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Negative Thermal Expansion Design Strategies in Metal-Organic Frameworks

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Sandia National Laboratories

National Interest

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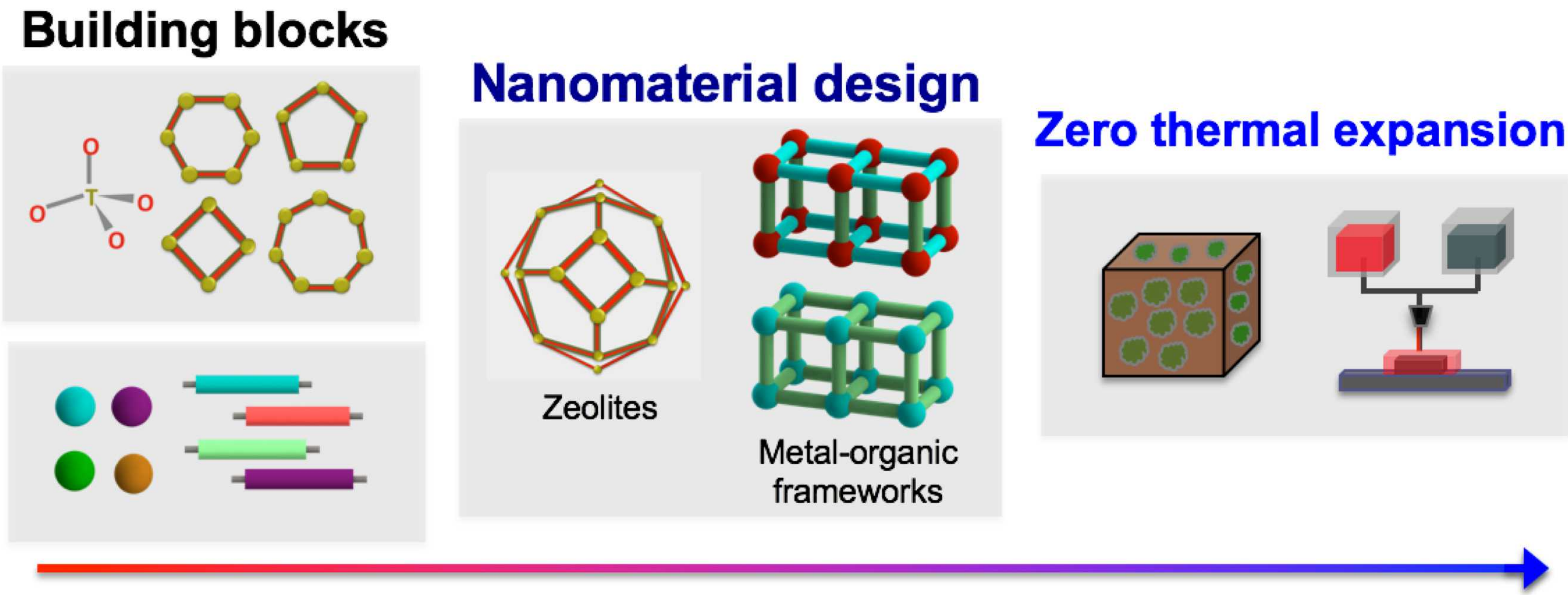
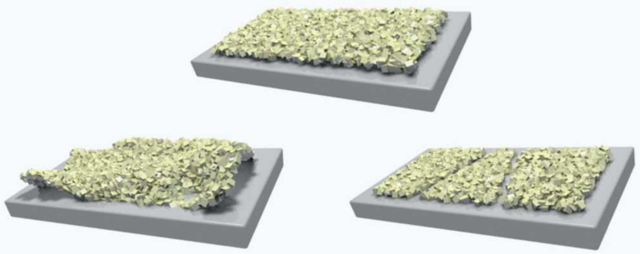
Project vision

Negative thermal expansion material design



Fundamental understanding

Material interfaces
Thin films and composite materials

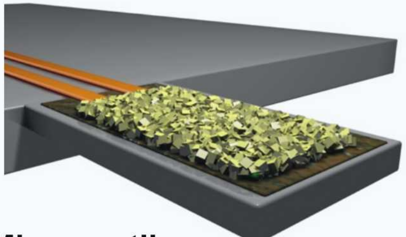


Poor adhesion **Strong adhesion**

Constrained materials
Nanoscale devices

Cracking

Material responses
Sensors and precision instruments



Microcantilever

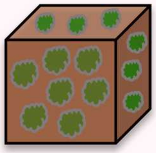
Stassen, Burtch, Talin, Falcaro, Allendorf, Ameloot, *Chem. Soc. Rev.* 2017, *46*, 3185.

Negative thermal expansion (NTE) application opportunities

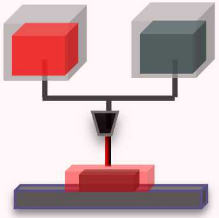
Composite materials

Doping into PTE matrix to produce

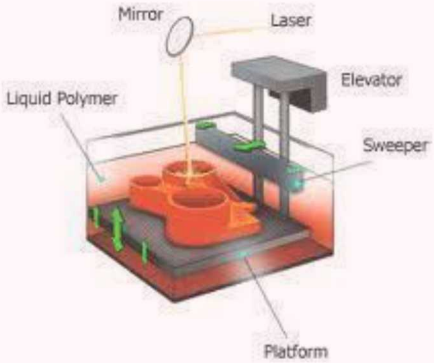
- Overall ZTE
- Better match CTE at interface



Additive manufacturing

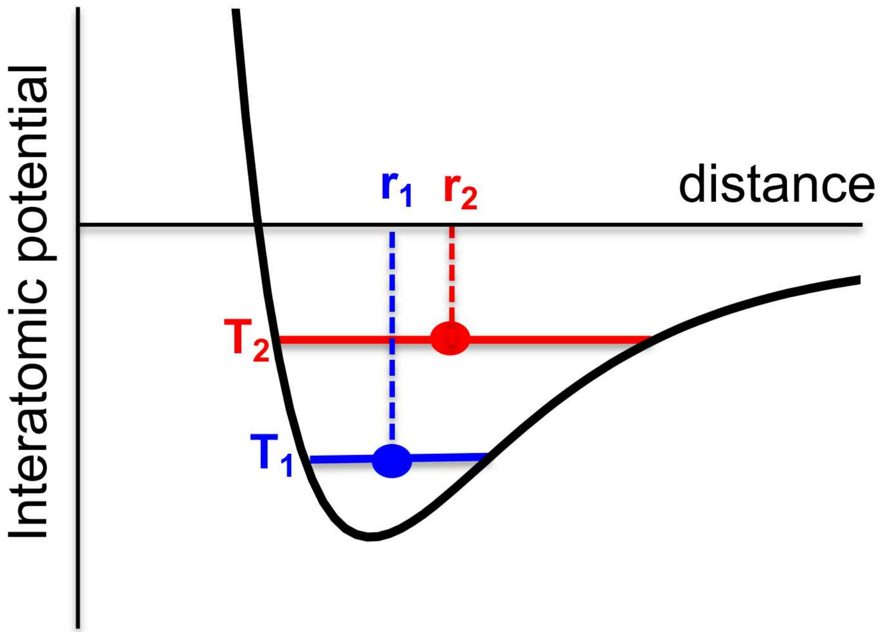


Material jetting



Stereolithography

Positive thermal expansion



Coefficient of thermal expansion (CTE)

