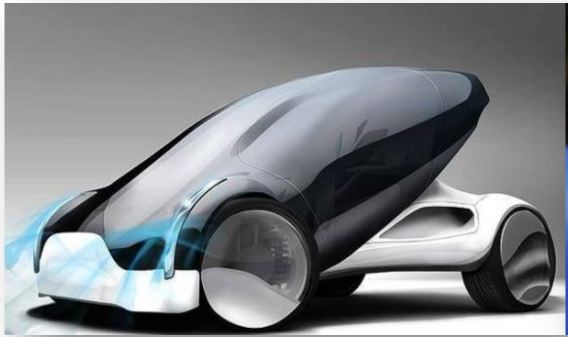
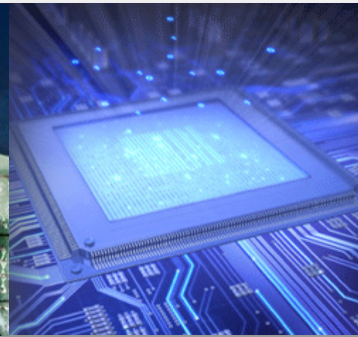
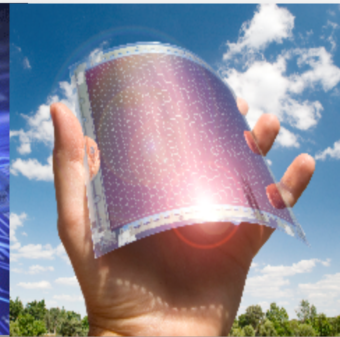
Processing, Properties and Reliability of Molecular Hybrids


light-weight vehicle


touch display


wearable


microelectronics


energy

WMF 2017 - designing high value solutions at minimum cost.

Use less — *reduce buy-to-use ratio, increase and use recycled materials.*

Use longer — *lenghten product's life span, configurable platforms for easy retrofits/upgrades.*

Use smarter — *increasing product performance.*

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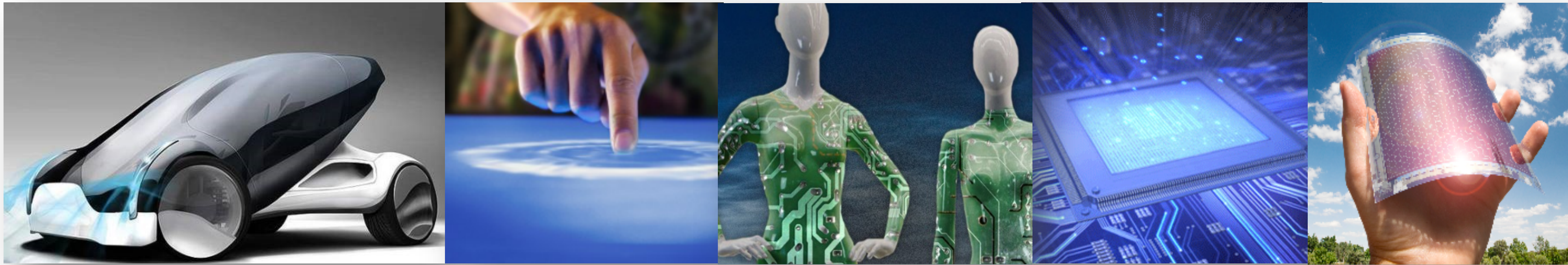
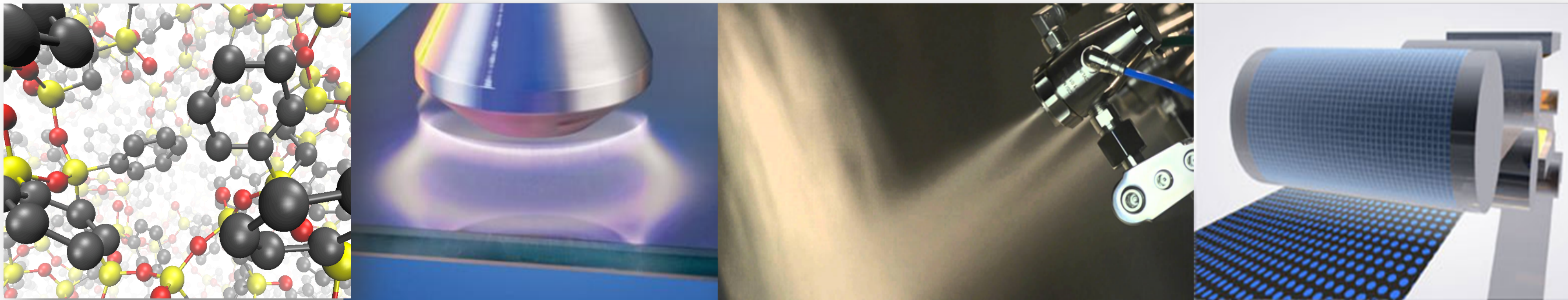
Processing, Properties and Reliability of Molecular Hybrids



light-weight vehicle touch display wearable microelectronics energy

WMF 2017 - designing high value solutions at minimum cost.

Progress through scientific innovation in materials design and processing…



molecular design atmospheric plasma spray coating roll-to-roll

… for inexpensive and durable materials with robust operational lifetimes!

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Opportunities for Multifunctional Hybrid Materials: *Molecular Design to Applications*

Organosilicate Films and Coatings

Joe Burg, Scott Isaacson, Siming Dong, Michael Hovish, Florian Hilt

Polymers and Hybrid Nanomaterials

Can Wang, Qiran Xiao, Zhenlin Zhao, Yichuan Ding, Farhan Ansari

Membranes for Fuel Cells and Batteries

Daisy Yuen, Can Cai

Complex Multi-Junction Device Structures

Ryan Brock, Oliver Zhang

Photovoltaic and Flexible Electronic Materials

Nick Rolston, Warren Cui, Adam Prinz

Human Skin Properties and Function

Jacob Bow, Chris Berkey, David Kanno, Ross Bennet-Kennet

Reinhold H. Dauskardt (dauskardt@stanford.edu)

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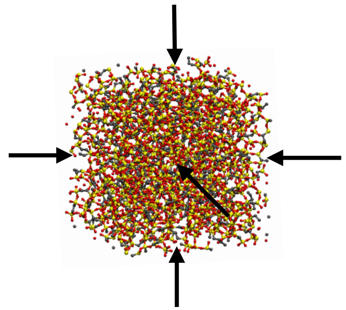
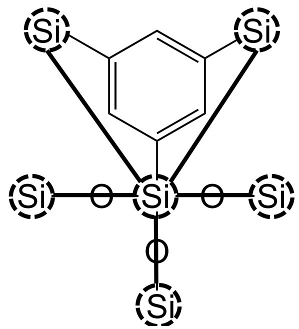
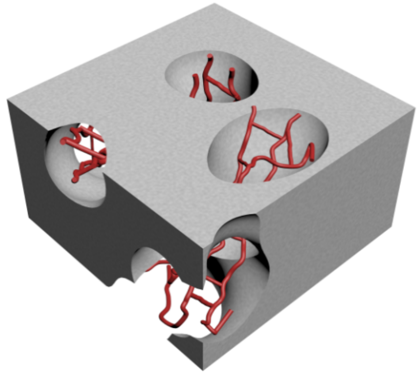
Outline

- Hybrid Molecular Design Strategies
  - unexpected elastic and thermal expansion properties





- Hyperconnected Network Architectures
  - designing network connectivity for exceptional mechanical properties



- Hyper Confined Molecular Hybrids
  - fundamental limits on toughening and strengthening

- Emerging Applications for Molecular Hybrids
  - thermal barriers and battery electrolytes

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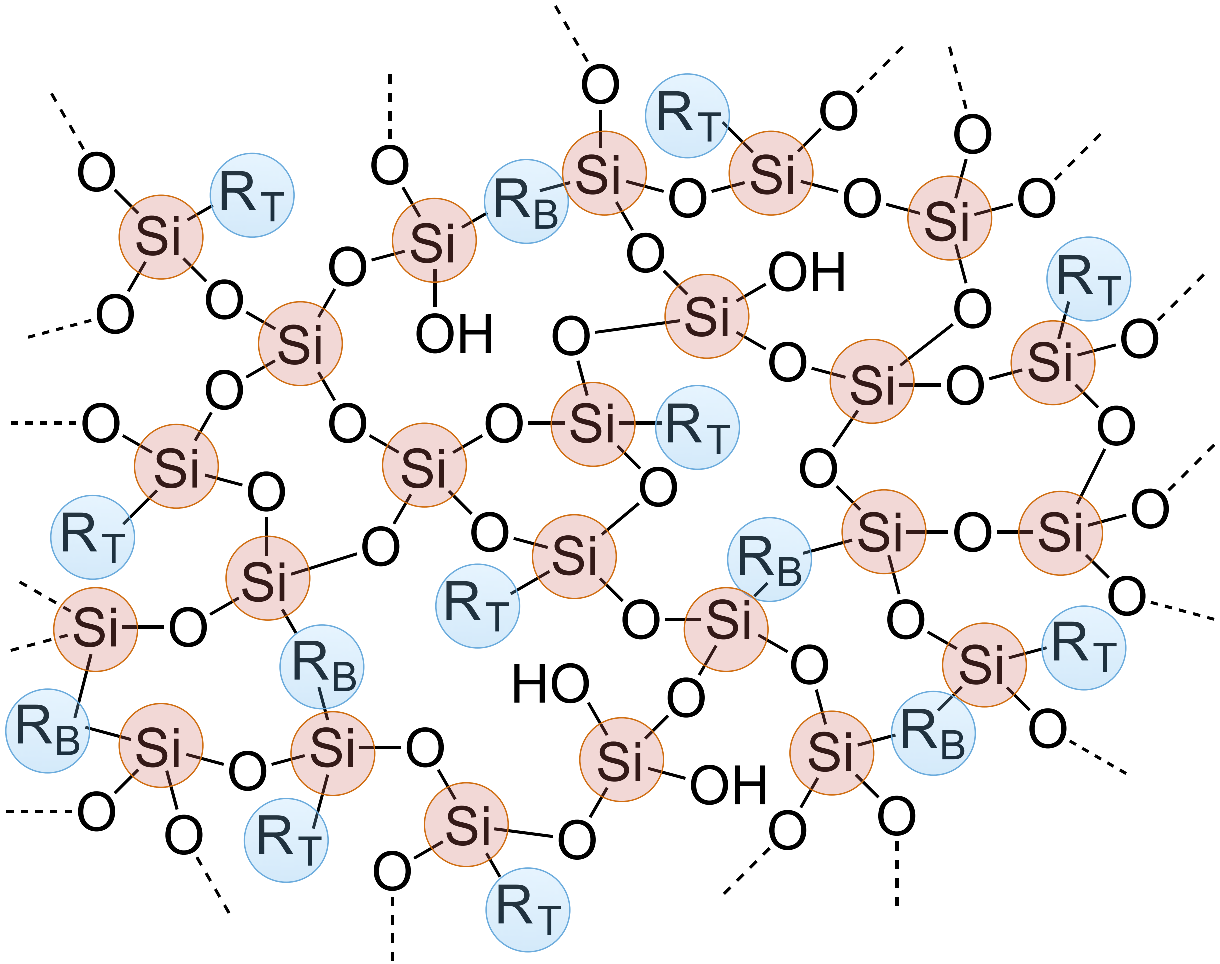
Hybrid Molecular Materials

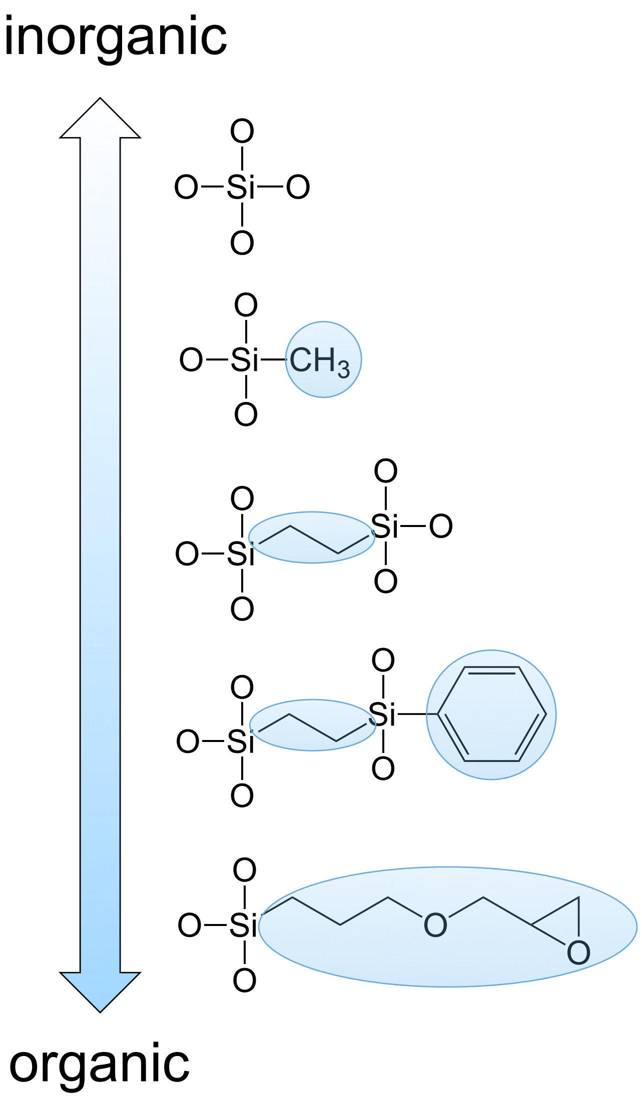
organic species

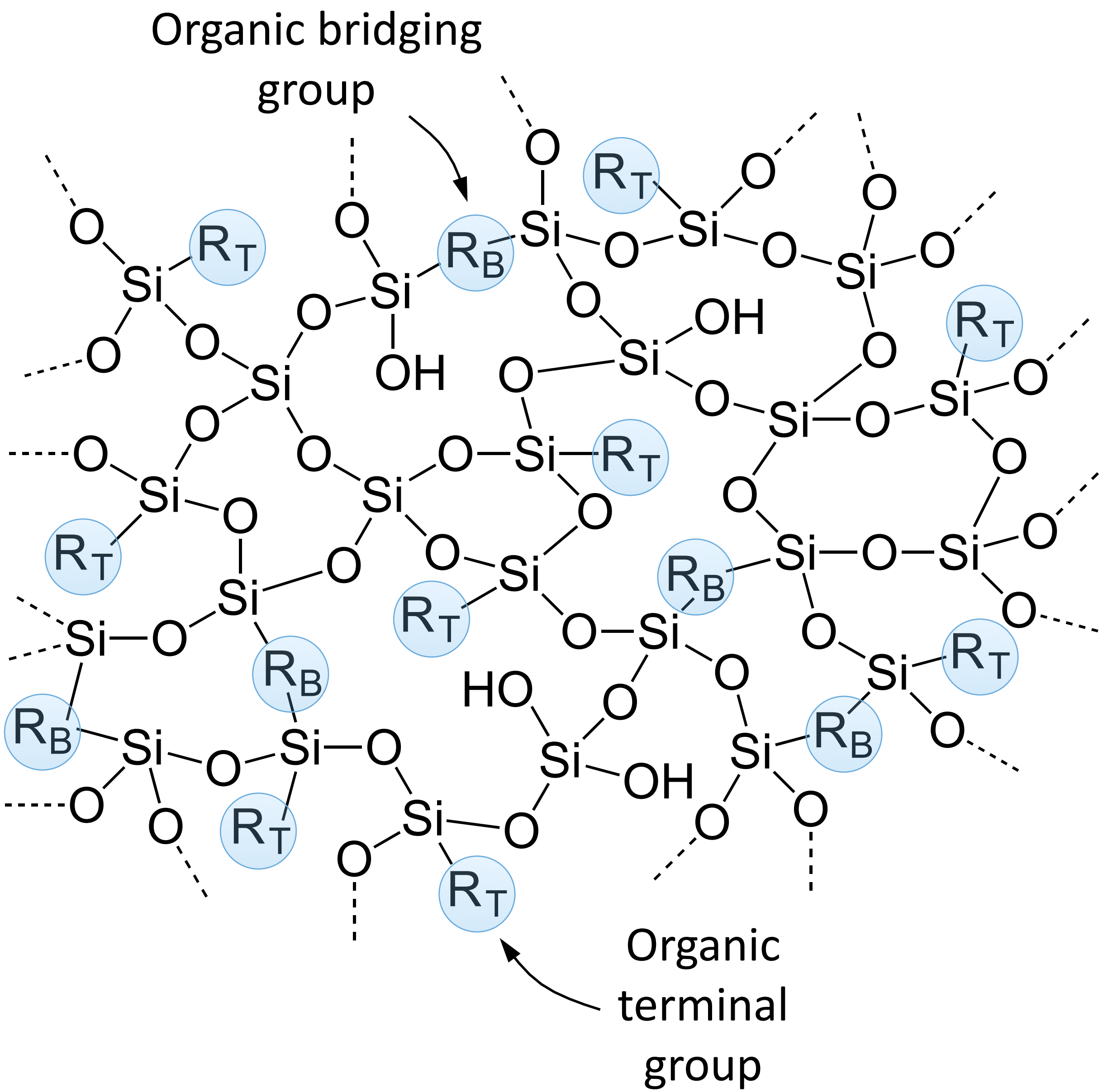
inorganic species

metal alkoxide
(<u>Si</u>, Ti, Zr, etc.)



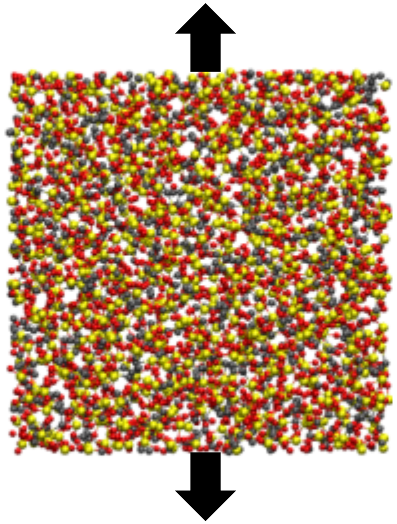
Hybrid Molecular Materials

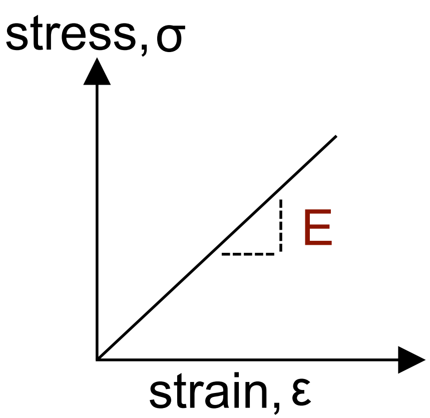




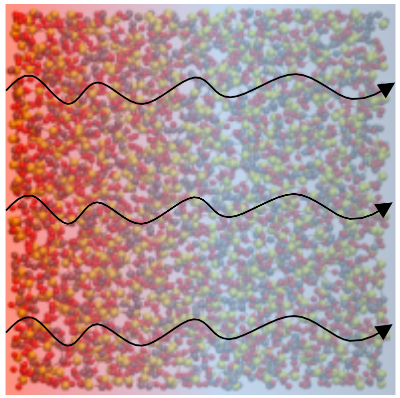
Mechanical and Thermal Properties

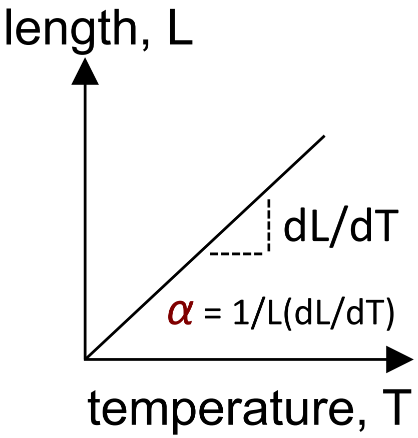
Elastic Modulus, E
“stiffness”



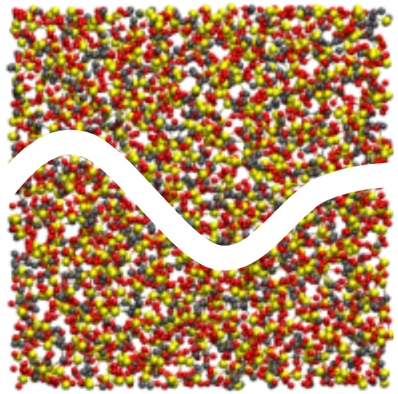


CTE, α
“response to ΔT”



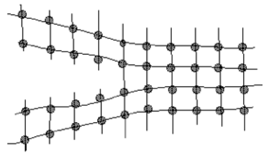


Fracture Energy, G_c
“toughness”

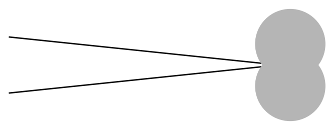


$$G \geq G_c \ (J/m^2)$$

G = energy release rate (driving force)

