



SCHOOL of ENGINEERING & APPLIED SCIENCE
UNIVERSITY of VIRGINIA

Tunable thermal transport and reversible thermal conductivity switching in topologically networked bio-inspired materials



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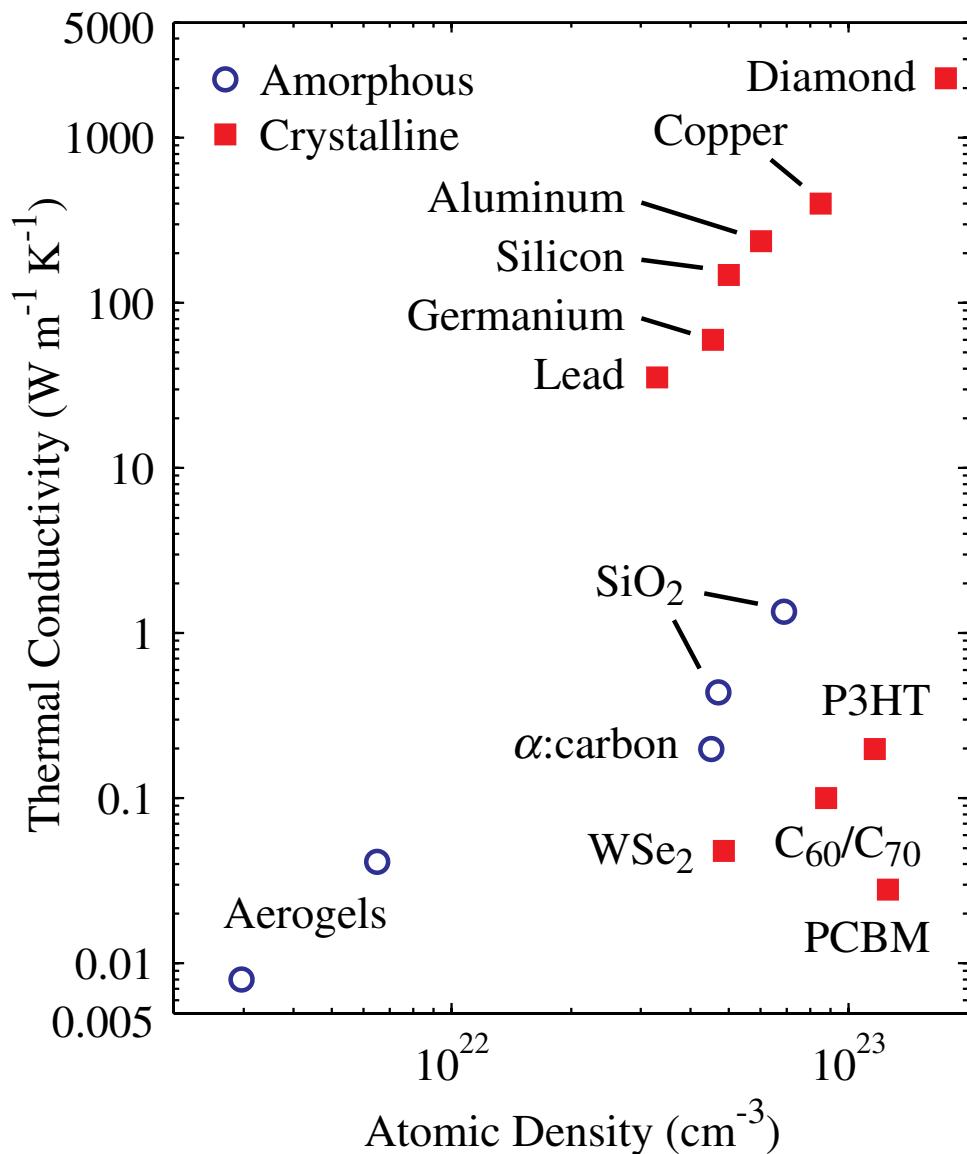
Dept. Mat. Sci. & Eng.

Dept. Physics

University of Virginia

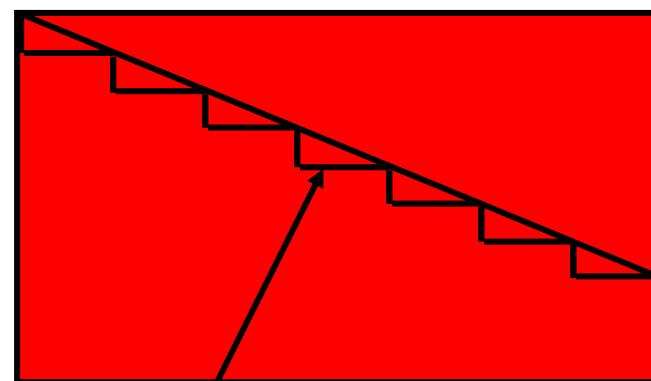
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Thermal conductivity of materials



PRL 110, 015902 (2013)

Microscopic Picture



λ = Mean free path

$$\kappa = \frac{1}{3} Cv \lambda = \frac{1}{3} Cv_g^2 \tau$$

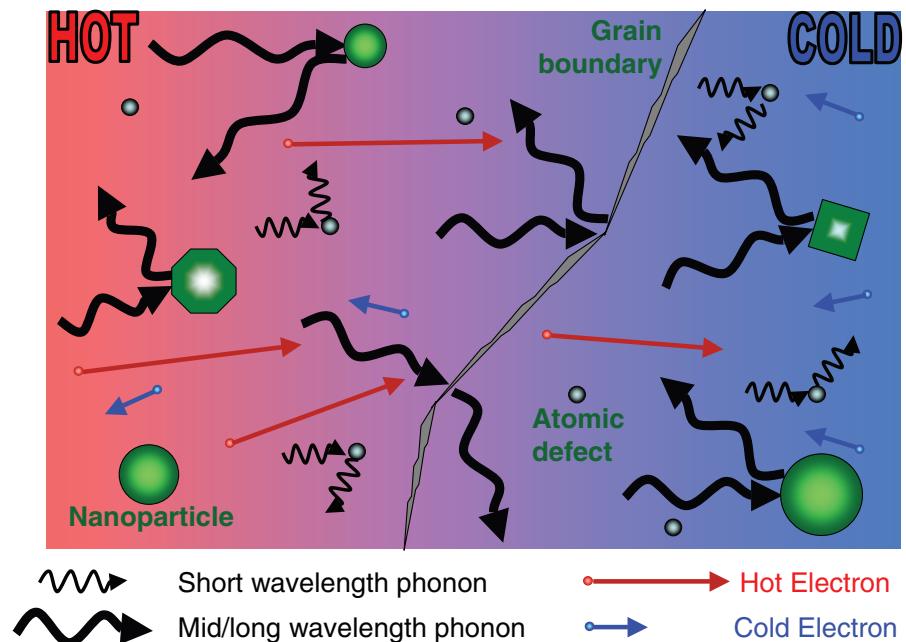
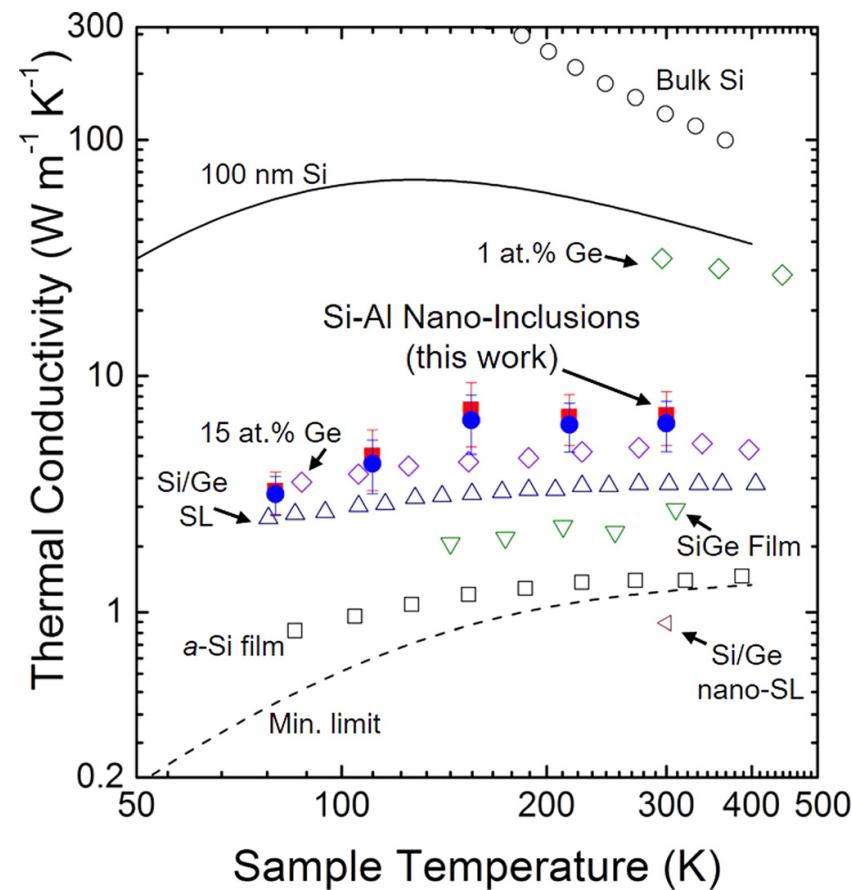
Heat capacity