$$\alpha_l = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P$$

Units: K^{-1}

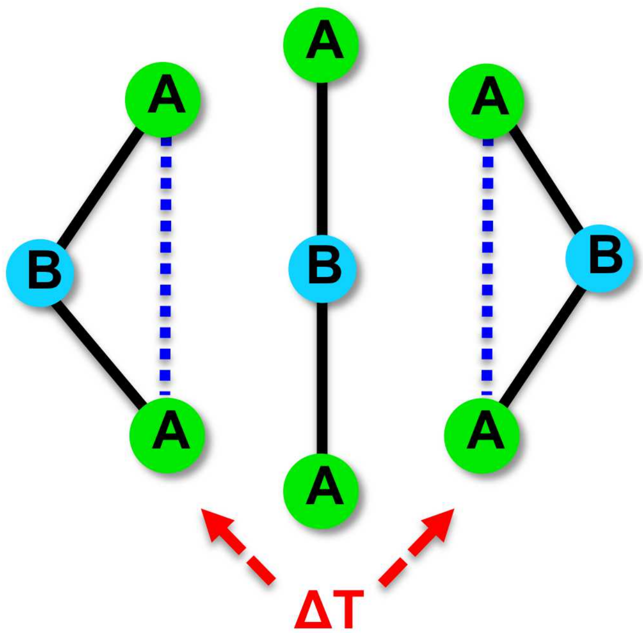
<u>C.T.E (298K)</u>[1,2]

Silicon:	2.6 ppm/K
Copper:	17 ppm/K
Gold:	13 ppm/K

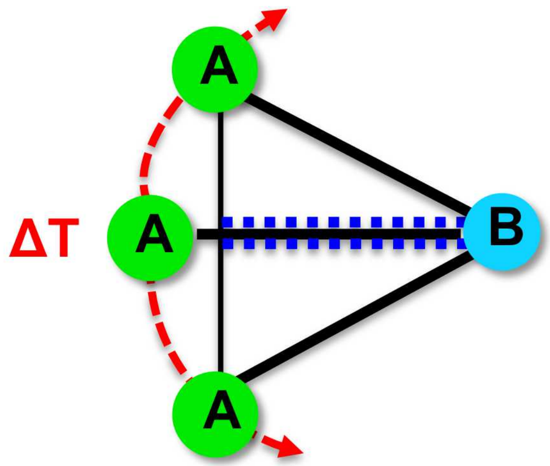
1. Swenson, *J. Phys. Chem. Ref. Data* 1983, 12, 179.
2. Buffington, R.; Latimer, W. *Coefficients Expans.* 1926, 48, 2305.

Negative thermal expansion in solids

Vibrational mechanisms of NTE[1]



Transverse motions

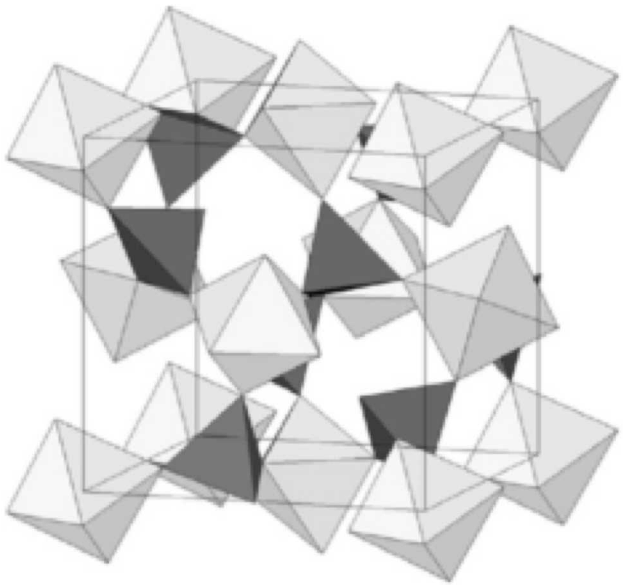


Librational motions

1. Barrera, Bruno, Barron, Allan. “Negative thermal expansion,” *J. Phys. Condens. Matter, 2005.*

Benchmark material

ZrW_2O_8



Pale gray = ZrO_6
Dark gray = WO_4

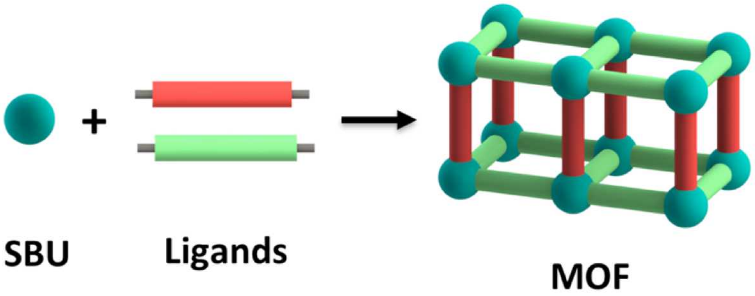
Negative thermal expansion from 0.3K to 1050K in ZrW_2O_8

Mary, Evans, Sleight, Vogt. ***Science***, 1996.

Limitations

(1) Limited NTE tunability
(2) Compatibility with PTE matrix

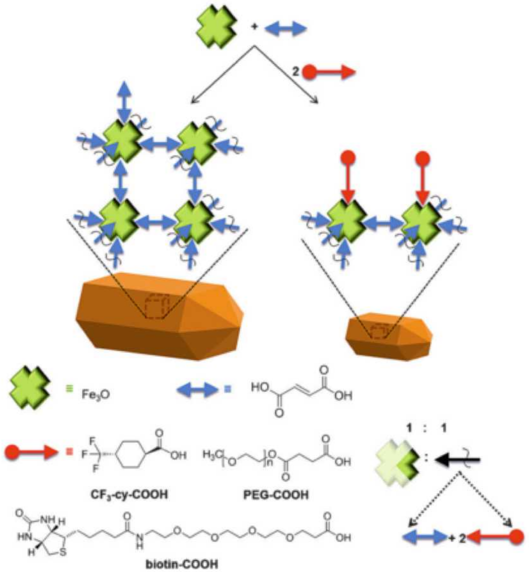
MOF opportunities



(1) Tunable structural chemistry

(2) Tailorable surface chemistry

(3) Low density (< 1 g/cm^3)



Rijnaarts et al. *Chem. Eur. J.* 2015, 21, 10296.