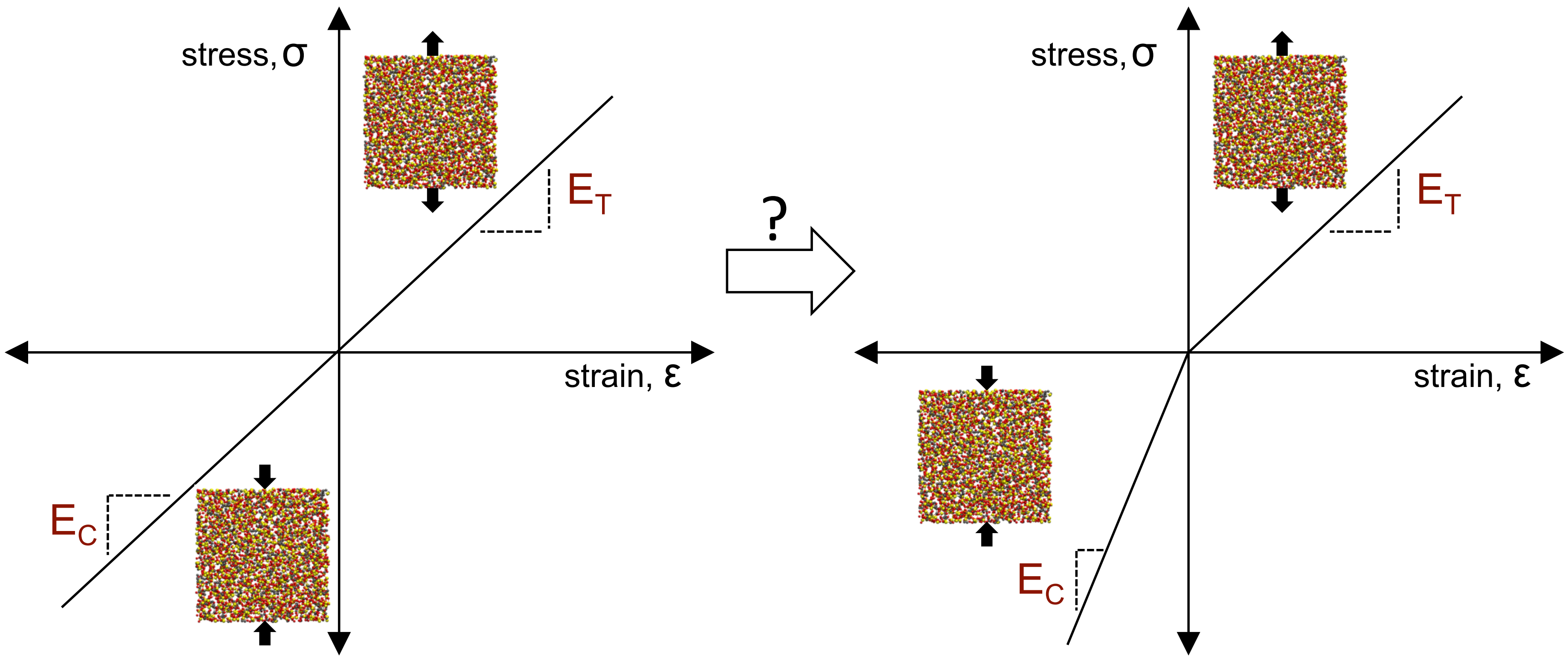


bond rupture

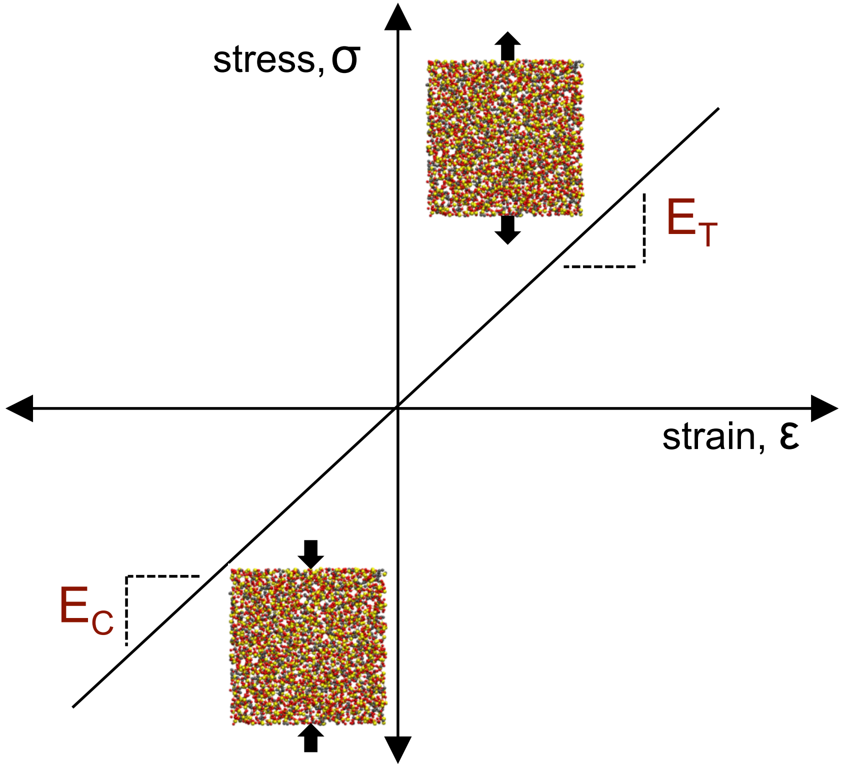


crack tip plasticity

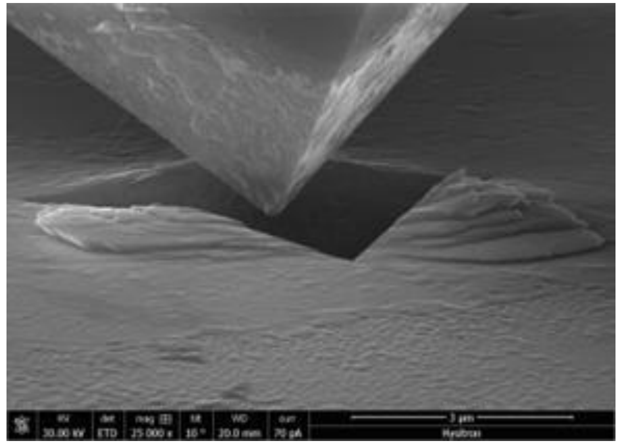
Are Elastic Properties Different in Compression and Tension?



Elastic Properties Assumed the Same in Compression and Tension – AND EXPERIMENTS CAN'T DISTINGUISH

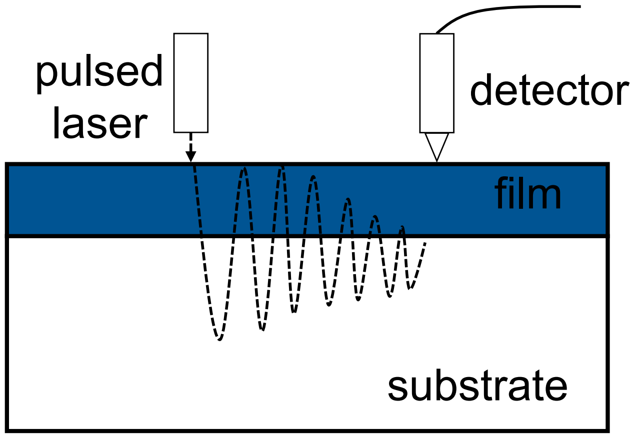


nanoindentation

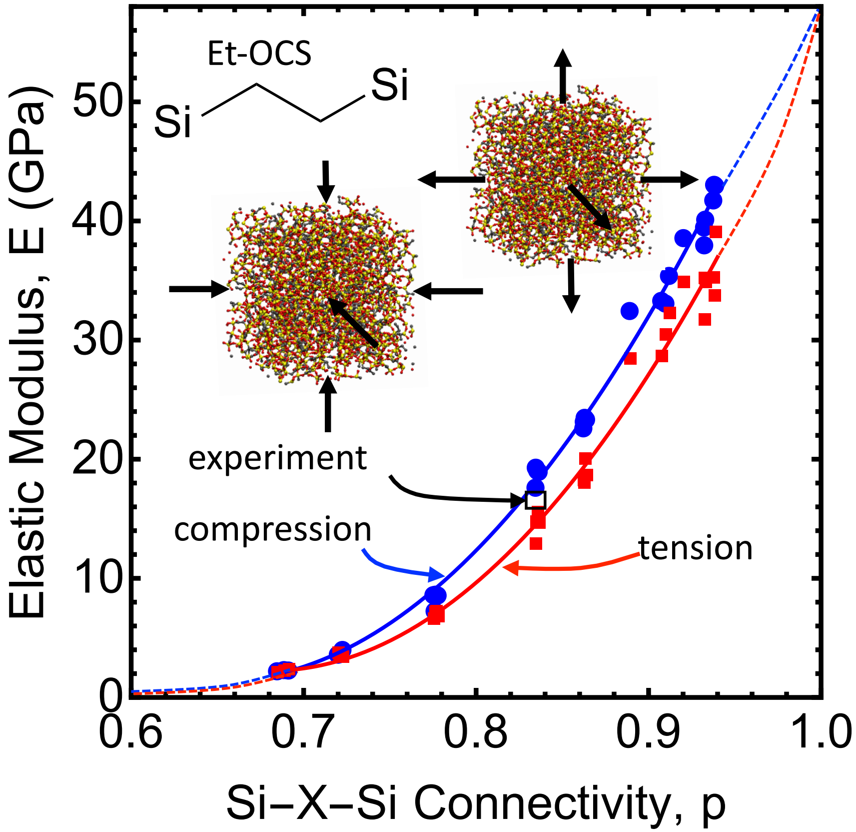


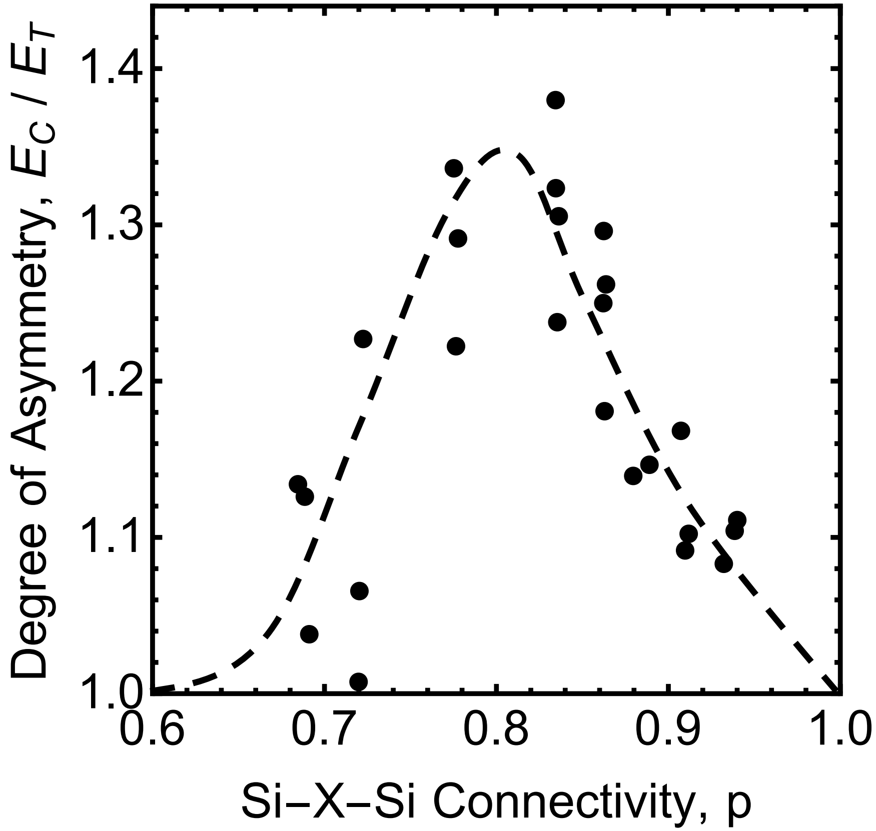
Blue Scientific

surface acoustic wave spectroscopy



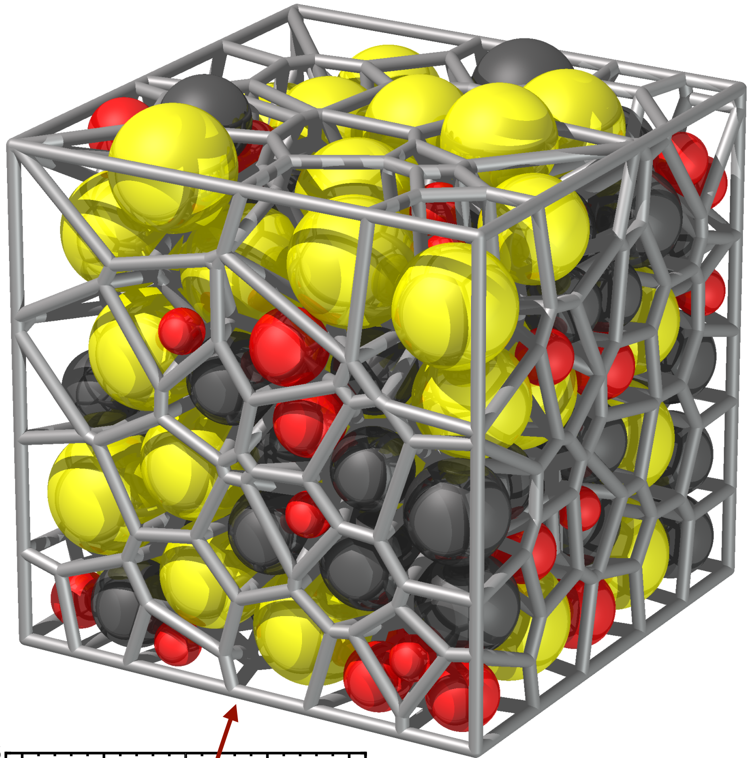
Asymmetric Elastic Behavior

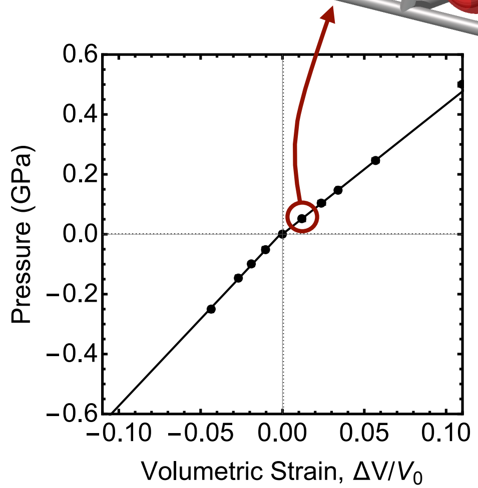


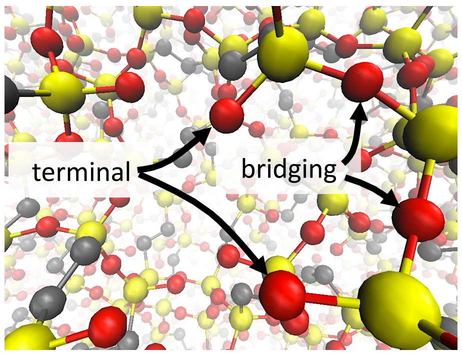


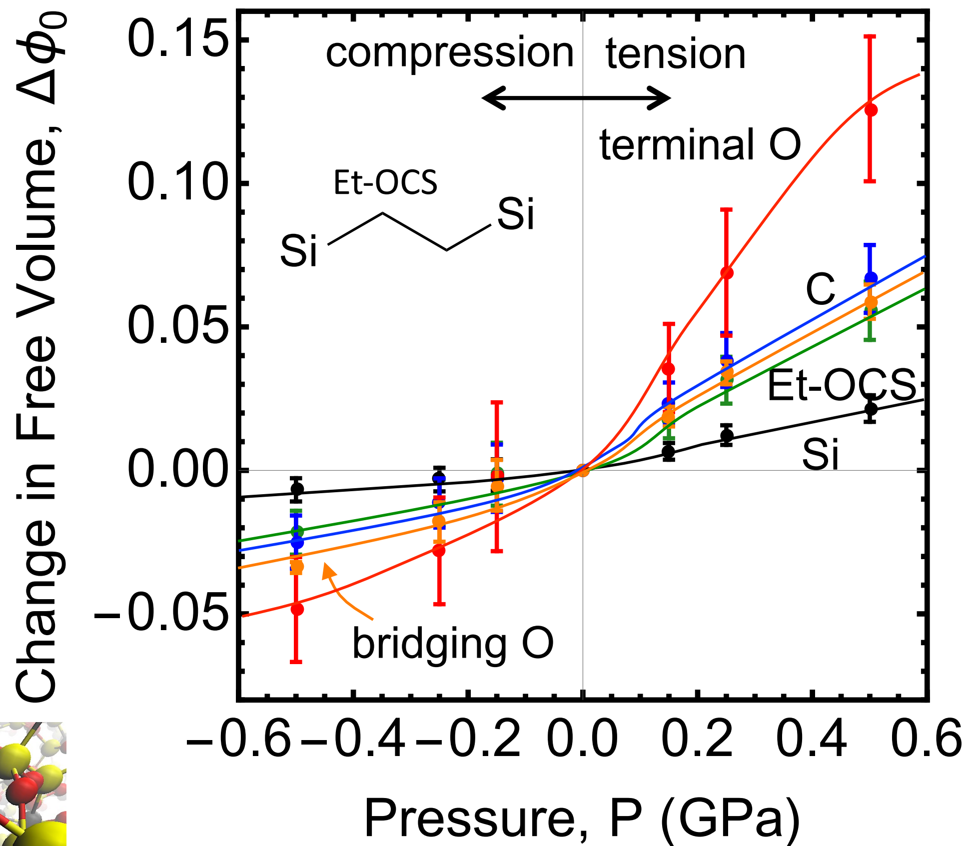
J.A Burg & R.H. Dauskardt, *Nature Materials*, 2016.

Atomic Free Volume Change Under Loading







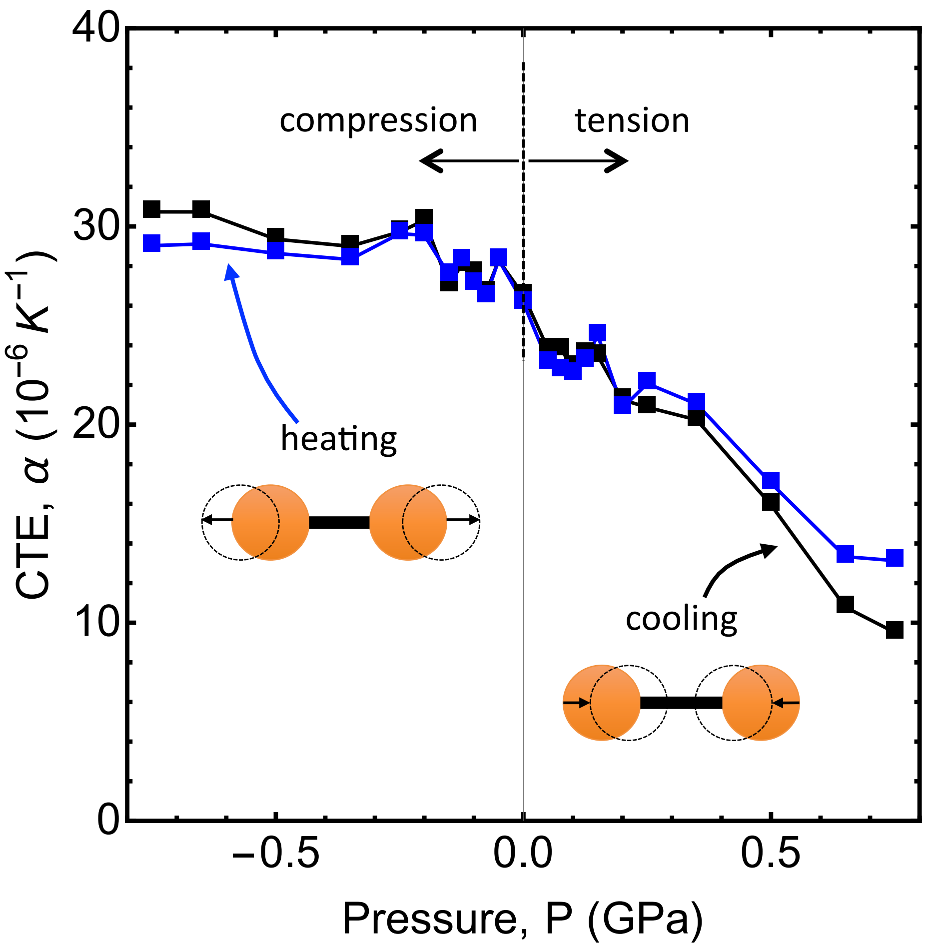


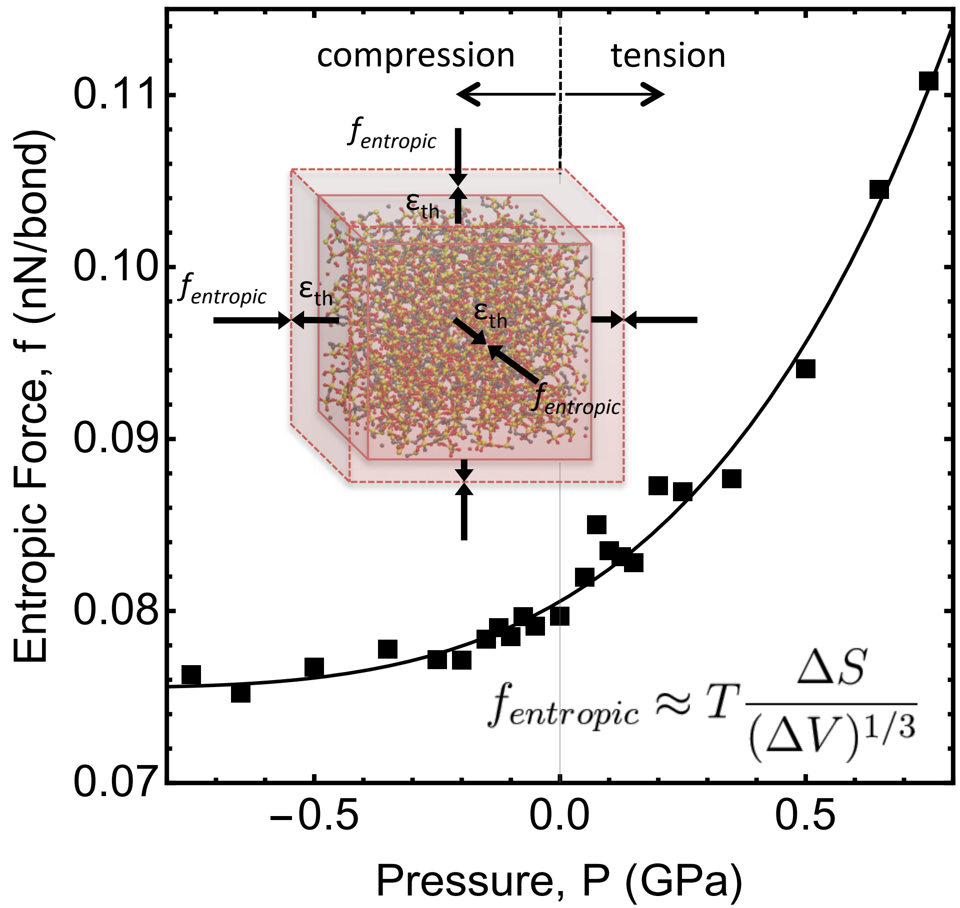
change in atomic free volume

$$\Delta\phi_0 = \sum_i \frac{\Omega_i - \Omega_i^{eq}}{\Omega_i^{eq}}$$

J.A Burg & R.H. Dauskardt, *Nature Materials*, 2016.

