

Identifying Energy-Structure-Property Relationships in Uranium Metal–Organic Frameworks Through Their Dynamic Crystalline Structural Transformations

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June 28, 2023

SSGF Outgoing Seminar

Uranium in Society: Why You Should Care

1942



Manhattan Project

How to remediate nuclear waste?

1951



First Nuclear Power Plant

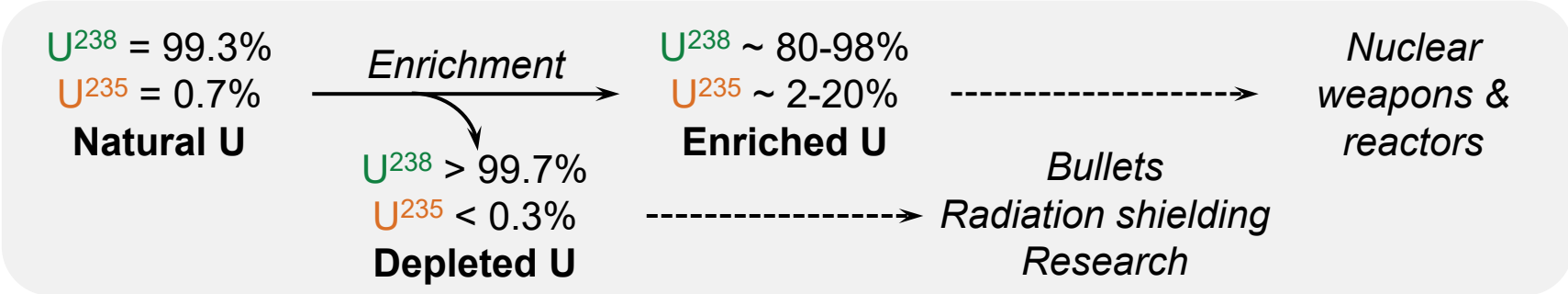
How to apply depleted U?

1963-2023



Nuclear Test Ban Treaty, Stockpile Stewardship

How to effectively steward the stockpile?

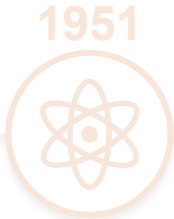


Uranium in Society: Why You Should Care



Manhattan Project

How to remediate nuclear waste?



First Nuclear Power Plant

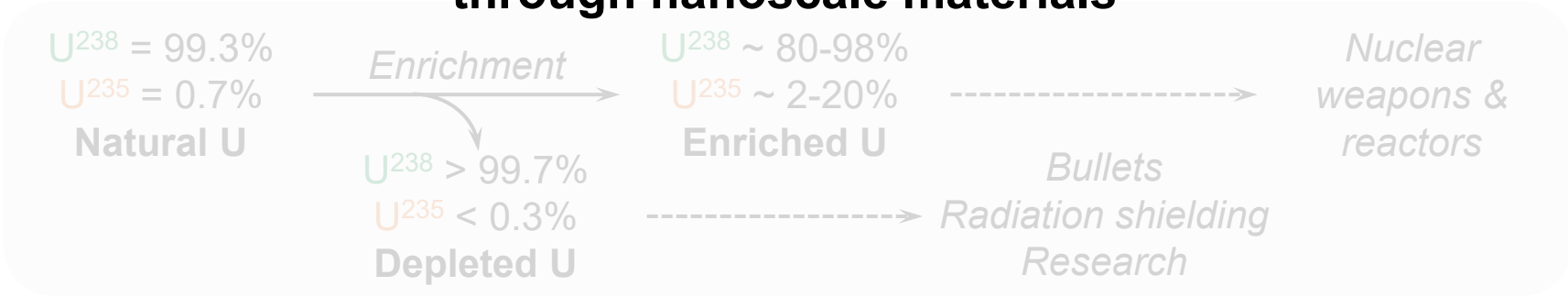
How to apply?



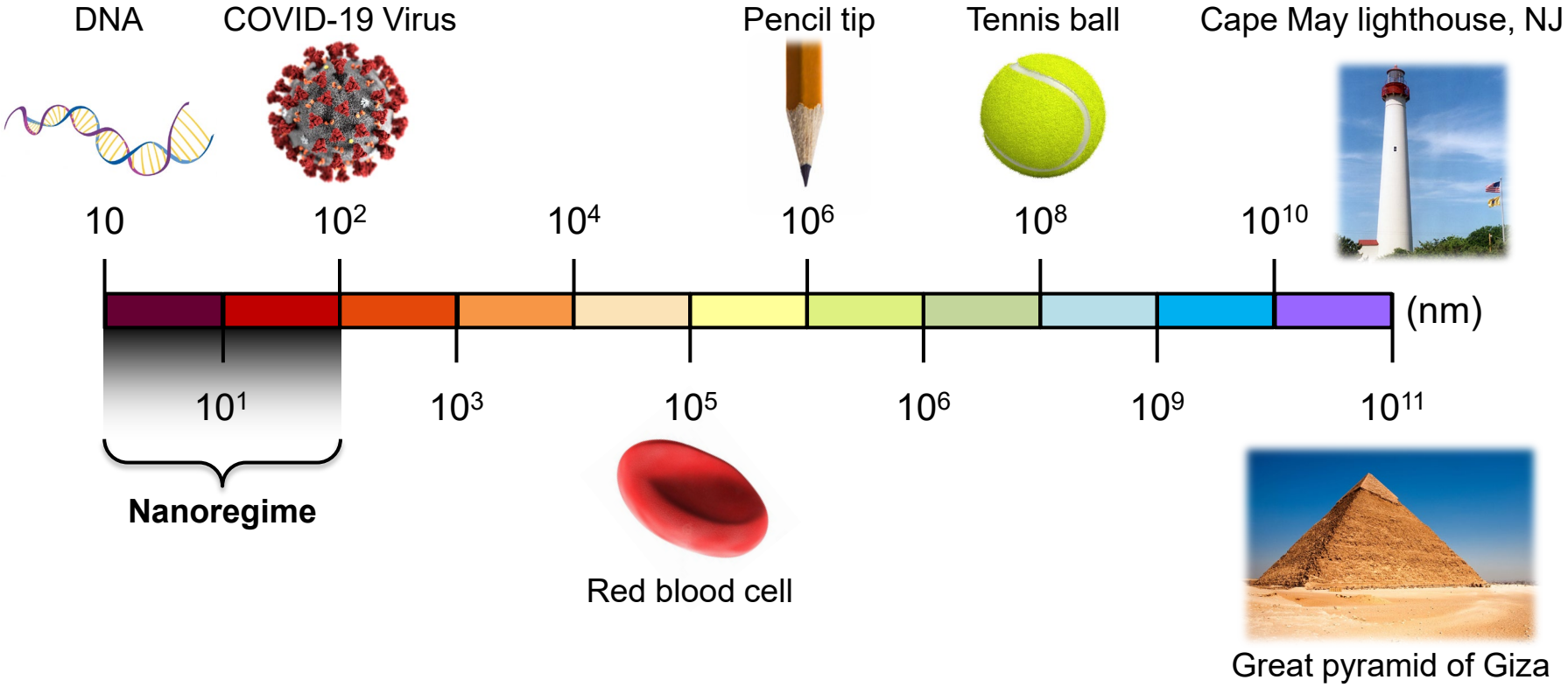
Nuclear Test Ban Treaty, Stockpile Stewardship

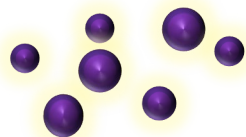
How to effectively steward the stockpile?

Address these questions by the study of uranium chemistry through nanoscale materials

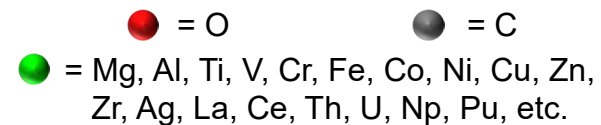
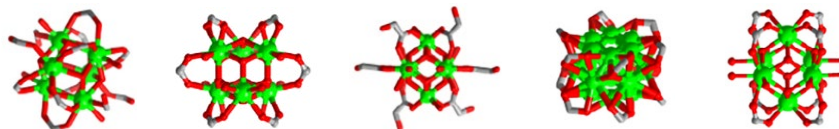


How Small are Nanoscale Materials?

