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Sandia National Laboratories

Identification of nominally nonporous H_2 physisorbents via graph theory-based descriptors of MOF flexibility

PRESENTED BY

Matthew Witman[1], Sanliang Ling[2], Andreas Schneemann[1,3], Pavithra Wijeratne[1], Robert Horton[1], Justin Wong[1], Vitalie Stavila[1], Mark Allendorf[1]

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[3] Technical University of Dresden, Dresden, Germany

HyMARC

LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Collaboration Group:

Nottingham University – Sanliang Ling

Sandia National Laboratories – Andreas Schneemann, Pavithra Wijeratne, Robert Horton, Justin Wong, Vitalie Stavila, and Mark Allendorf

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The authors gratefully acknowledge research support from the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office through the Hydrogen Storage Materials Advanced Research Consortium (HyMARC).

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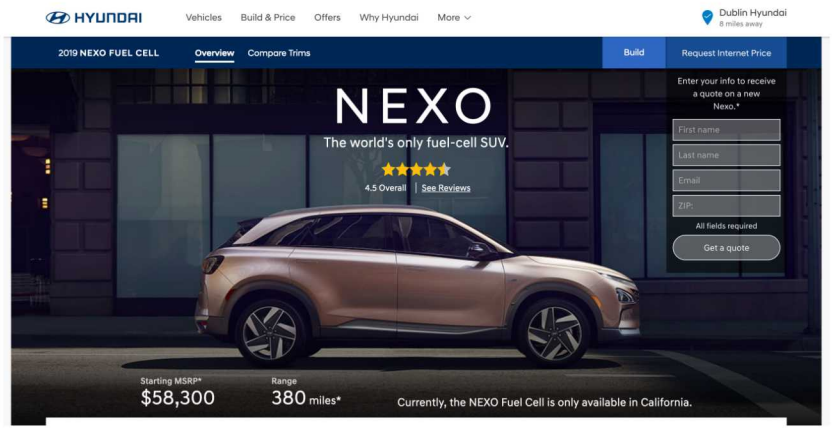
HyMARC
Hydrogen Materials Advanced Research Consortium

Economical storage of hydrogen is critical for enabling a variety of zero emission technologies

Commercially available fuel cell vehicles with physical-based hydrogen storage:

https://www.businessinsider.com/this-toyota-fuel-cell-car-can-power-your-house-2014-11



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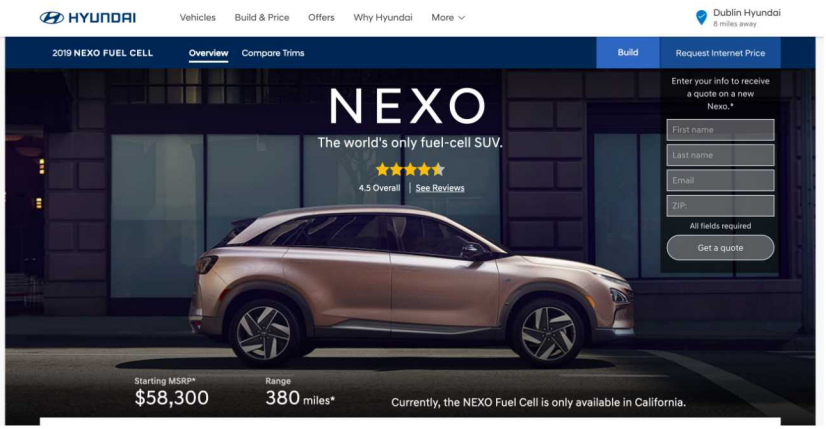

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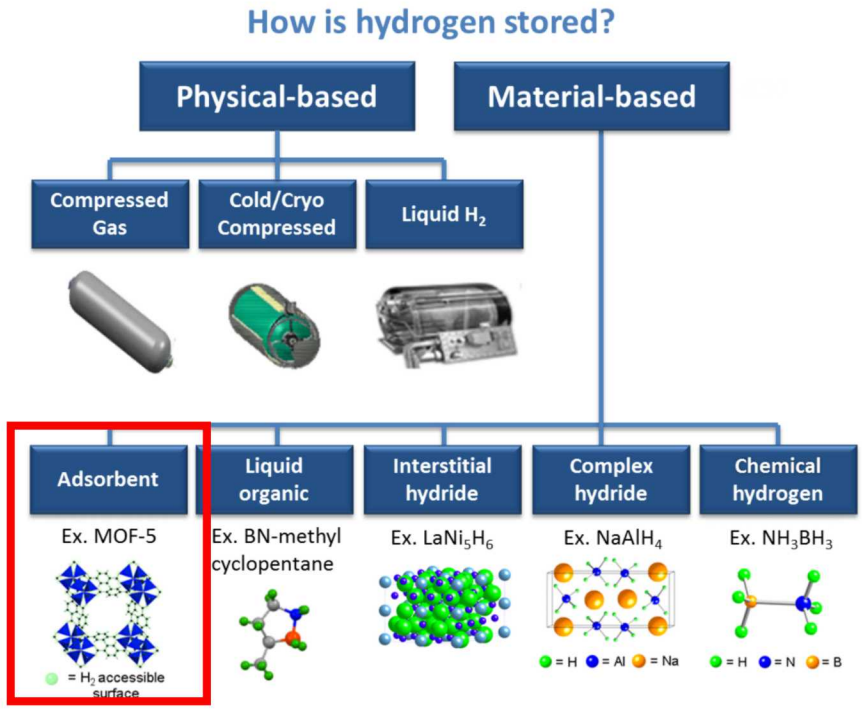
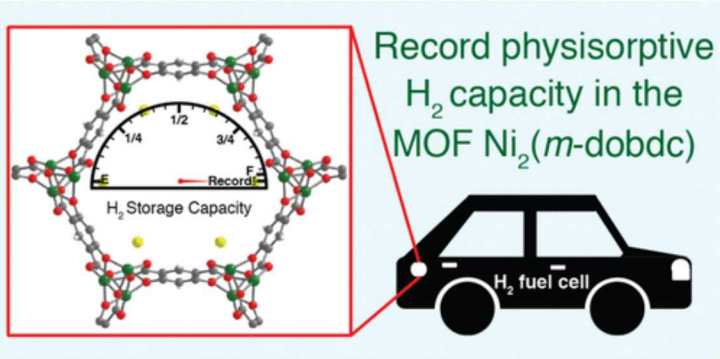
A material that meets all DOE technical targets for on board hydrogen storage could help send the technology mainstream:



https://www.energy.gov/eere/fuelcells/hydrogen-storage

Physisorbents are attractive due to fast kinetics, but suffer from low volumetric capacities due to weak H_2 interactions