Velocity

Controlling thermal conductivity - Static

Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity



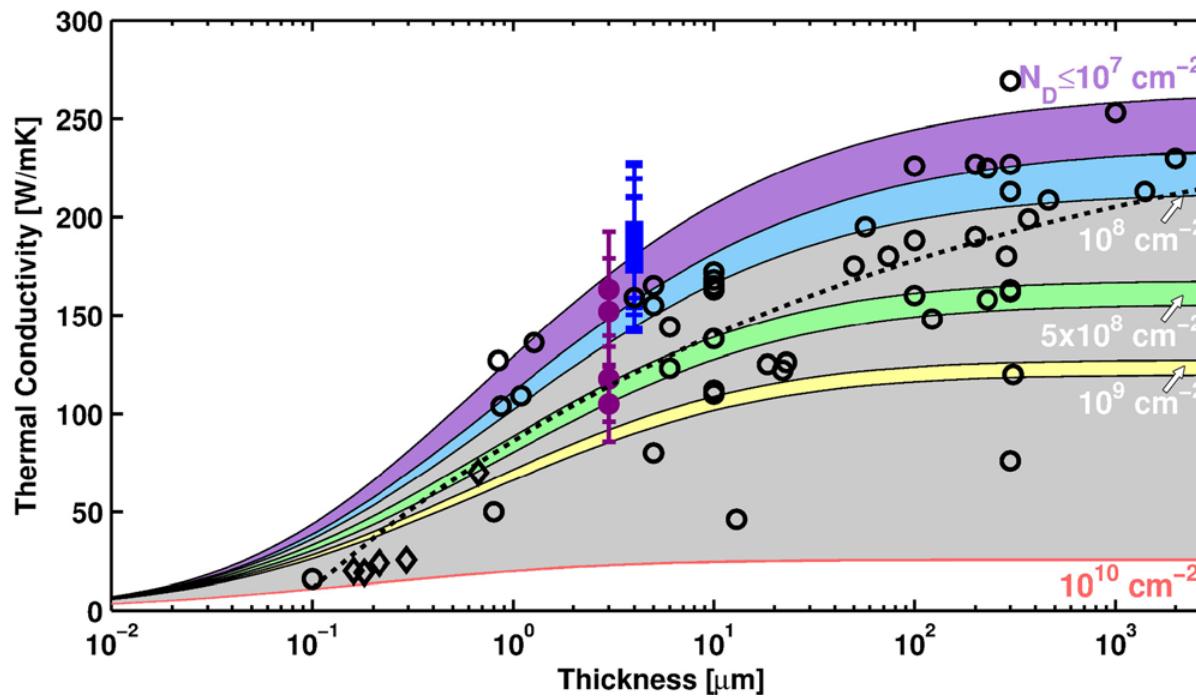
Adv. Mat. 22, 3970

Controlling thermal conductivity - Static

Nanoscale heat transfer

Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity

Thermal conductivity of GaN films



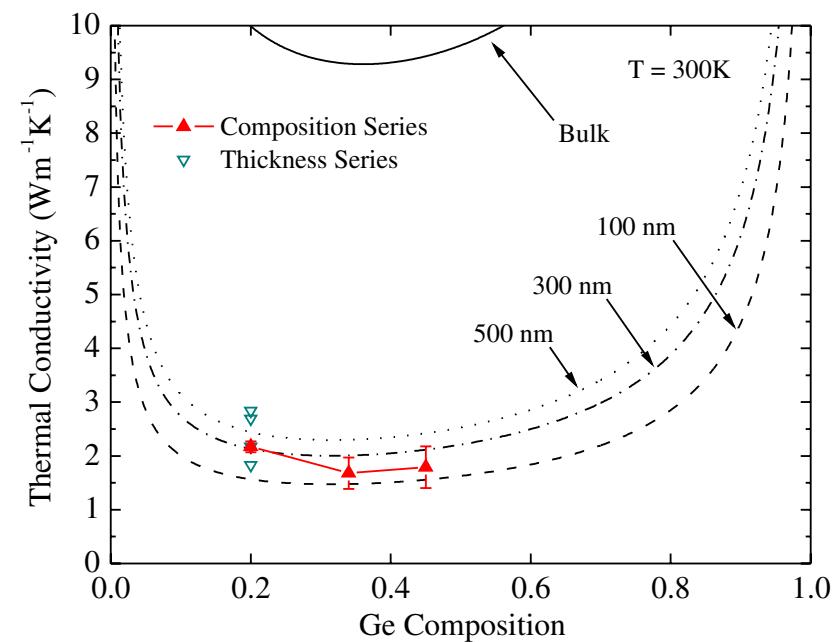
Controlling thermal conductivity - Static

Nanoscale heat transfer

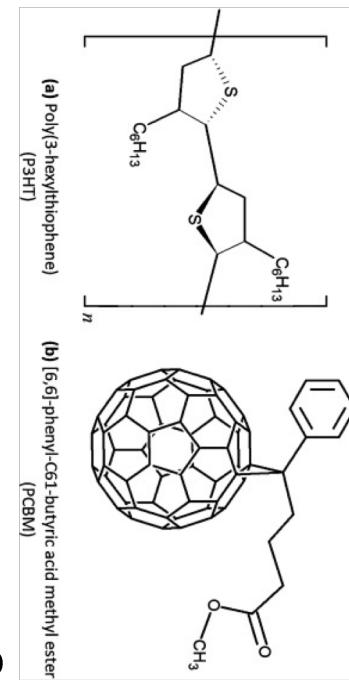
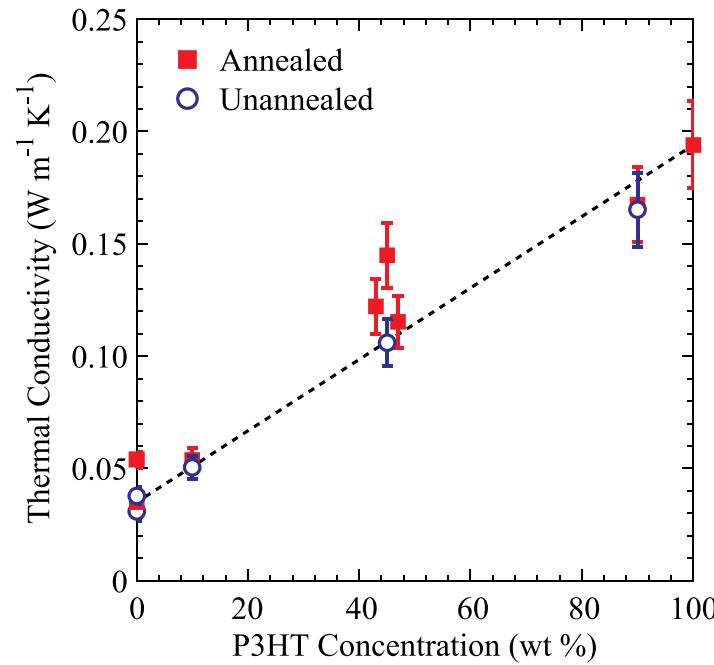
Well controlled and prescribed inclusions, defects, or interfaces to *permanently* change thermal conductivity