Asymmetric Thermal Expansion Properties





J.A Burg & R.H. Dauskardt, *Nature Materials*, 2016.

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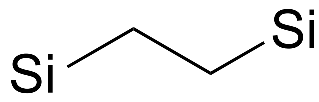
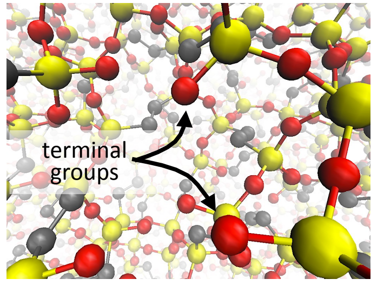
Effect of Other Common Terminal Groups

non-terminated

$m_{Si} = 1 + 3g$

EtOCS

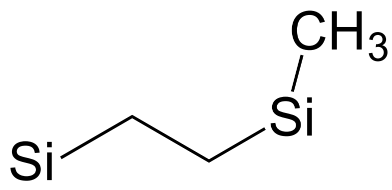


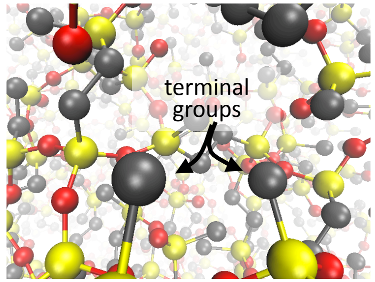


intrinsically terminated

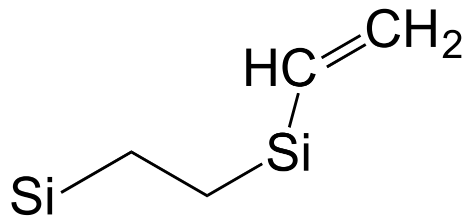
$m_{Si} = 1 + 2.5g$

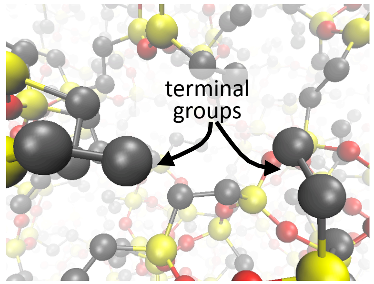
EtOCS-Methyl



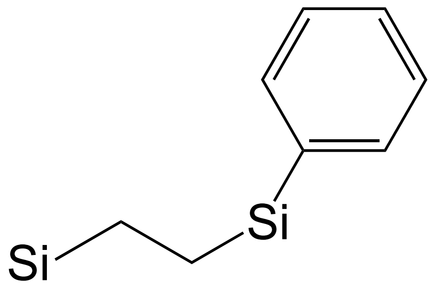


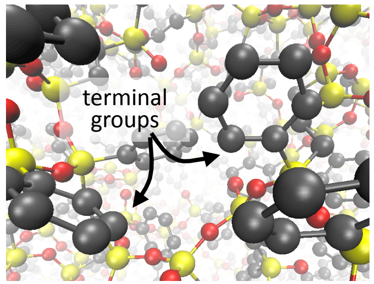
EtOCS-Vinyl





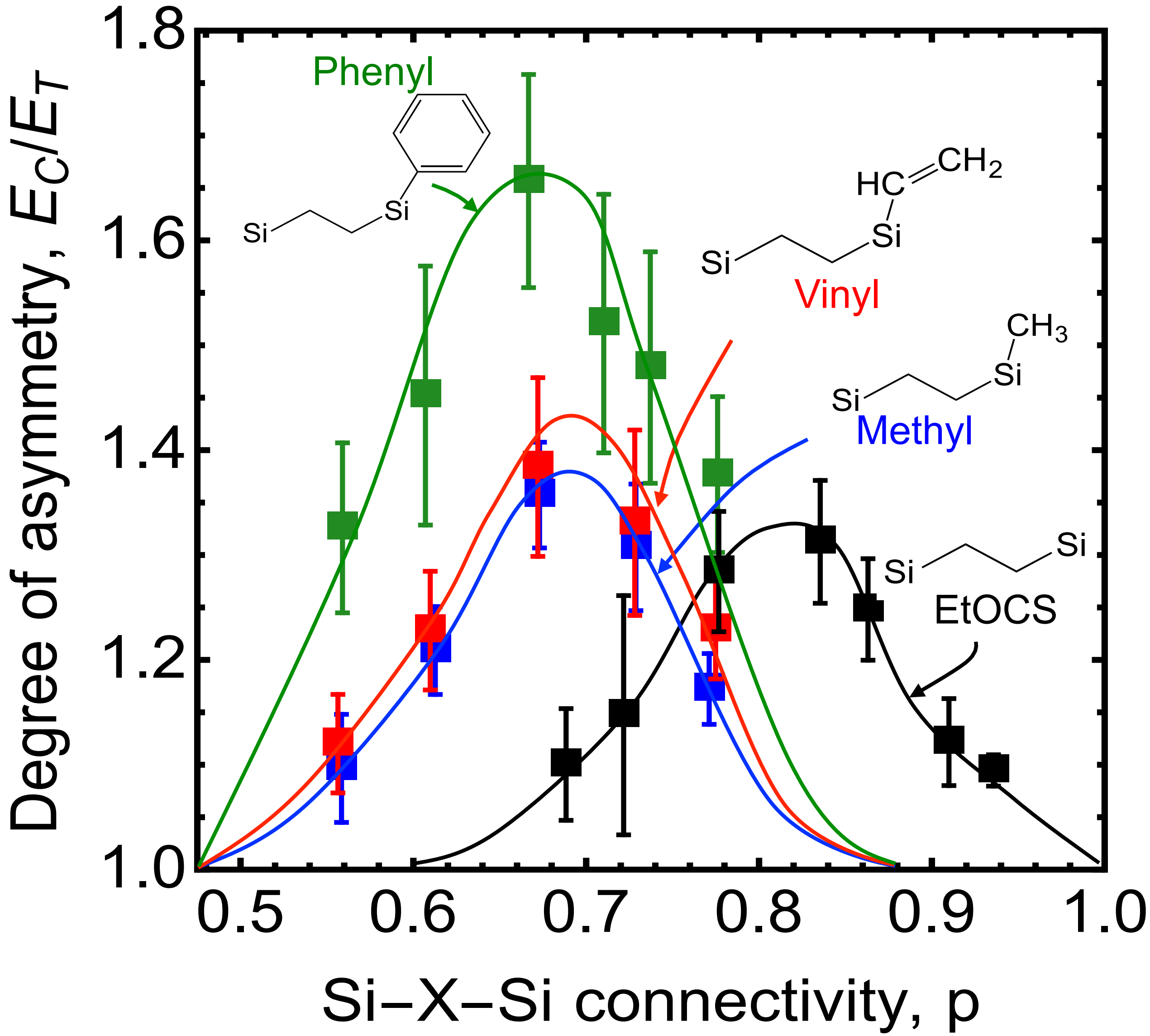
EtOCS-Phenyl

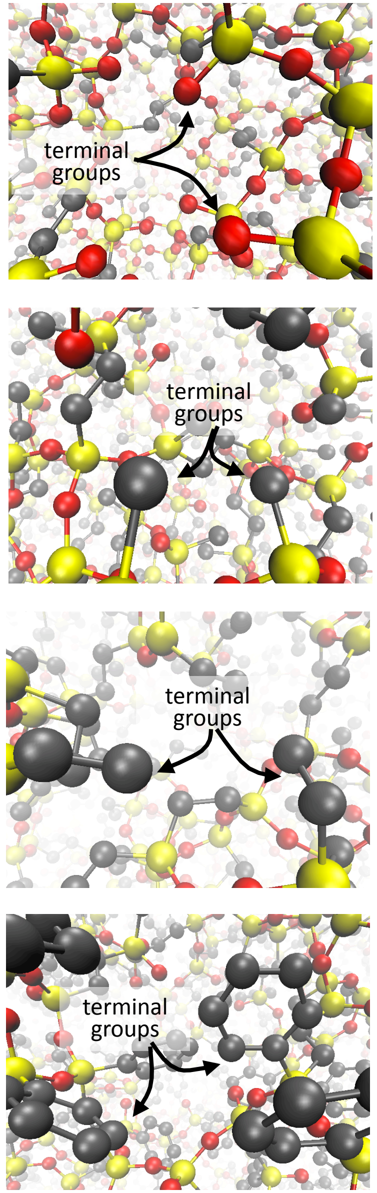




J.A Burg & R.H. Dauskardt, *Nature Communications*, in review, 2017.

Effect of Other Common Terminal Groups





J.A Burg & R.H. Dauskardt, *Nature Communications*, in review, 2017.

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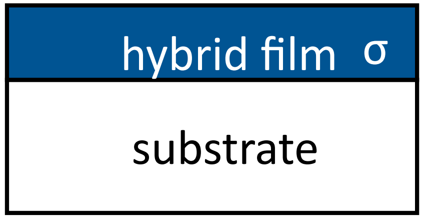
Implications of Asymmetries for Device Reliability

film stress, σ

- residual
- applied
- thermal (α)

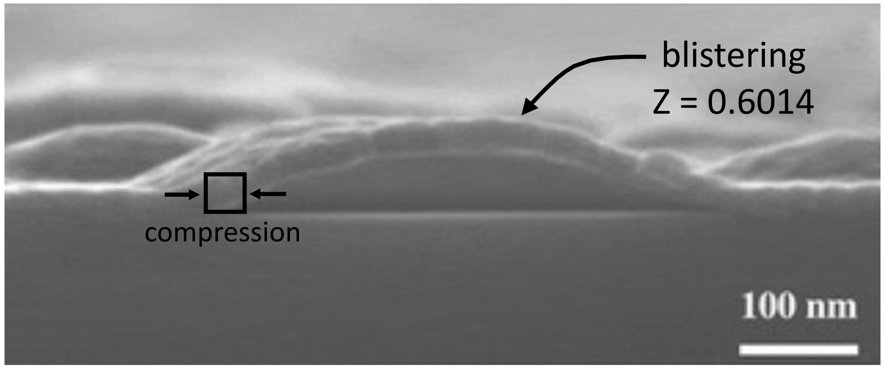


α: coefficient of thermal expansion

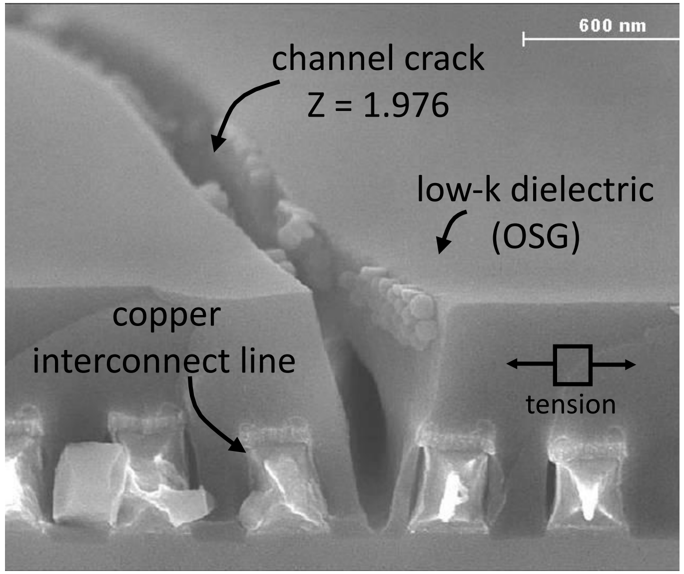
$$\sigma_{failure} = \sqrt{\frac{G_c E'}{Z h}}$$

G_c: fracture energy, E: elastic modulus

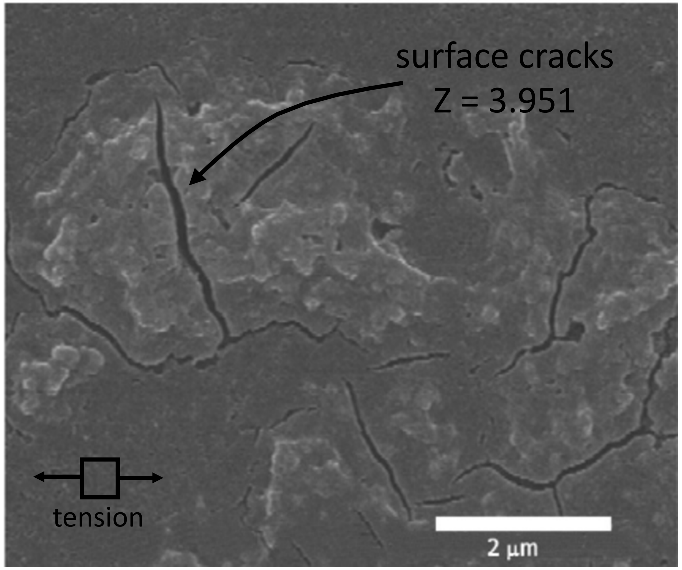
Z: crack configuration, h: film thickness



Papadatos et al (2007)

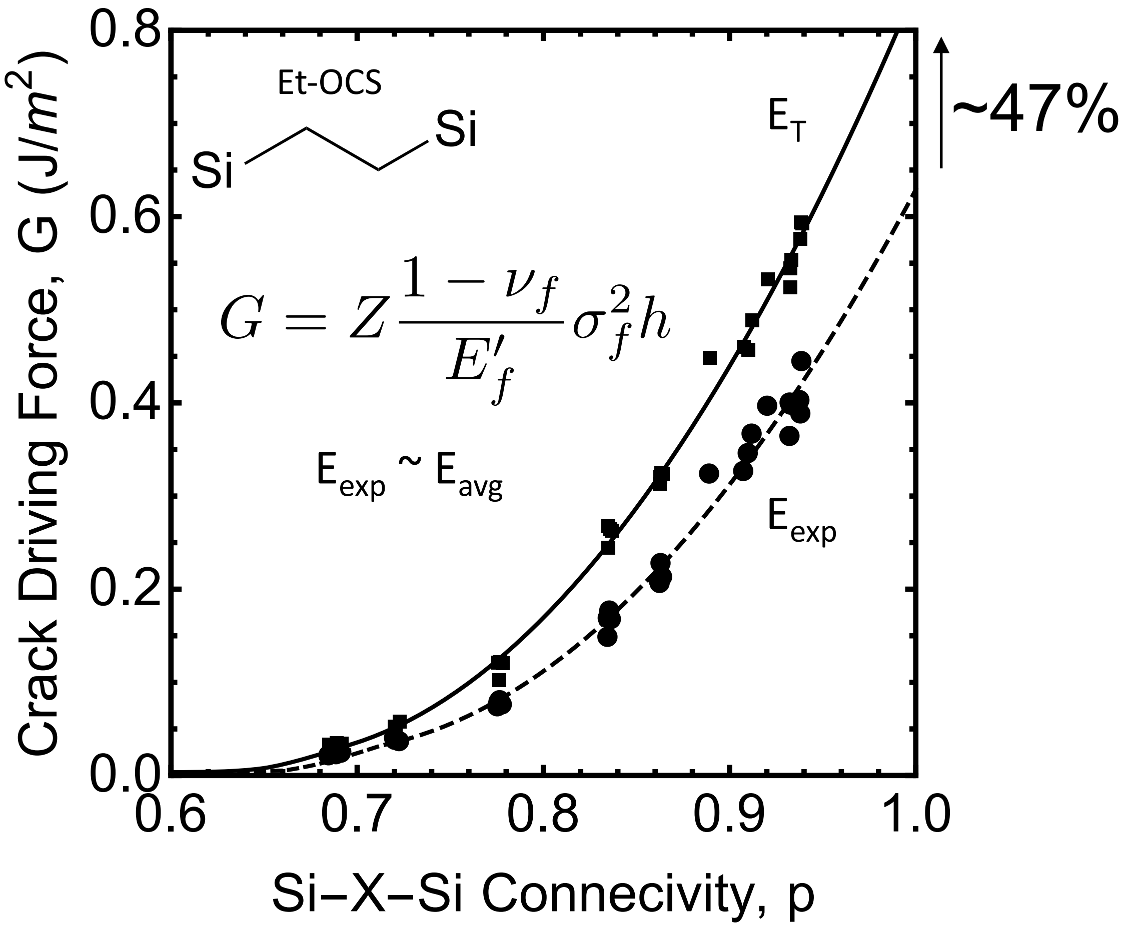


Garitagoitia et al (2014)



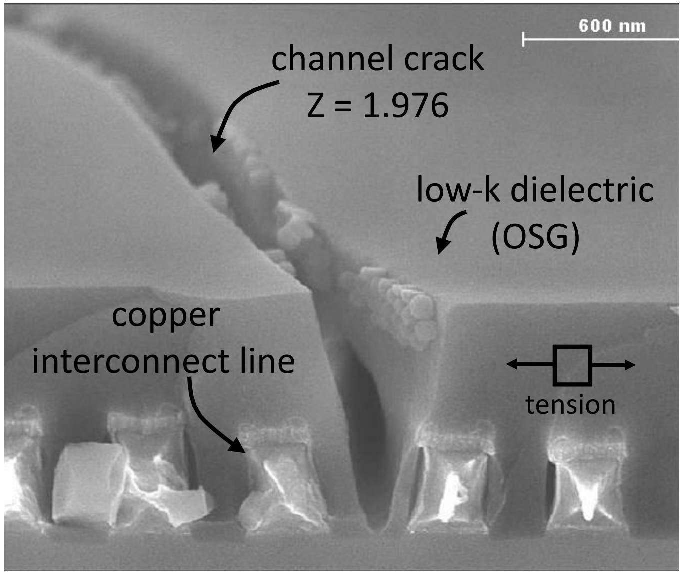
Sierros et al (2009)

Implications of Asymmetries for Device Reliability

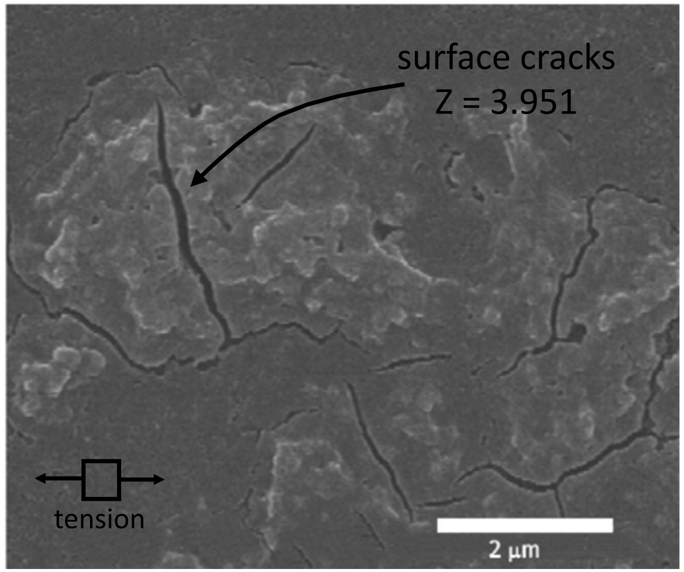


failure criterion:
$G \geq G_c$ (J/m^2)

J.A Burg & R.H. Dauskardt, *IEEE*, 2016.