Solution 1: Rationally design best H_2 binding sites at highest possible volumetric density



Kapelewski, M. et al. *Chem. Mater.* 2018, 30, 22, 8179-8189

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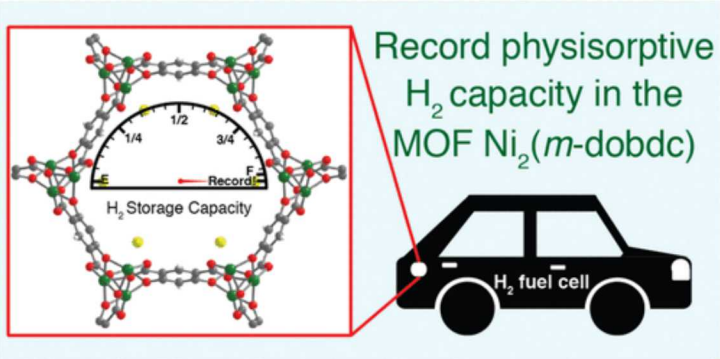

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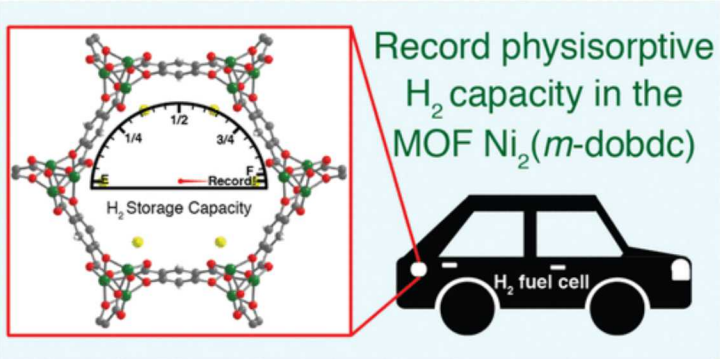

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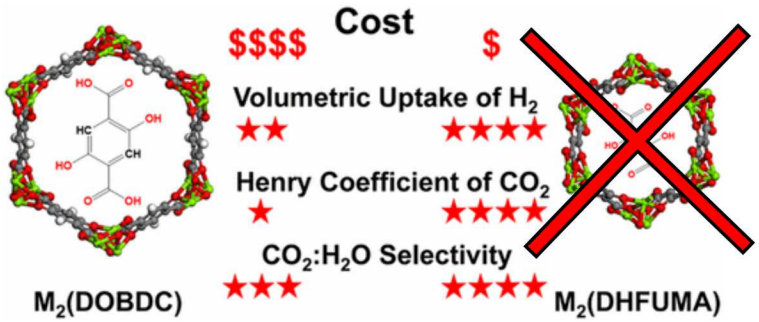

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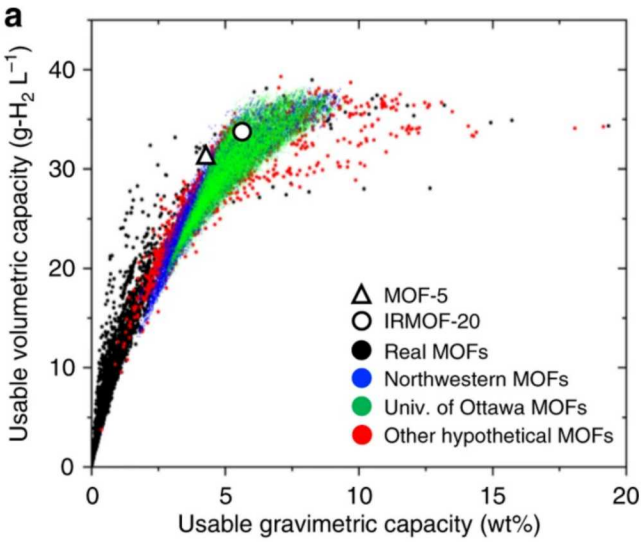
Solution 2: High-throughput screening of known chemical space to identify top adsorbents



Ahmed, A. et al. *Nat. Commun.* 2019, 10, 1568

High-throughput screening may miss promising H_2 physisorbents due to two approximations (made for computational tractability)

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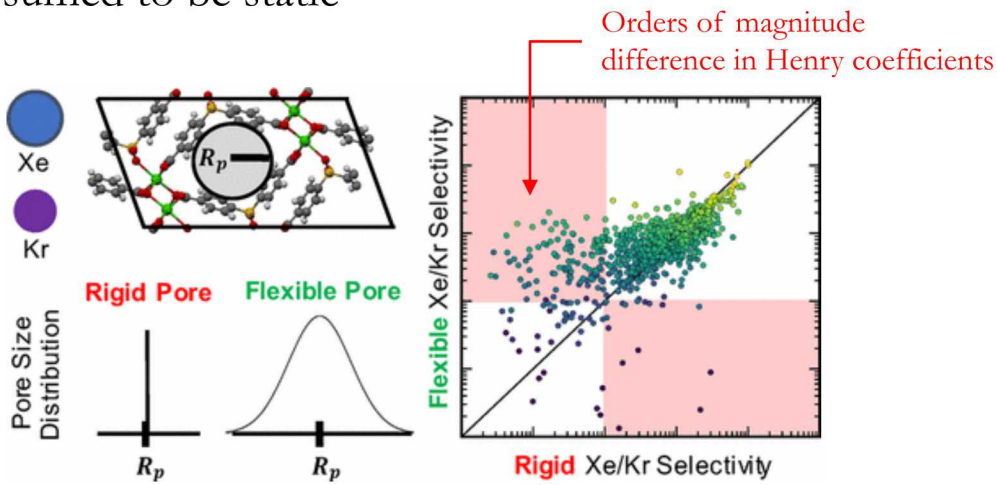

