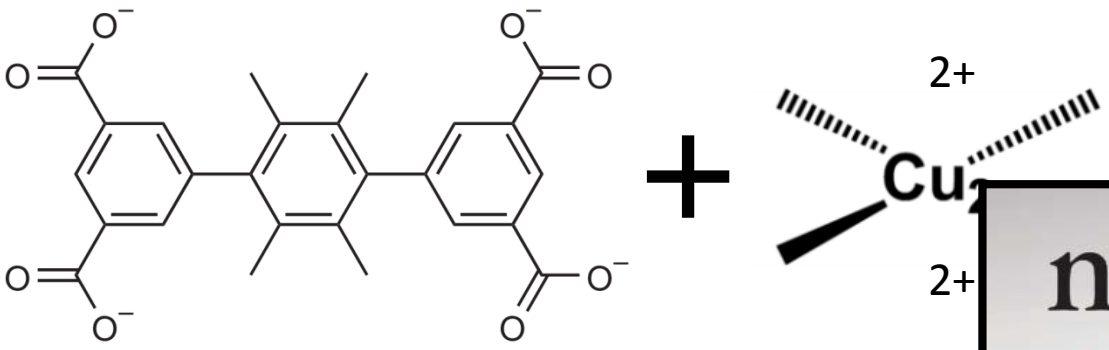
→ 137,953 MOFs

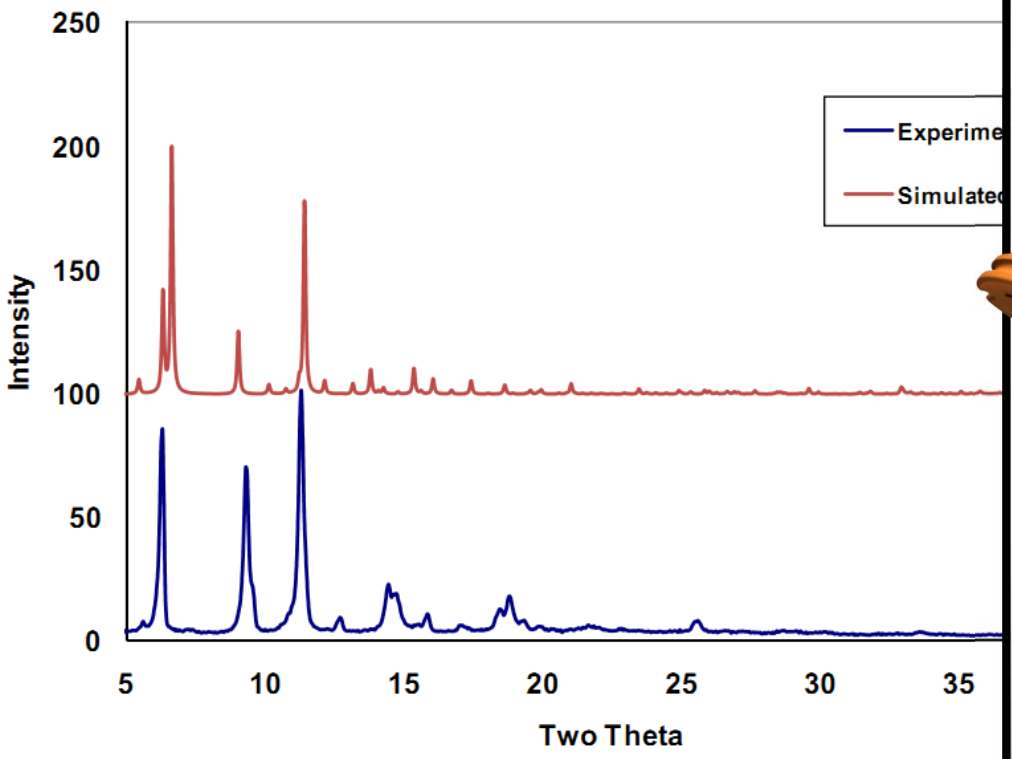
Finding Improved Methane Storage Materials