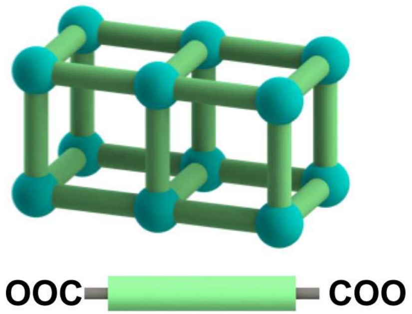
Coordination modulation

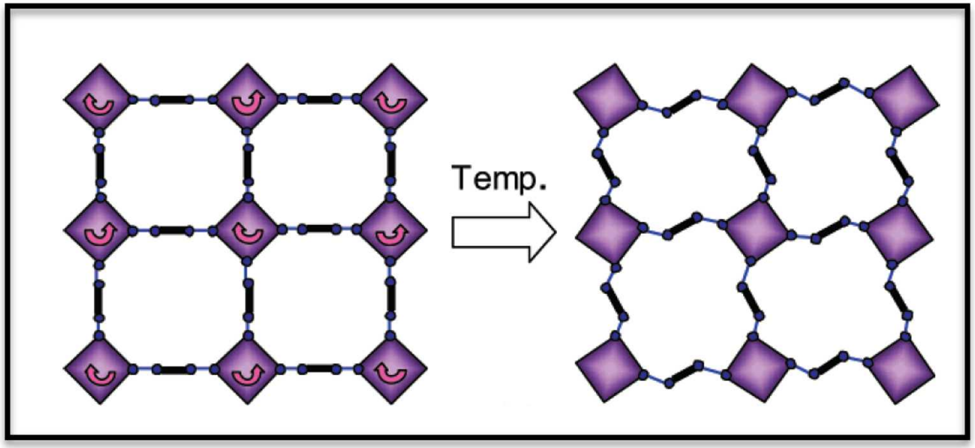
"**growth**" vs. "**capping**" ligands

Negative Thermal Expansion in MOFs

IRMOF-1/MOF-5

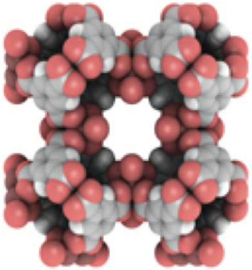
Dubbeldam, Walton, Ellis, Snurr *Angew. Chemie,* 2007, 46, 4496.
Han, Goddard, *J. Phys. Chem. C.* 2007, 111, 15185.
Greathouse, Allendorf *J. Phys. Chem. C.* 2008, 112, 5795.

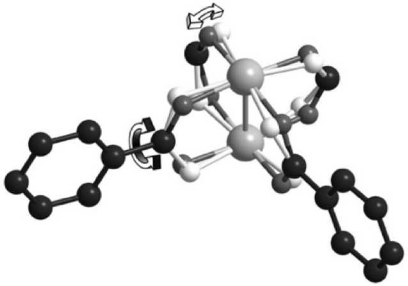




HKUST-1/Cu-BTC

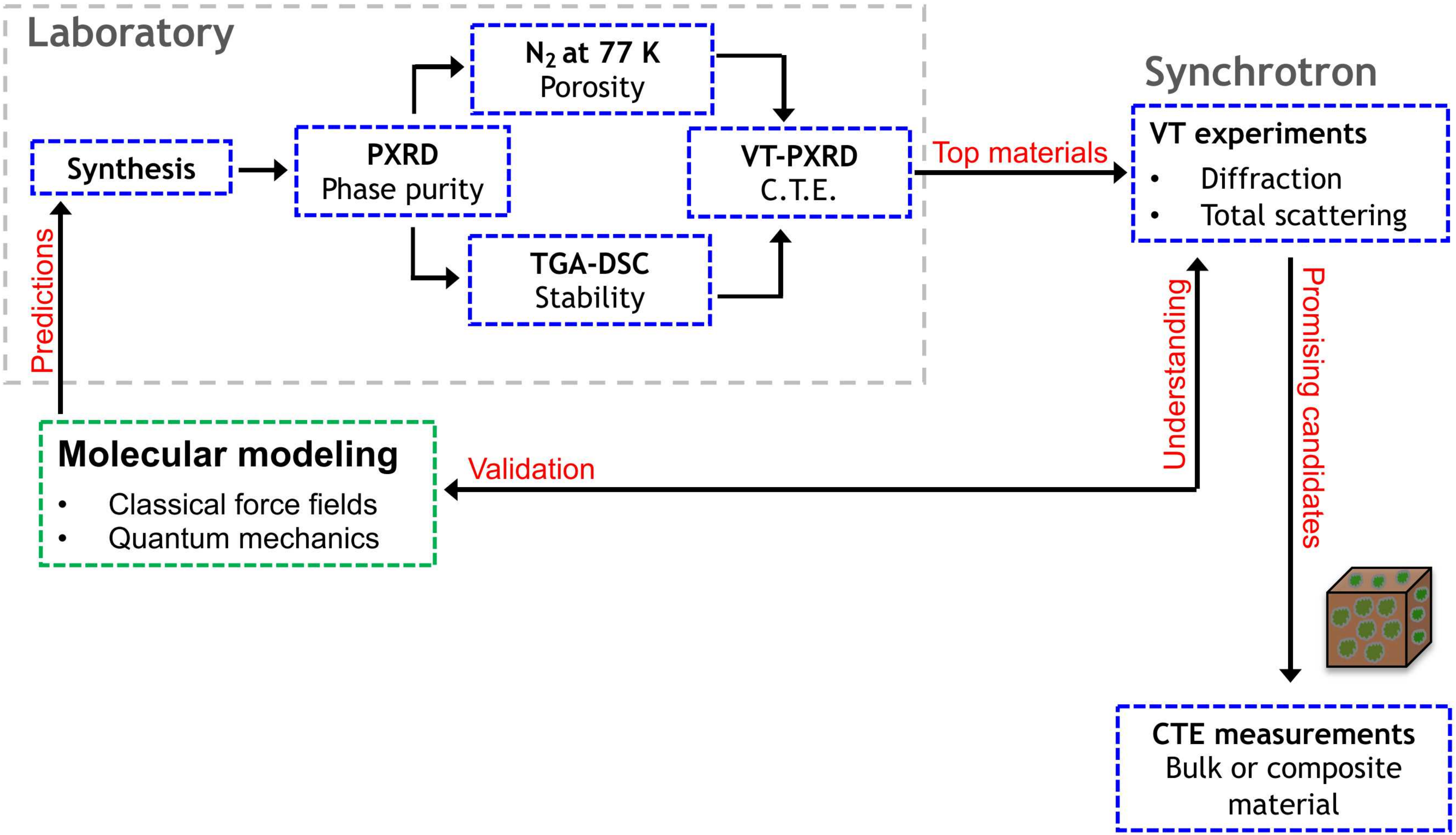
Wu et al., *Angew. Chemie,* 2008, 120, 9061.