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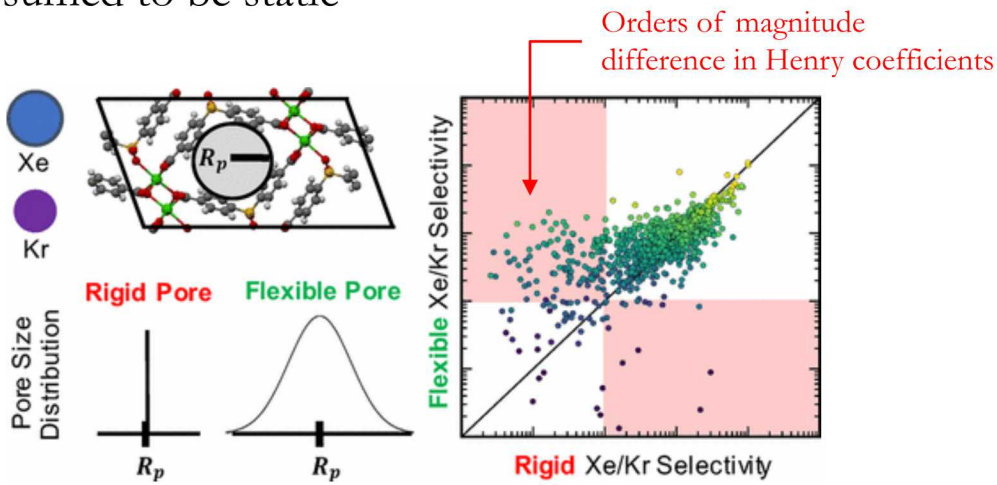

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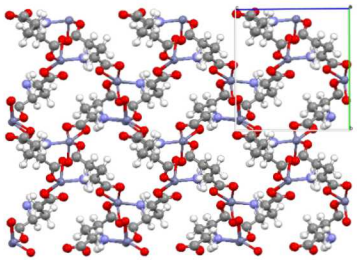
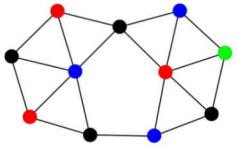
3. Research question: How do we efficiently identify these materials that are nominally non-porous, but are sufficiently flexible that H_2 adsorption is energetically favorable?

Graph theory-based, high-throughput porous materials' analyses are enabled by open-source **LAMMPS Interface**