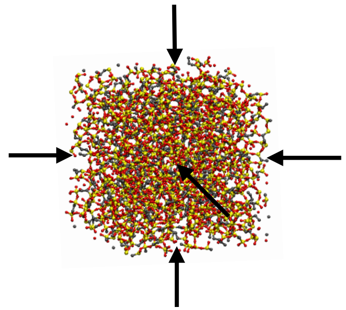
Garitagoitia et al (2014)

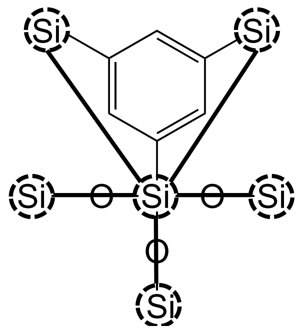


Sierros et al (2009)

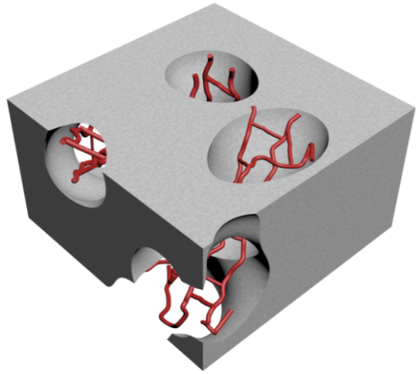
Outline

- Hybrid Molecular Design Strategies
  - unexpected elastic and thermal expansion properties





- Hyperconnected Network Architectures
  - designing network connectivity for exceptional mechanical properties



- Hyper Confined Molecular Hybrids
  - fundamental limits on toughening and strengthening

- Emerging Applications for Molecular Hybrids
  - thermal barriers and battery electrolytes

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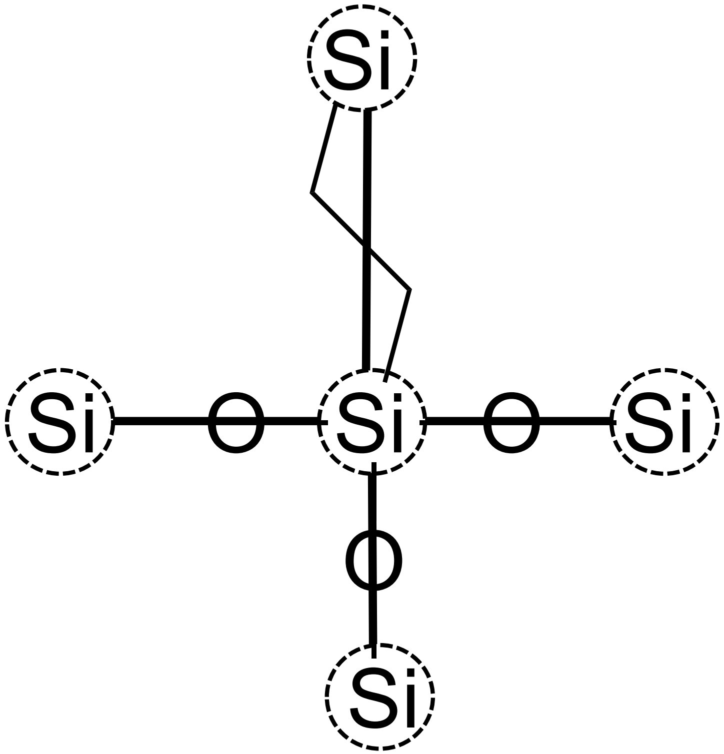
Designing a Hyperconnected Network Architecture

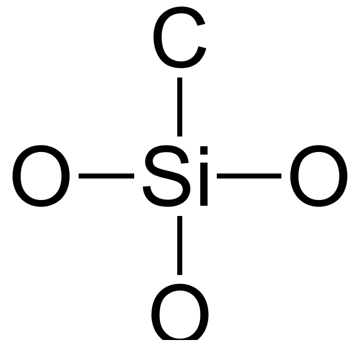
network connectivity



$$m_{Si} = 1 + 3a$$

$$m_{Si} = 4$$

coordination number



hyperconnected network:

$$m_{Si} > CN - 4$$

J.A Burg et al, *Nature Communications*, in review, 2017.

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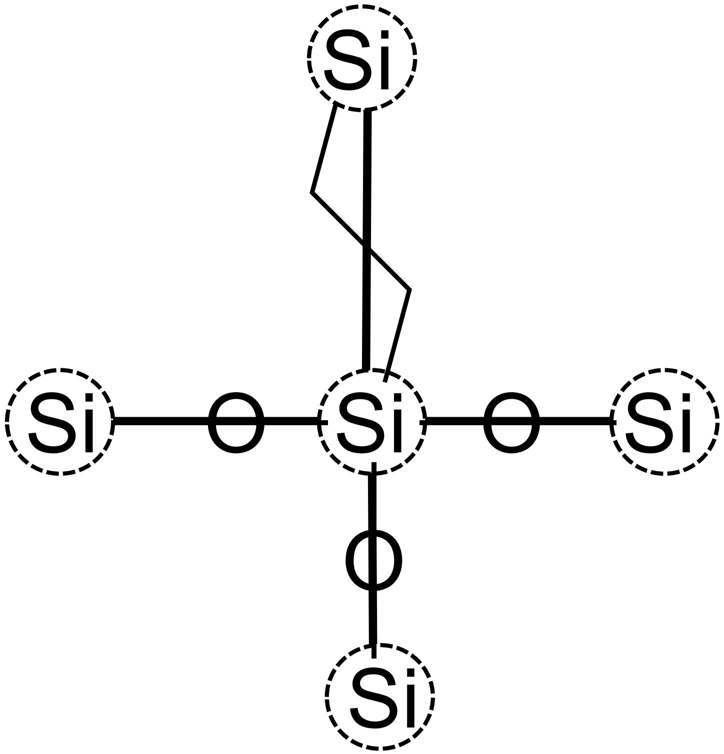
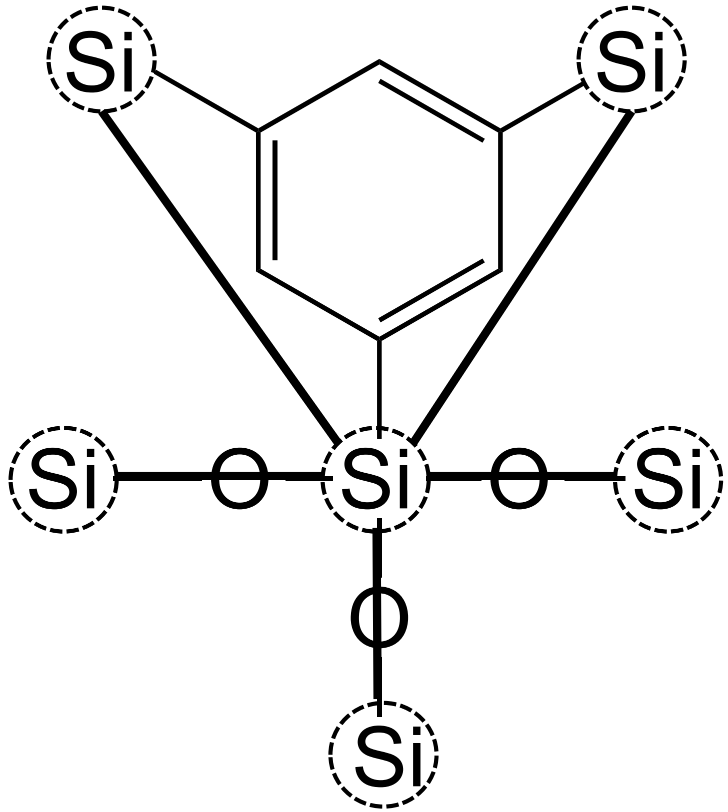
Designing a Hyperconnected Network Architecture

network connectivity



1,3,5-Benzene



$$m_{Si} = 1 + 3a$$

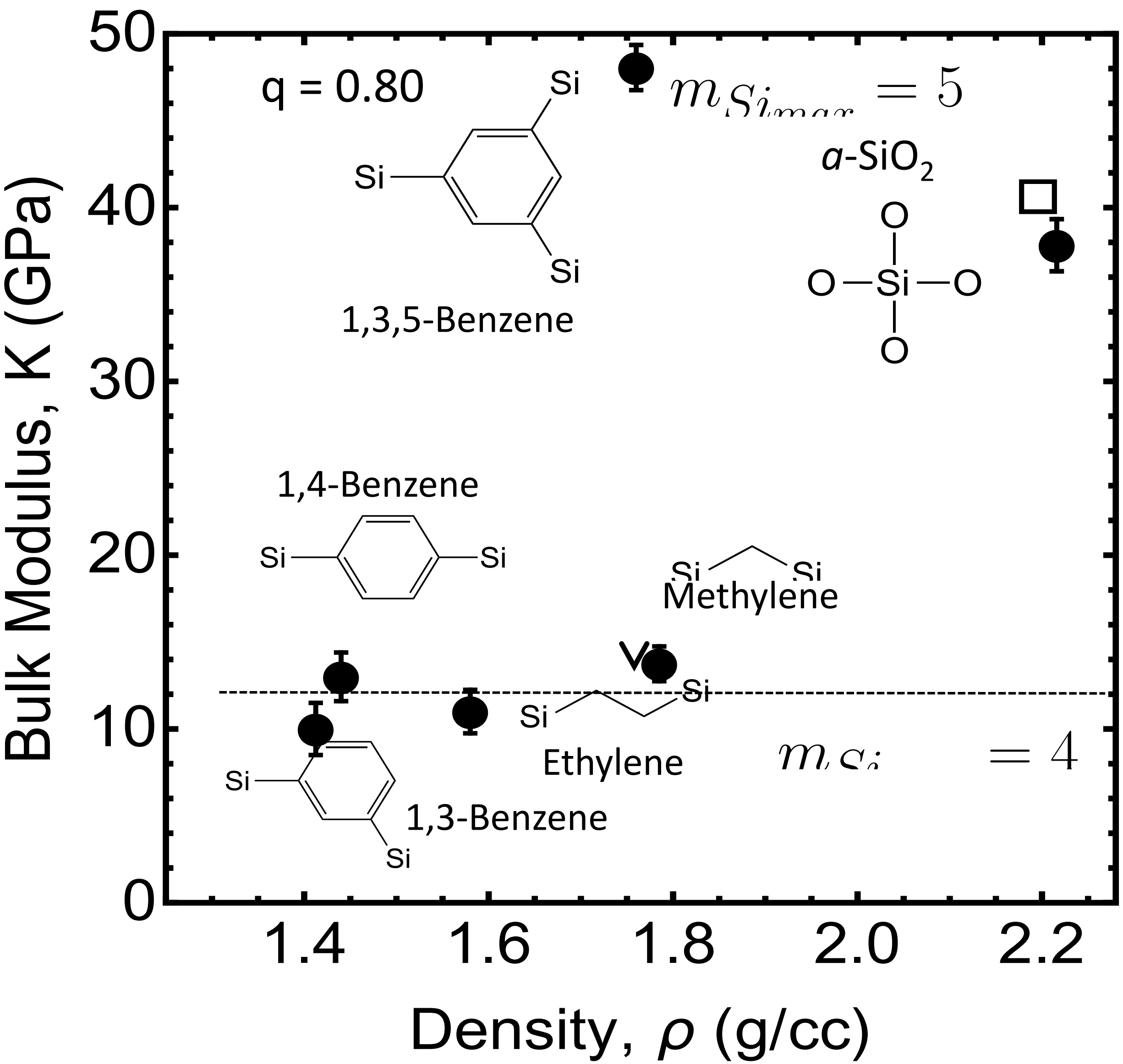
$$m_{Si} = 4$$

$$m_{Si} = 2 + 3a$$

$$m_{Si_{max}} = 5$$

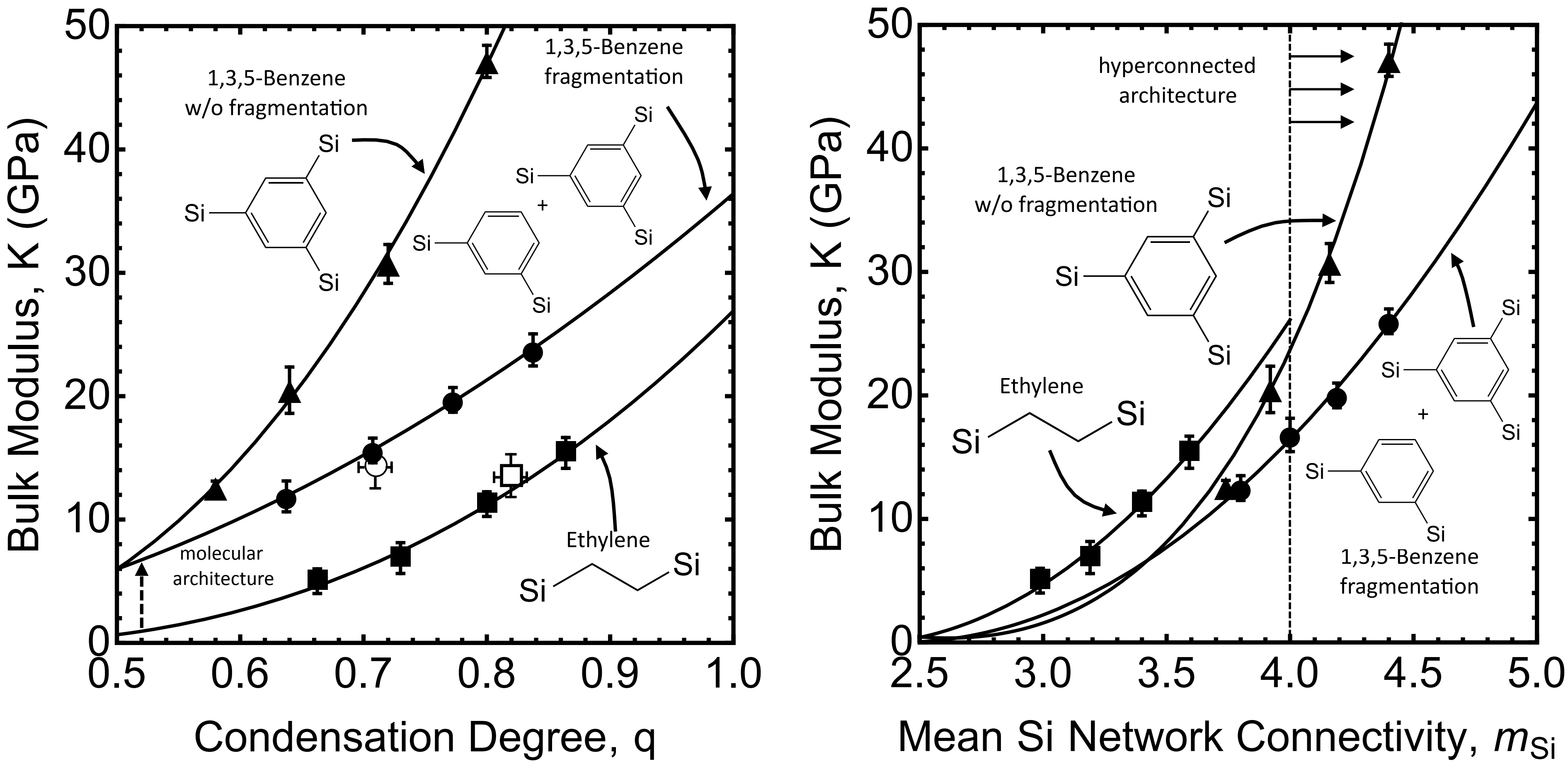
J.A Burg et al, *Nature Communications*, in review, 2017.

Prediction of Exceptional Mechanical Properties



J.A Burg et al, *Nature Communications*, in review, 2017.

Validating Model Predictions through Synthesis



J.A Burg et al, *Nature Communications*, in review, 2017.

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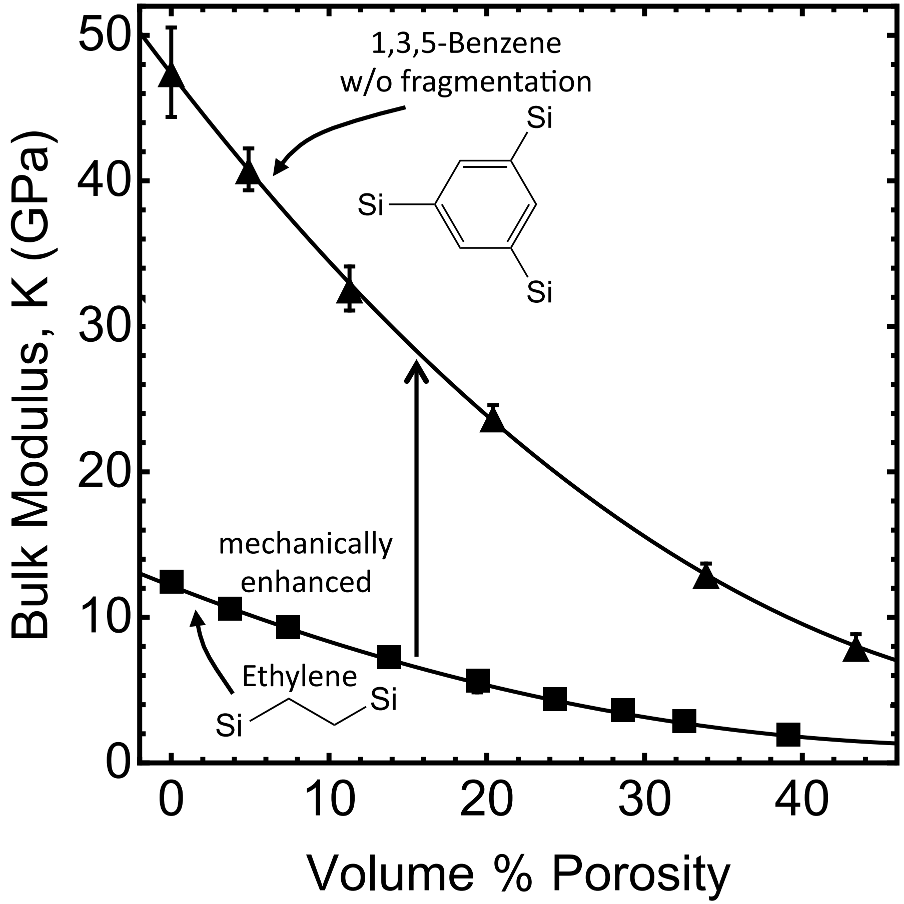
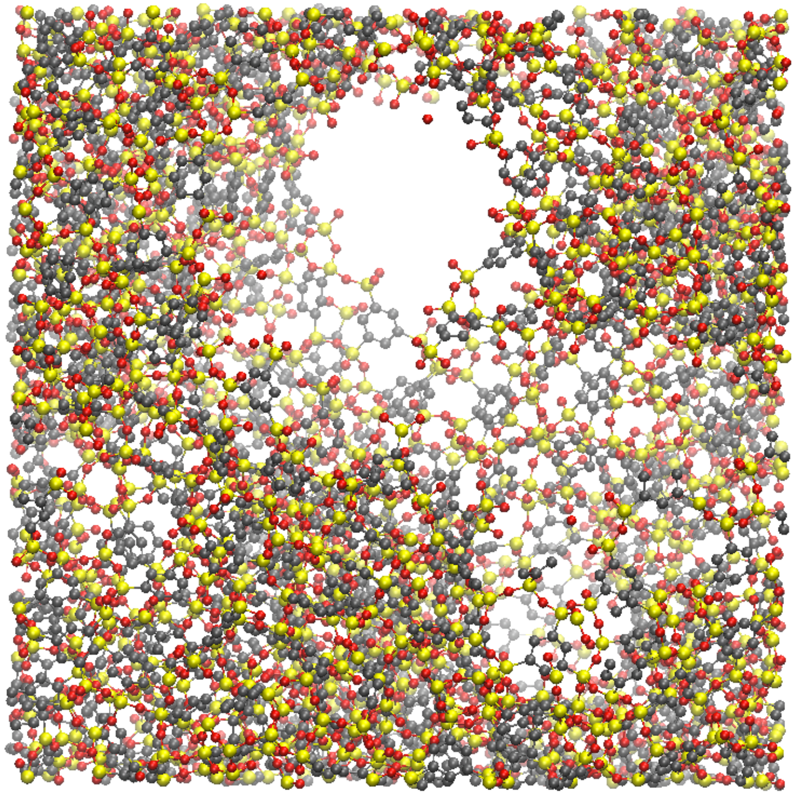
Hyperconnected Molecular Network Enhances Nanoporous Hybrids





J.A Burg et al, *Nature Communications*, in review, 2017.