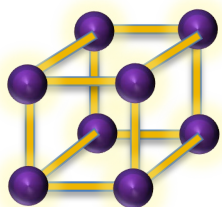
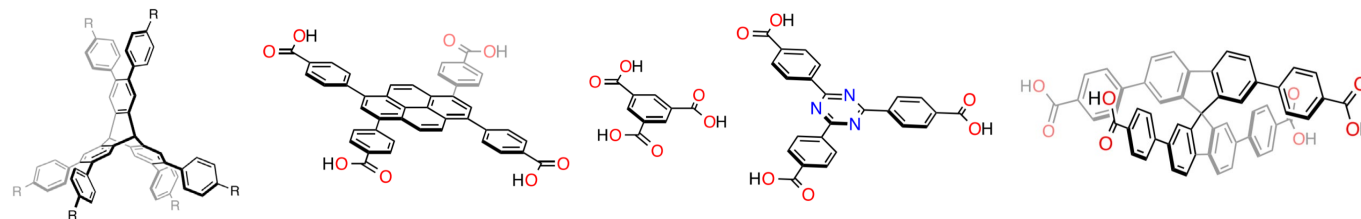




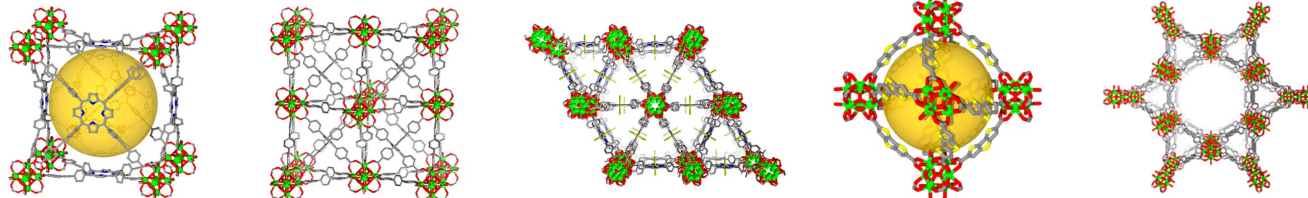
Inorganic Nodes



Organic Linkers

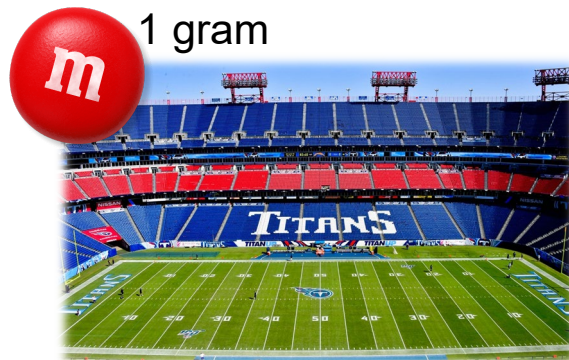


Self-assembled MOF



MOF Characteristics and Applications

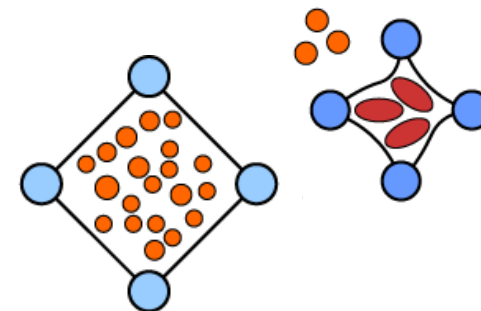
- Porous
- High Surface Area
- Tunable
- Facile Synthesis
- Stable
- Atomically Precise



Thousands of m²



Detoxify Chemical Weapons



Gas Storage & Separations

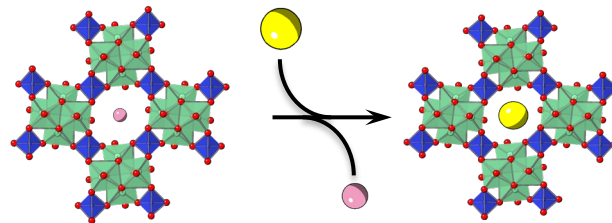


Harvest Water From Air

Q

How to remediate nuclear waste?

A

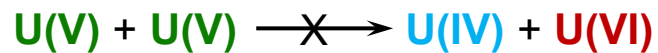


Uranium MOFs to capture radioactive waste

Q

How to apply depleted U?

A

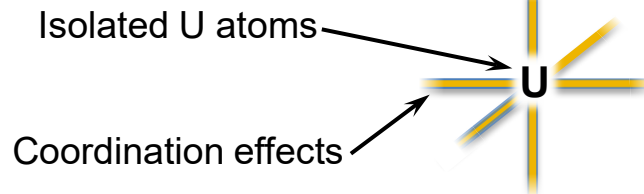


MOFs discourage disproportionation

Q

How to effectively steward the stockpile?

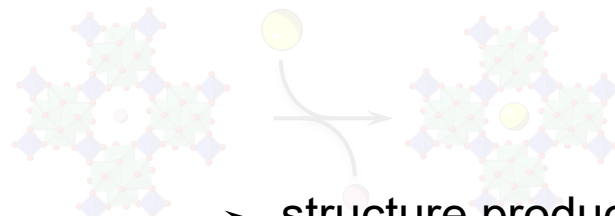
A



Fundamental structure/property studies



How to remediate nuclear waste?



Uranium MOFs to capture radioactive waste

Structure-Property → structure produces function



Energy-Structure-Property

How to apply depleted U?

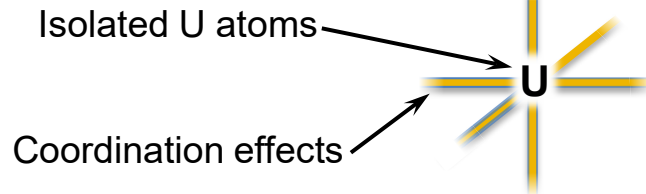


MOFs discourage disproportionation

why structure produces function



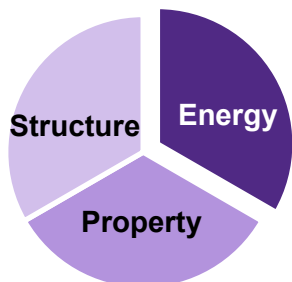
How to effectively steward the stockpile?



Fundamental structure/property studies

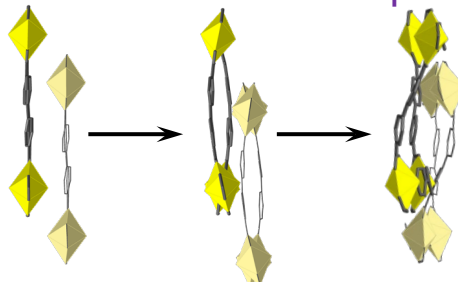
Identifying Energy-Structure-Property Relationships in U-MOFs Through Their Dynamic Crystalline Structural Transformations

Ch. 1 - Introduction



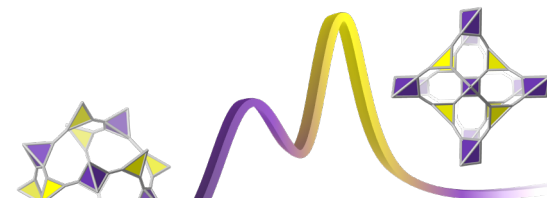
Hanna, S.L. et. al. *Chem. Sci.* 2023

Ch. 2 – Structure/Property



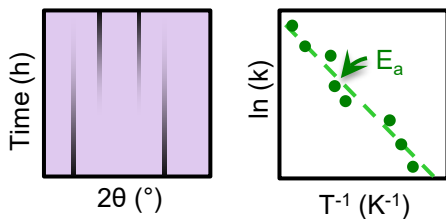
Hanna, S.L. et. al. *Cryst. Growth Des.* 2018

Ch. 3 – Energy/Structure



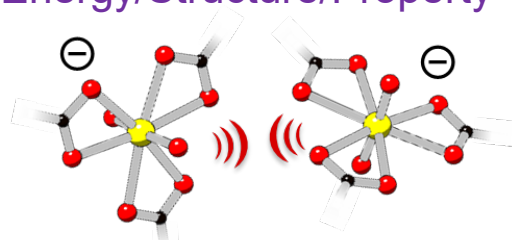
Hanna, S.L. et. al. *Chem. Sci.* 2022

Ch. 4 – Energy/Property



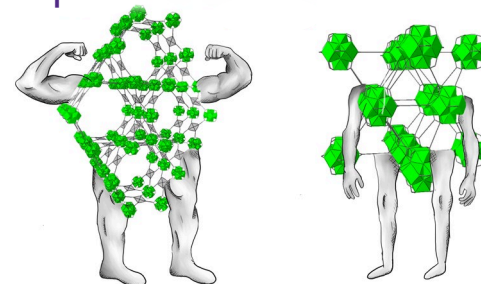
Hanna, S.L. et. al. *Under Revision.* 2023