build passing docs passing pypi package 0.1.2

LAMMPS Interface



```
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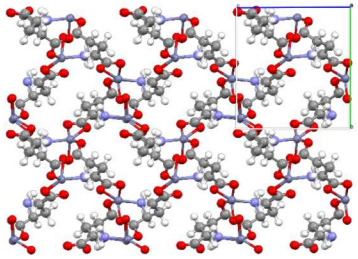

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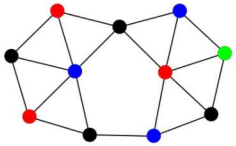

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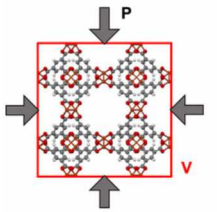

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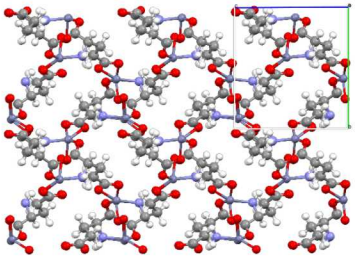

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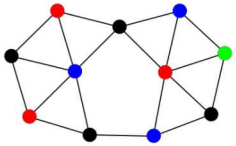

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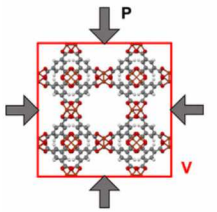

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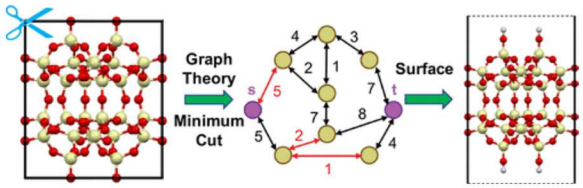

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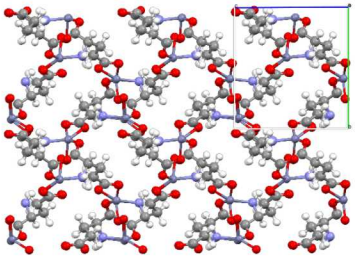

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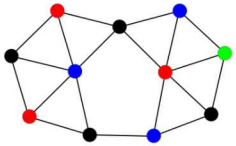

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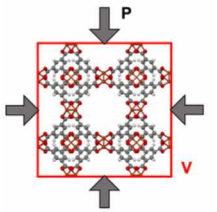

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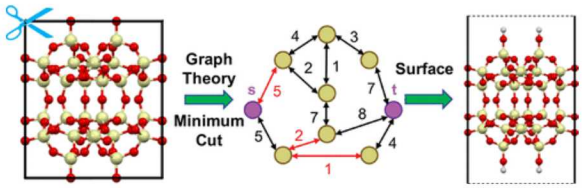

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3. High-throughput identification of flexible MOFs via graph search