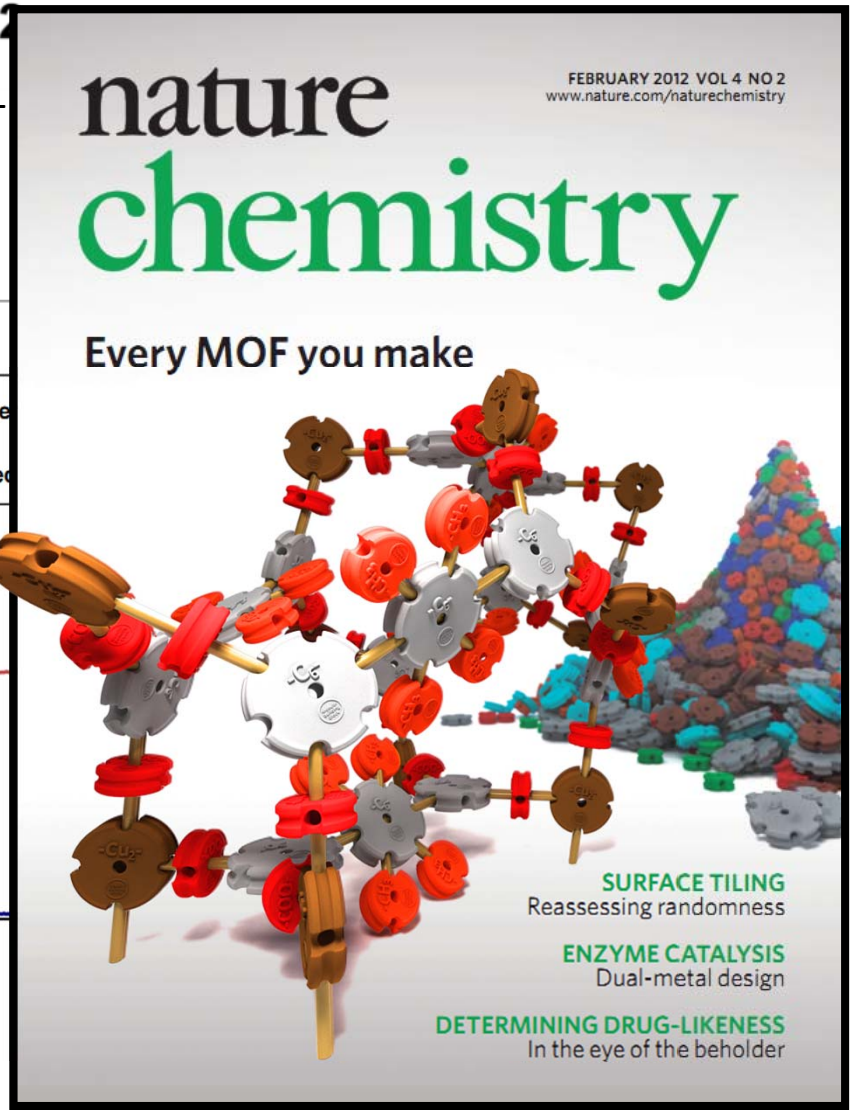


Wilmer, Leaf, Lee, Farha, Hauser, Hupp, Snurr, *Nature Chem.*, 2012.