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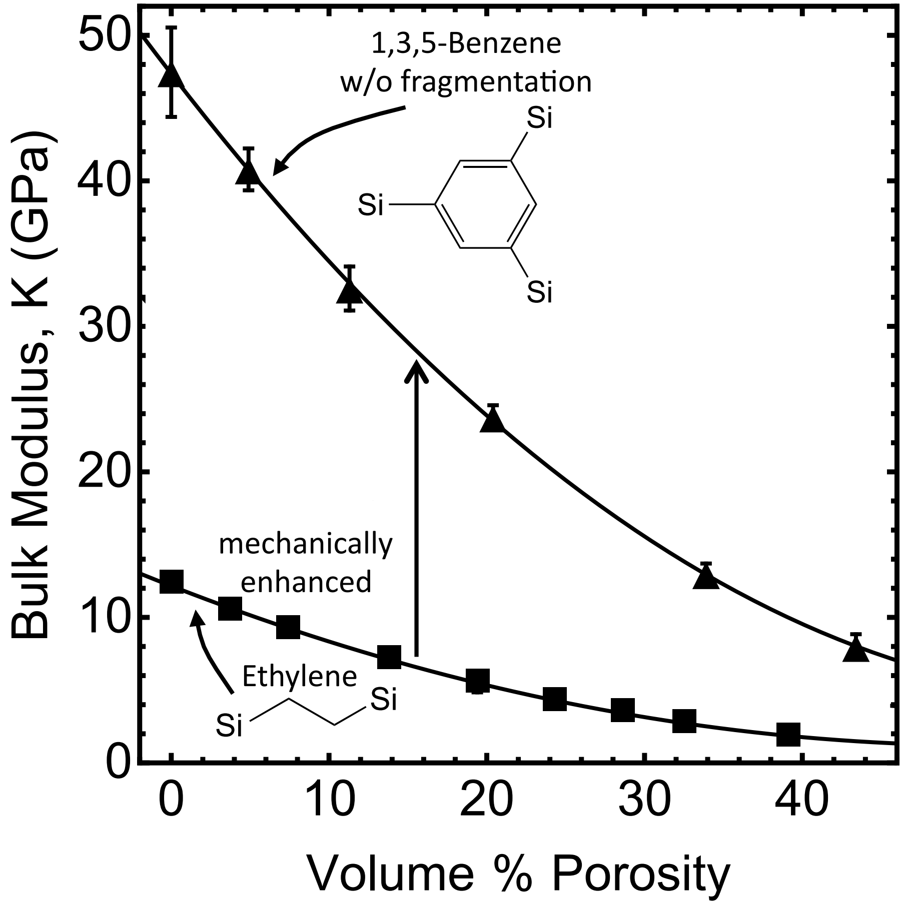
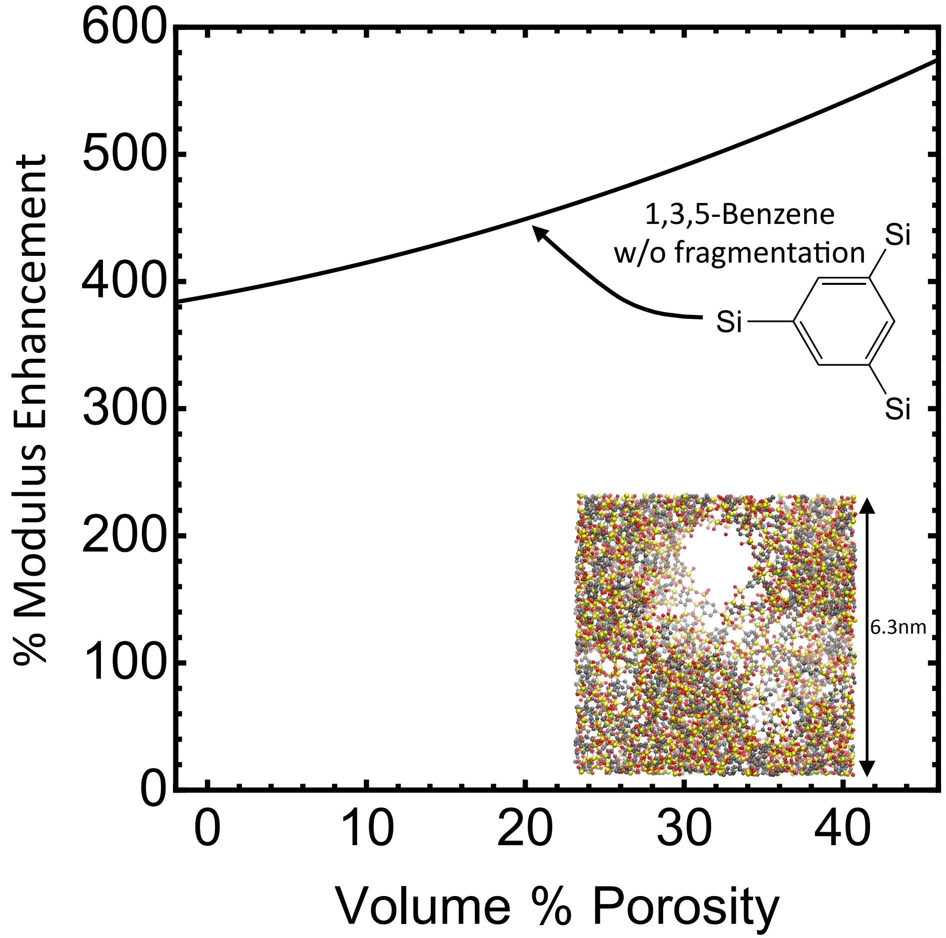
Hyperconnected Molecular Network Enhances Nanoporous Hybrids





J.A Burg et al, *Nature Communications*, in review, 2017.

Outline

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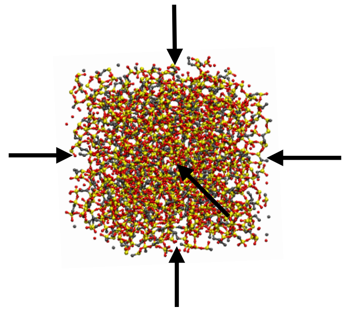
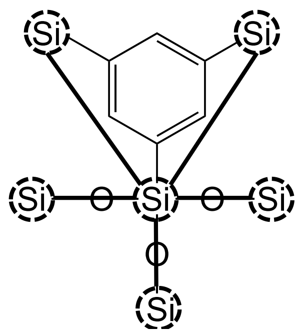
  - unexpected elastic and thermal expansion properties





- Hyperconnected Network Architectures
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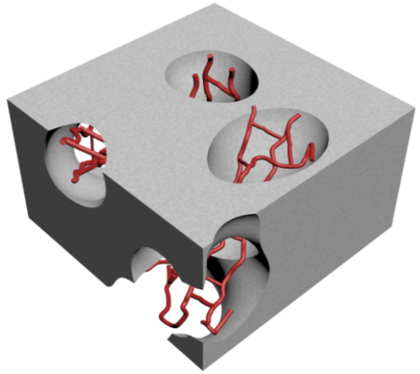
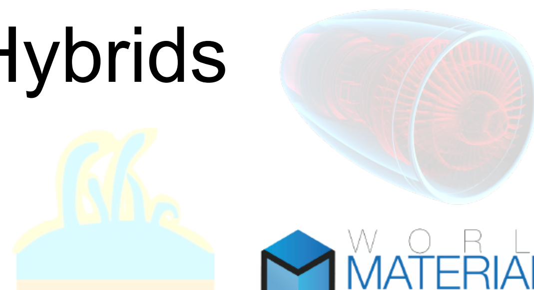
- Hyper Confined Molecular Hybrids
  - fundamental limits on toughening and strengthening



- Emerging Applications for Molecular Hybrids
  - thermal barriers and battery electrolytes



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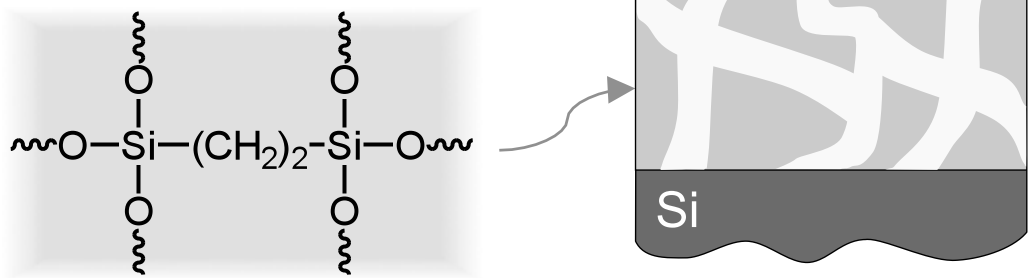
Hybrid Nanocomposites Materials System

Matrix

- nanoporous organosilicate glass (ethylene oxycarbosilane, Et-OCS)
- cylindrical pores, 7 nm diameter
- porosity: 50 vol. %



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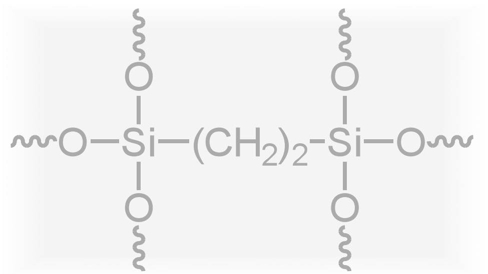
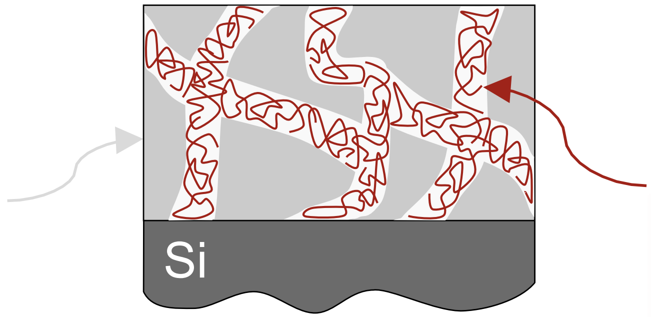
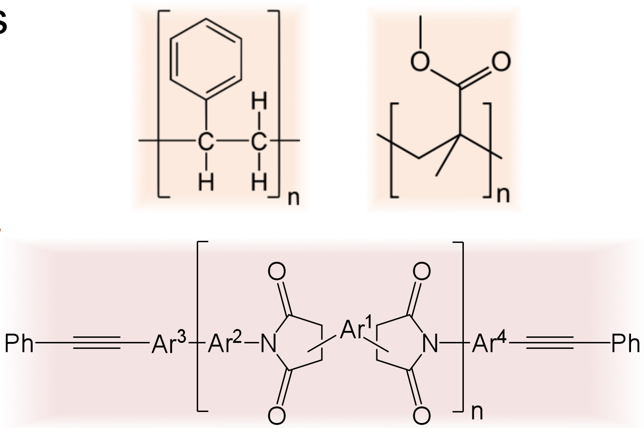


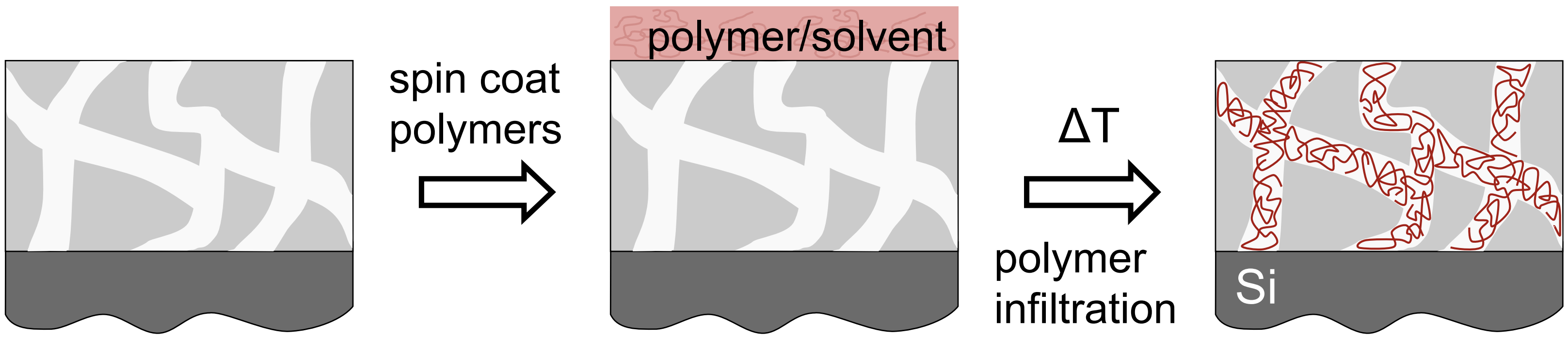


Filler

- polystyrene
- acrylics
- polyimide (thermally crosslinkable)
- others



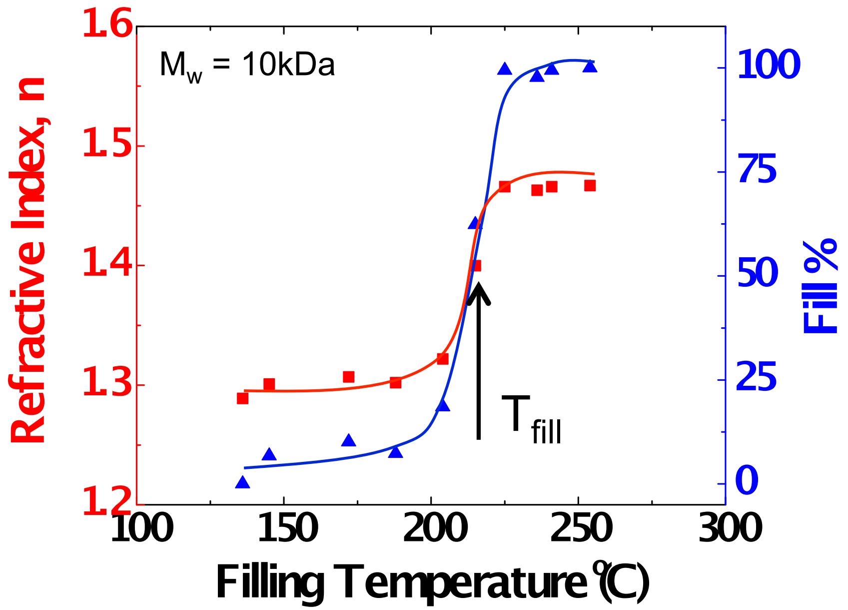
Second phase backfill strategy for porous hybrids



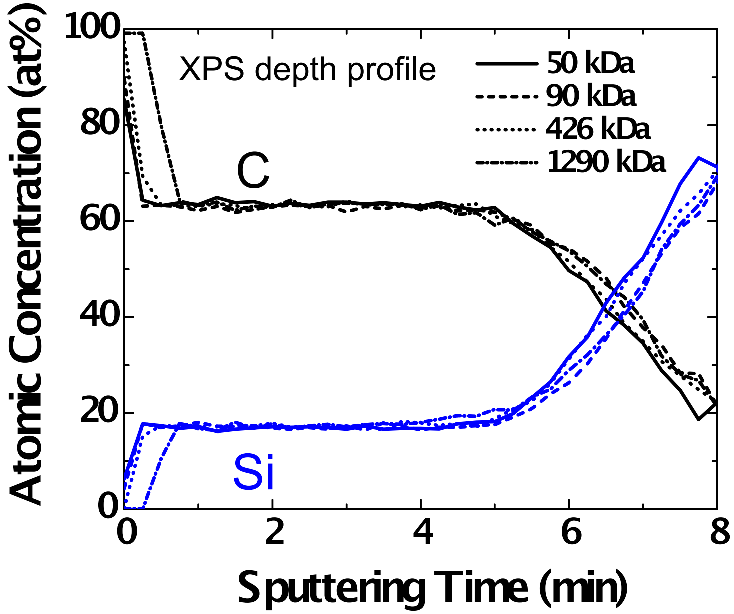
Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

Uniform and Controllable Pore Filling

Precise control of fill level



Uniform filling



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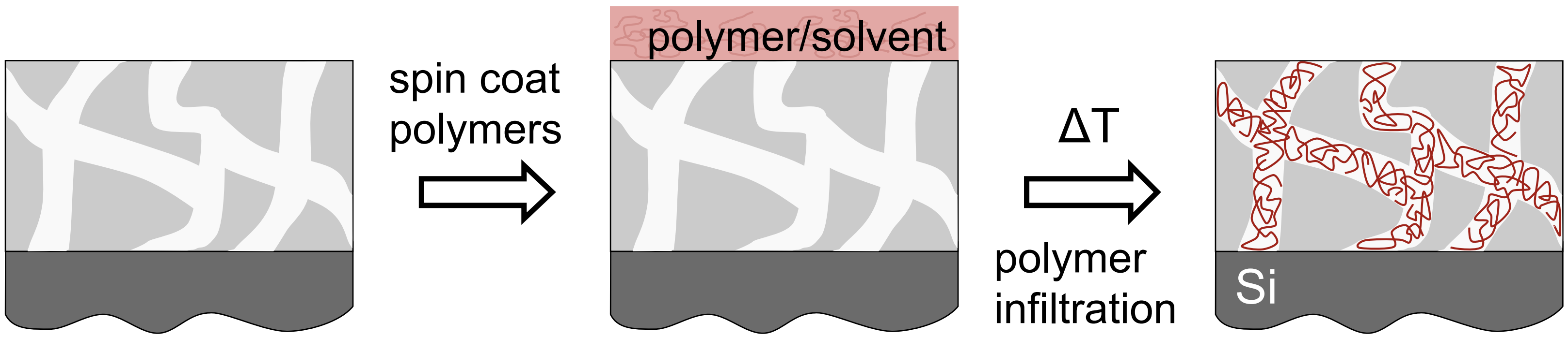
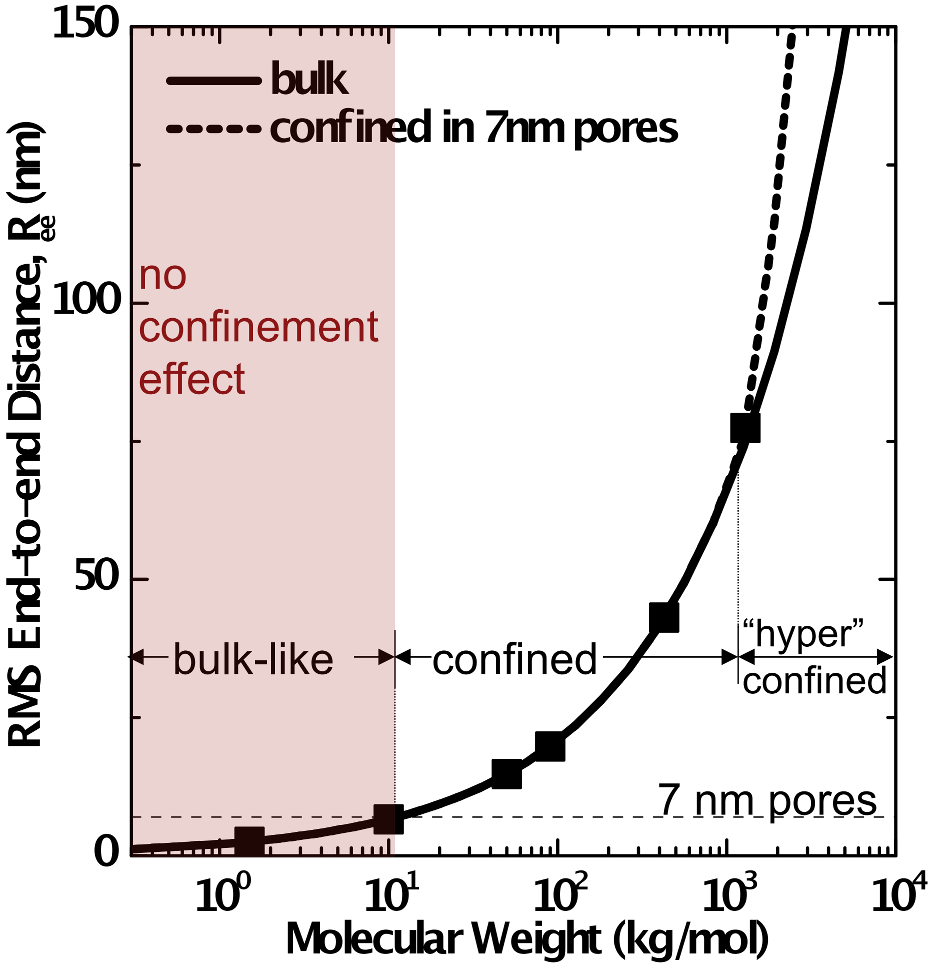
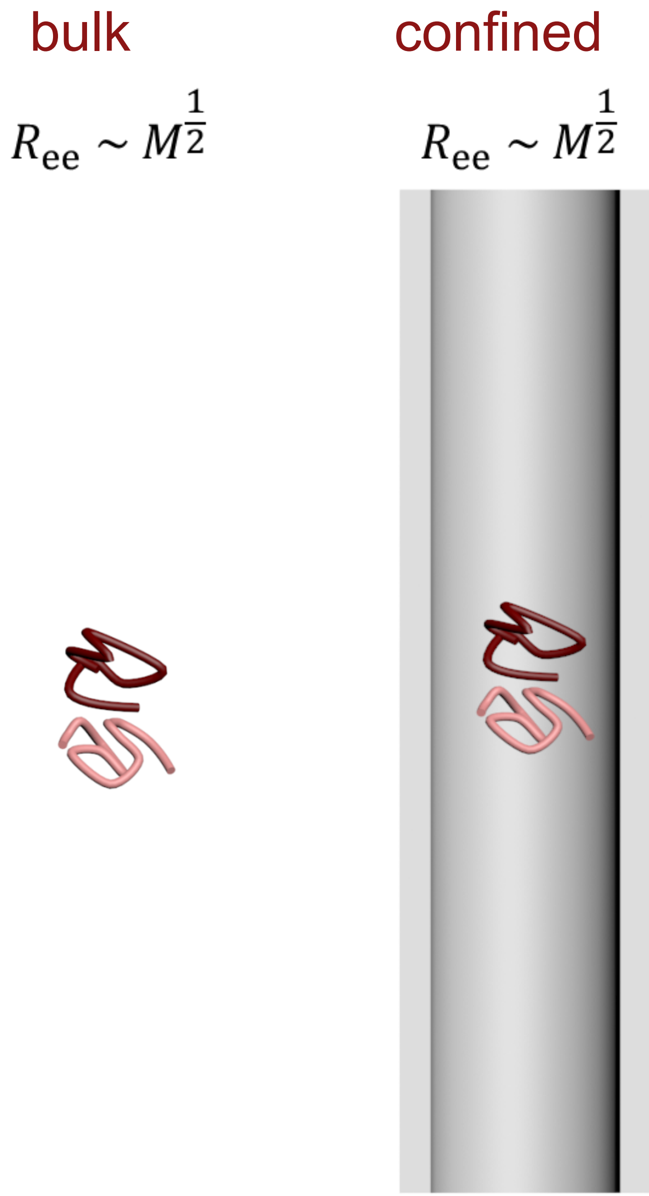


Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

Polymer Confinement in Hybrid Nanocomposites





Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

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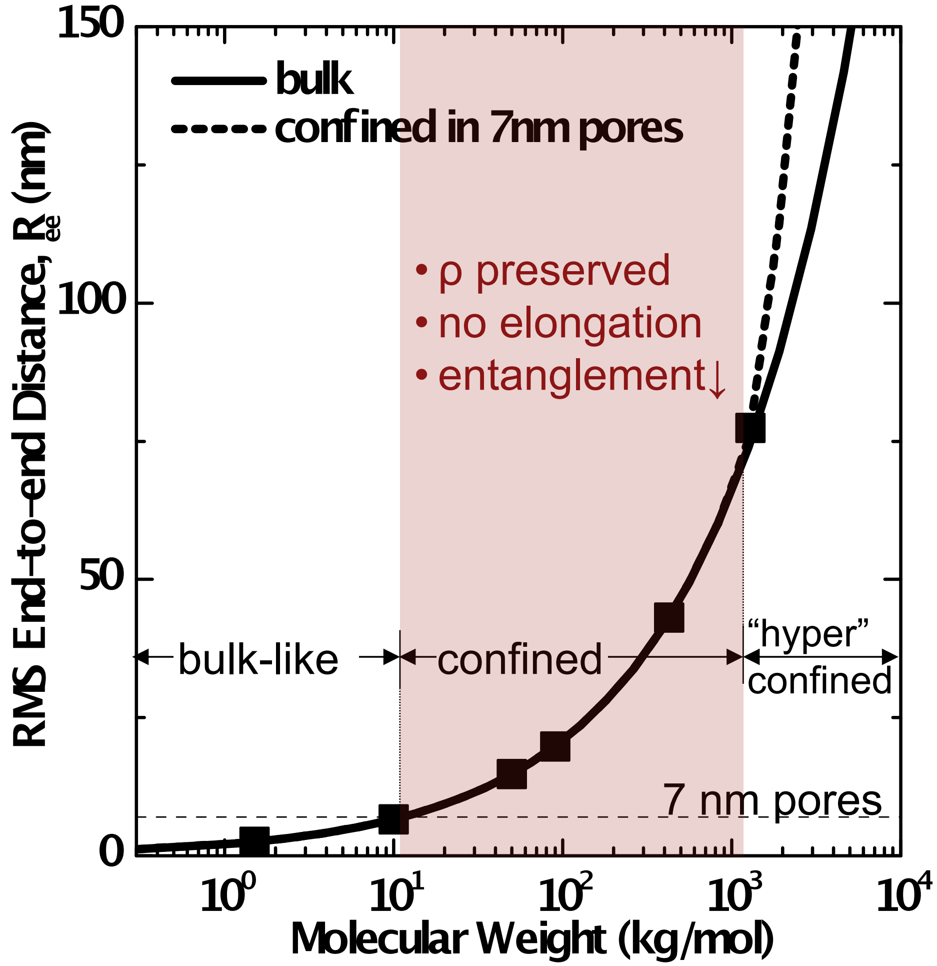

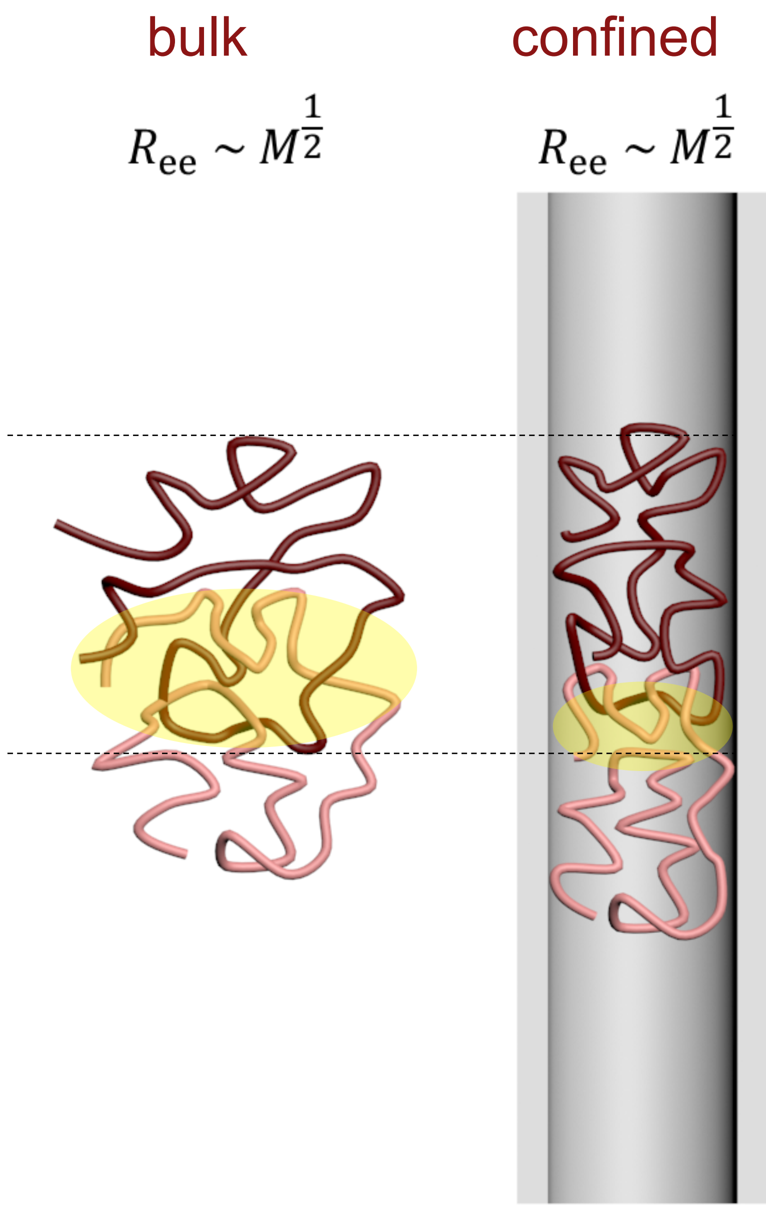

Isaacson, Dauskardt, *et al. Nature Materials*, 2016.

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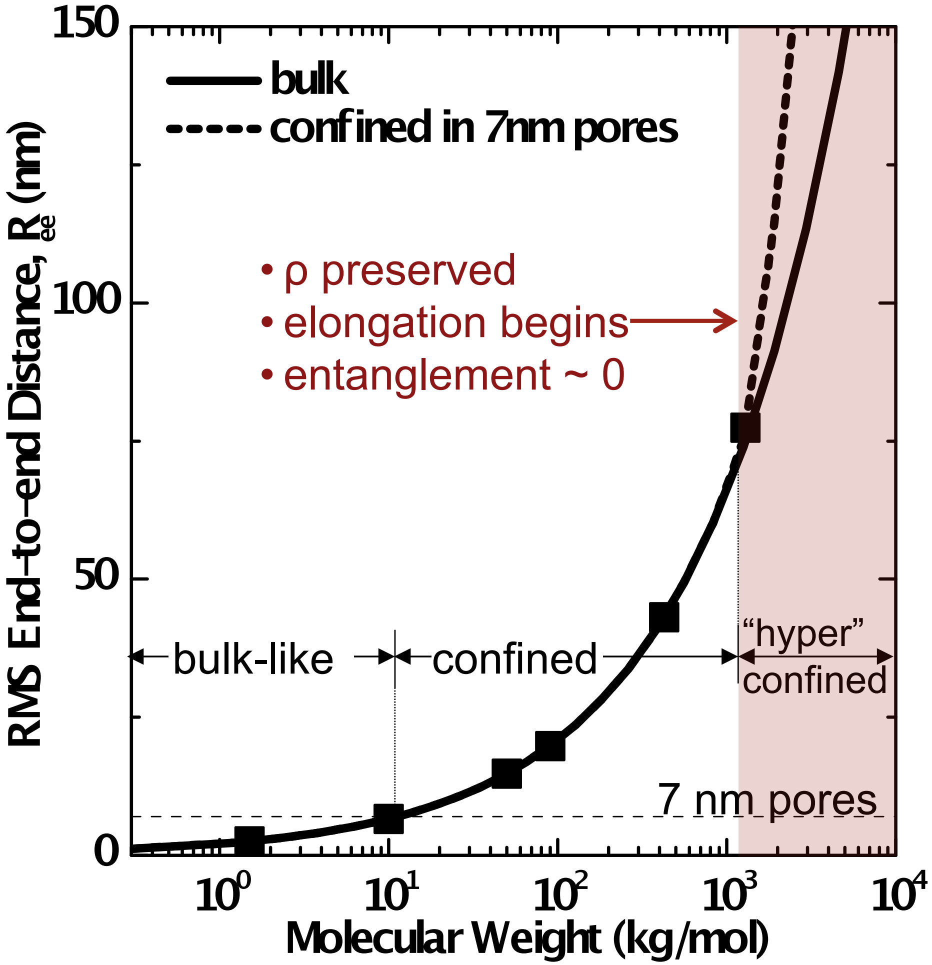

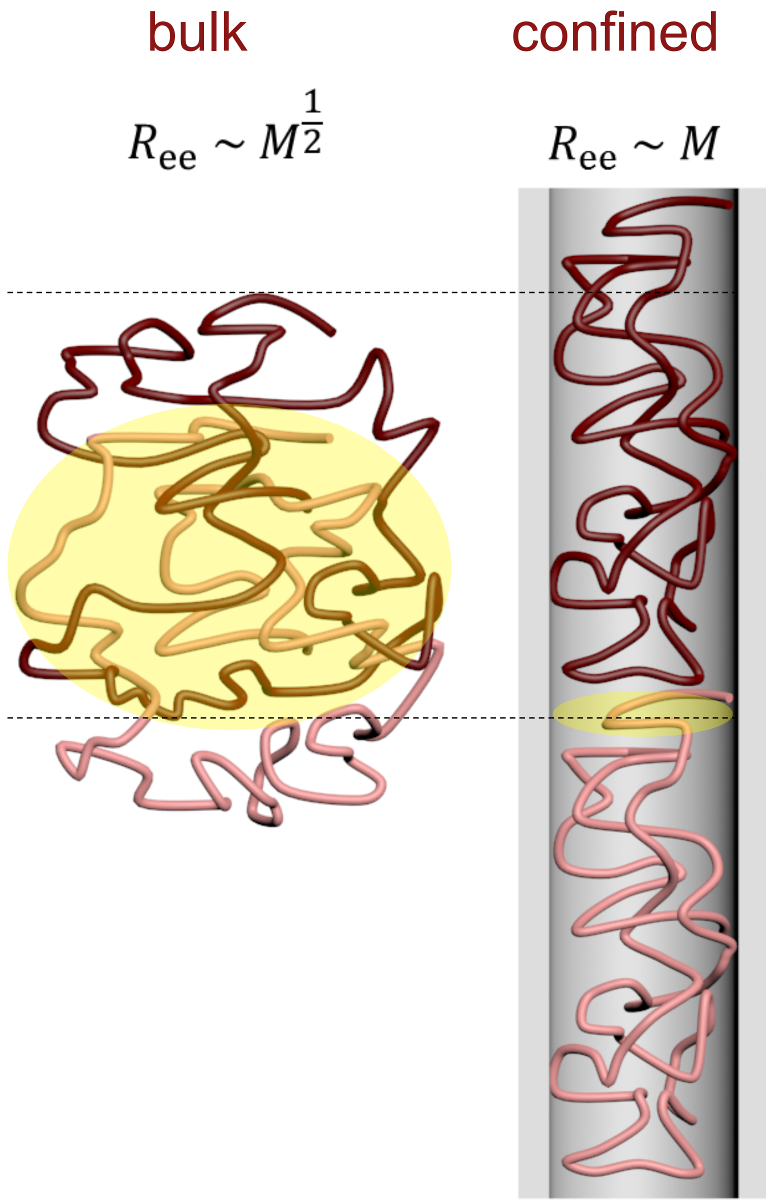

Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

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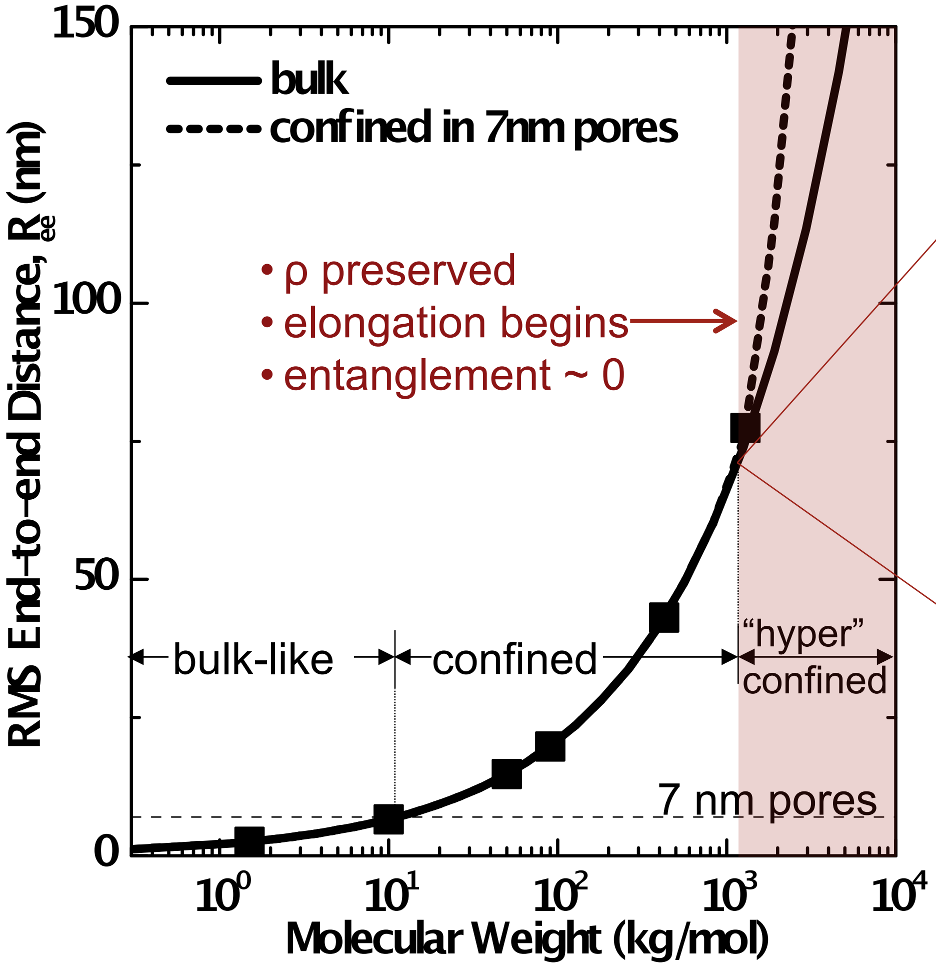
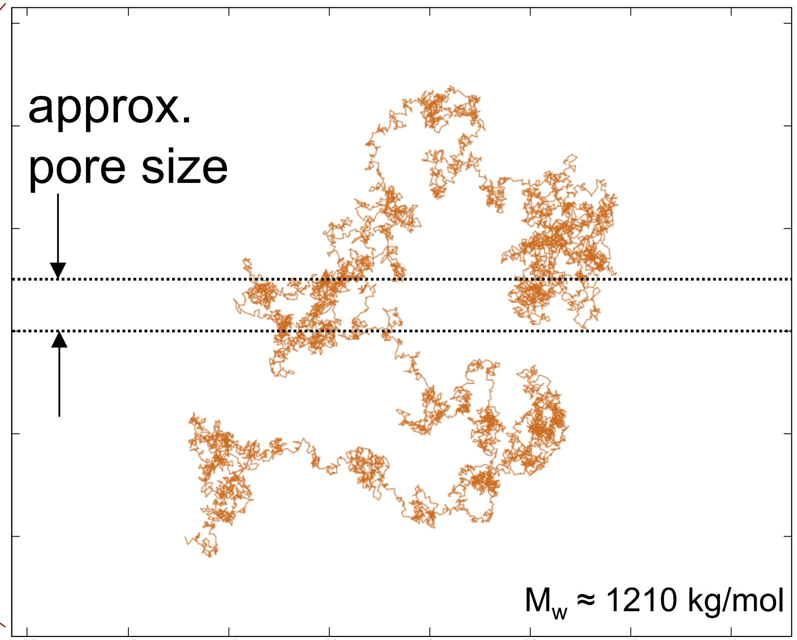


simulated polymer chain



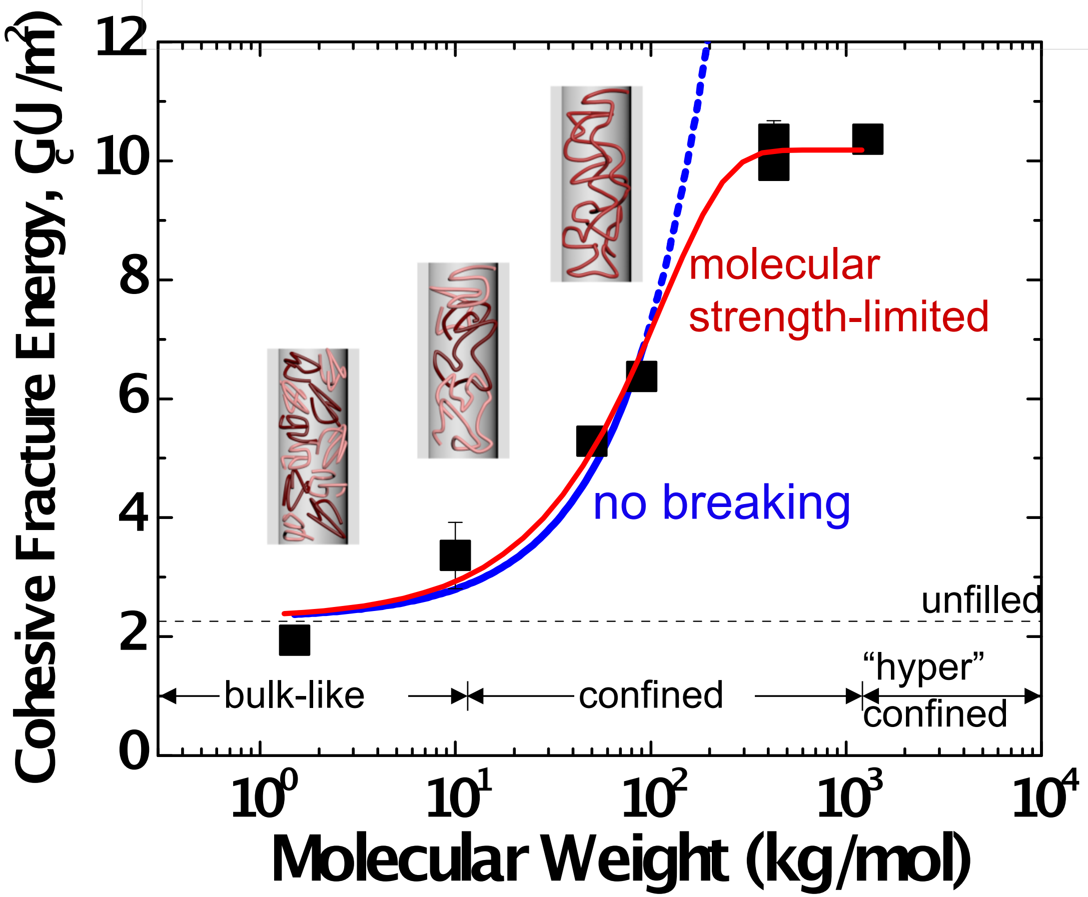
$R_{ee} \approx 75$ nm, extended length ≈ 8 μm

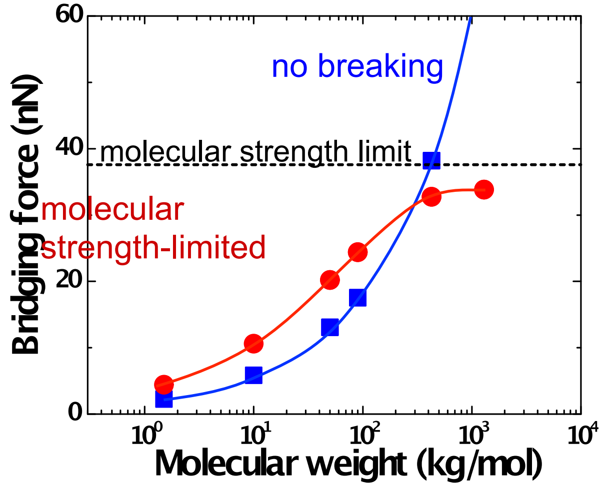
Isaacson, Dauskardt, *et al. Nature Materials*, 2016.