This Work

Hypothesis: MOFs containing saturated organic components are likely to display a significant degree of flexibility

1. Preliminaries:

$G = (V, E)$ be the MOF's connected, undirected graph

$R \equiv$ the set of all nodes considered rigid

$F \equiv$ the set of all nodes considered flexible

$V' \equiv$ the vertices in a connected subgraph of G

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   f_α: a node belongs to F if it is an sp3 hybridized, non-metal atom

   f_β: a node belongs to F if it is an sp3 hybridized, non-metal atom and is bonded to at most two other (non-H) atoms

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4. Objectives:

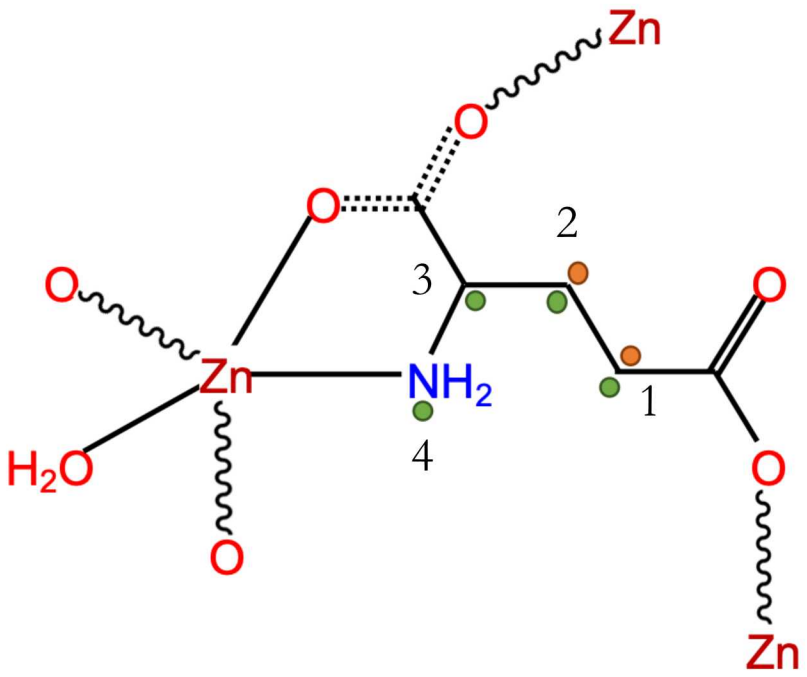
   $$L = \{V_1', V_2', \ldots, V_{|L|}'\} \mid (V_1' \cap V_2' \ldots \cap V_{|L|}' = \emptyset) \wedge (V_1' \cup V_2' \ldots \cup V_{|L|}' = F)$$

   $$N = \{|V_1'|, |V_2'|, \ldots, |V_{|L|}'|\}$$

I.e. what are all the independent, flexible subgroups in the MOF (L_α) and how big are they (N_α) ?

Visualized: Graph theoretic identification of flexible subunits

2D sketch of a MOF building unit (4 linkers per unit cell):