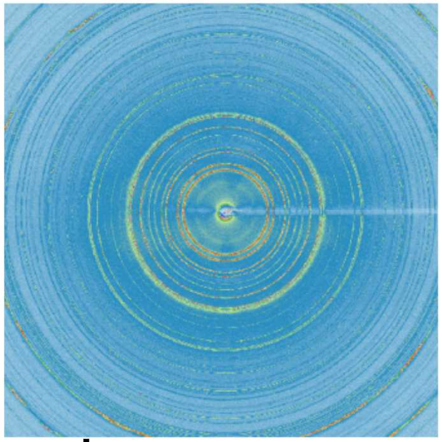
Characterization approach

Complimentary **experiments** and **molecular modeling**

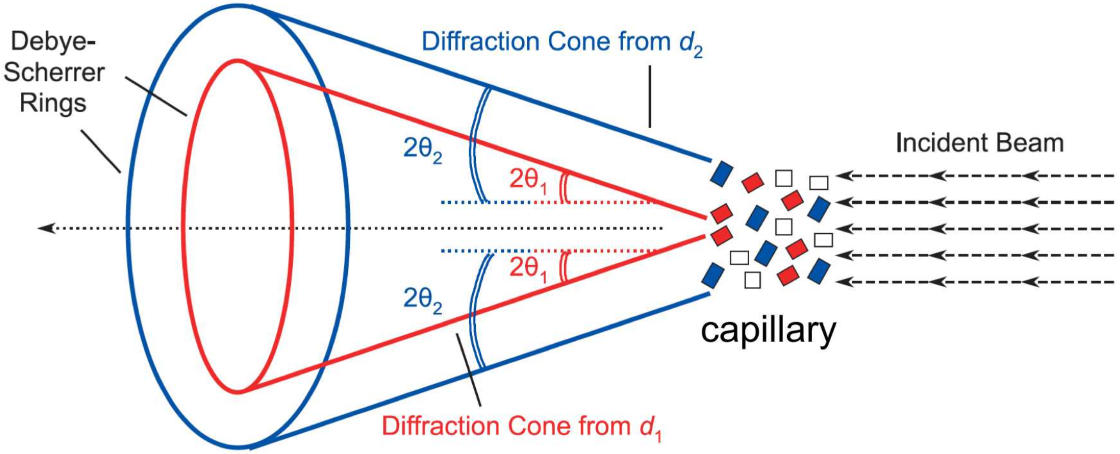


Quantifying thermal expansion: XRD

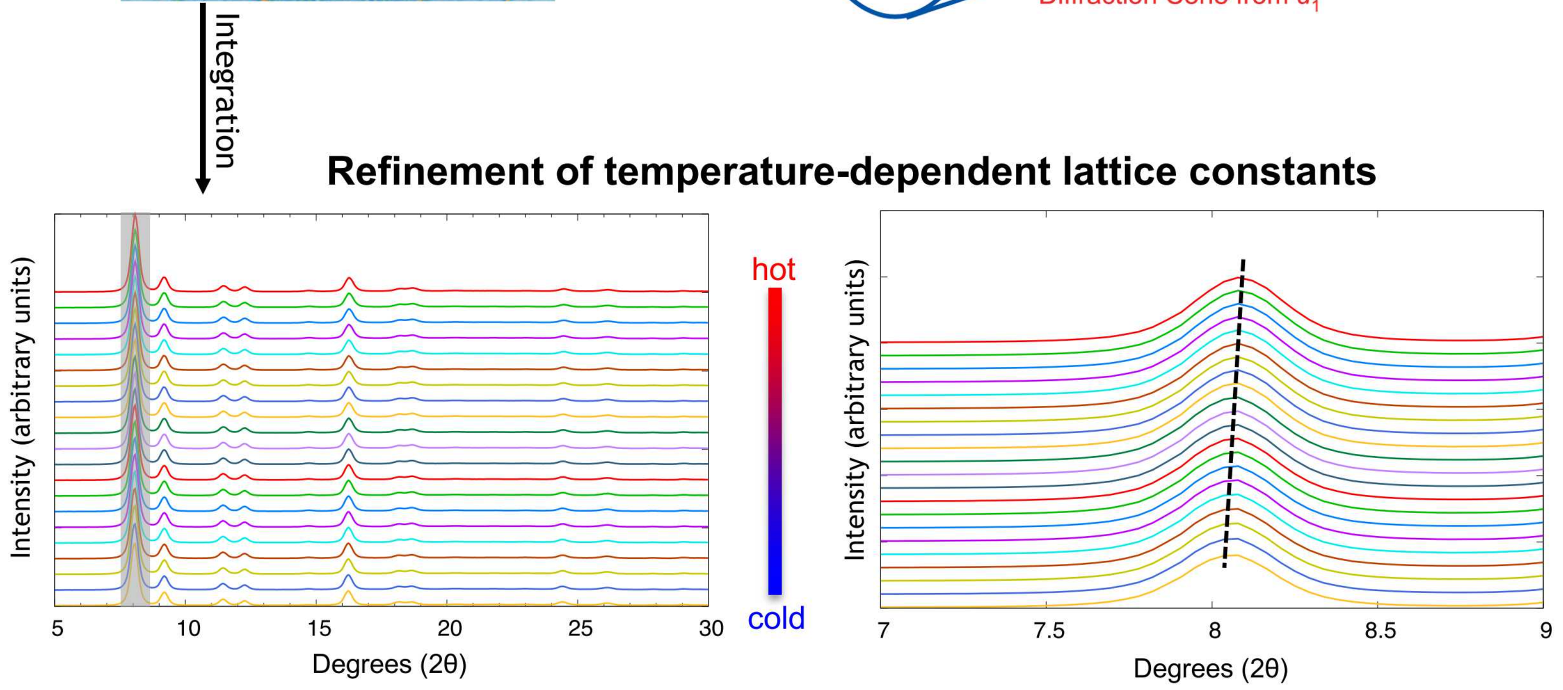
2D detector



Transmission mode powder diffraction



Refinement of temperature-dependent lattice constants

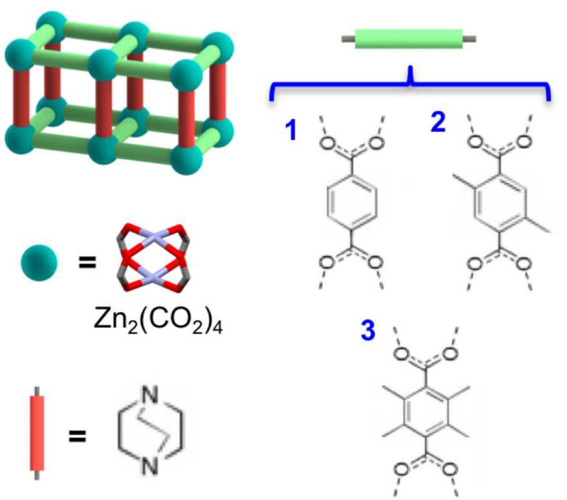


Systems for thermal expansion understanding

Pillared DABCO-based MOFs

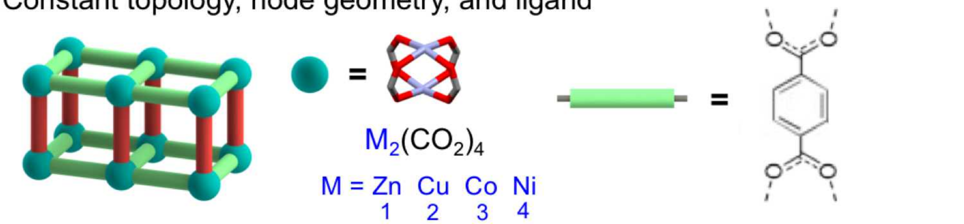
Ligand sterics

Constant topology, node geometry, metal species

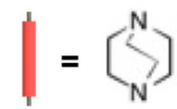


Metal identity

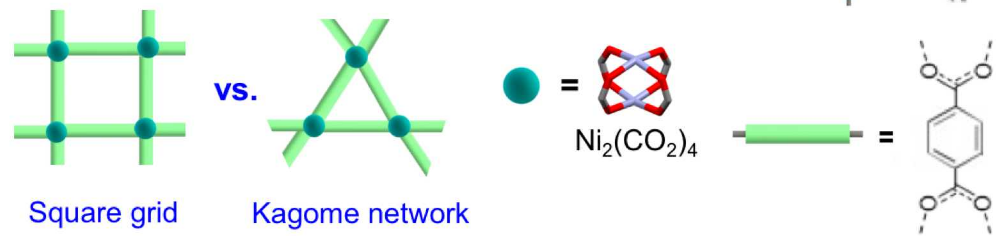
Constant topology, node geometry, and ligand