Ch. 5 – Energy/Structure/Property



Hanna, S.L. et. al. *Chem.* 2022
Hanna, S. L. *Chem.* 2022

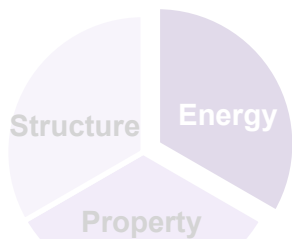
Ap. A – Radiation Stability



Hanna, S.L. et. al. *Ind. Eng. Chem. Res.* 2020

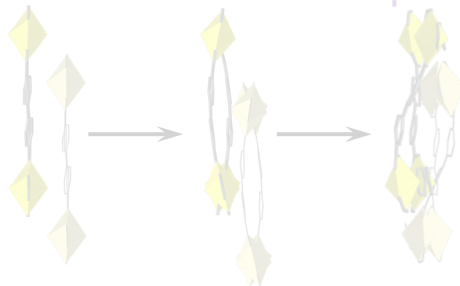
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Ch. 1 - Introduction



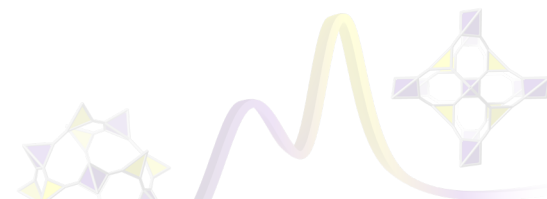
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Ch. 2 – Structure/Property



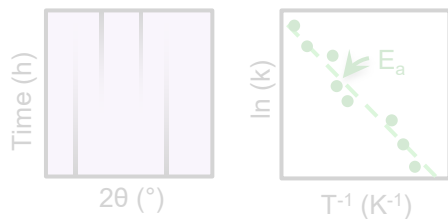
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Ch. 3 – Energy/Structure



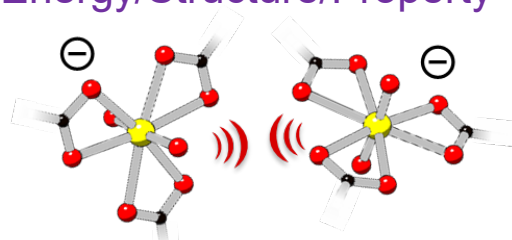
Hanna, S.L. et. al. *Chem. Sci.* 2022

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Hanna, S.L. et. al. *Under Revision.* 2023

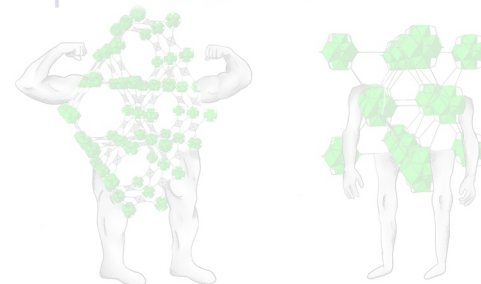
Ch. 5 – Energy/Structure/Property



Hanna, S.L. et. al. *Chem.* 2022

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Ap. A – Radiation Stability



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Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

Background

Network entanglement reduces void space



Driving Force

Repulsions of charges change thermodynamics



Experimental Control

Entangled systems that remain entangled



Discovery

Spontaneous dis-entanglement observed



Role of H₂O

Removing water speeds up dis-entanglement



Implications

Self-generate valuable pore space

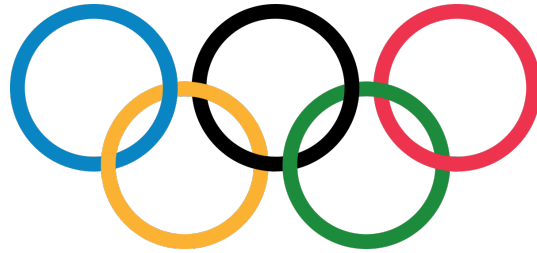
Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

Background

Network entanglement
reduces void space



Entanglement is the entwining of multiple lattices, such that **the lattices must be broken** in order to be separated



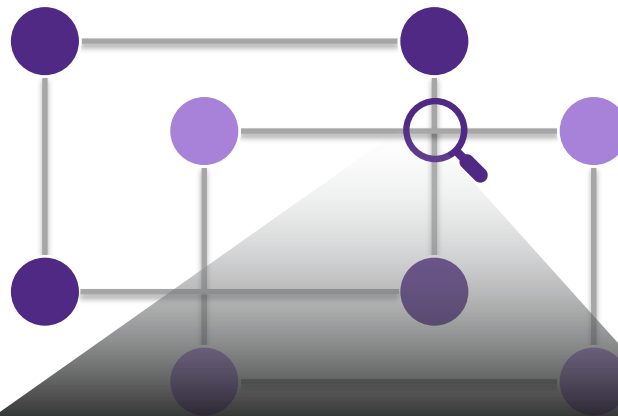
Network Entanglement is Energetically Favorable



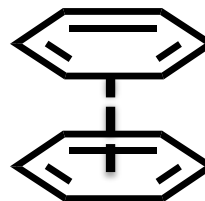
Energetically favorable



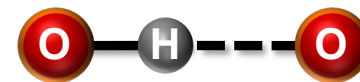
Ubiquitous in Nature and synthetic systems



π - π Stacking

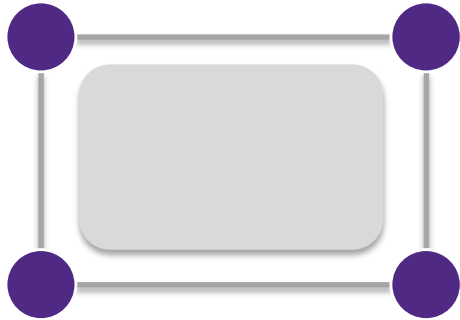


Hydrogen Bonding



Network Entanglement Reduces Valuable Pore Space

Accessible Surface Area

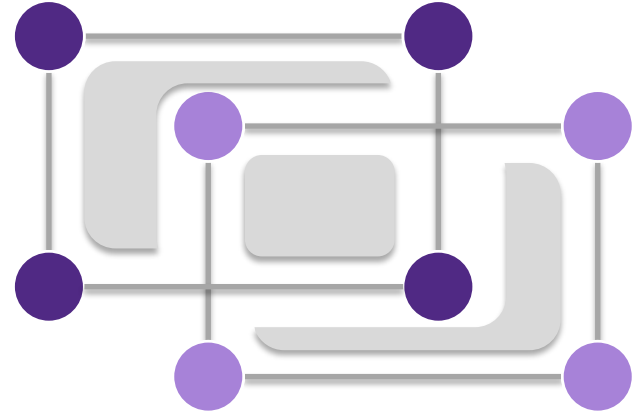


Energetically favorable

→

←

Confined Pore Space



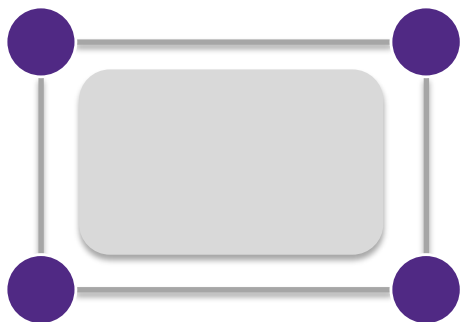
Enhanced Function

- Gas storage (gravimetric)
- Catalysis
- Chemical sensing
- Medical diagnostics
- Electronics

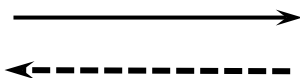
Reduced Function

- Gas storage (gravimetric)
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Accessible Surface Area