Thermal conductivity of alloy thin films

$\text{Si}_{1-x}\text{Ge}_x$



PCBM/P3HT

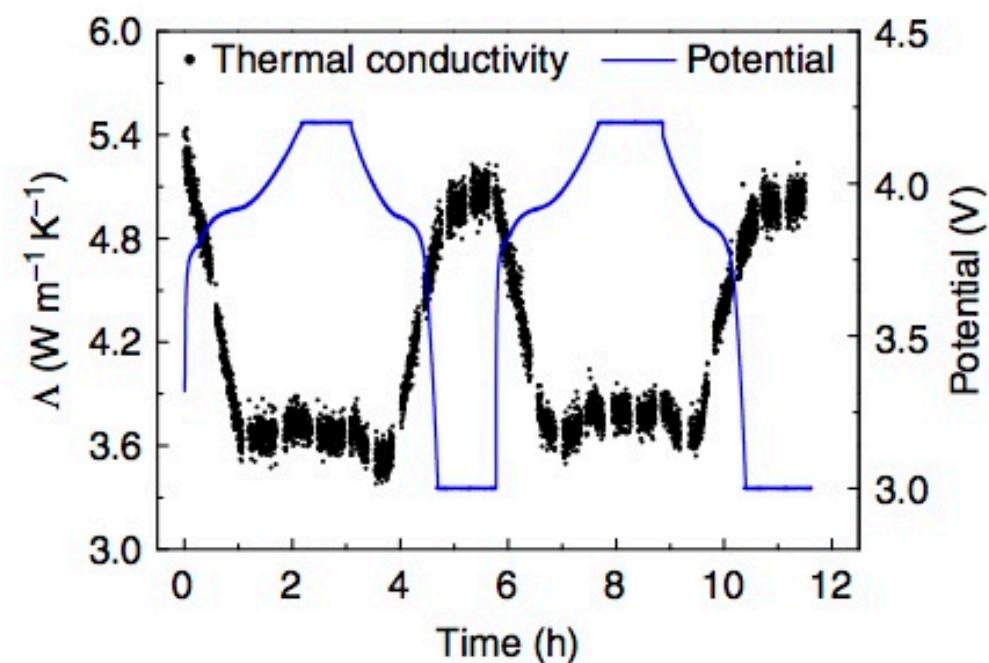
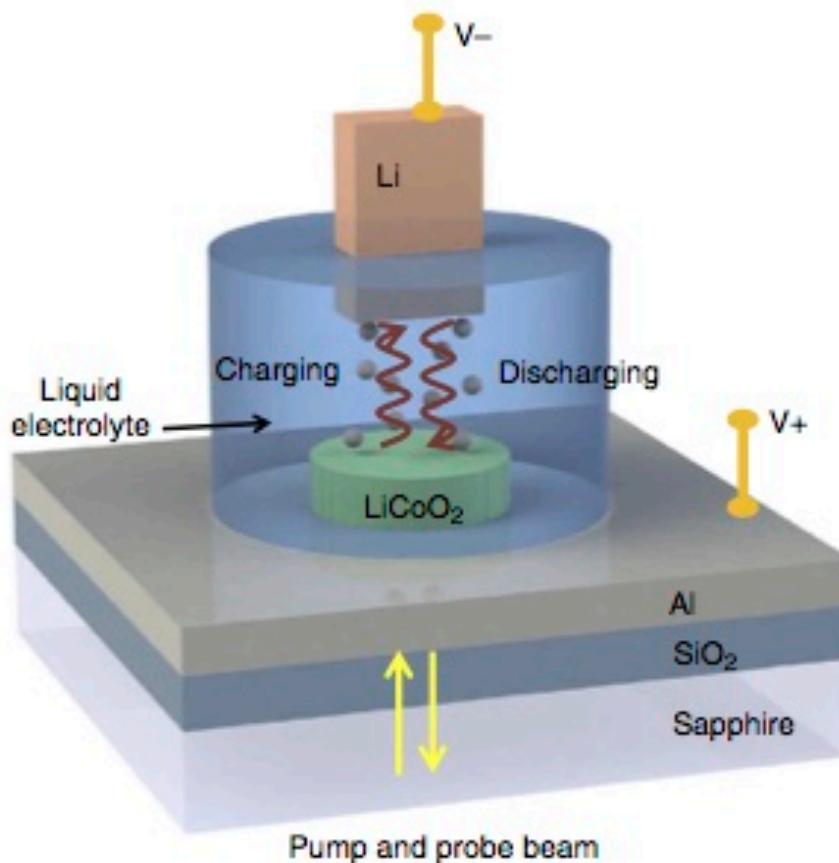


Controlling thermal conductivity - Dynamic

The thermal conductivity switch

Reversibly switching the thermal conductivity of a material via an external stimulus

Defect diffusion, e.g., “de-litiation” of LiCoO_2

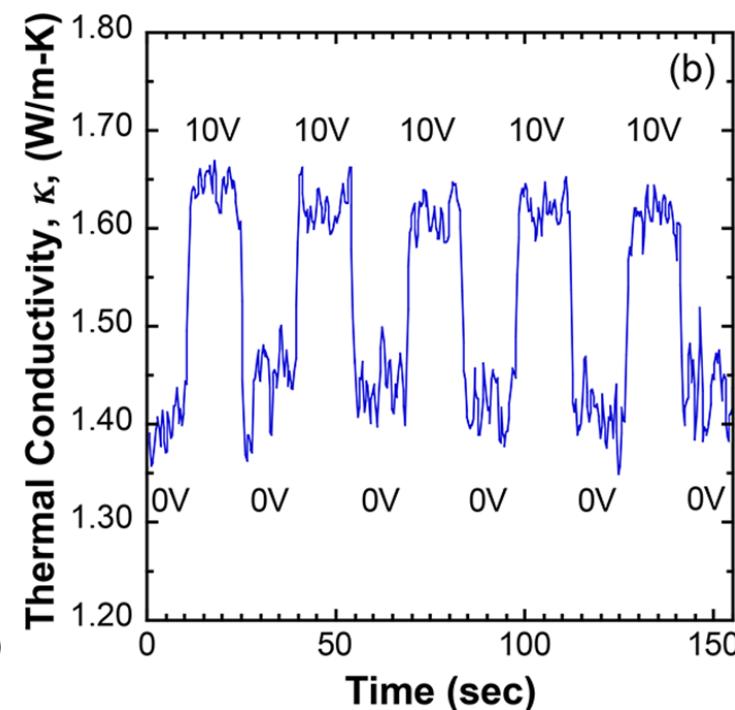
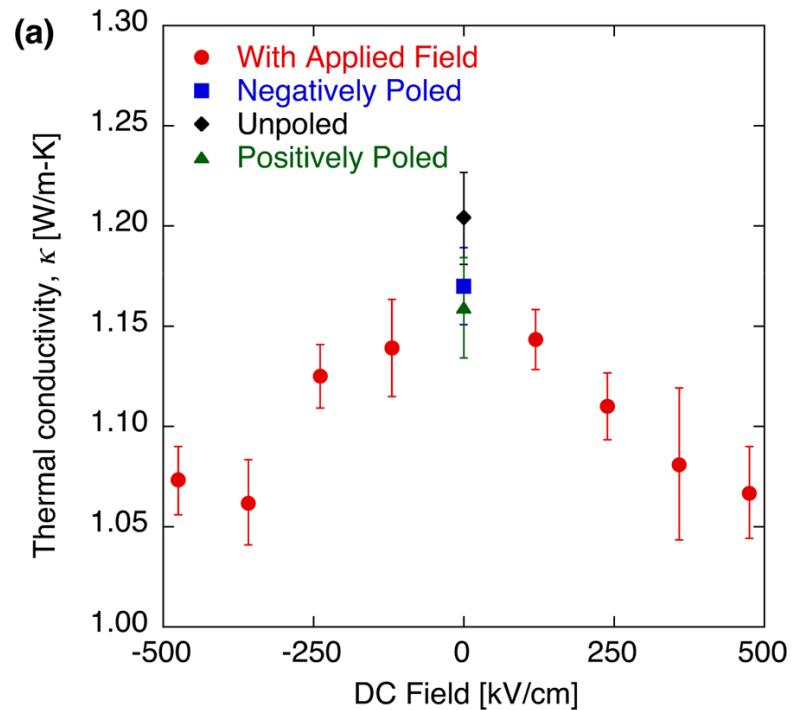
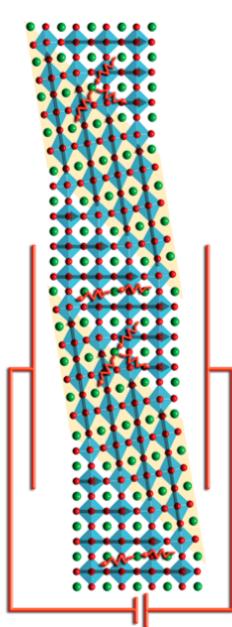