Molecular Toughening in Hybrid Nanocomposites

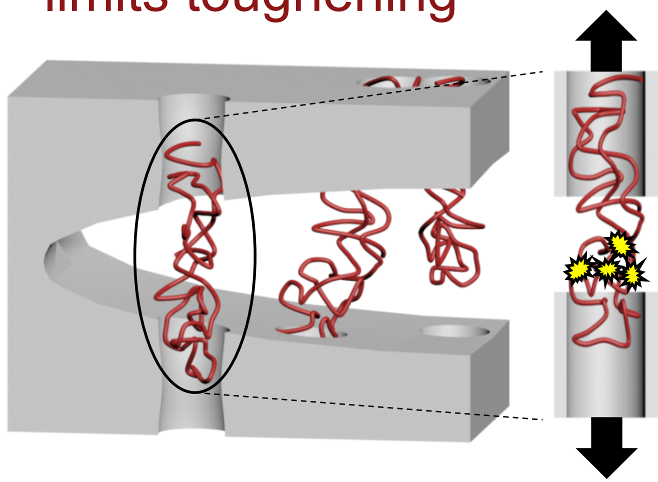
La partie de l'image avec l'ID de relation rld14 n'a pas été trouvée dans le fichier.

La partie de l'image avec l'ID de relation rld13 n'a pas été trouvée dans le fichier.





molecular strength
limits toughening



toughening through collective action of individual molecules

Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

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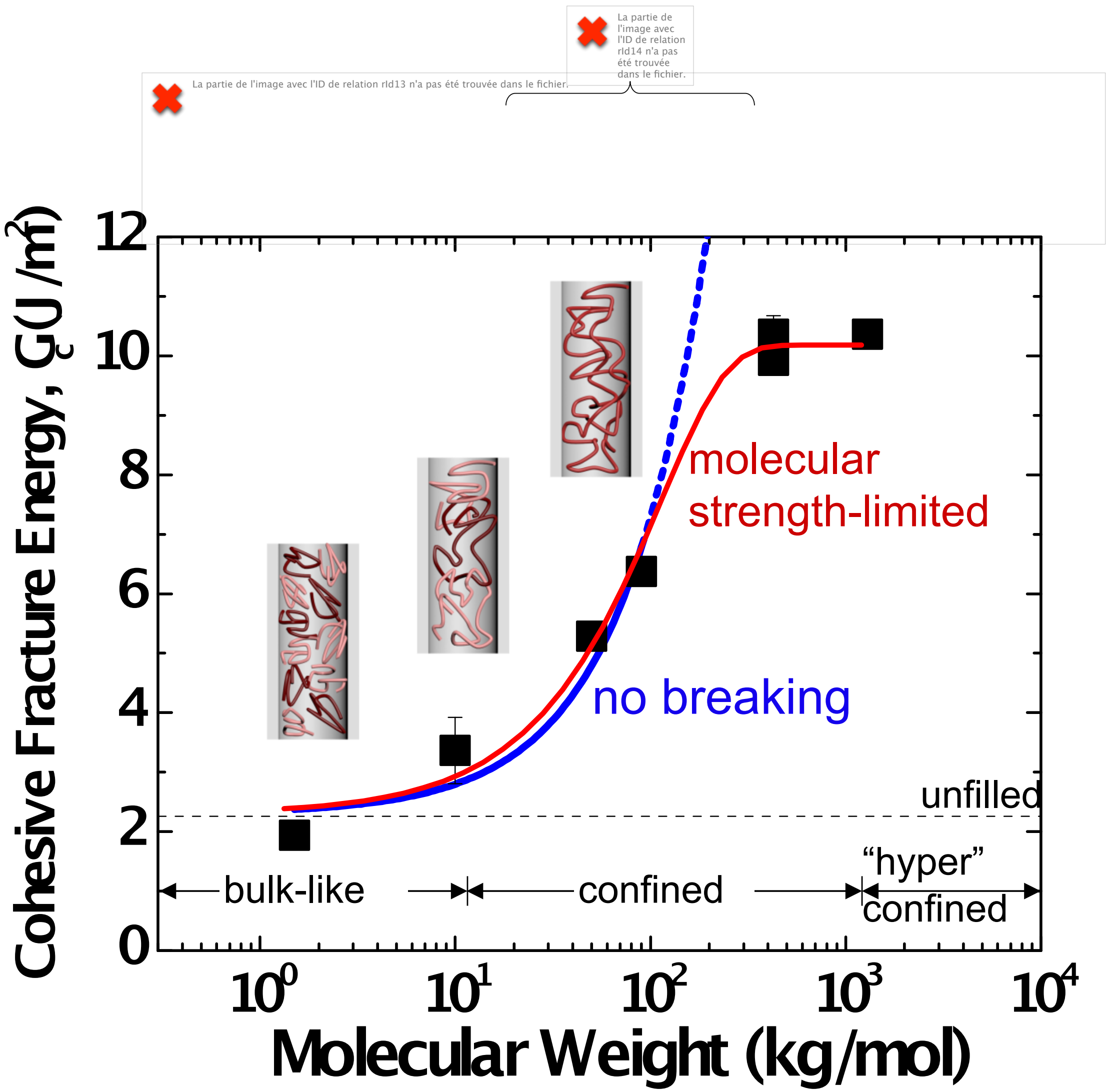
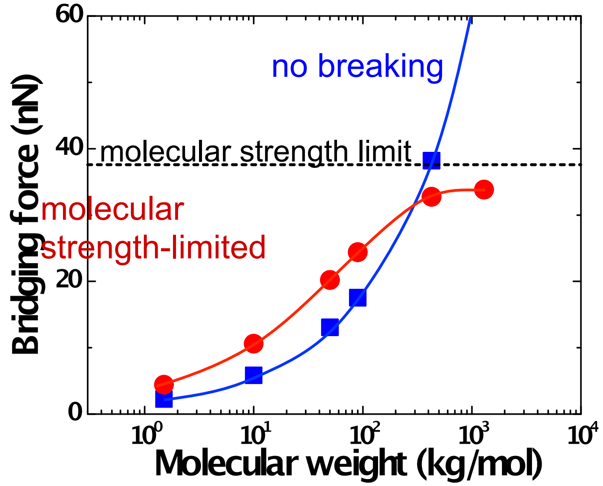
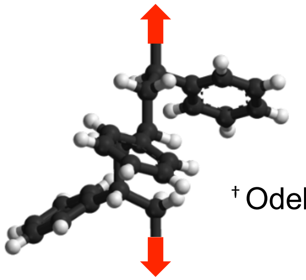
Molecular Toughening in Hybrid Nanocomposites





molecular strength limits toughening



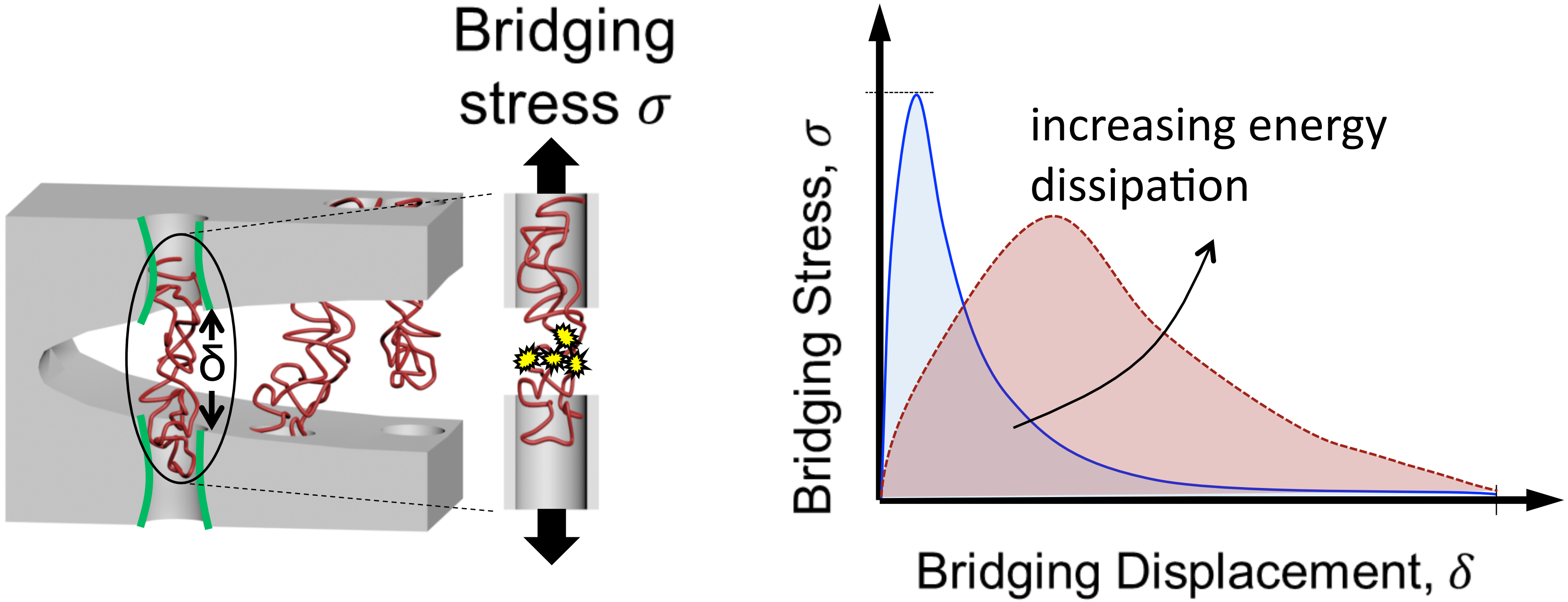
Force to break a single chain: ~8 nN/bond†

† Odell and Keller, *J. Polym. Sci.* (1986).

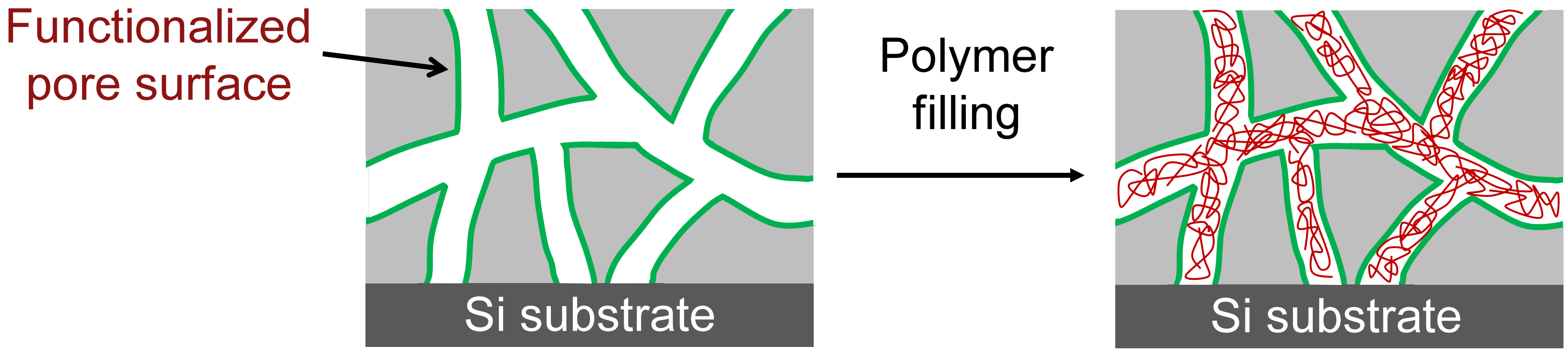
$$\left(\frac{8\ \text{nN}}{\text{bond}}\right)\left(\frac{4.7\ \text{load bearing bonds}}{\text{bridging molecule}}\right) = 38\ \text{nN/molecule}$$

Isaacson, Dauskardt, *et al*. *Nature Materials*, 2016.

Tuning Polymer-Surface Interactions

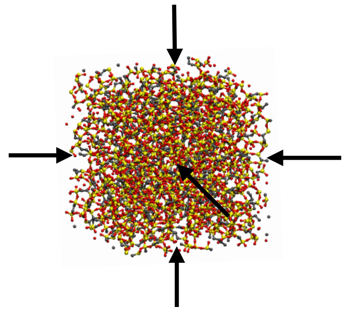


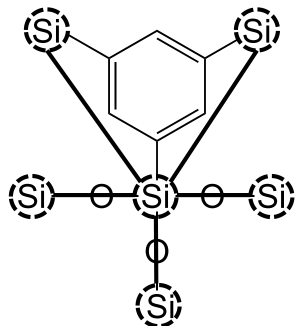
Strategy: surface chemical functionalization



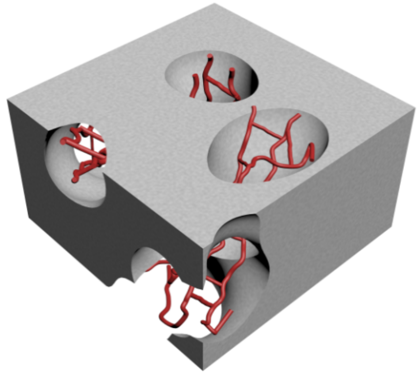
Outline

- Hybrid Molecular Design Strategies
  - unexpected elastic and thermal expansion properties





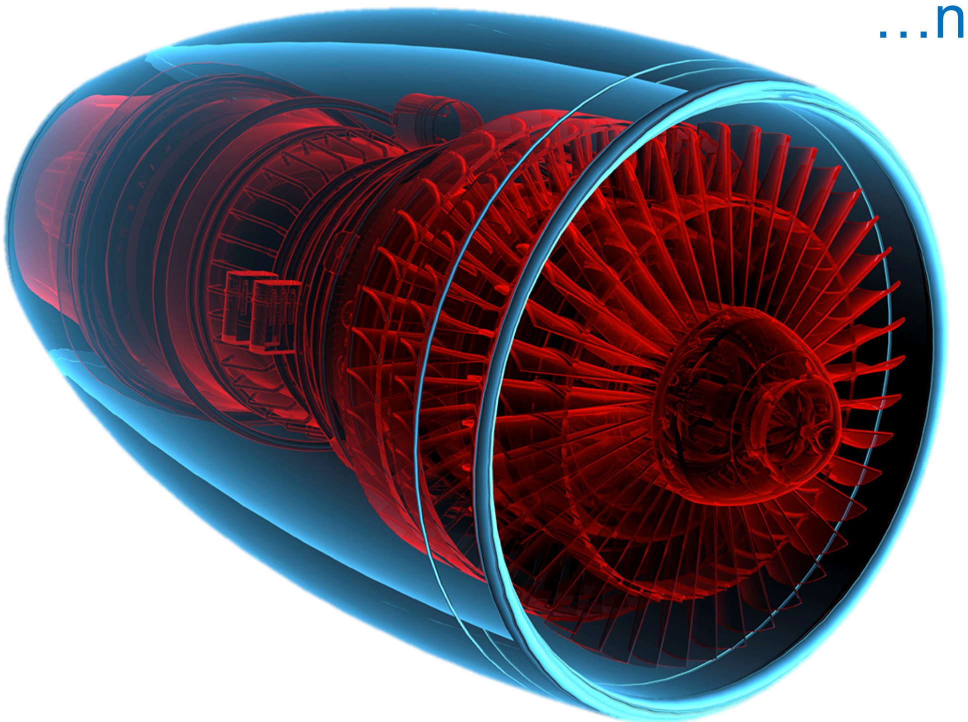
- Hyperconnected Network Architectures
  - designing network connectivity for exceptional mechanical properties



- Hyper Confined Molecular Hybrids
  - fundamental limits on toughening and strengthening

- Emerging Applications for Molecular Hybrids
  - thermal barriers and battery electrolytes

Polyimide Hybrid Nanocomposites Coatings

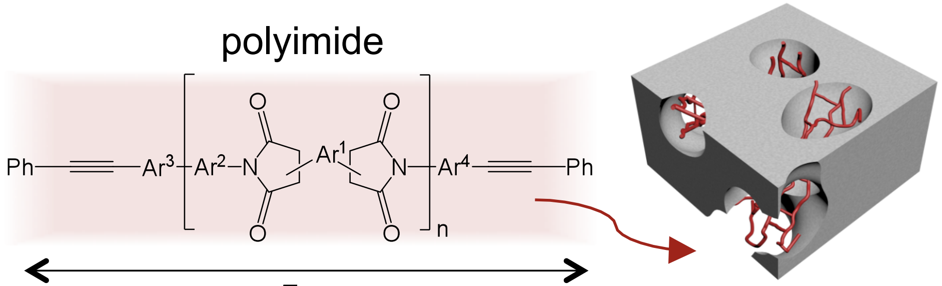


…need for high temperature thermal barrier coatings for plastics

Polyimide Filler

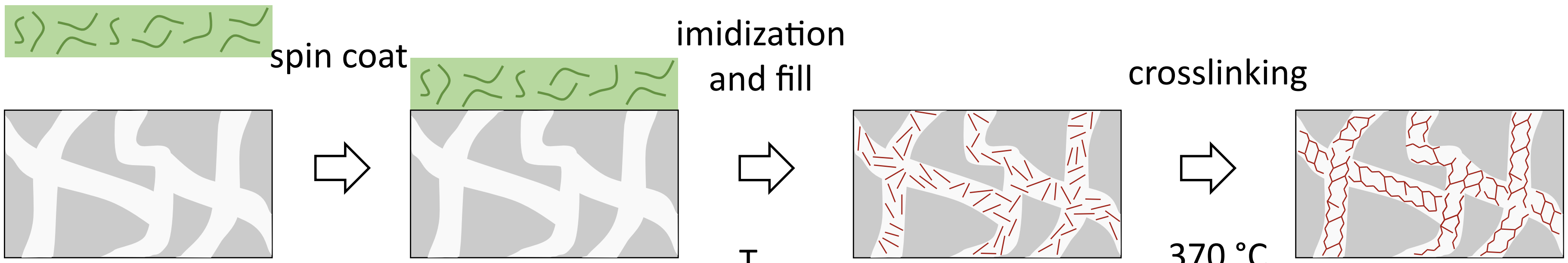
- high temperature organic phase
- stiff molecular backbone, high T_g
- poor solubility
- reactions in nanoscale confinement

polyimide



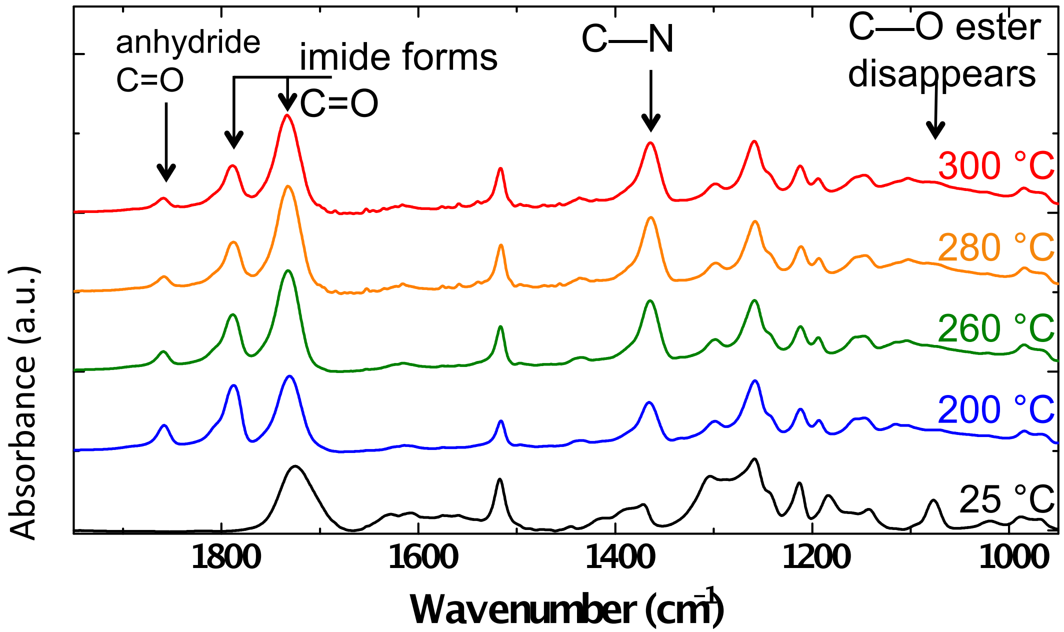
~5 nm

poly(amic ester)