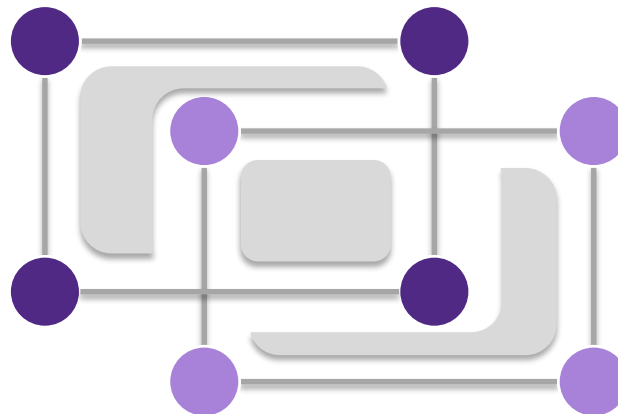


Energetically favorable



Requires external stimuli

Confined Pore Space



Temperature



Pressure



Solvent



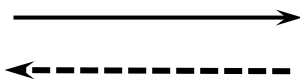
Guest

Discovery of Spontaneous Phenomenon Which Leads to Dis-Entanglement

Accessible Surface Area



Energetically favorable

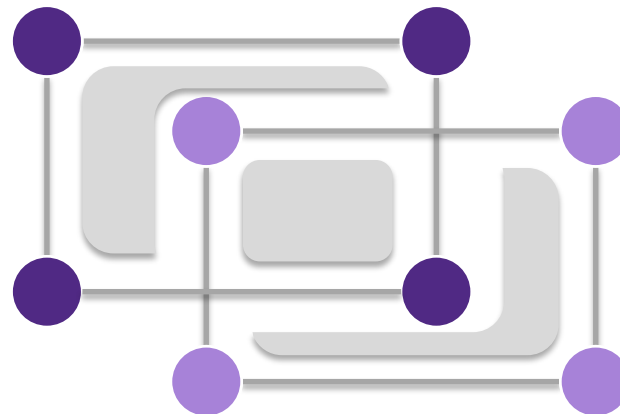


Charged Point-Point Repulsions



No external stimuli required

Confined Pore Space



Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

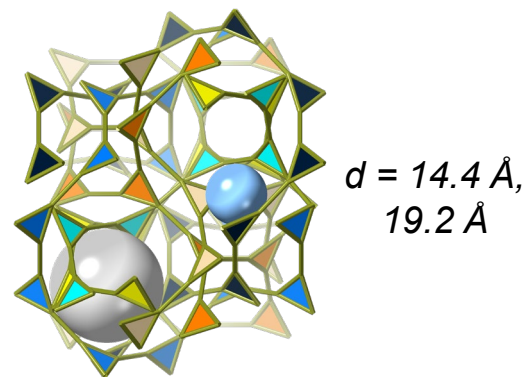
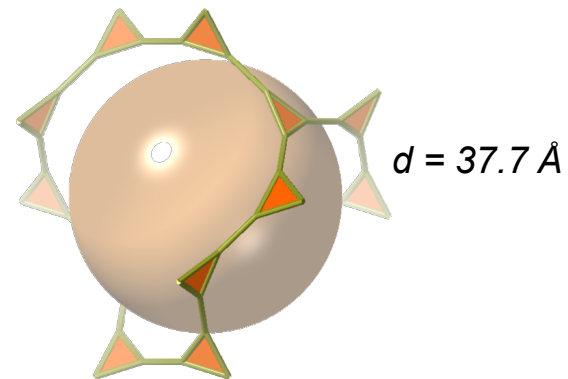
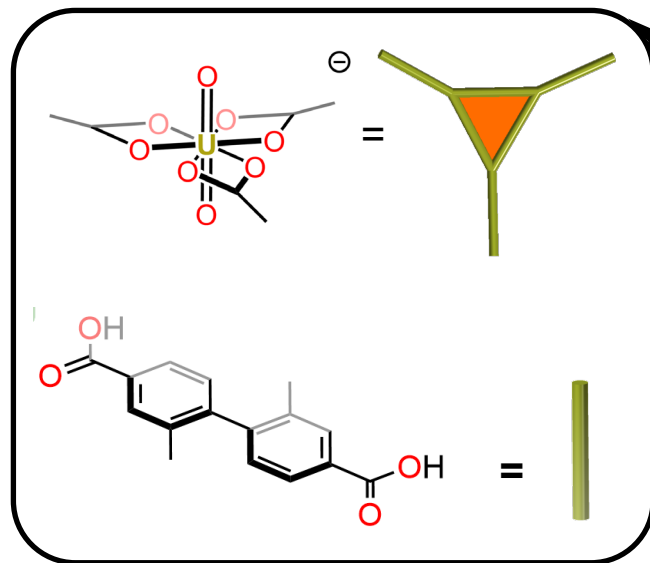
Background

Network entanglement
reduces void space

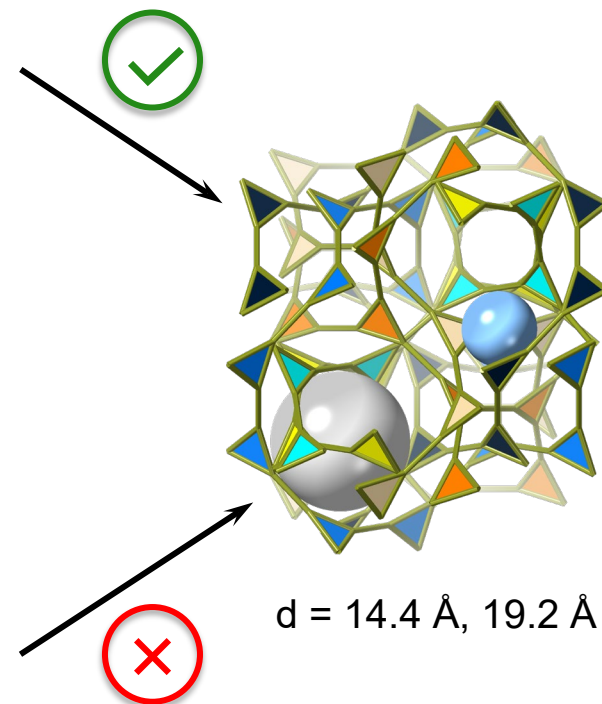
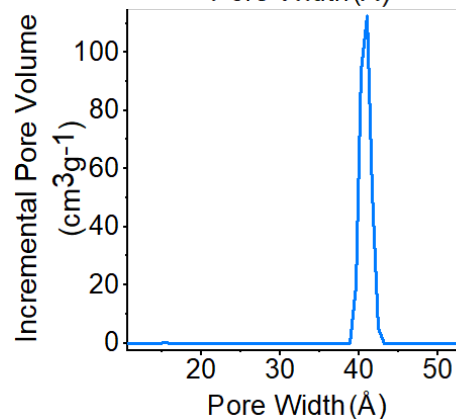
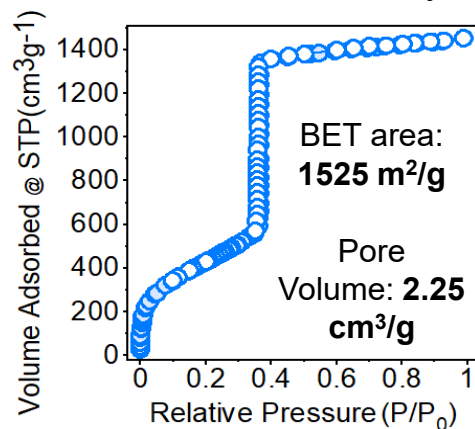
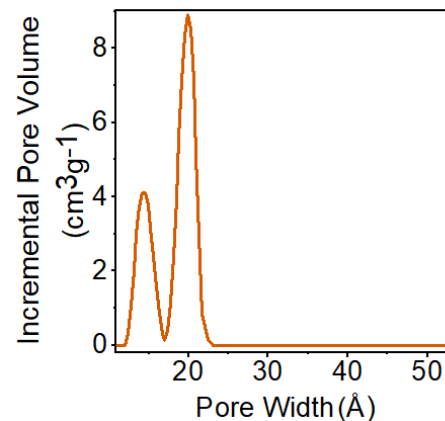
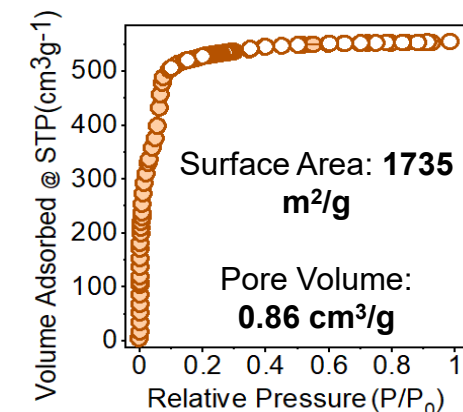