Controlling thermal conductivity - Dynamic

The thermal conductivity switch

Reversibly switching the thermal conductivity of a material via an external stimulus

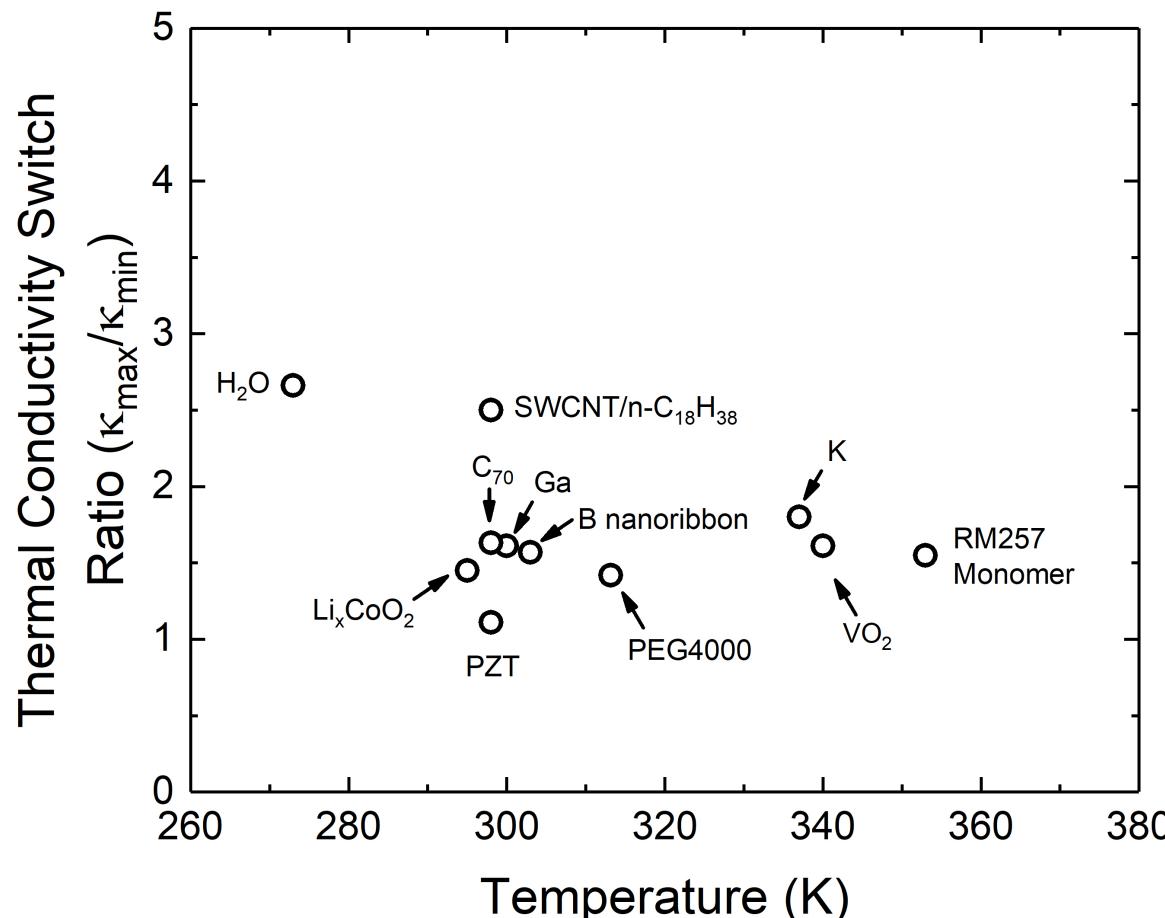
Field controlled ferroelastic domain mobility in PZT



Controlling thermal conductivity - Dynamic

The thermal conductivity switch

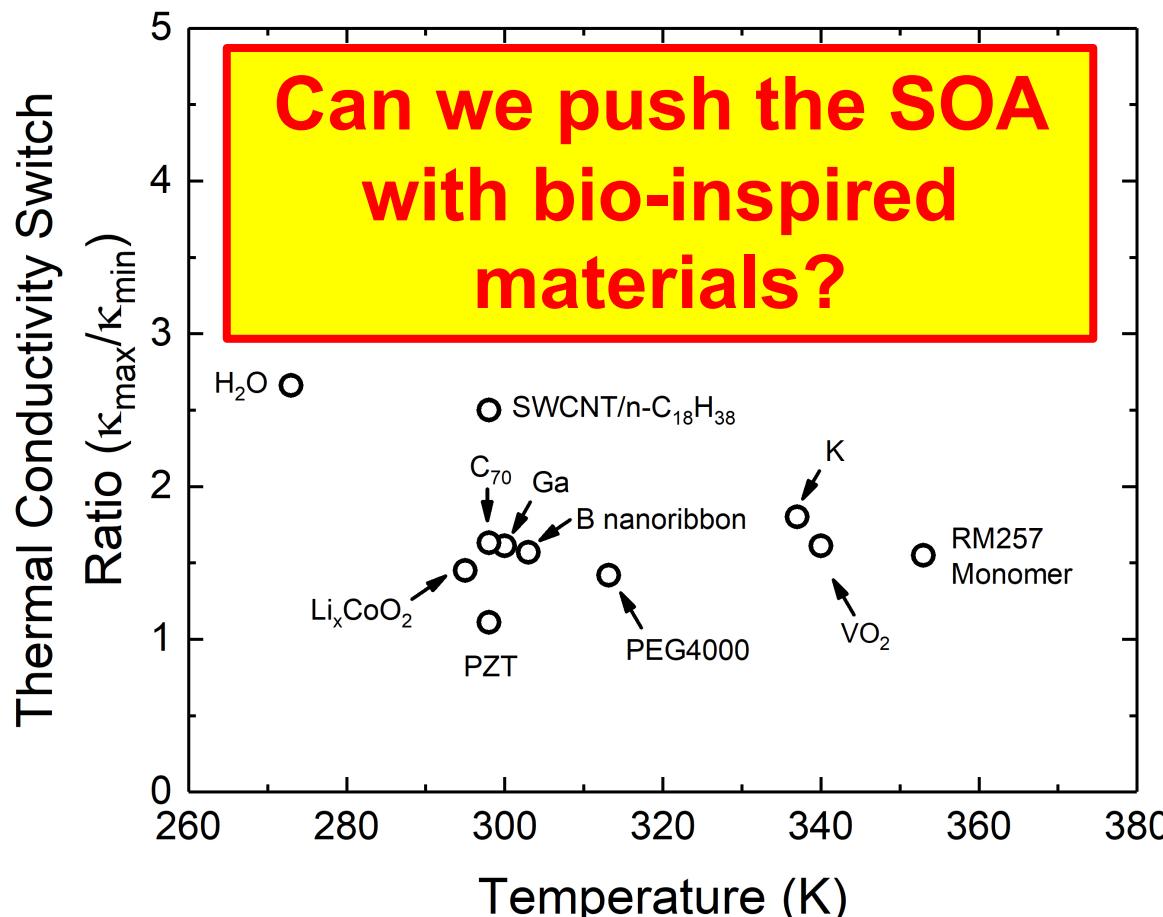
State of the art around biologically relevant temperatures