Topology effects



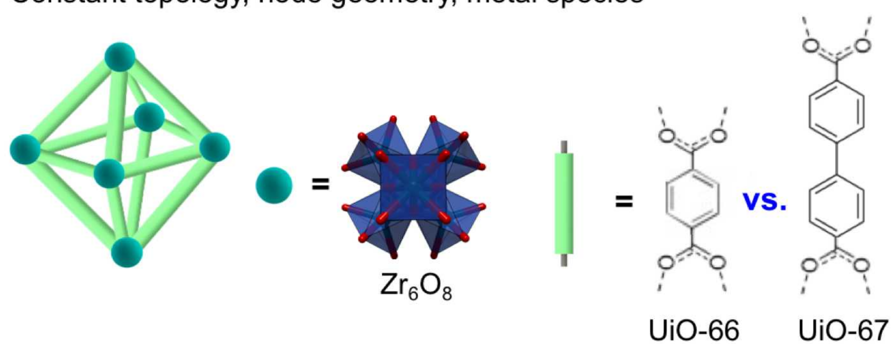
Constant metal cluster geometry, metal identity, and ligand



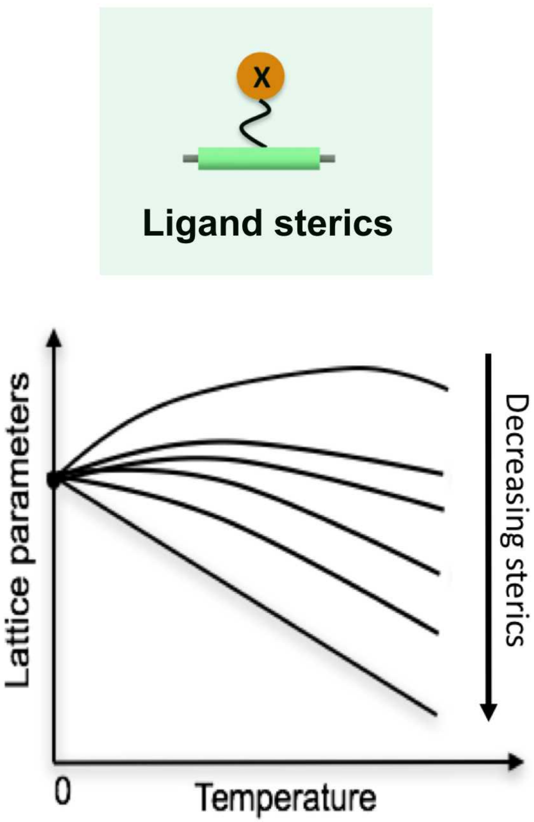
Guest species

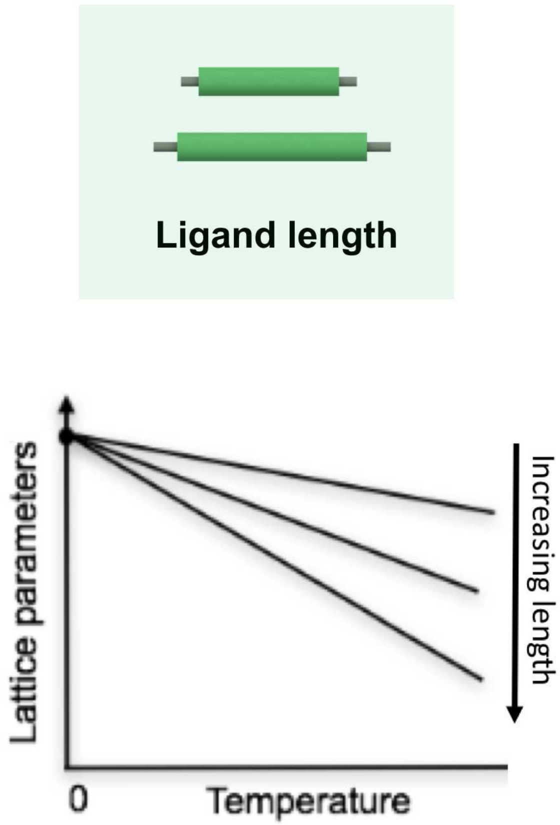
Ligand length

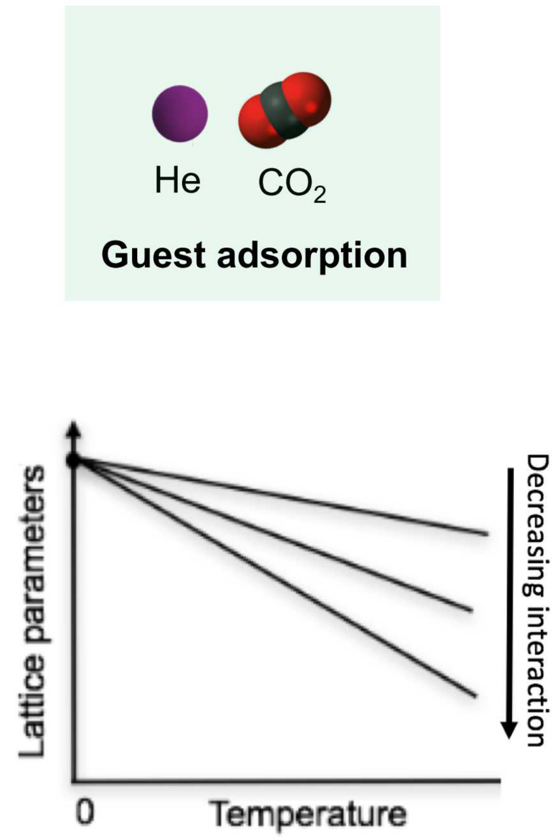
Constant topology, node geometry, metal species