Discovery

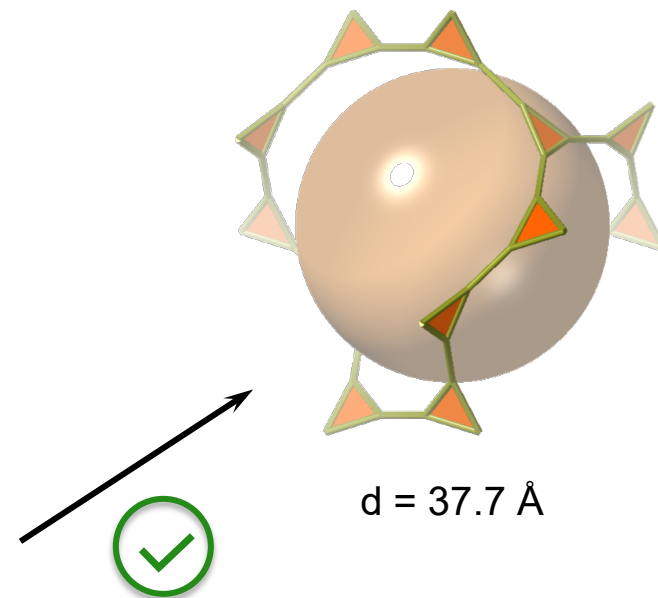
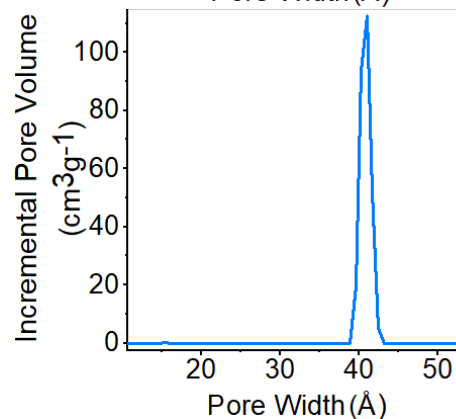
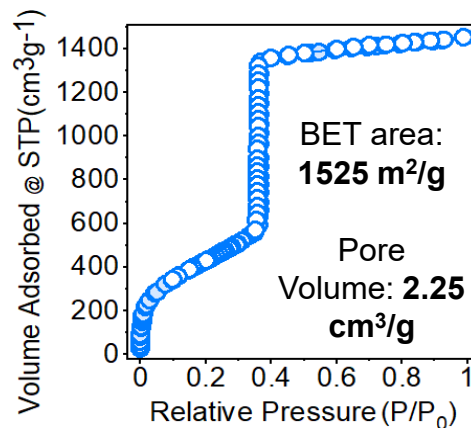
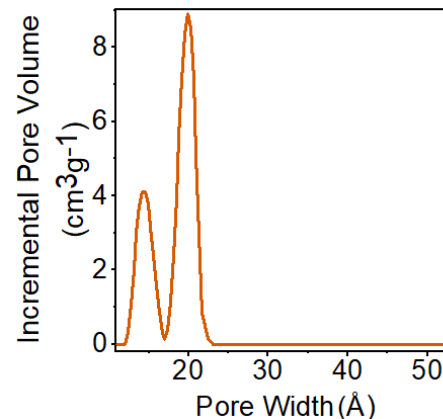
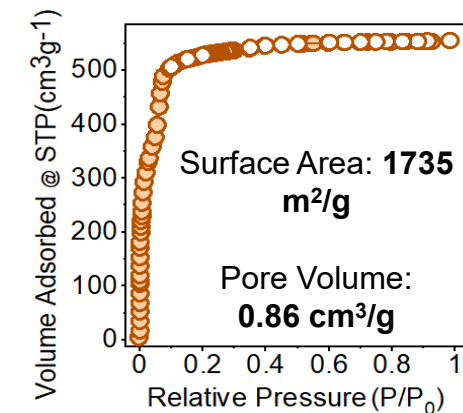
Spontaneous dis-
entanglement observed



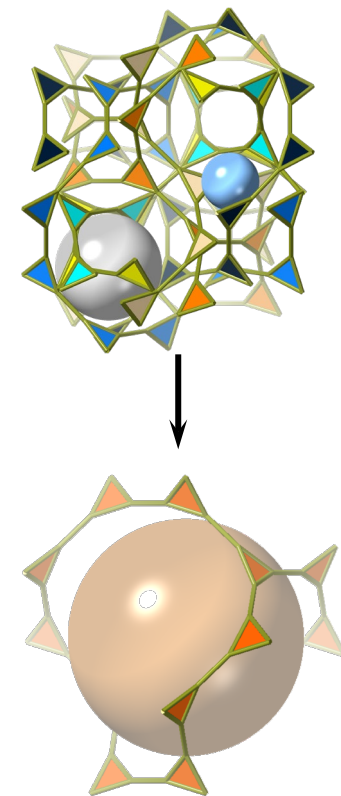
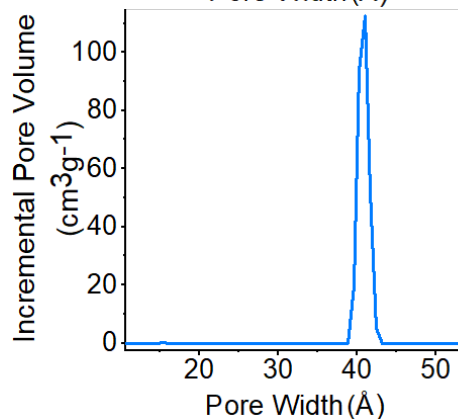
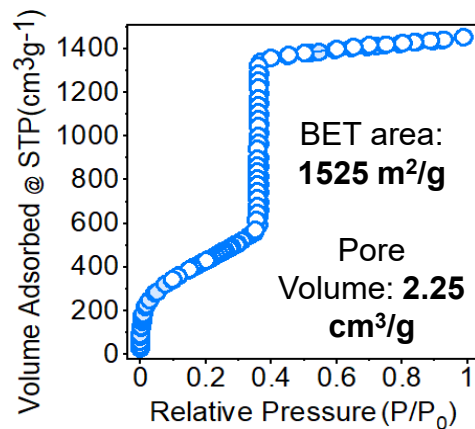
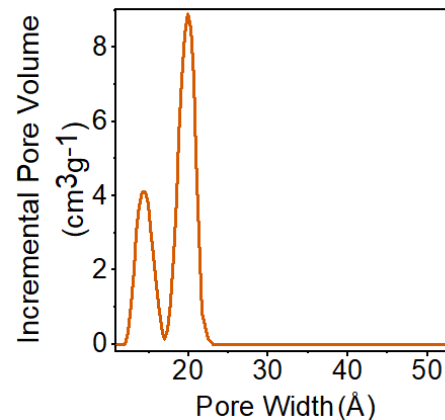
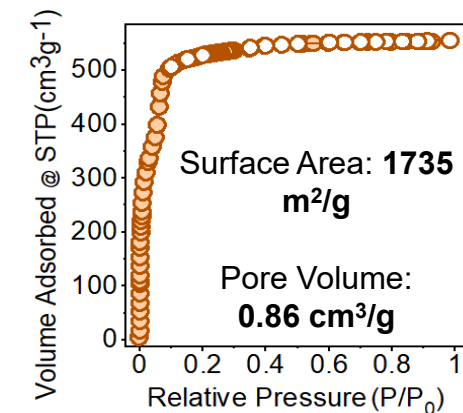
De-Interpenetration Discovered After 5 Months of Soaking in Solvent at Room Temperature



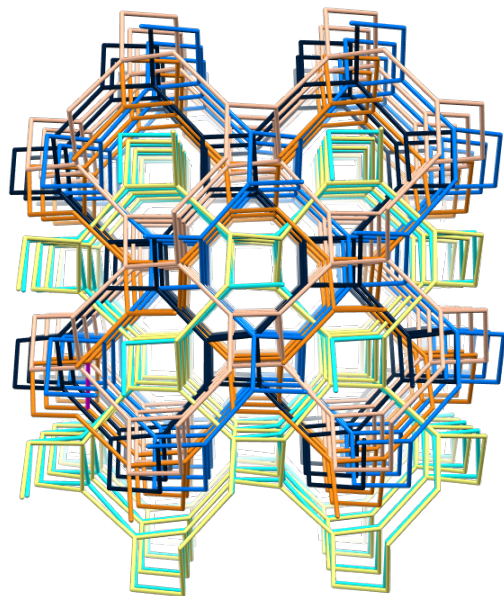
De-Interpenetration Discovered After 5 Months of Soaking in Solvent at Room Temperature