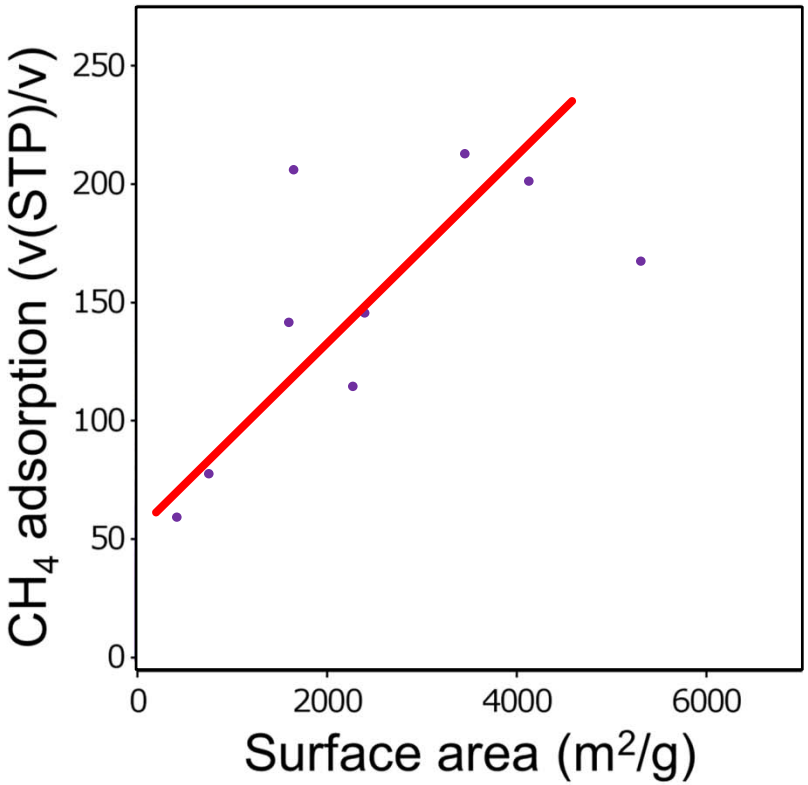
NOTT-107

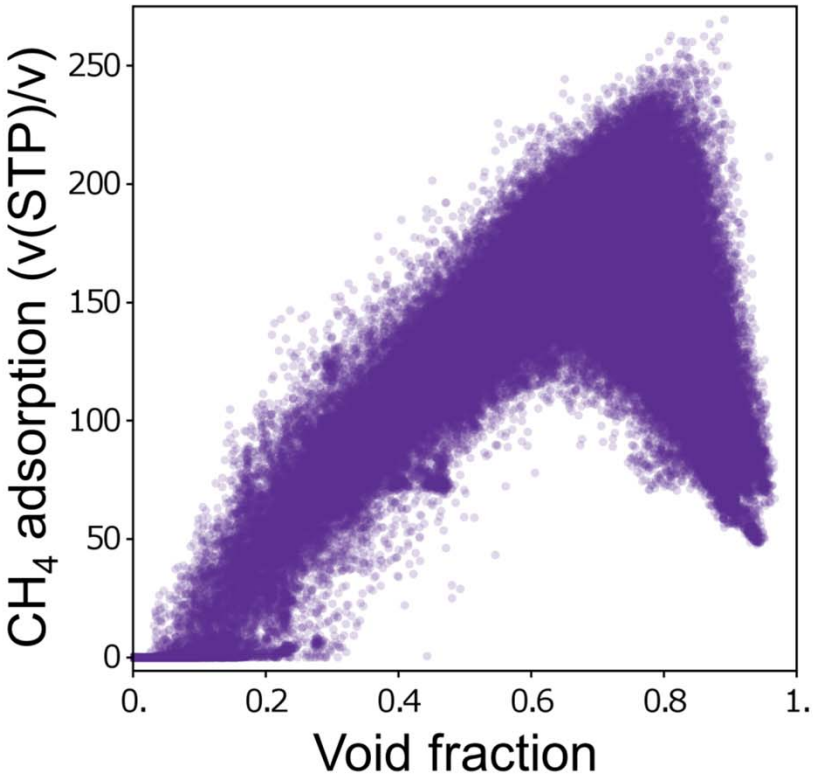

2+
Cu
2+


250
200
150
100
50
0
Intensity
5
10
15
20
25
30
35
Two Theta
Experime
Simulate

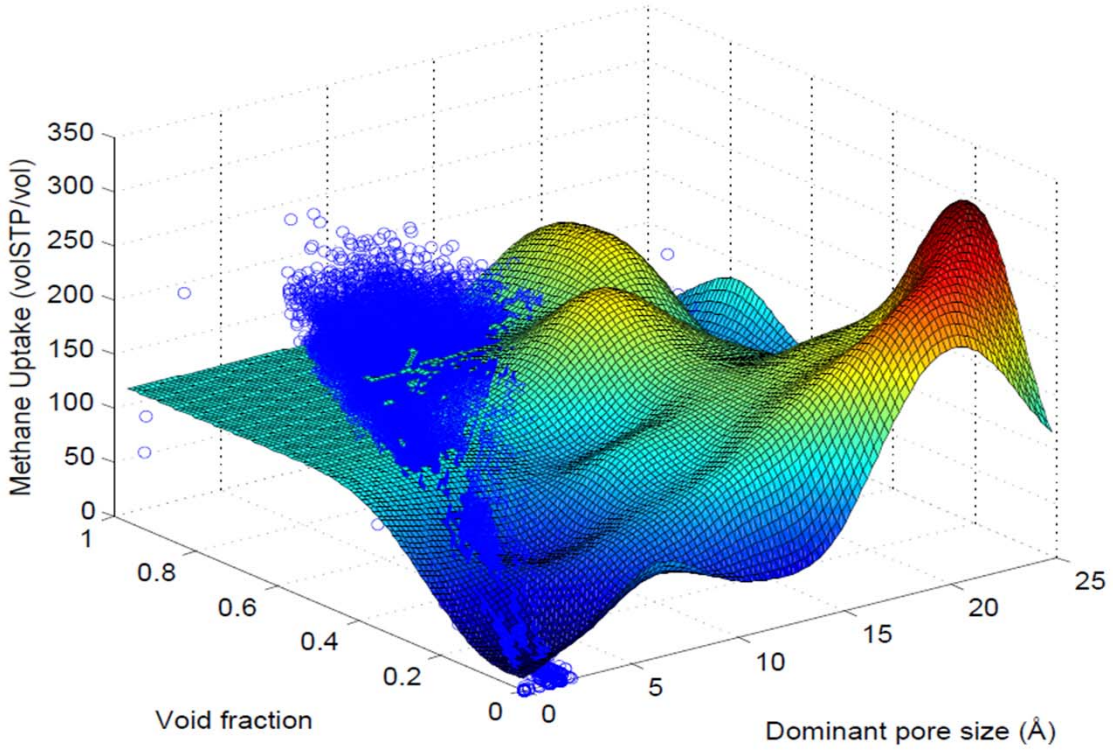

nature
chemistry
FEBRUARY 2012 VOL 4 NO 2
www.nature.com/naturechemistry
Every MOF you make
SURFACE TILING
Reassessing randomness
ENZYME CATALYSIS
Dual-metal design
DETERMINING DRUG-LIKENESS
In the eye of the beholder