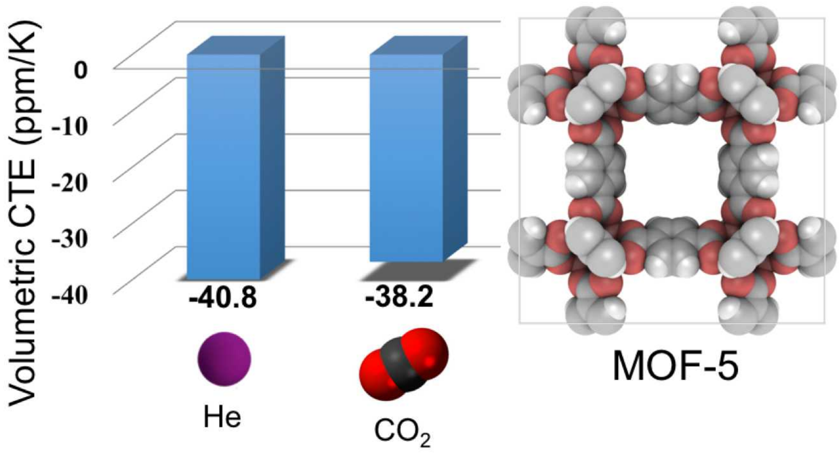
Design strategies

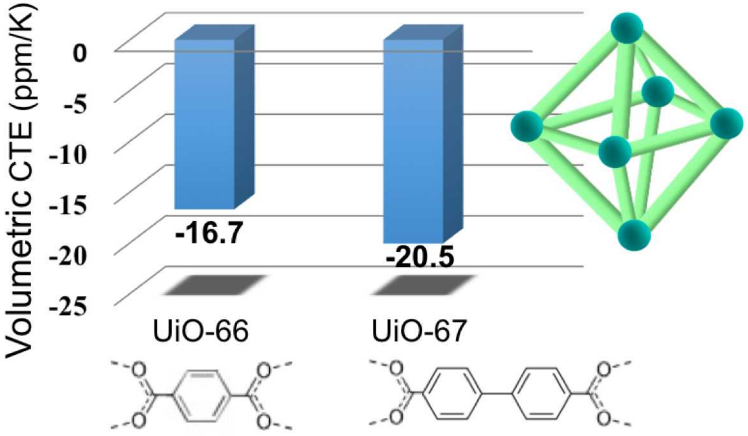


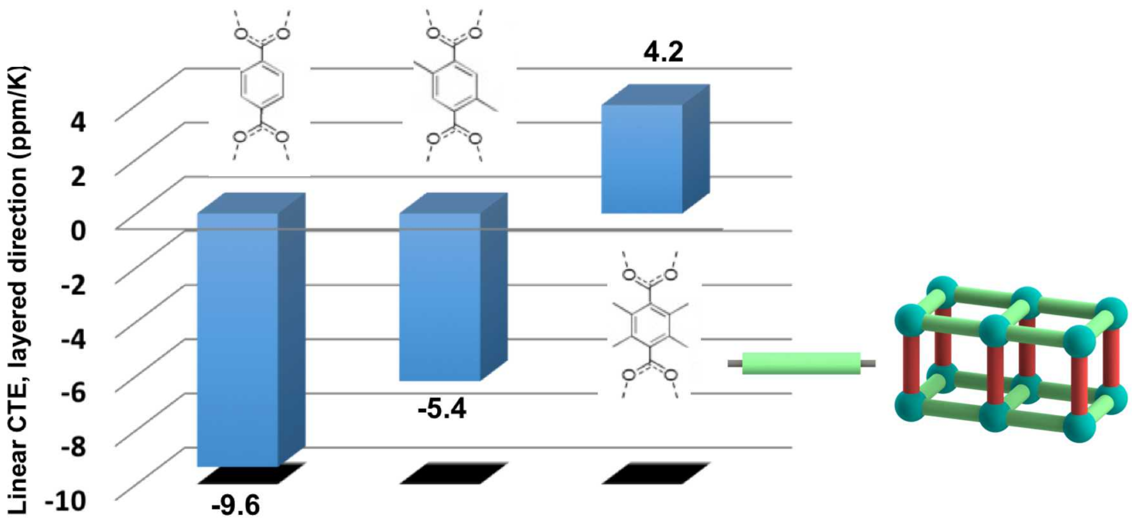




Average CTE values from ~0ºC to 100ºC

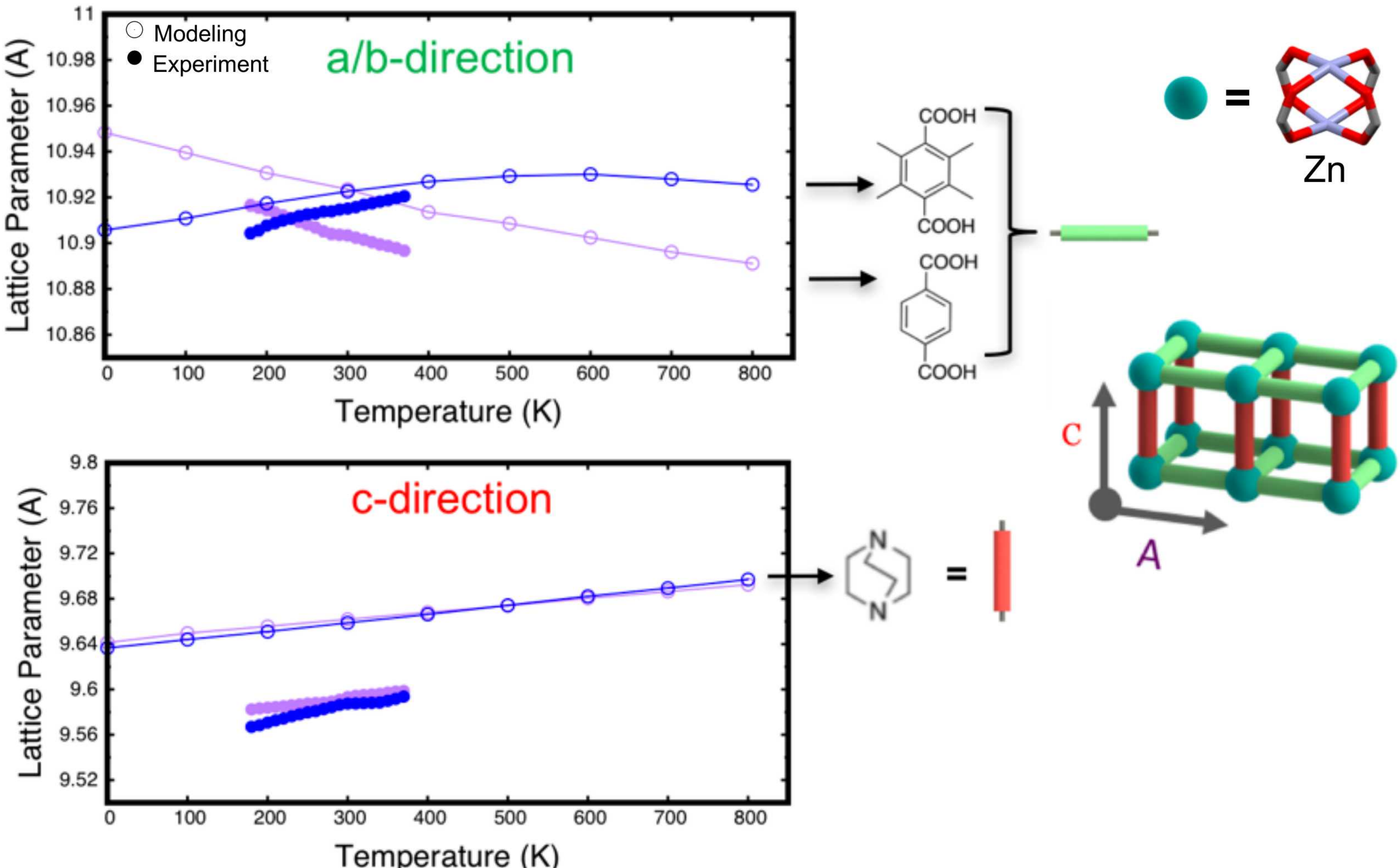






Comparing models to experiments

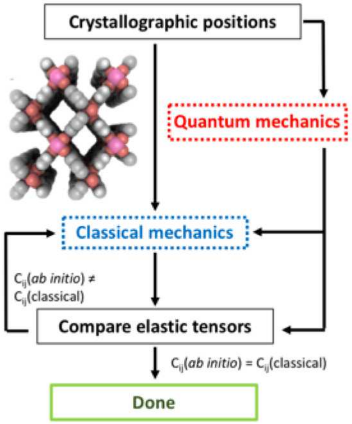
Thermal expansion predictions from molecular mechanics (prior to experiment)



Burtch, Dubbeldam, Walton, *Molecular Simulation*, 2015, 41, 1379.