De-Interpenetration Discovered After 5 Months of Soaking in Solvent at Room Temperature

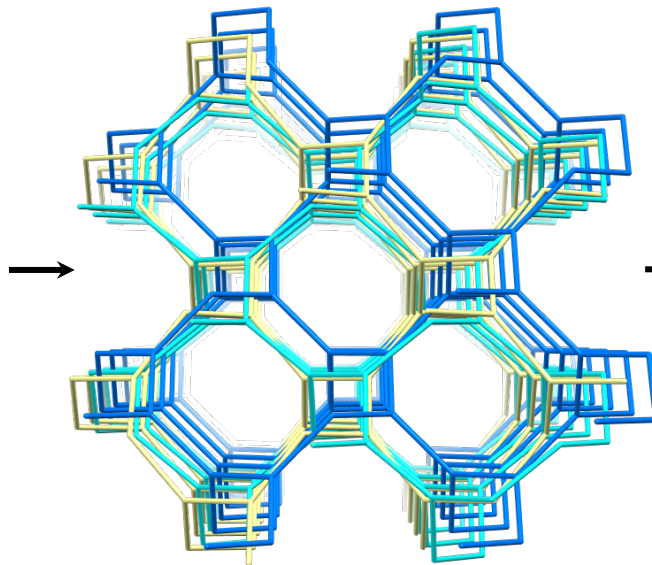


Interpenetrated



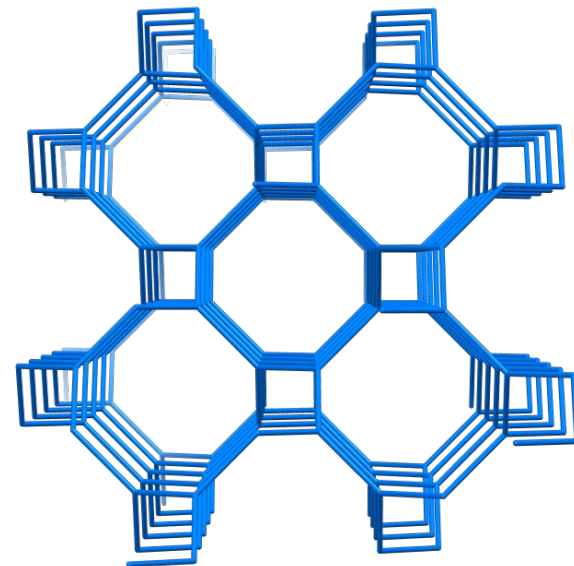
NU-1303-6

De-Interpenetration Intermediate



NU-1303-3

De-Interpenetrated



NU-1303-1

Interpenetrated

De-Interpenetration Intermediate

De-Interpenetrated

Highest porosity of any MOF reported to date:

96.6% free volume

9.2 cm³ g⁻¹ pore volume

Dense framework transformed into the most open MOF material

NU-1303-6

NU-1303-3

NU-1303-1

Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

Background

Network entanglement
reduces void space



Driving Force

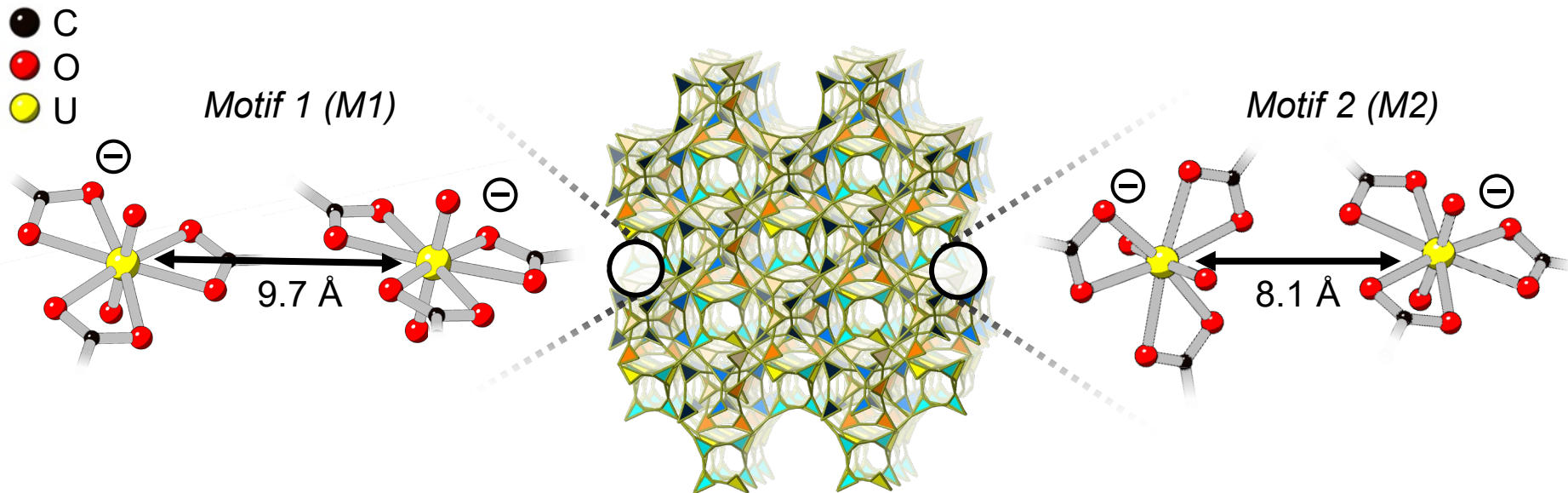
Repulsions of charges
change thermodynamics



Discovery

Spontaneous dis-
entanglement observed

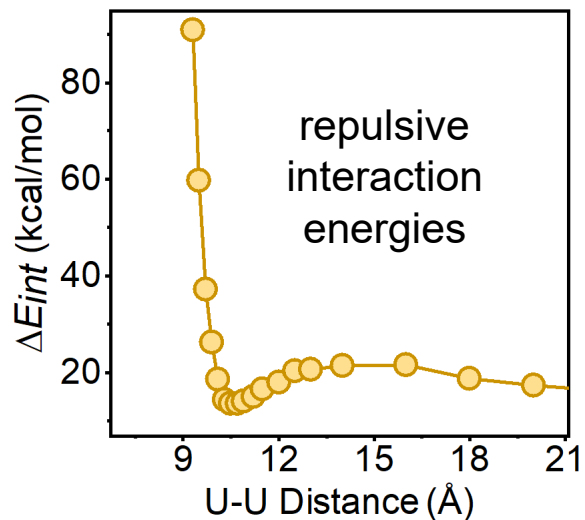
What Drives De-Interpenetration in NU-1303-6?



Hypothesis

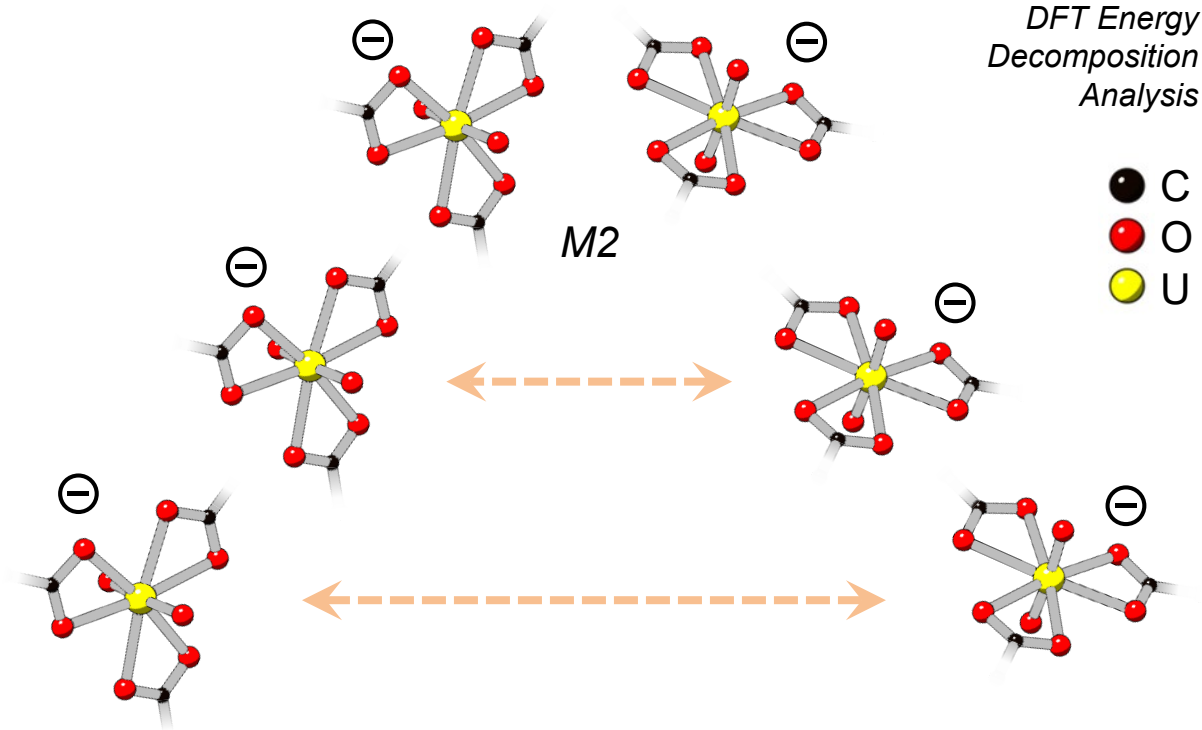
Since charged points are closely spaced, unfavored **charged point-point repulsions** drive dis-entanglement