Structure-Property Relationships



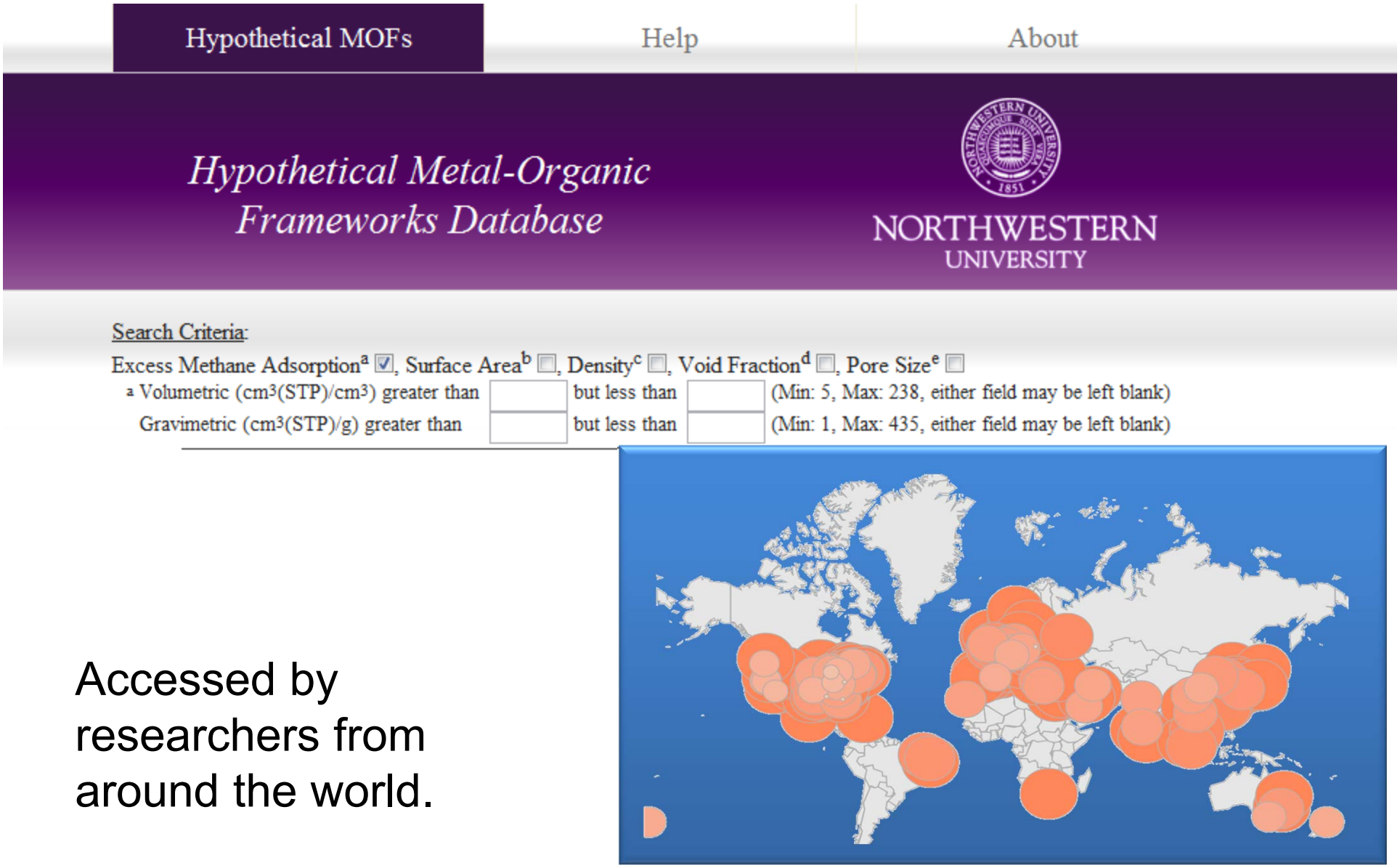


Quantitative Structure-Property Relationships



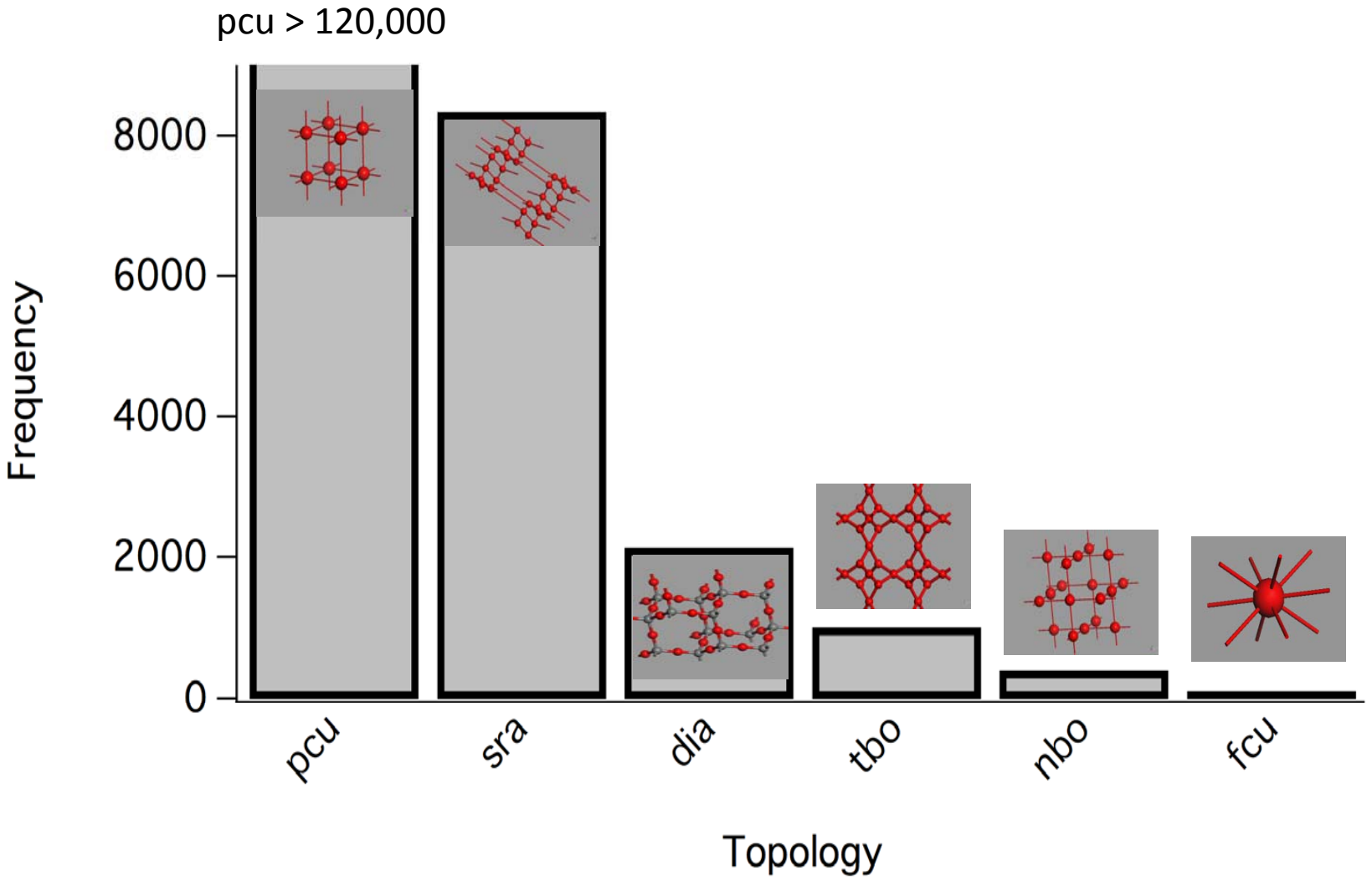
Large-scale Quantitative Structure-Property Relationship (QSPR) Analysis of Methane Storage in Metal-organic Frameworks.