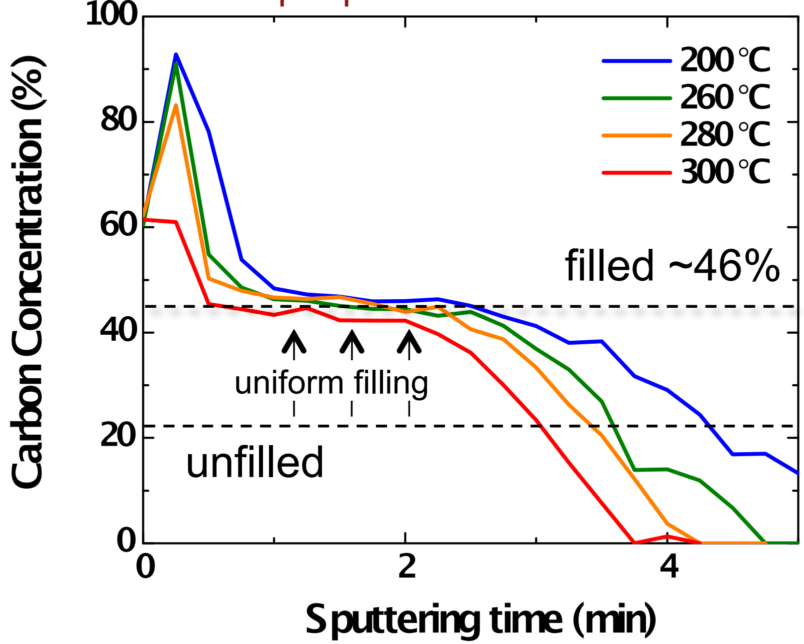


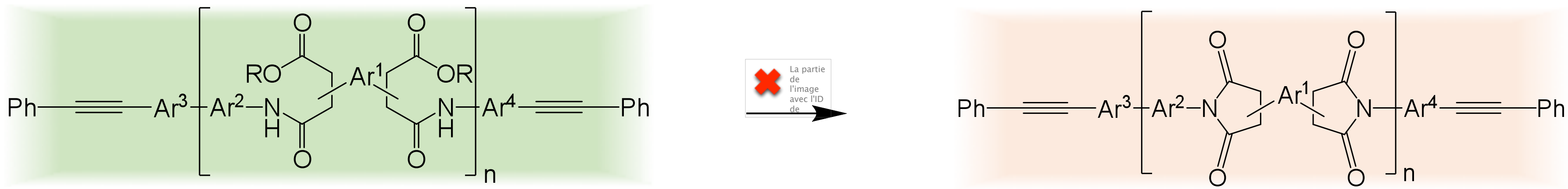
Simultaneous Filling and Confined Imidization

FTIR spectrum ring-closing imidization

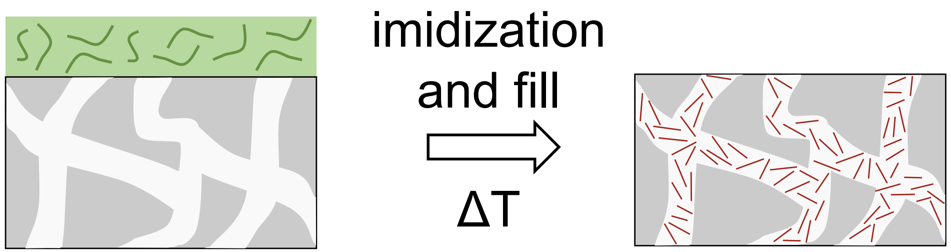


XPS depth profile



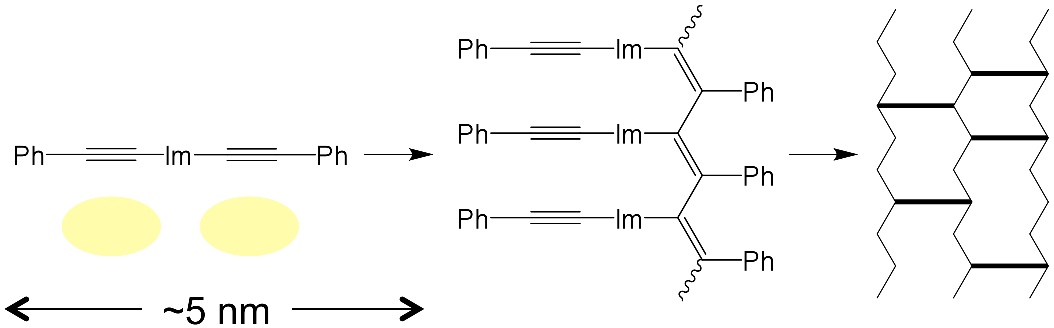


poly(amic ester) polyimide

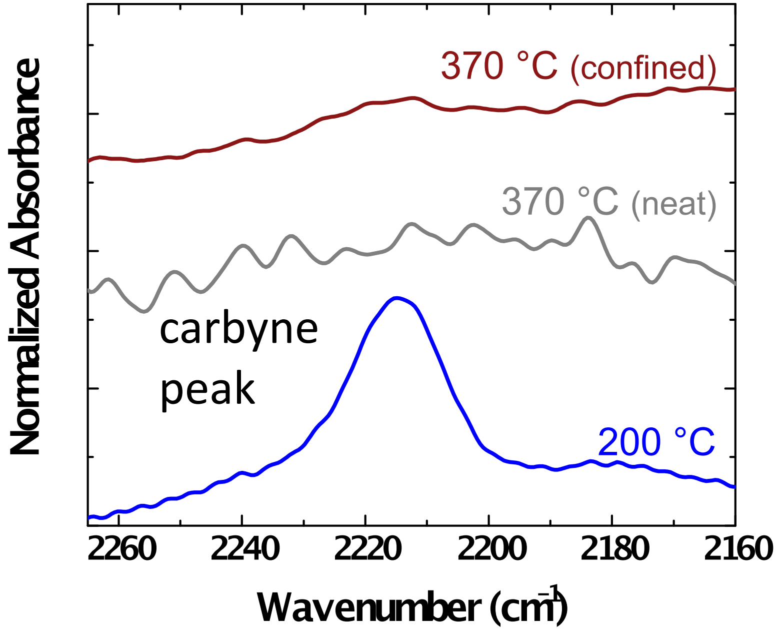


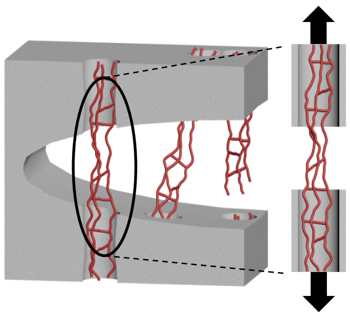
Polyimide Crosslinking in Nanoscale Confinement

polyimide crosslinking reaction



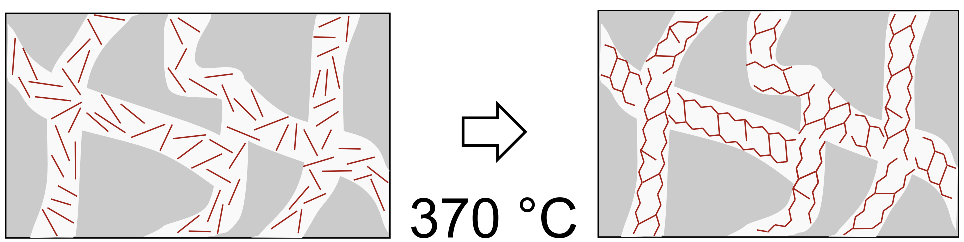
phenylethynyl endcaps undergo radical addition reactions and aromatic formation to crosslink network

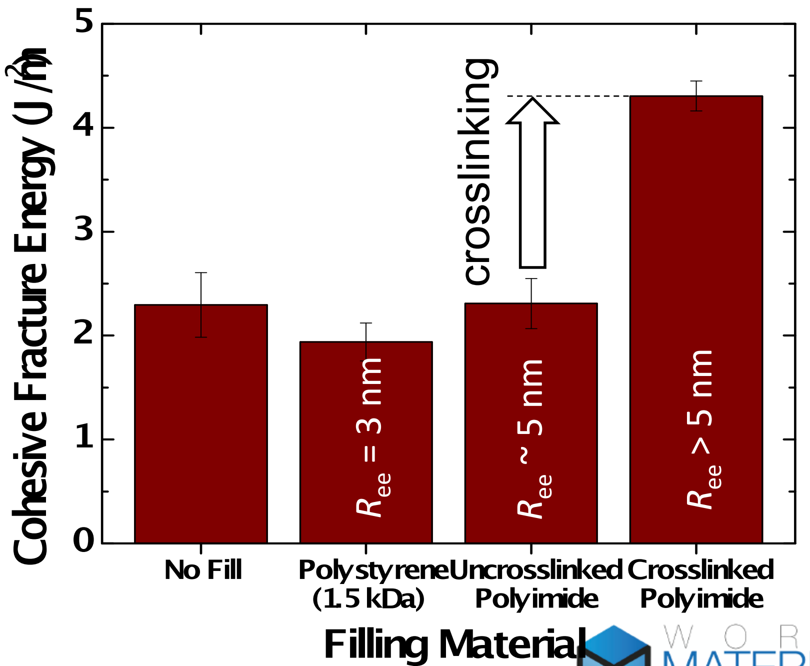




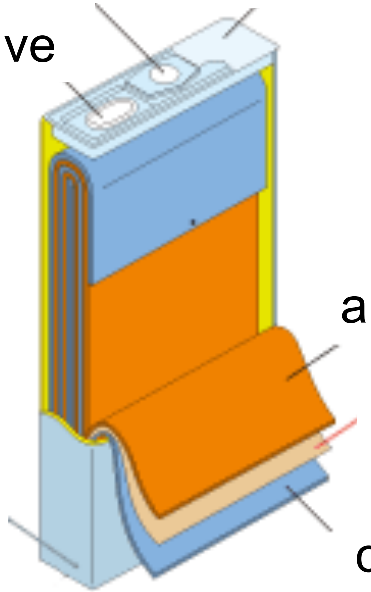
molecular bridging toughening mechanism

crosslinking





Reinforced Solid Polymer Hybrid Electrolyte

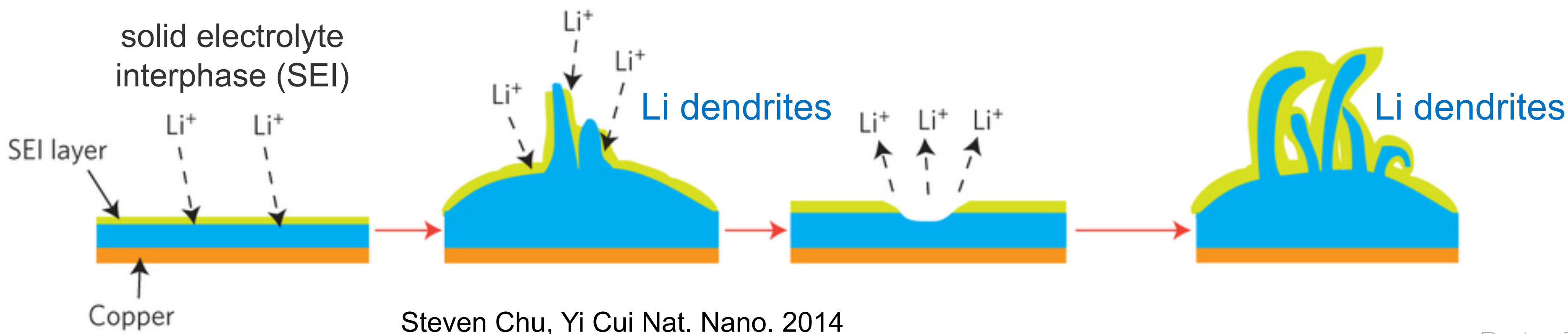


…need for high-energy and safe Li-anode batteries

polymer-based electrolytes attractive

- low density
- low cost
- excellent processability

...however, lower ionic conductivity for reasonable kinetics and too mechanically weak to suppress Li dendrite formation



Steven Chu, Yi Cui Nat. Nano. 2014

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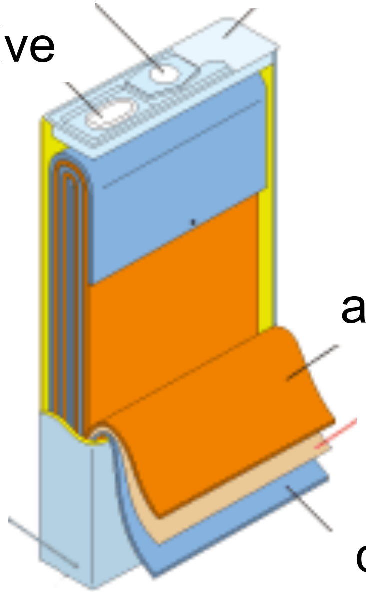
Reinforced Solid Polymer Hybrid Electrolyte



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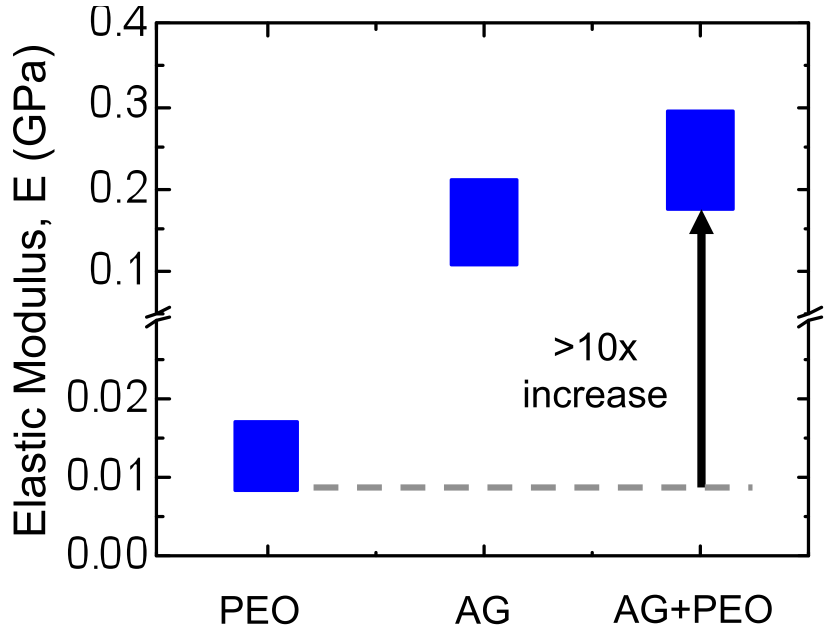


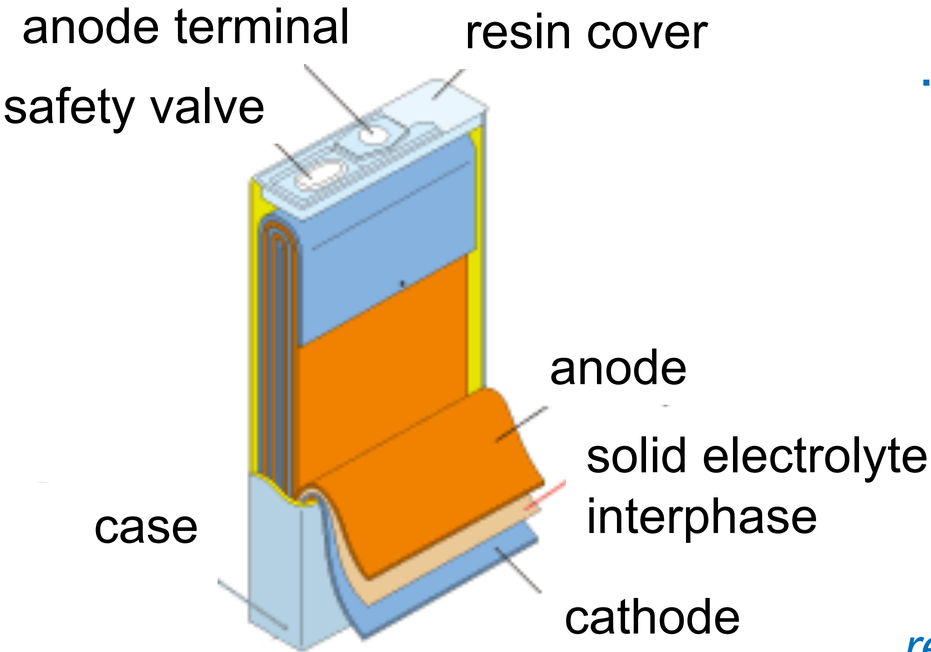
reinforced composite polymer electrolyte with high ionic conductivity and high modulus

SiO_2 aerogel (AG) polyethylene oxide (PEO) w/ Li+

porosity = 85%, t ~ 600μm

Dauskardt, Cui, et. al. In review, 2017

Reinforced Solid Polymer Hybrid Electrolyte



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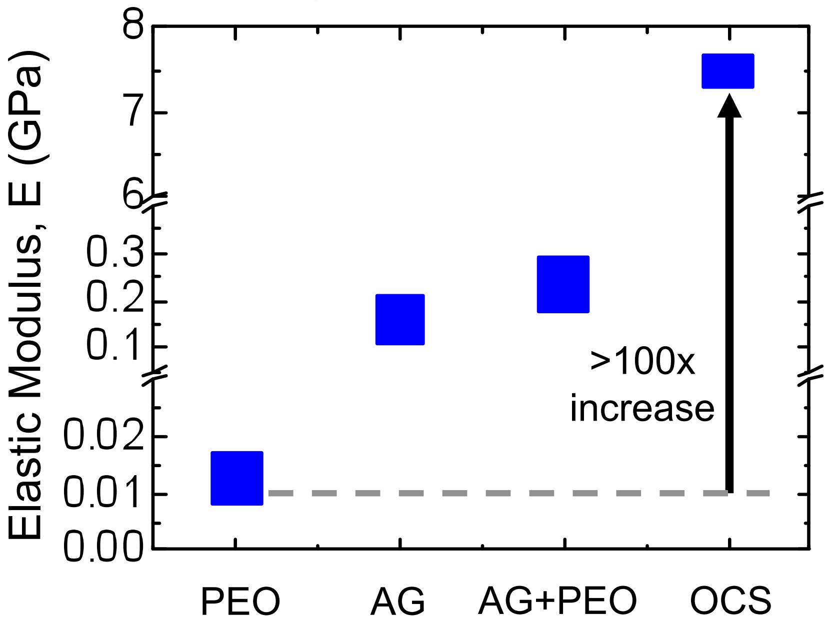

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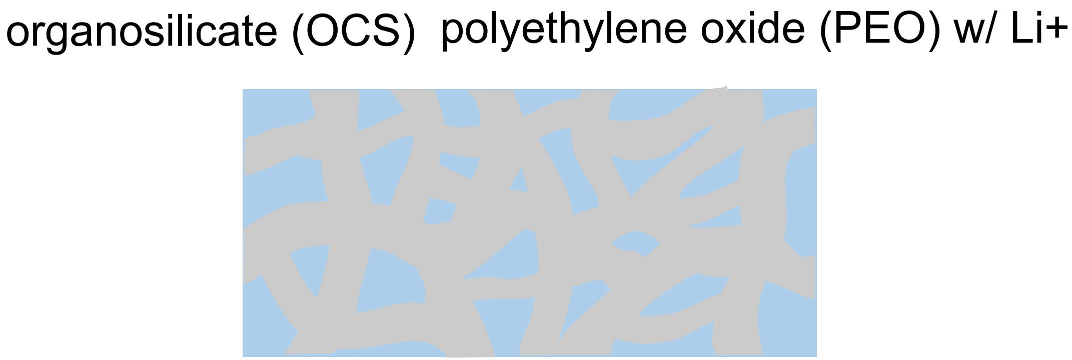

porosity = 44%, t ~ 480nm

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Dauskardt, Cui, et. al. In review, 2017

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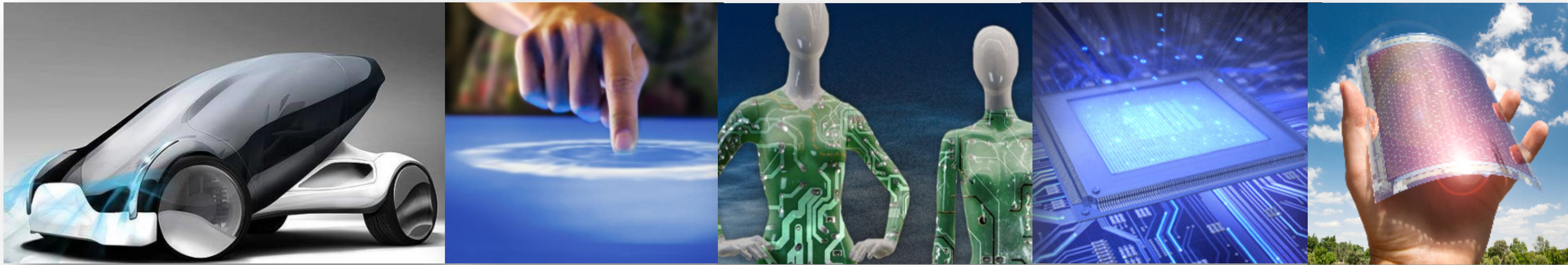
Processing, Properties and Reliability of Molecular Hybrids



light-weight vehicle | touch display | wearable | microelectronics | energy

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… for inexpensive and durable materials with robust operational lifetimes!

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