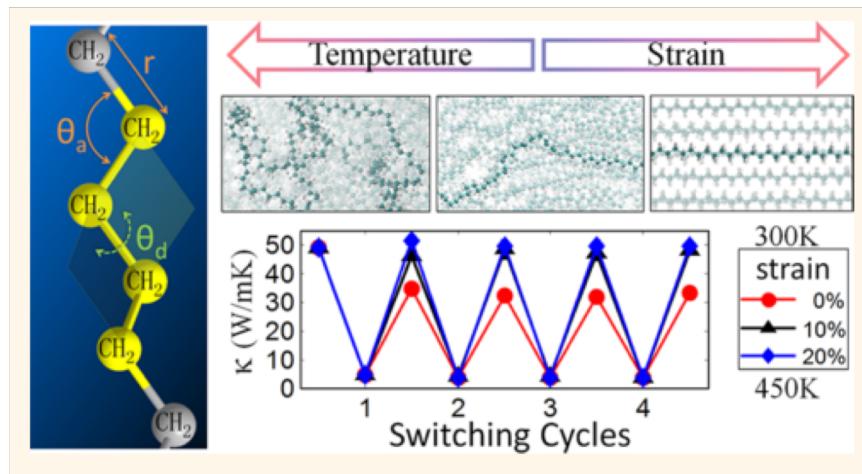
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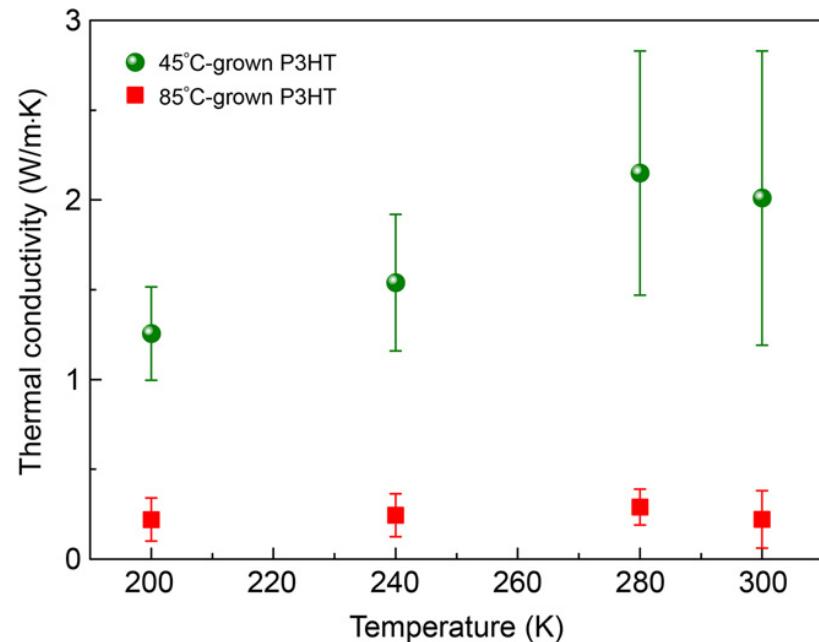
Heat transfer and thermal conductivity in polymers



ACS Nano 7, 7592

Increased inter- and intramolecular bonding has been shown to **create polymers with $\sim 10x$ higher κ than conventional polymers**

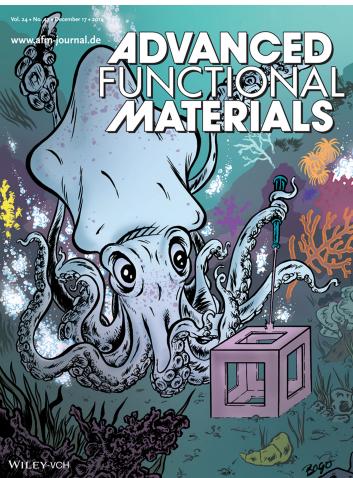
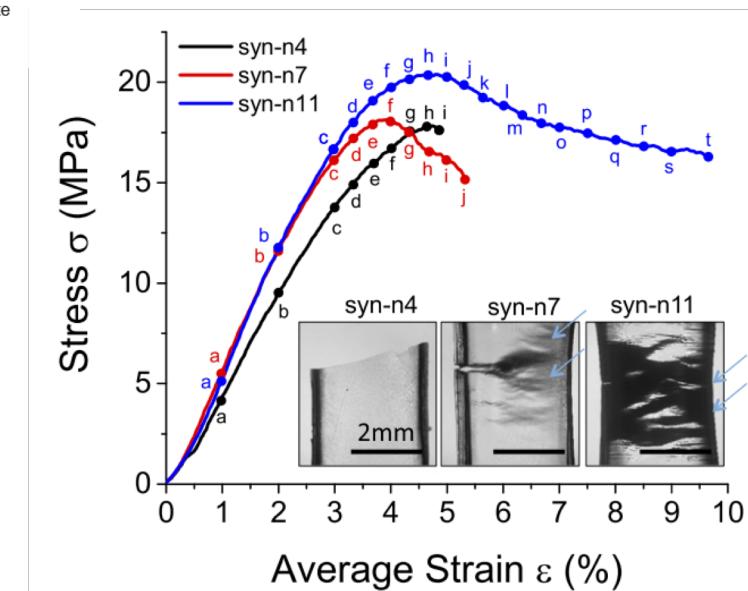
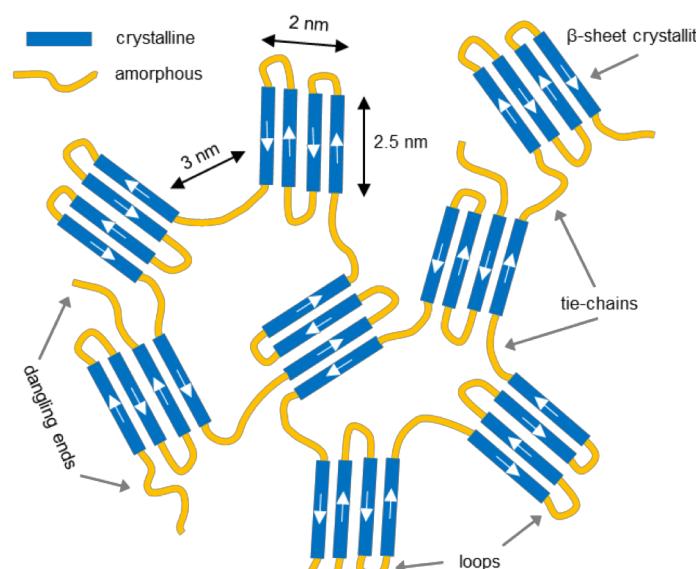
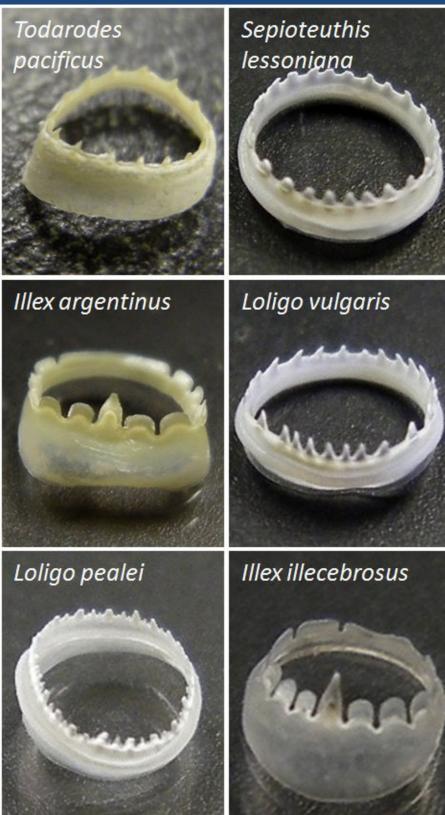
Polyethylene predicted to vary thermal conductivity by a **factor of 12**



Science Advances 4, eaar3031

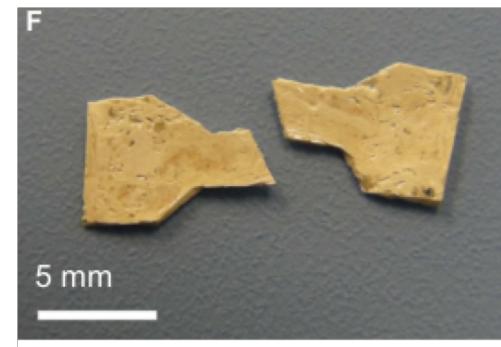
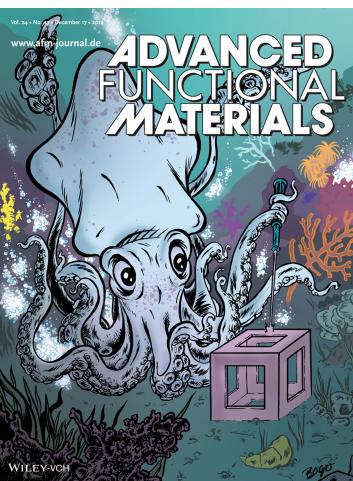
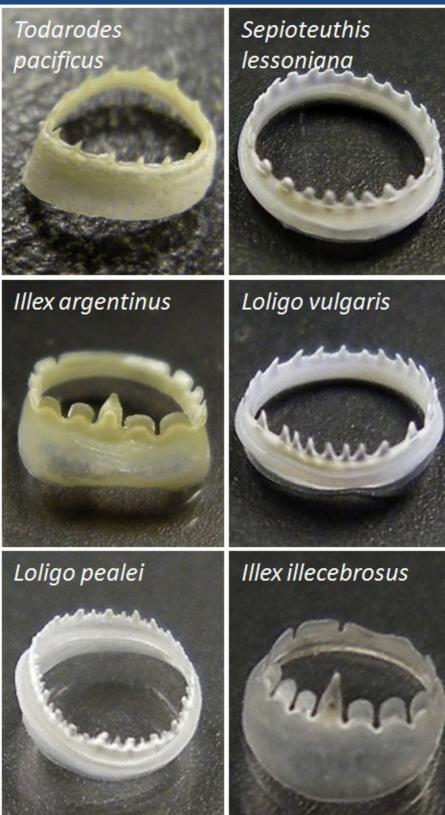
Strain, chain alignment and crystallinity lead to large changes in polymer thermal conductivity (static)