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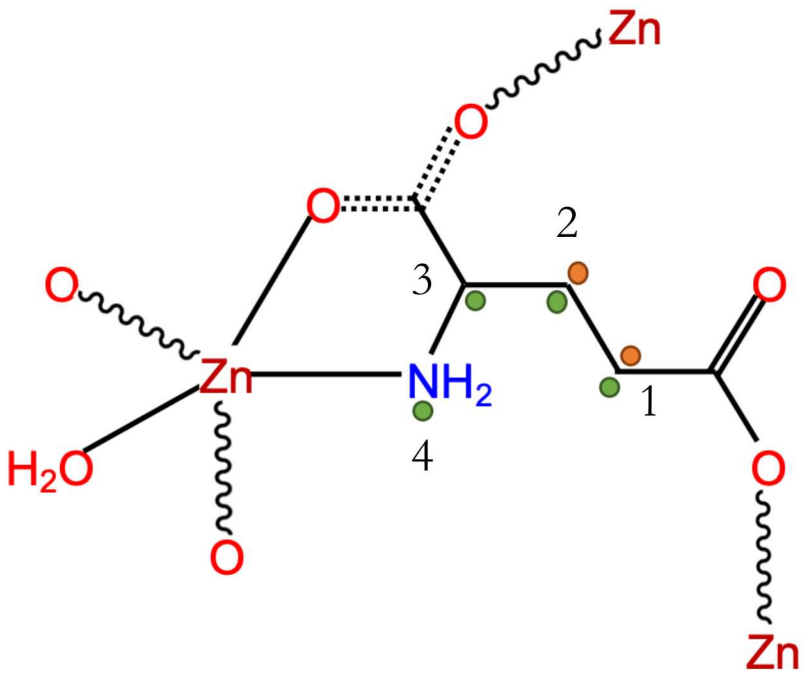

f_α objectives:
$L_\alpha = \{\{1,2,3,4\}, \ldots\}$
$N_\alpha = \{4,4,4,4\}$

f_β objectives:
$L_\beta = \{\{1,2\}, \ldots\}$
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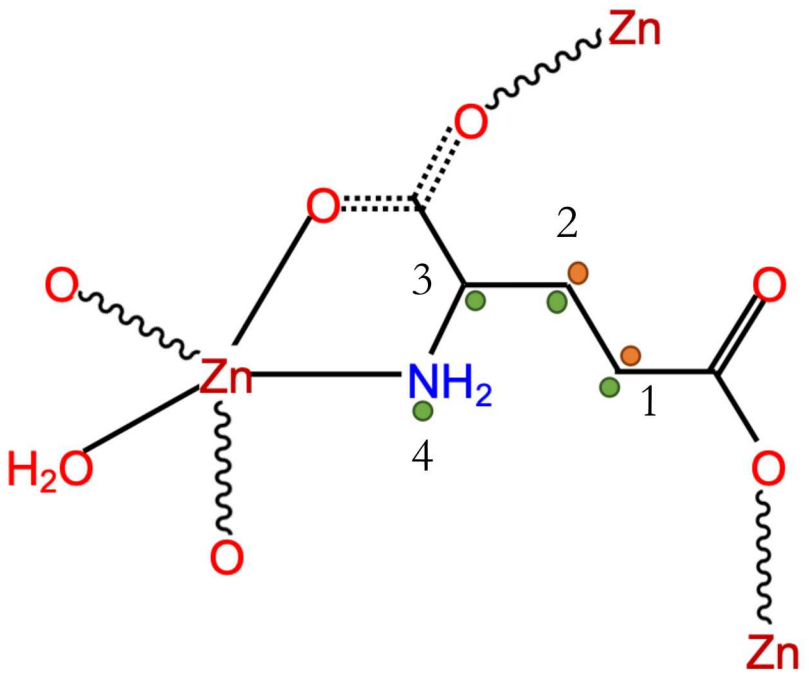

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f_α descriptors:

$\min(N_\alpha) = 4$

$\phi = \frac{\sum N_\alpha}{\#\ atoms}$

f_β objectives:

$L_\beta = \{\{1,2\}, \ldots\}$

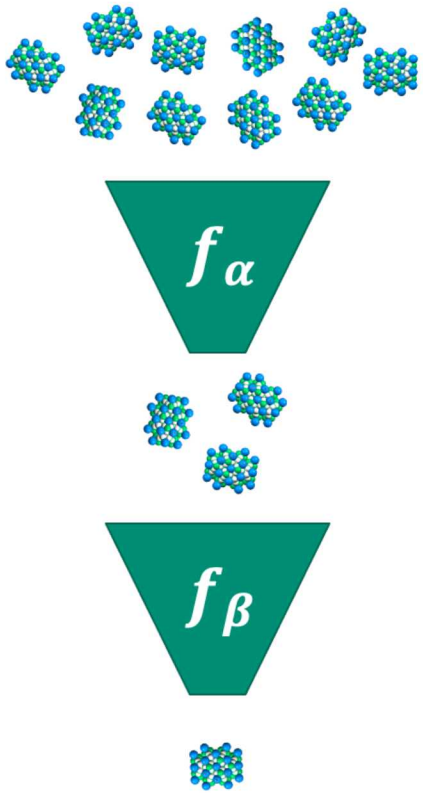
$N_\beta = \{2,2,2,2\}$

f_β descriptors:

$\min(N_\beta) = 2$

$\phi = \frac{\sum N_\beta}{\#\ atoms}$

Automated extraction of CoRE MOFs deemed to be flexible from graph theory descriptors

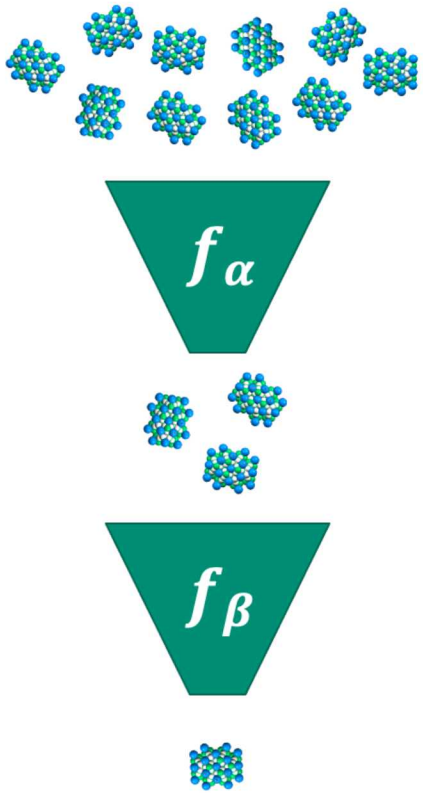


~10,000 CoRE MOFs

~2600 with $\min(N_\alpha) > 2$

~1500 with $\min(N_\beta) > 2$

Automated extraction of CoRE MOFs deemed to be flexible from graph theory descriptors



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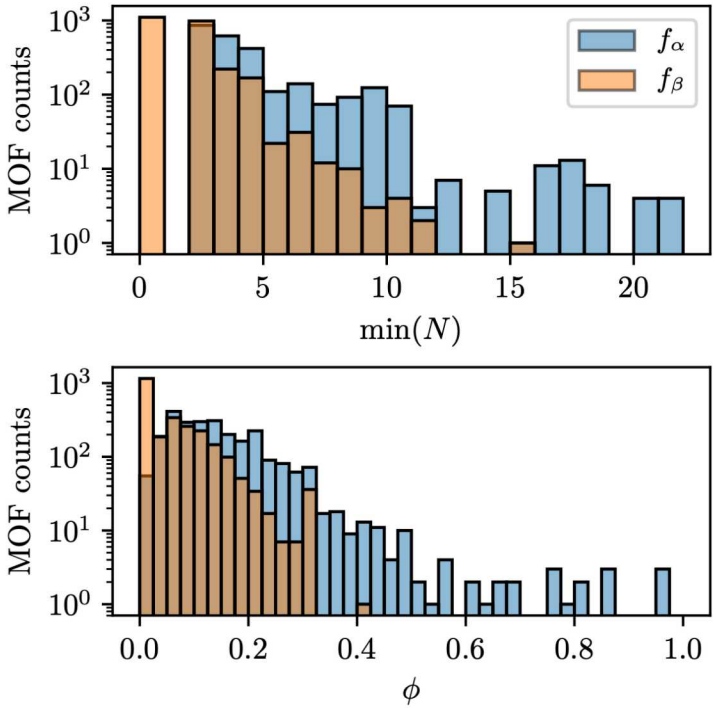
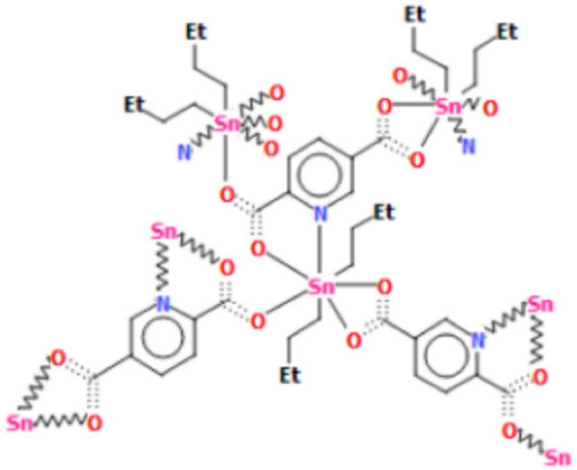
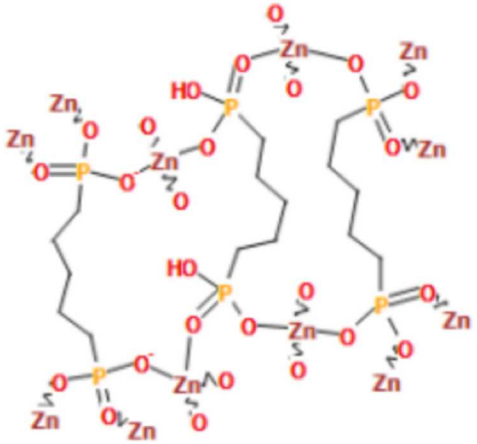


Structurally diverse flexible moieties are identified by the graph theory screening

Flexible side chains:



Fully aliphatic backbone:



Saturated ring backbone:

Aliphatic backbone hinges:

Computational adsorption experiments portend favorable H_2 adsorption despite "non-porous" 0K structure

DFT calculations on materials with:

1. $\min(N_\beta) > 2$
2. Pore size similar/slightly smaller than H_2
3. Contain open metal sites (strong H_2 binding sites)

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DFT calculations on materials with:

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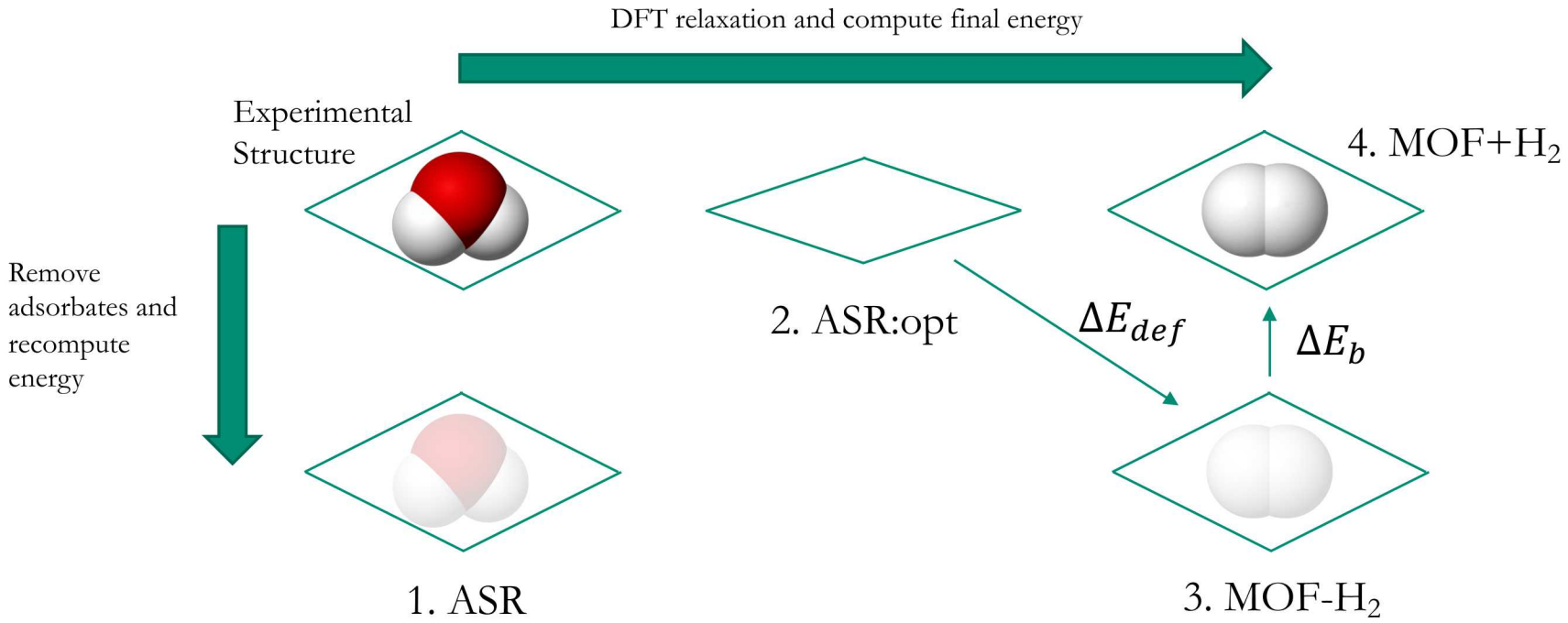
Compute energies/geometries of various adsorption states:



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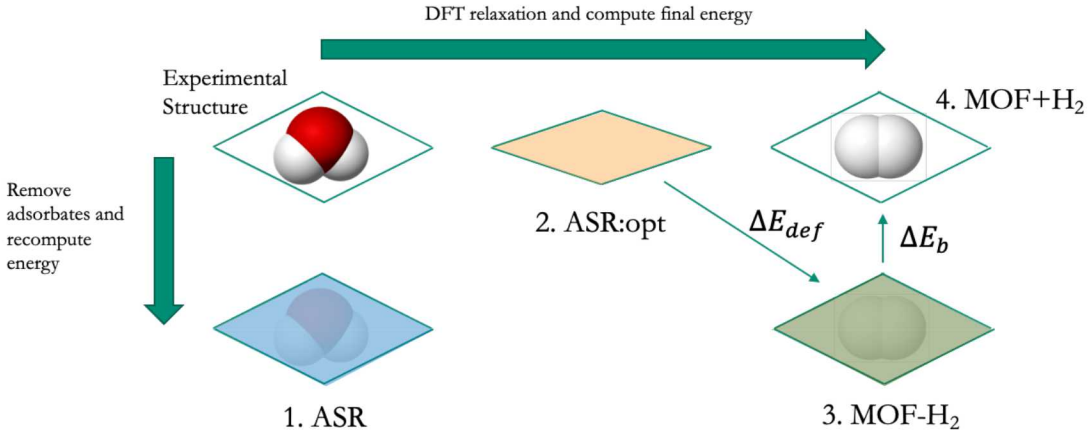

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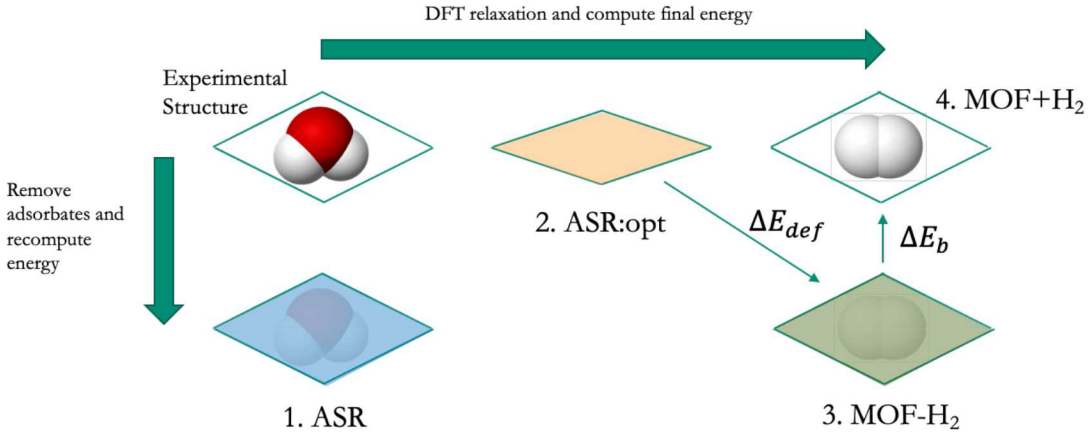
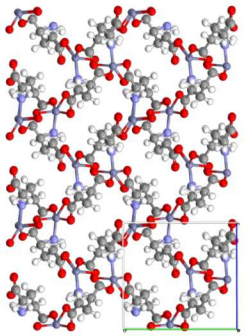
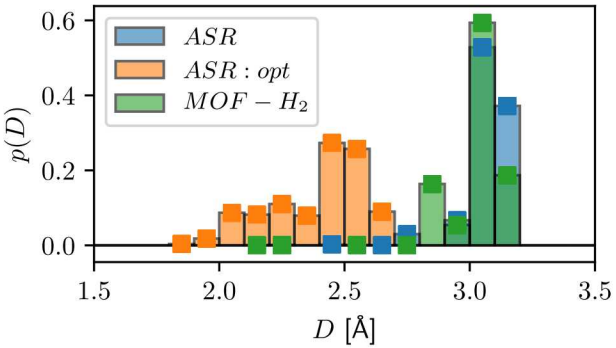
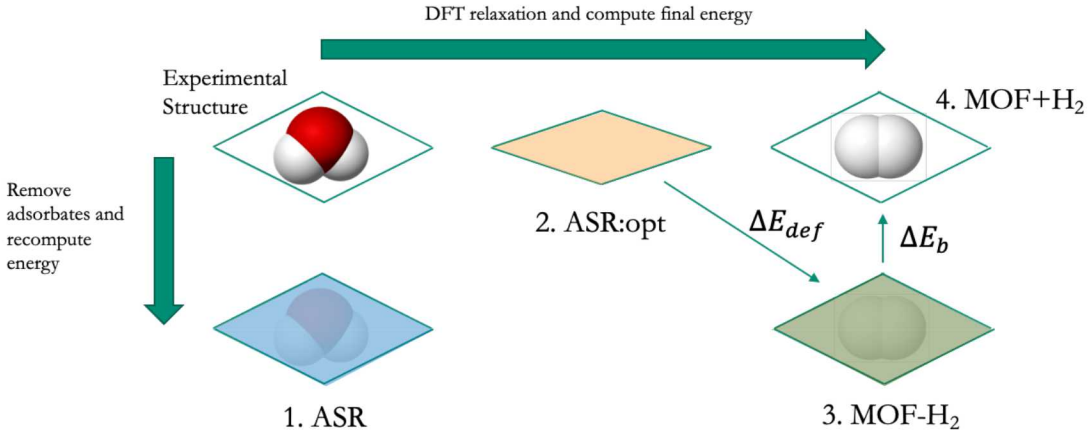


1. Entirely non-porous minimum energy state:





Computational adsorption experiments portend favorable H_2 adsorption despite non-porous 0K structure



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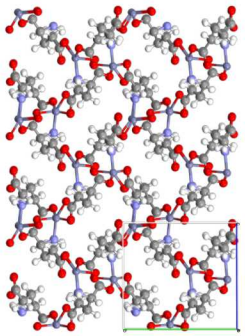
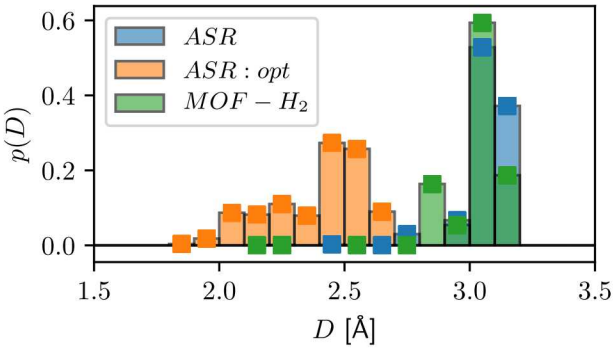