M. Fernandez, T.K. Woo, C.E. Wilmer, R.Q. Snurr, *J. Phys. Chem. C* 2013.

hmofs.northwestern.edu



Accessed by researchers from around the world.

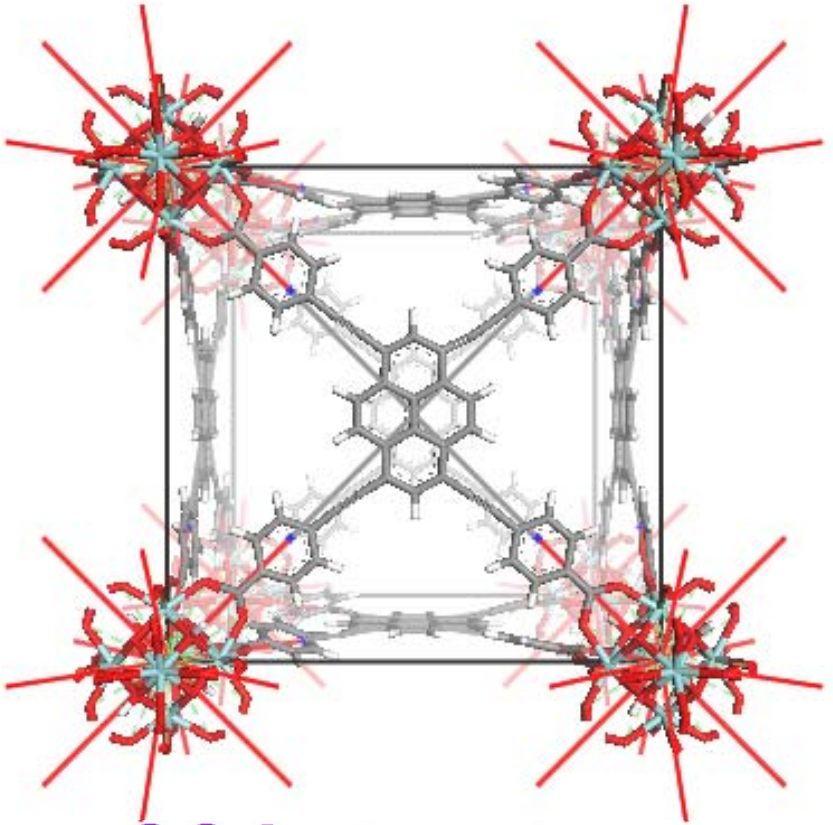
Framework Topologies in the Database



Sikora, Winnegar, Proserpio, Snurr, *Microporous Mesoporous Mater*., 2014.