Squid ring teeth proteins – Prof. Melik Demirel (Penn State)

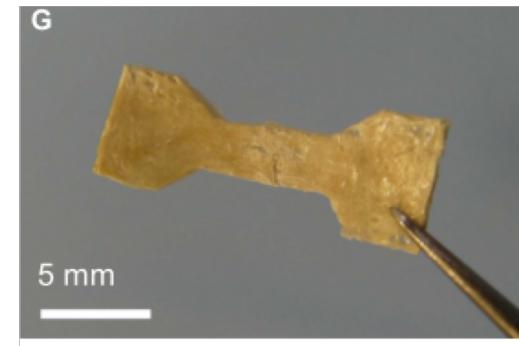


High strength protein due to semi crystalline (beta sheets) hydrogen bonded network

Squid ring teeth proteins – Prof. Melik Demirel (Penn State)

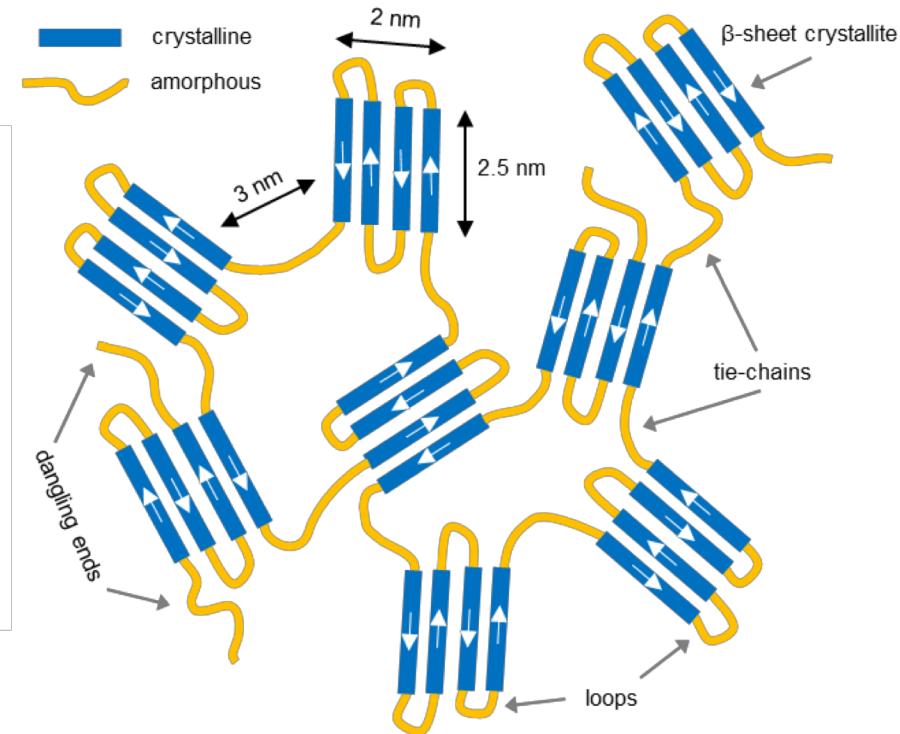
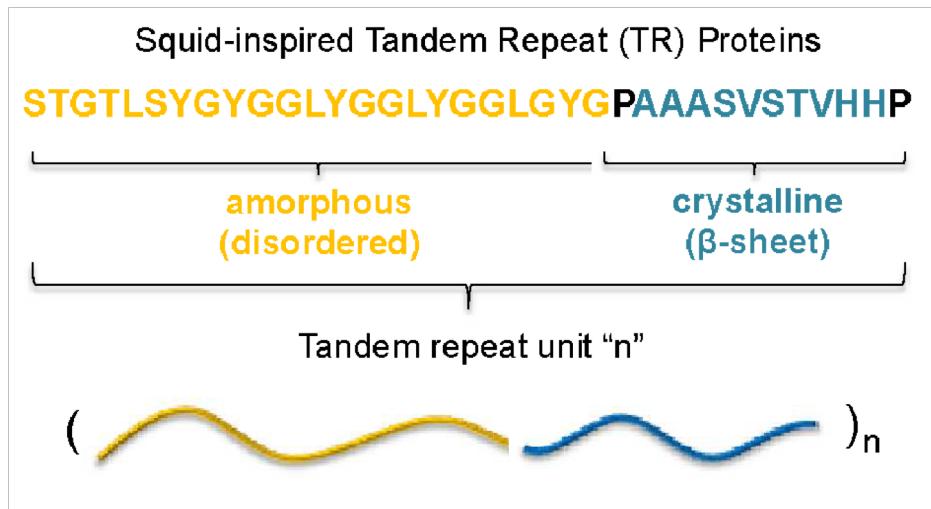


Add water!



Self healing when hydrated
(with a little bit of heat)

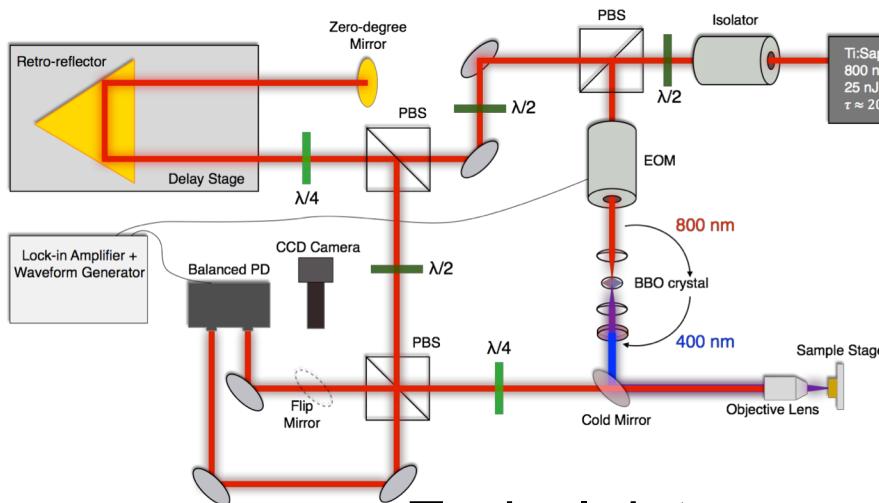
Squid ring teeth proteins – Prof. Melik Demirel (Penn State)