Charged Point-Point Repulsions Drive De-Interpenetration



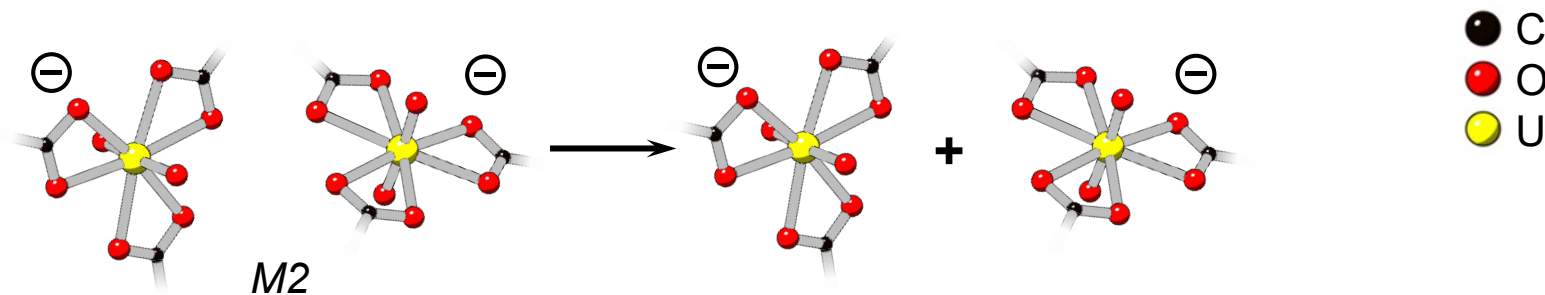
Key Point

U-U repulsions dominate the electronic energy landscape



with Saumil Chheda & Debmalya Ray, Gagliardi Group (University of Chicago)

Free Energy of Transformation DFT Models



$$\Delta G = \frac{2 * G_{NU-1303-1} - G_{NU-1303-6}}{2} = -15.8 \text{ kcal mol}^{-1}$$

Key Point

Negative ΔG shows that de-interpenetration is spontaneous and thermodynamically favored

with Saumil Chheda & Debmalya Ray, Gagliardi Group (University of Chicago)

Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

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change thermodynamics



Discovery

Spontaneous dis-
entanglement observed



Role of H₂O

Removing water speeds
up dis-entanglement

Faster De-Interpenetration Under Low Humidity, Slower De-Interpenetration Under High Humidity