“Top-down” MOF construction

- Selection of appropriate net template
- Scaling of unit cell based on targeted building blocks
- Placement of inorganic “nodes”
- Placement of organic “nodes”
- Placement of organic “linkers”
- Classical force field optimization of hypothetical structures
- Characterization of textural properties
- Simulation of methane adsorption isotherm up to 65 bar



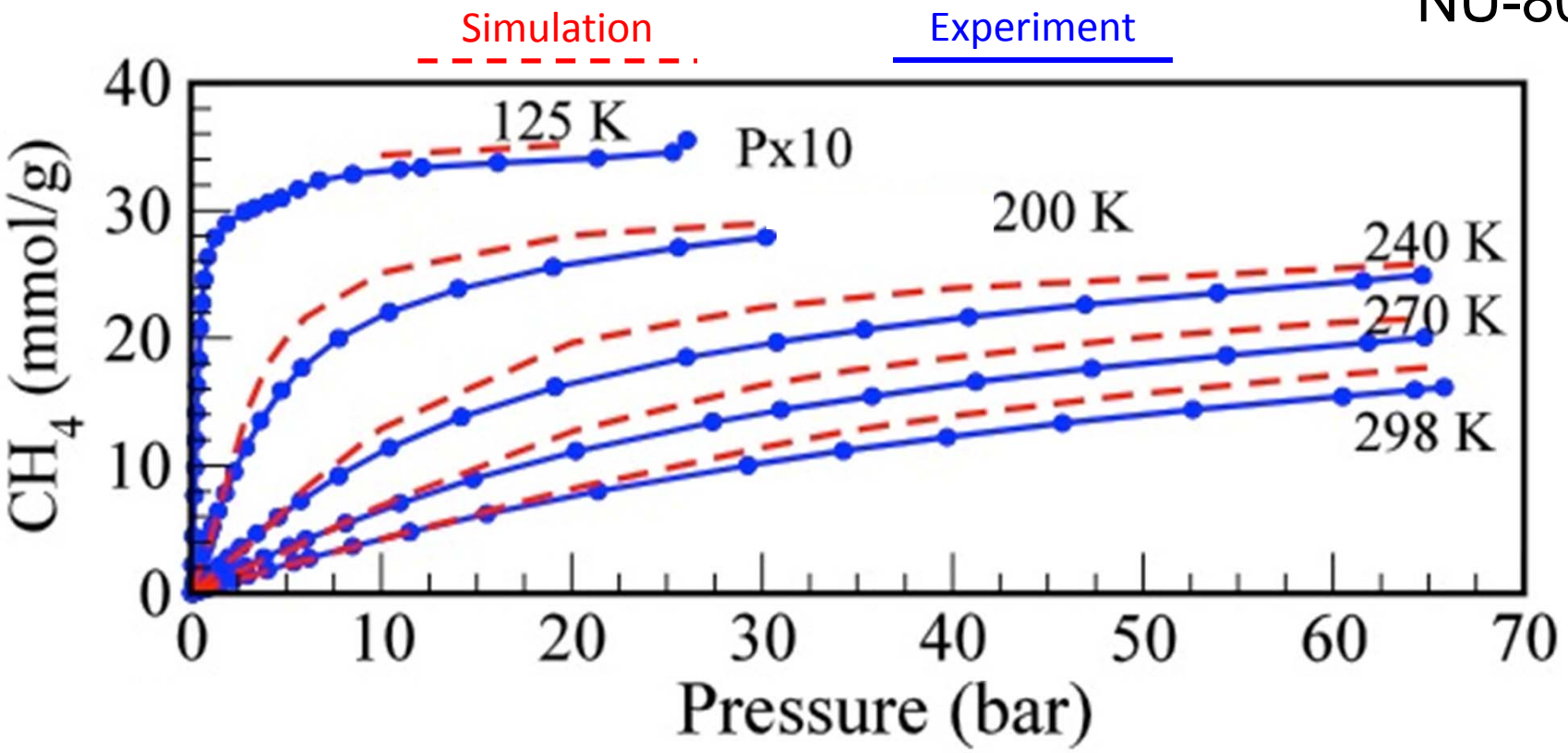
204 structures

D.A. Gomez-Gualdron, O. V. Gutov, V. Krungleviciute, B. Borah, J.E. Mondloch, J.T. Hupp, T. Yildirim, O.K. Farha, R.Q. Snurr, Computational design of metal-organic frameworks based on stable zirconium building units for storage and delivery of methane, *Chem. Mater.*, in press.