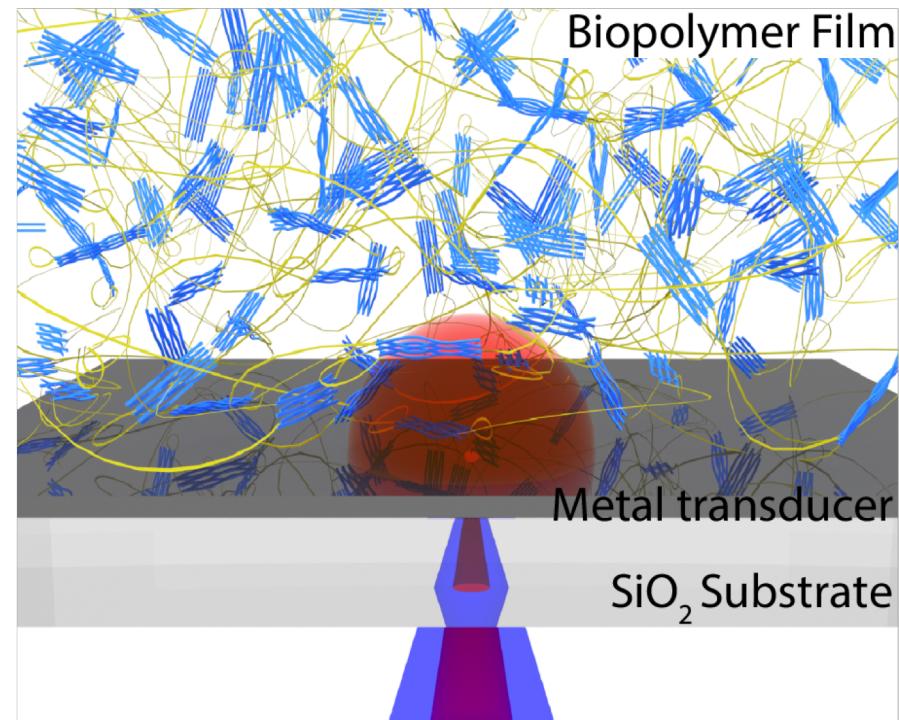
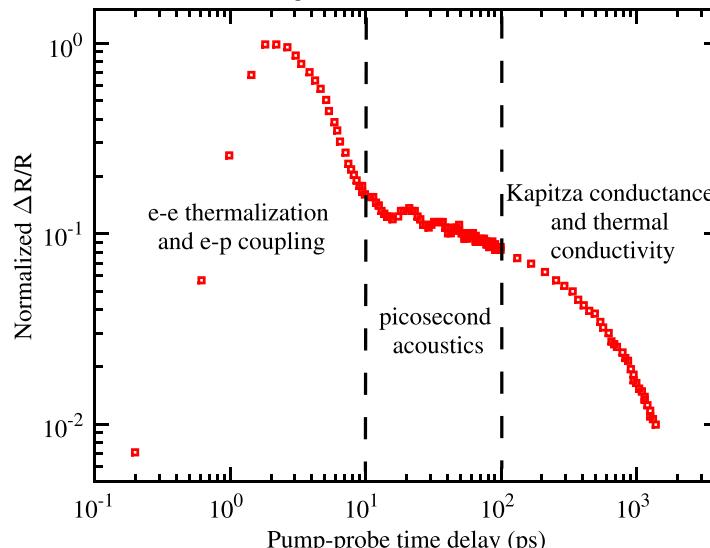
- Can we tune the thermal conductivity by changing the molecular structure? (static)
- Can we dynamically control the thermal conductivity with hydration? (dynamic thermal conductivity switch)

Time domain thermoreflectance (TDTR)

A typical sub-picosecond pump-probe system

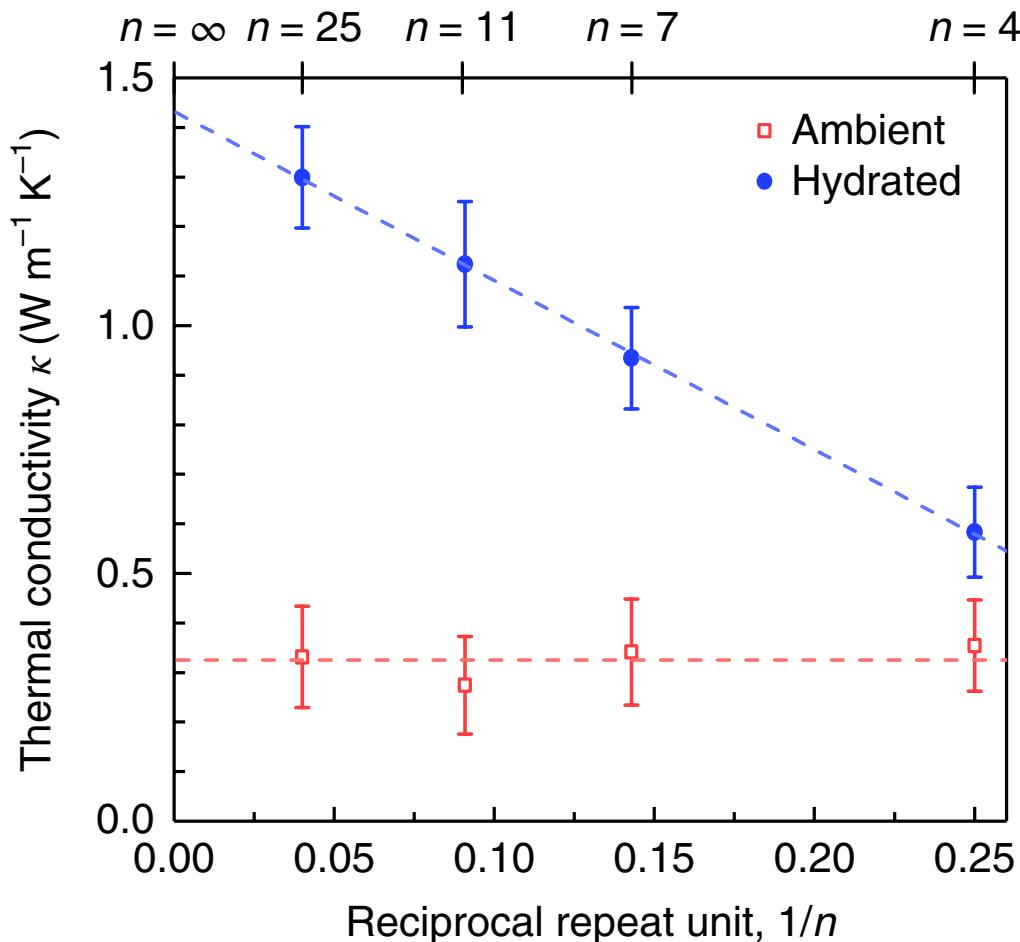


Typical data



Data from: Giri *et al.* *J. Appl. Phys.* **117**, 105105 (2015)

Results – Programmable thermal conductivity



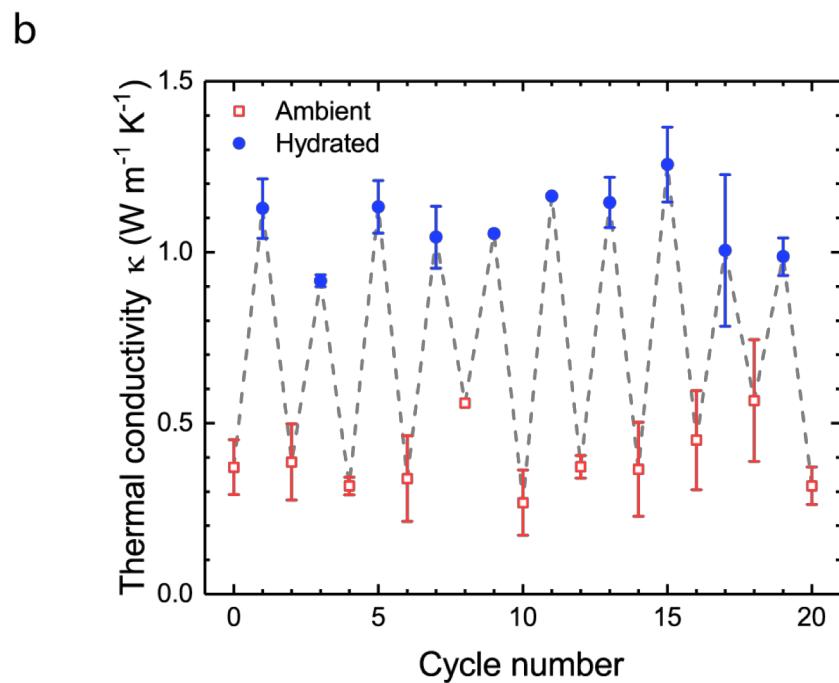
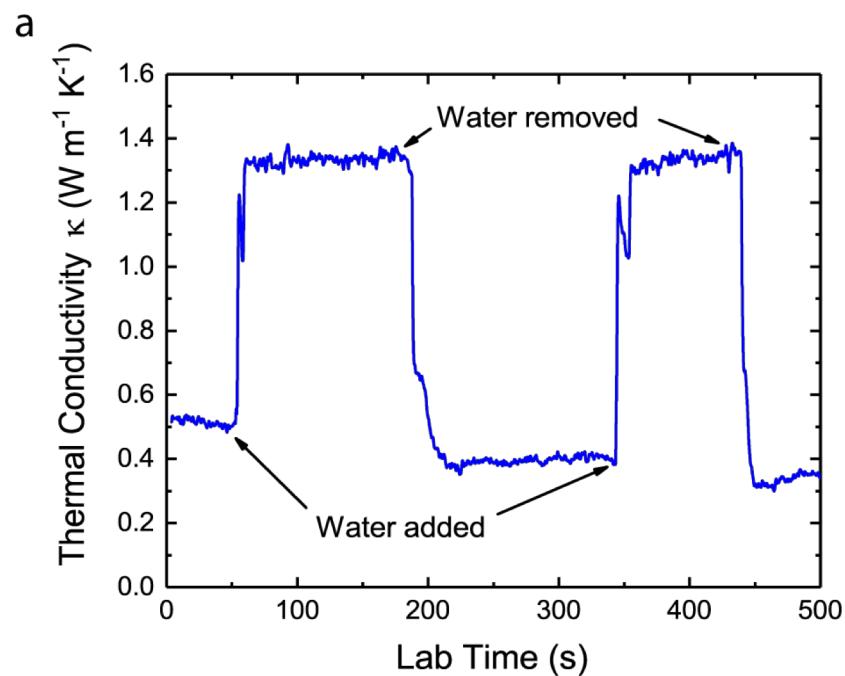
κ ambient