NEWS CHICAGO WEATHER

Chicago set new cold weather records

Rockford and Illinois broke all-time record temperatures

By Sara Freund | Updated Feb 1, 2019, 9:43am CST

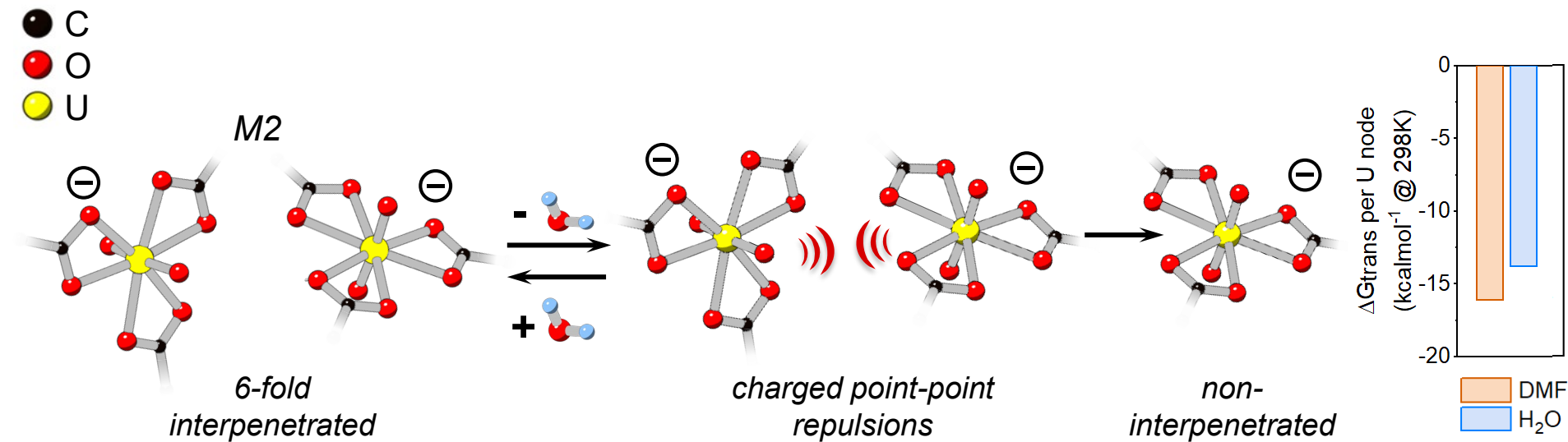


CHICAGO WEATHER

Heat Wave, Humidity Continue Into the Week for Chicago

The heat index could reach 100 by Wednesday





Key Point

Removing H₂O increases the speed of de-interpenetration by 36 times

Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

Background

Network entanglement reduces void space



Driving Force

Repulsions of charges change thermodynamics



Experimental Control

Entangled systems that remain entangled



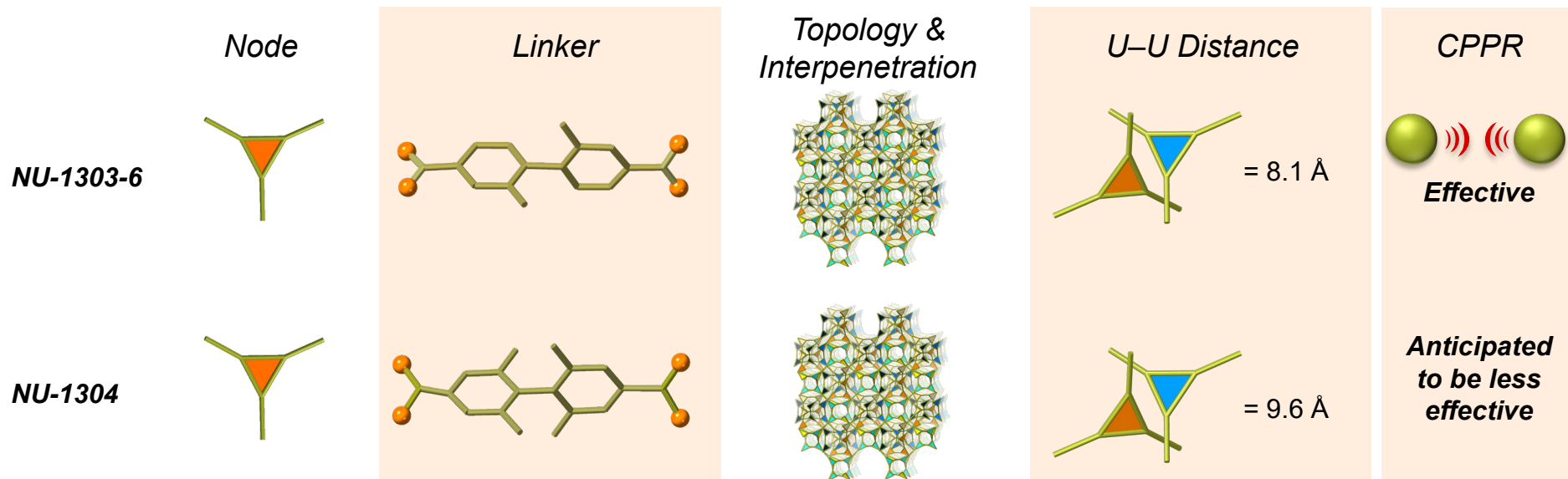
Discovery

Spontaneous dis-entanglement observed



Role of H₂O

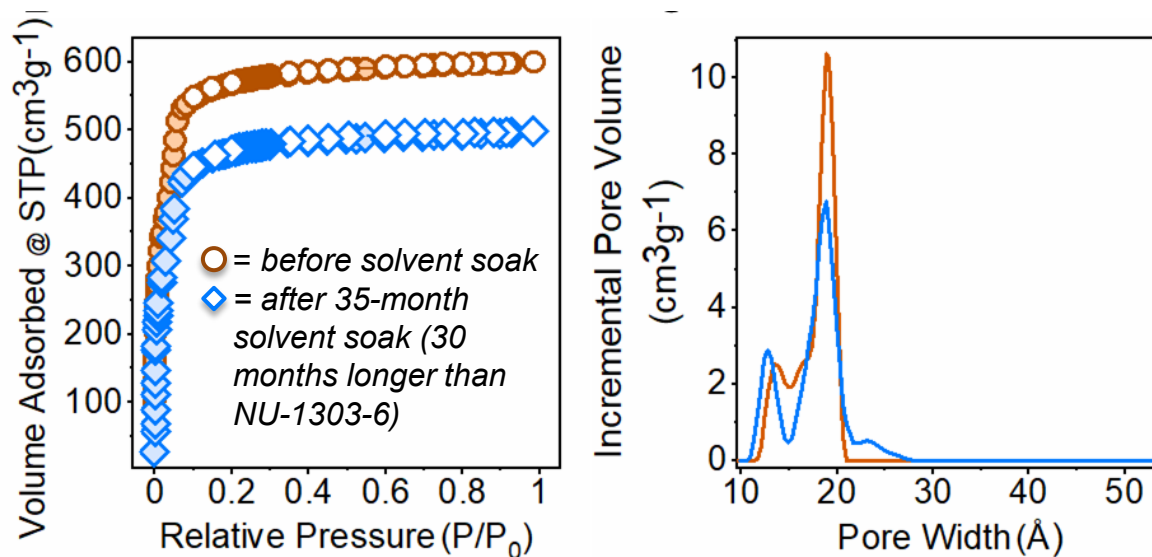
Removing water speeds up dis-entanglement



Hypothesis

Less effective CPPR anticipated for NU-1304 since larger distance between closest nodes

with Ryther Anderson & Katarina Zosel, Gomez-Gualdron Group (Colorado School of Mines)
with Penghao Li, Stoddart Group (Northwestern University)



Key Point

NU-1304 remains interpenetrated under the same conditions that led to de-interpenetration in NU-1303-6

Discovery of Spontaneous De-Interpenetration Through Charged Point-Point Repulsions

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Driving Force

Repulsions of charges change thermodynamics



Experimental Control

Entangled systems that remain entangled



Discovery

Spontaneous dis-entanglement observed



Role of H₂O

Removing water speeds up dis-entanglement



Implications

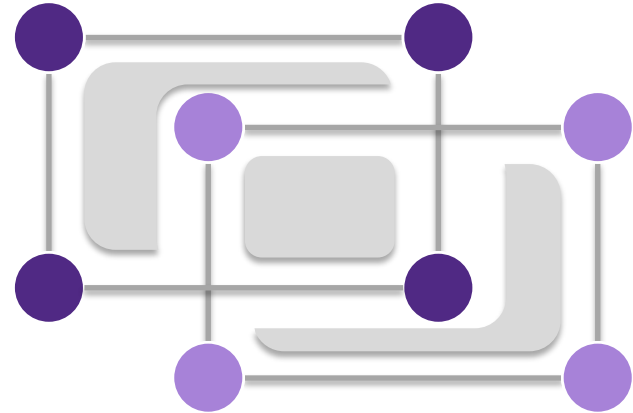
Self-generate valuable pore space

Accessible Surface Area



Energetically favorable
→
charged point-point repulsions

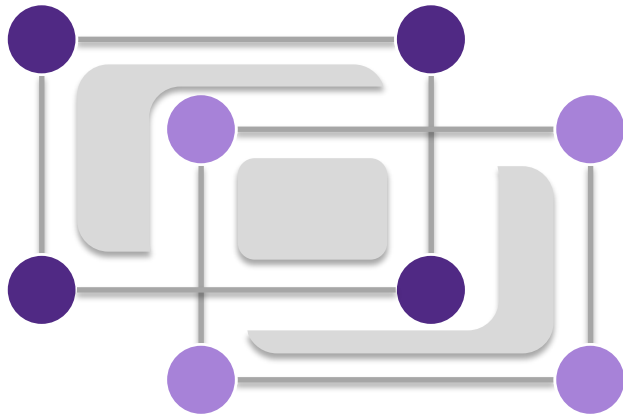
Reduced Void Space



First reported spontaneous network disentanglement,
allowing for ultra-high porosity and enhanced function

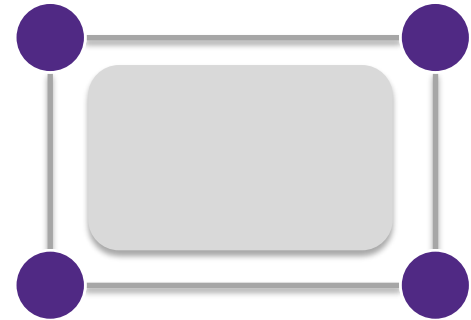
Impact of Charged Point-Point Repulsions (CPPR)

Reduced Void Space



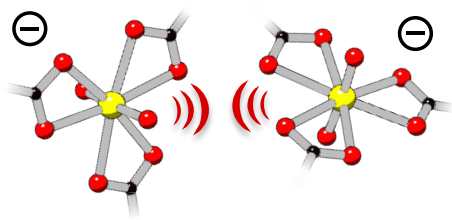
Energetically
favorable
→
*charged point-
point repulsions*

Accessible Surface Area



First reported spontaneous network disentanglement,
allowing for ultra-high porosity and enhanced function

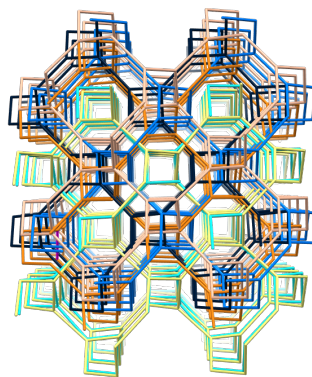
Energetics



CPPR Discovered

Reversing universal thermodynamics of porosity

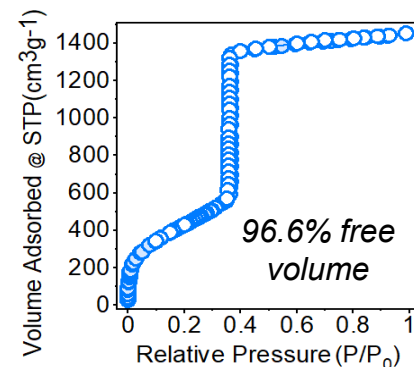
Structure



Observed in NU-1303-6

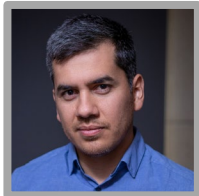
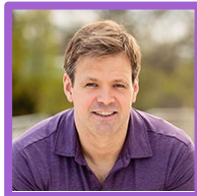
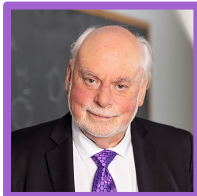
Crystallography, DFT computation, gas physisorption

Property



Void Space Generated

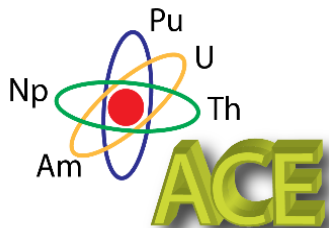
Record high pore volume and void fraction



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