More accurate parameterization approaches

Enabling more accurate thermal expansion predictions



Novel parameterization approach

Traditional approaches
- Bottom-up (cluster-based) →
- Generic F.F. libraries →

Problematic for low frequency modes
- Neglect periodicity
- Not parametrized for inorganics

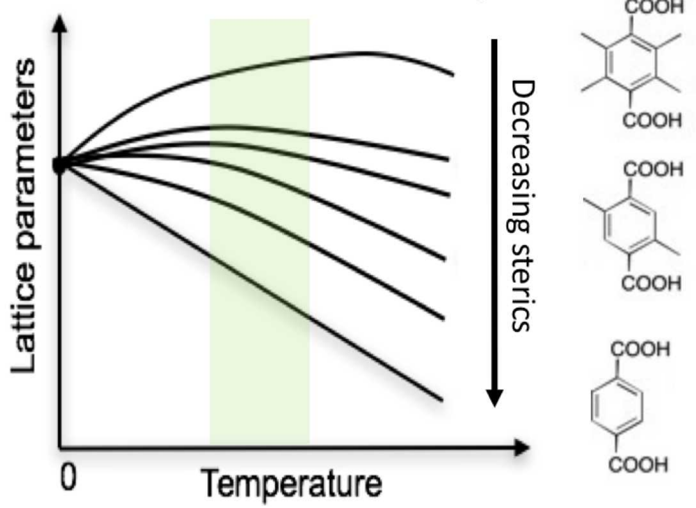
Top-down approach[1]
Fit classical model to reproduce *ab initio* elastic tensor

Periodic mechanical behavior captured
- Accurately captures low frequency modes
- Identify missing functional forms

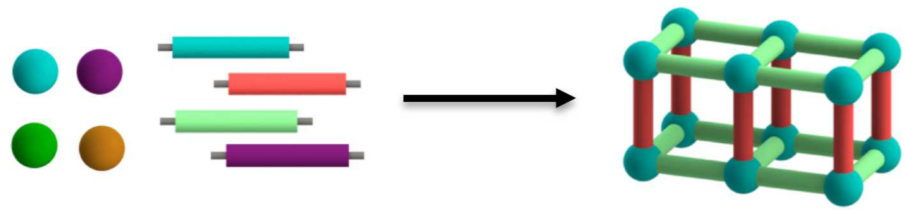
Heinen, Burtch, Walton, Dubbeldam, *Journal of Chemical Theory and Computation*, 2017, 13 (8), 3722-3730.

Fine-tuning thermal expansion

Discrete CTE changes

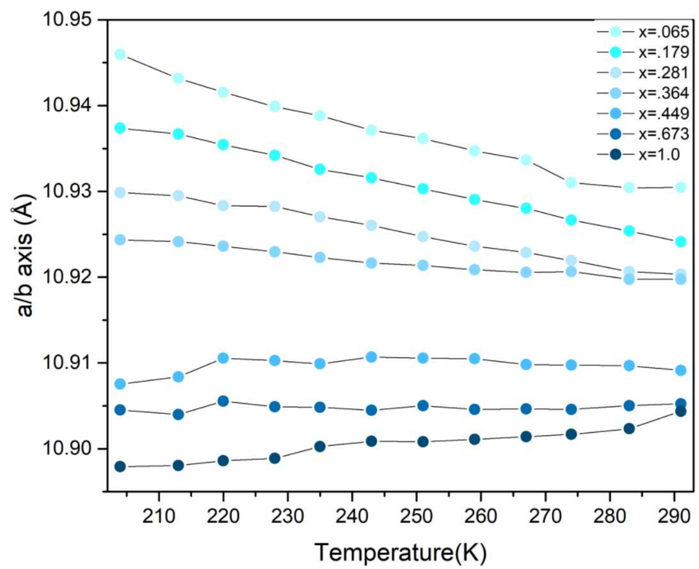


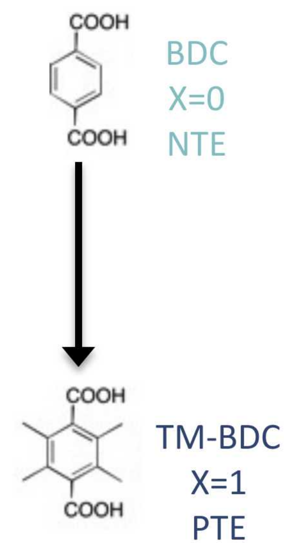
MOF solid solutions: precisely tailored CTE control



Multiple ligands within a single phase

$Zn_2(BDC)_{2-2x}(TM\text{-}BDC)_{2x}(DABCO)$

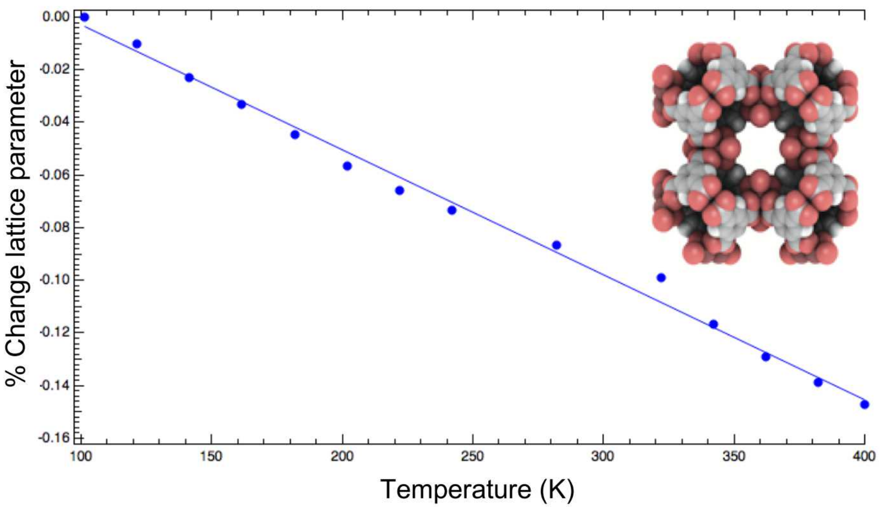




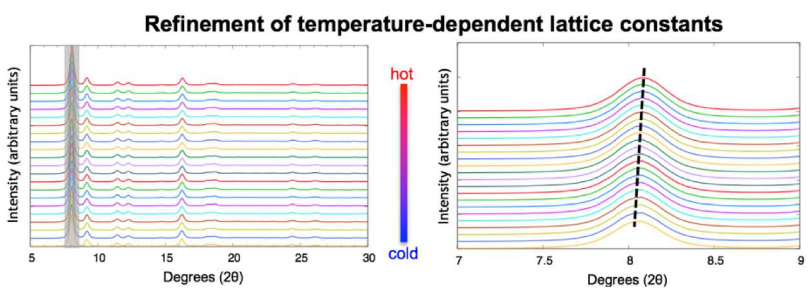
NTE translates to the particle length-scale

Diffraction results

Crystallographic changes (atomic-scale)