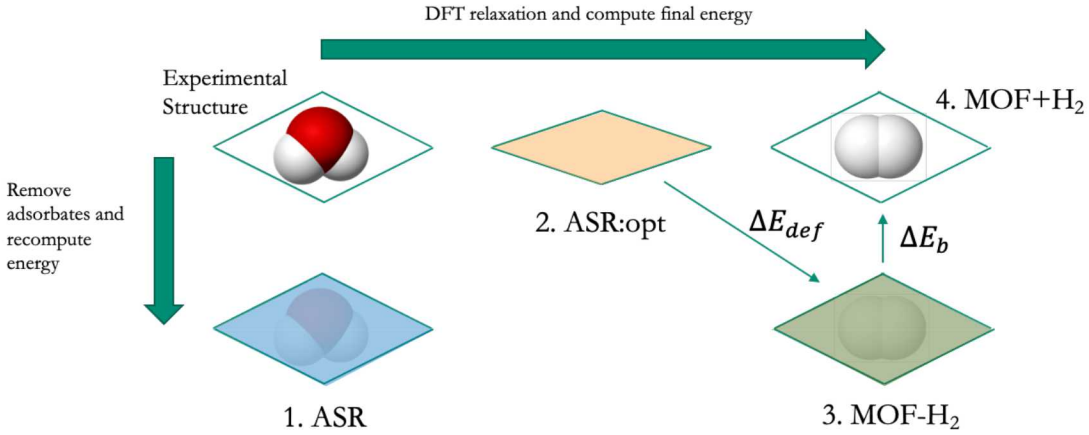




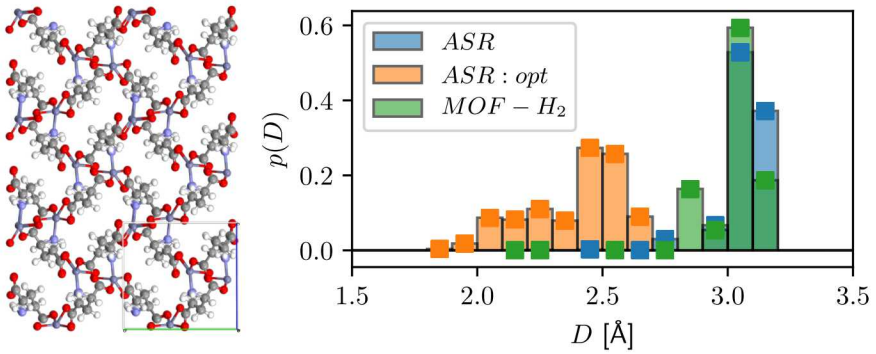
2. Highly favorable H_2 binding yields overall favorable process

$$\Delta E_{def} = 7.1\ \mathrm{kJ/molH_2}$$
$$\Delta E_b = -11.3\ \mathrm{kJ/molH_2}$$

Computational adsorption experiments portend favorable H_2 adsorption despite non-porous 0K structure



1. Entirely non-porous minimum energy state:



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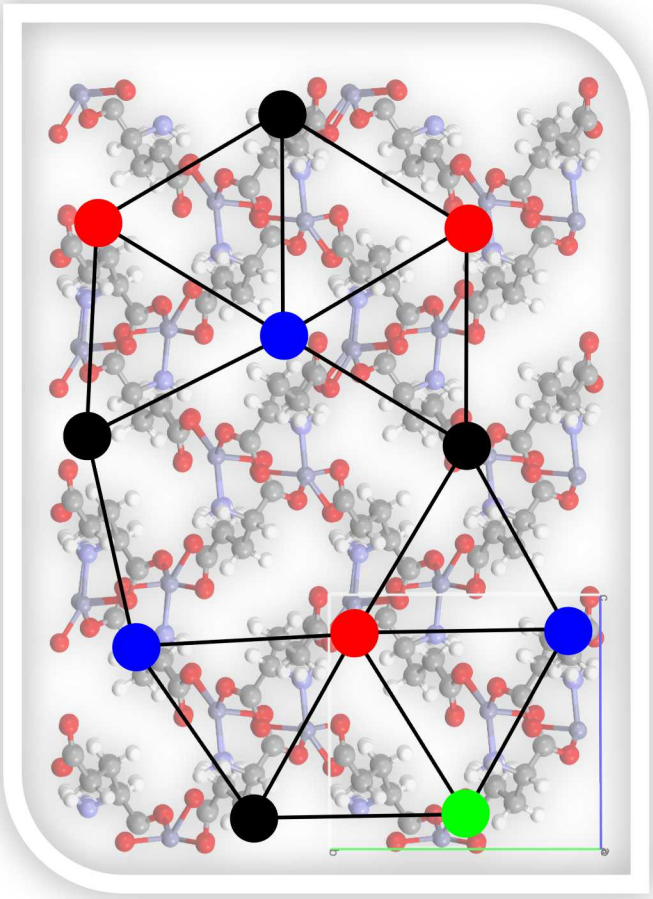
3. Rigorous isotherm prediction would require osmotic ensemble simulations and *ab initio* accuracy, how to circumvent?

Experimental adsorption studies are ongoing to validate computational predictions

To be determined

Key Takeaways



1. H_2 adsorption in nominally (i.e., 0 K DFT optimized) nonporous can still be an energetically favorable process

2. 10,000s of porous materials can be efficiently screened with graph-theory based indicators of flexibility

3. DFT can be used to assess the adsorption viability of a handful of high potential, flexible candidates

4. For robust quantitative screening of adsorption, we need *ab initio* accuracy in the osmotic ensemble... How to circumvent?

Thank you for your attention.

Questions?