Validation of simulation: methane adsorption

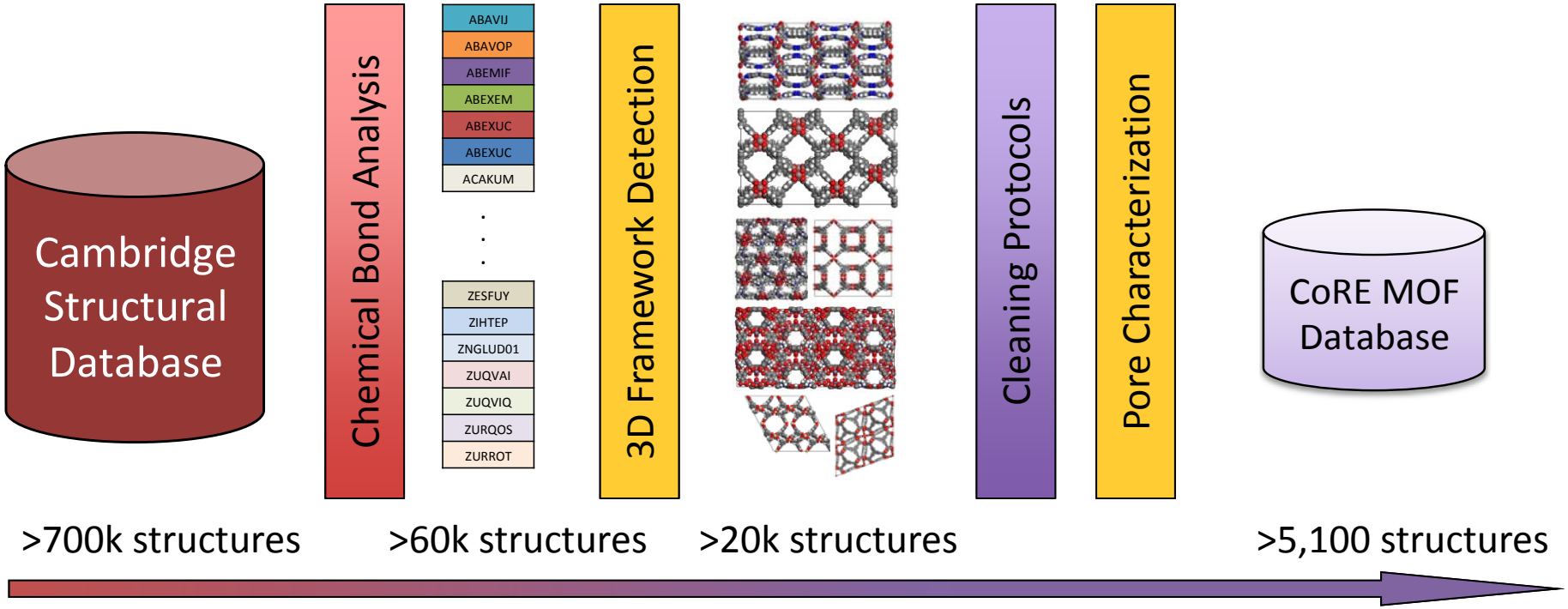
Ratio between simulated deliverable capacity (~190 cc(STP)/cc) and measured one (~170 cc(STP)/cc) is 0.895, which correlates well with the 0.884 ratio between simulated and measured BET surface area

NU-800



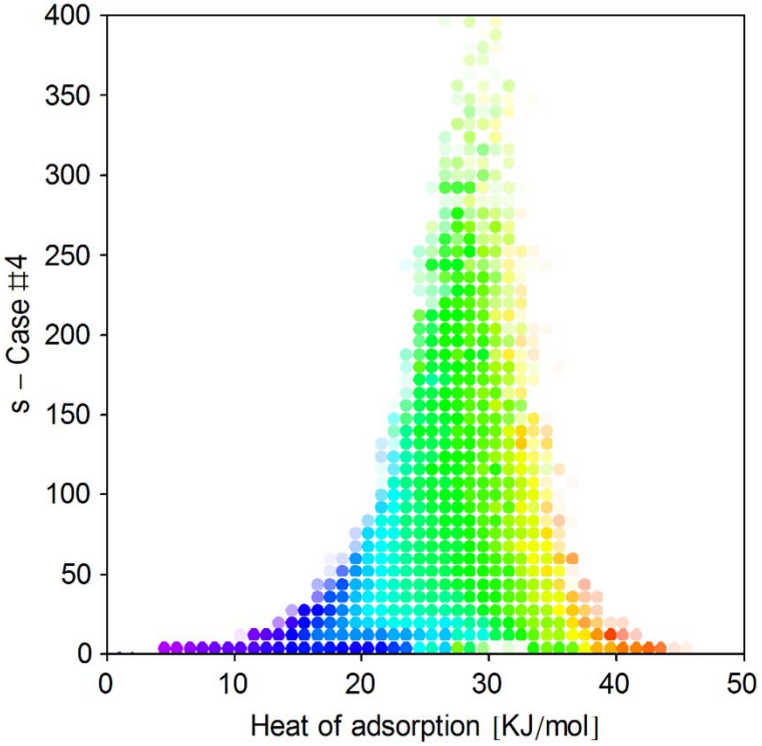
D.A. Gomez-Gualdron, O. V. Gutov, V. Krungleviciute, B. Borah, J.E. Mondloch, J.T. Hupp, T. Yildirim, O.K. Farha, R.Q. Snurr, Computational design of metal-organic frameworks based on stable zirconium building units for storage and delivery of methane, *Chem. Mater.,* in press.