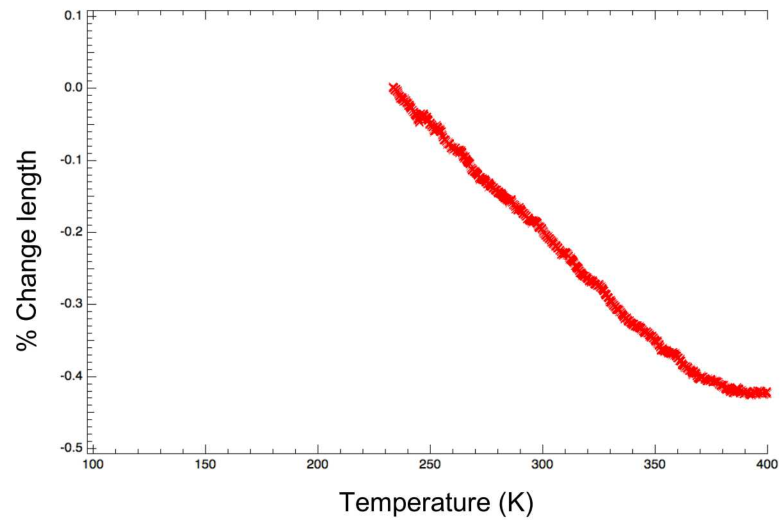


Characterization approach

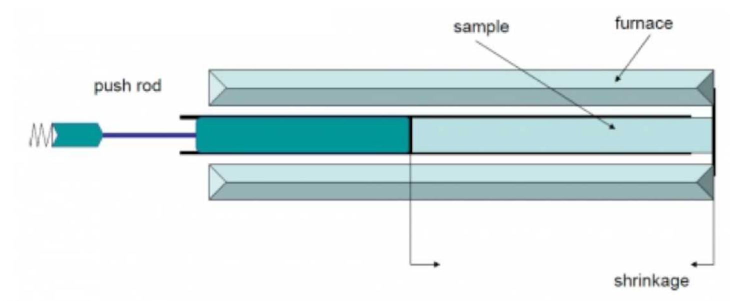


Thermomechanical analysis results

Powder height changes (macro-scale)

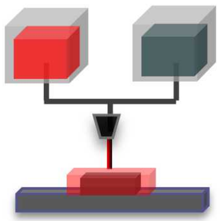


Characterization approach

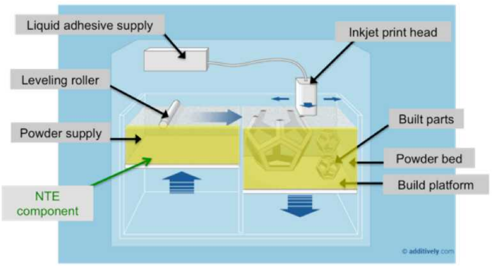


Composite material studies

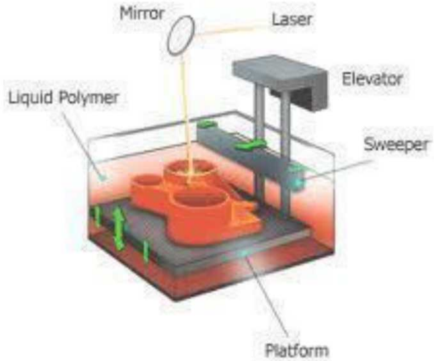
Incorporating NTE additives as material feeds for 3D printing technologies



Material jetting



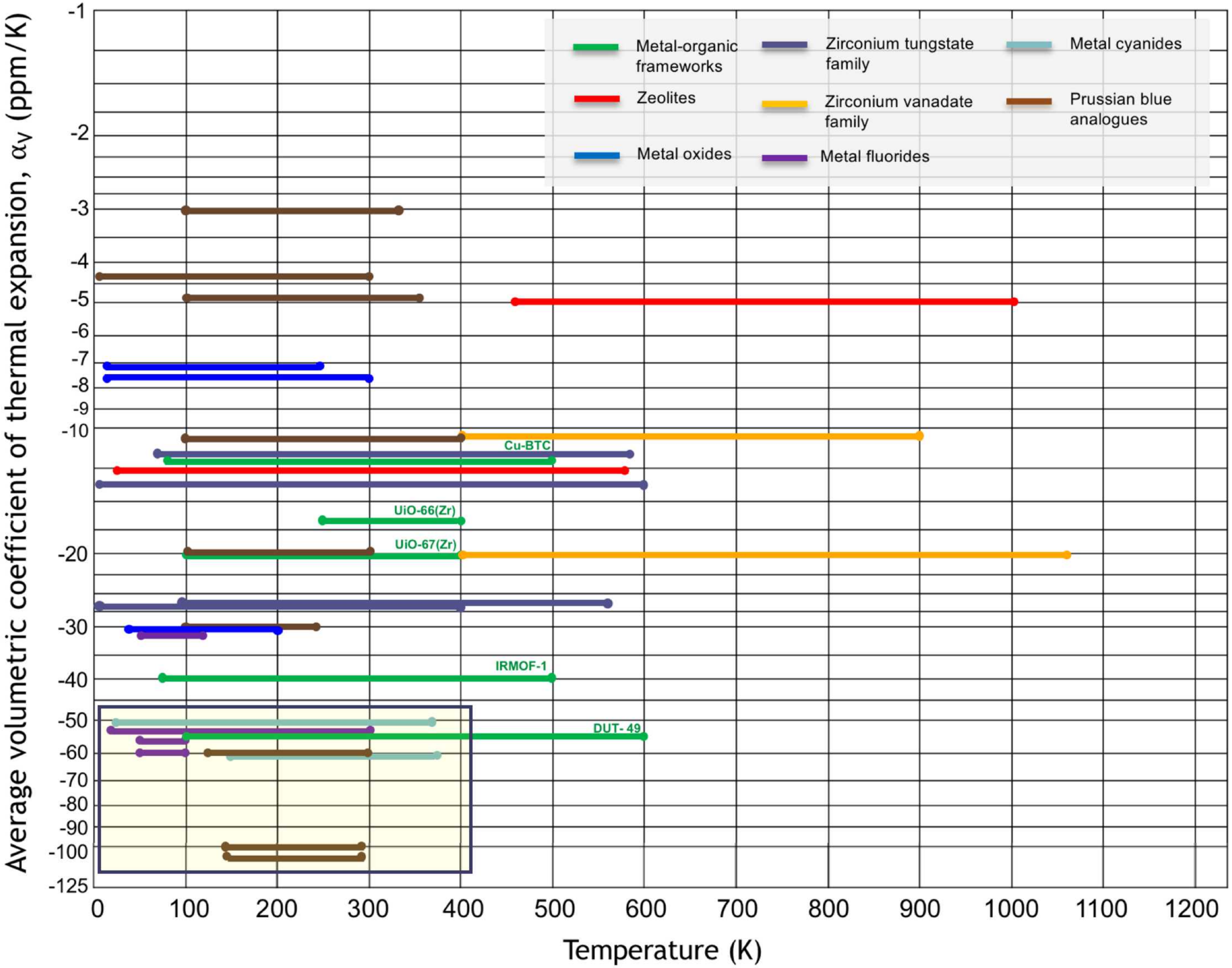
Binder jetting



Stereolithography

Burtch. Method for Tuning Thermal Expansion in an Additive Manufacturing Feedstock Material. U.S. Patent Serial No. 15/717,265 filed Sept. 27, 2017.

MOFs as an emergent NTE material class



Conclusions

MOFs as an emergent NTE material class

- Precisely *tailored* NTE characteristics
- NTE exists at the *crystallographic* and *particle* scale

Acknowledgements

Sandia National Laboratories

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Universiteit van Amsterdam

Argonne National Laboratory

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