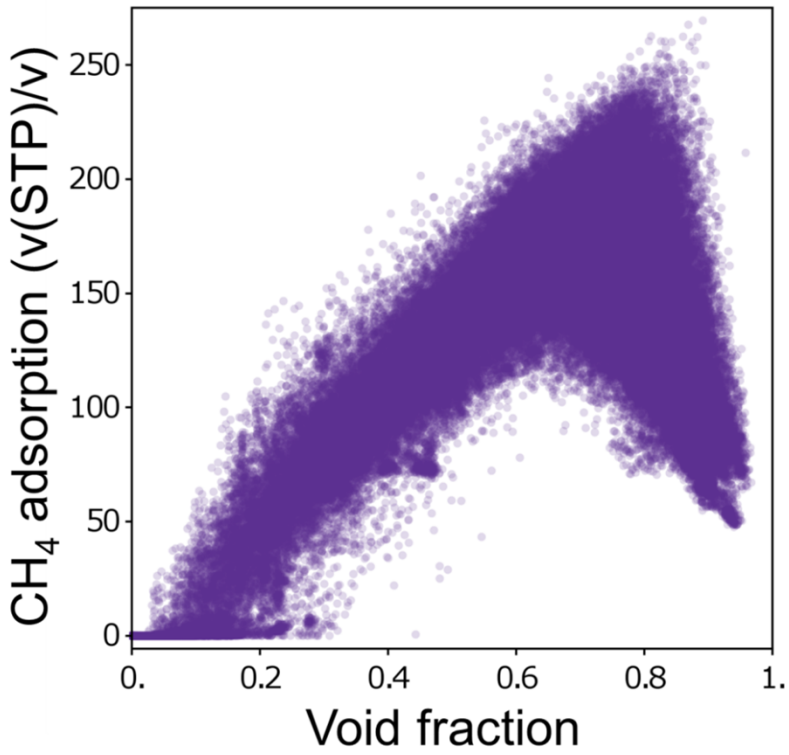
Computation-Ready, Experimental (CoRE) MOF Database



- MOF structures identified in the CSD
- Automated routines developed to “clean up” original crystal structures
  - Solvents (free & coordinated) are removed
  - Ions are retained
  - Structures with missing hydrogen atoms are identified and fixed
  - Mislabeled structures are recovered by text-mining
- >5,100 “computation-ready” structures with PLD > 2.4 Å

Chung, Camp, Haranczyk, Sikora, Bury, Krungleviciute, Yildirim, Farha, Sholl, Snurr, *Chem. Mater.*, in press.


s – Case #4
Heat of adsorption [KJ/mol]
0
50
100
150
200
250
300
350
400
0
10
20
30
40
50


CH4 adsorption (v(STP)/v)
Void fraction
0
50
100
150
200
250
0.
0.2
0.4
0.6
0.8
1.

Conclusions

How close are we to designing MOFs on the computer?

- Molecular simulation can provide (and has provided) inspiration for new materials.
- Proposed MOFs can be evaluated readily on the computer for their ability to store and separate simple gases.
- High-throughput computational screening is still in its infancy. It requires
  - Generation tools
  - Methods to calculate properties
  - Metrics for evaluation
  - Data mining

Acknowledgments

Current group

- Dr. Greg Chung
- Dr. Diego Gomez-Gualdron
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- David Chen
- Jiayi Chen
- Yamil Colon
- Stephanie Kwon
- Karson Leperi
- Casey Whitford
- Hongda Zhang

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- Dr. Bhaskar Borah (Charotar U.)
- Dr. David Fairen-Jimenez (U. Cambridge)
- Dr. Rachel Getman (Clemson U.)
- Pritha Ghosh (Inst. for Defense Analyses)
- Dr. Ivan Konstantinov (Dow Chemical)
- Ben Sikora (U. Montpellier)
- Chris Wilmer (U. Pittsburgh)
- Dr. A. Ozgur Yazaydin (UC London)
- Dr. Decai Yu (Dow Chemical)

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- Prof. Omar Farha
- Prof. Mercouri Kanatzidis
- Prof. SonBinh Nguyen
- Prof. Fengqi You

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- Global Climate & Energy Project
- Dow Chemical Company
- XSEDE and NERSC Computing

30 minutes total