- No dependence on n
- Typical κ for polymer/protein
- Disorder dominates

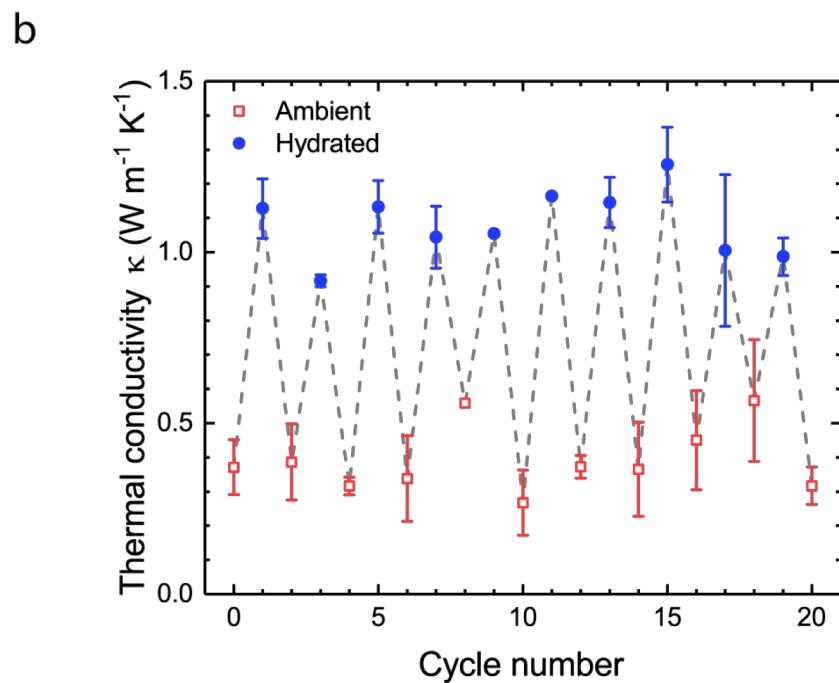
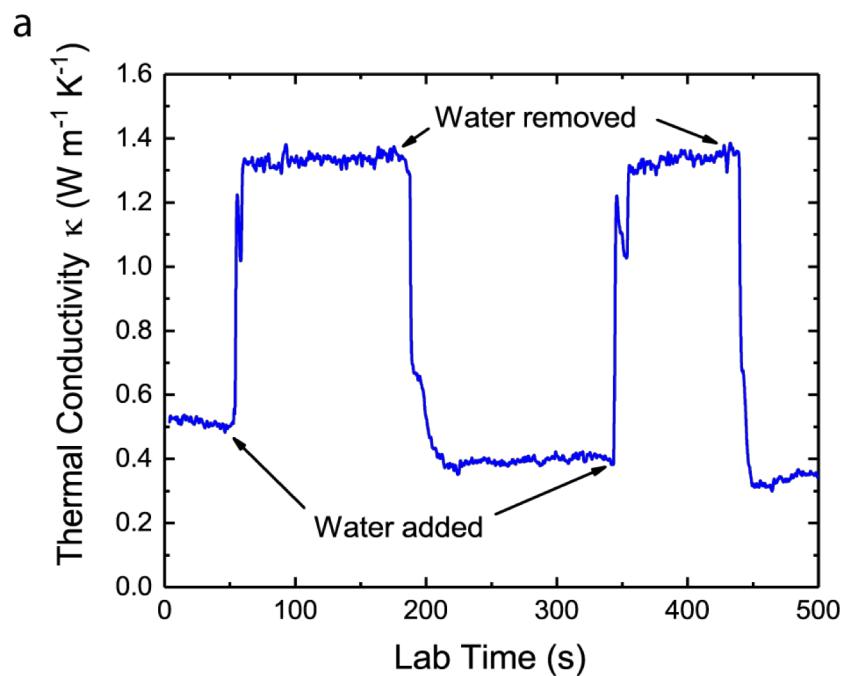
κ hydrated

- Linear dependent on $1/n$
- Up to 4X increase in κ compared to ambient

Results – Switchable thermal conductivity

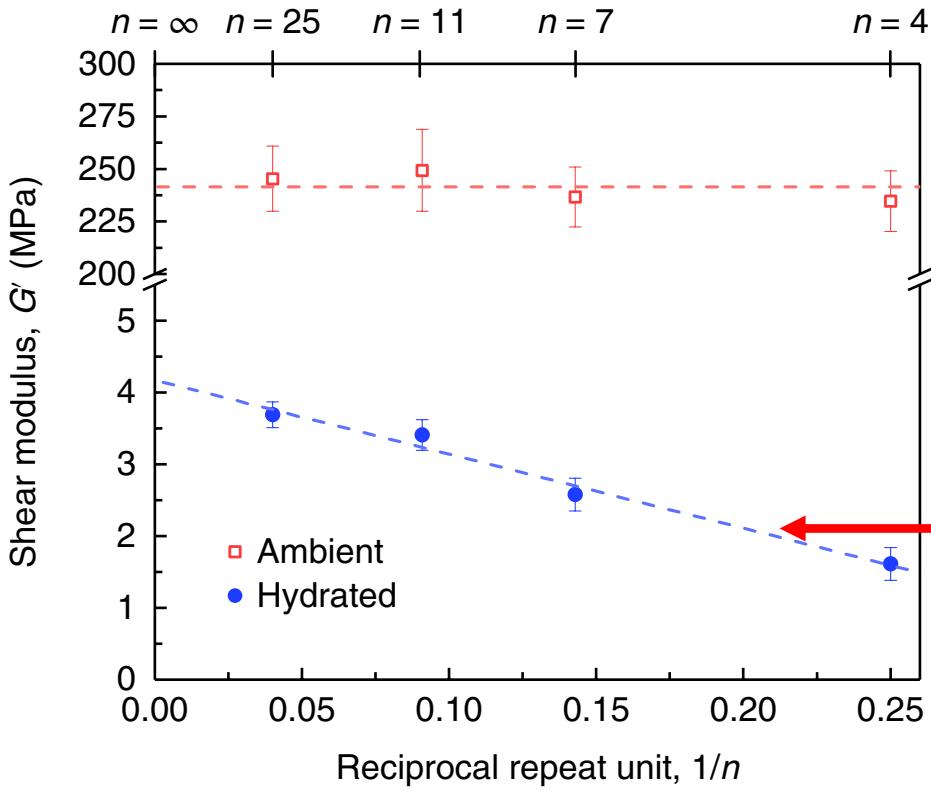


Results – Switchable thermal conductivity



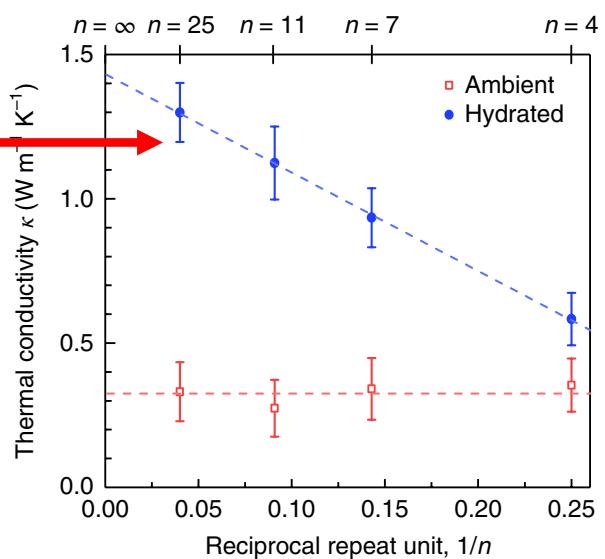
But why???

Results – Rheology

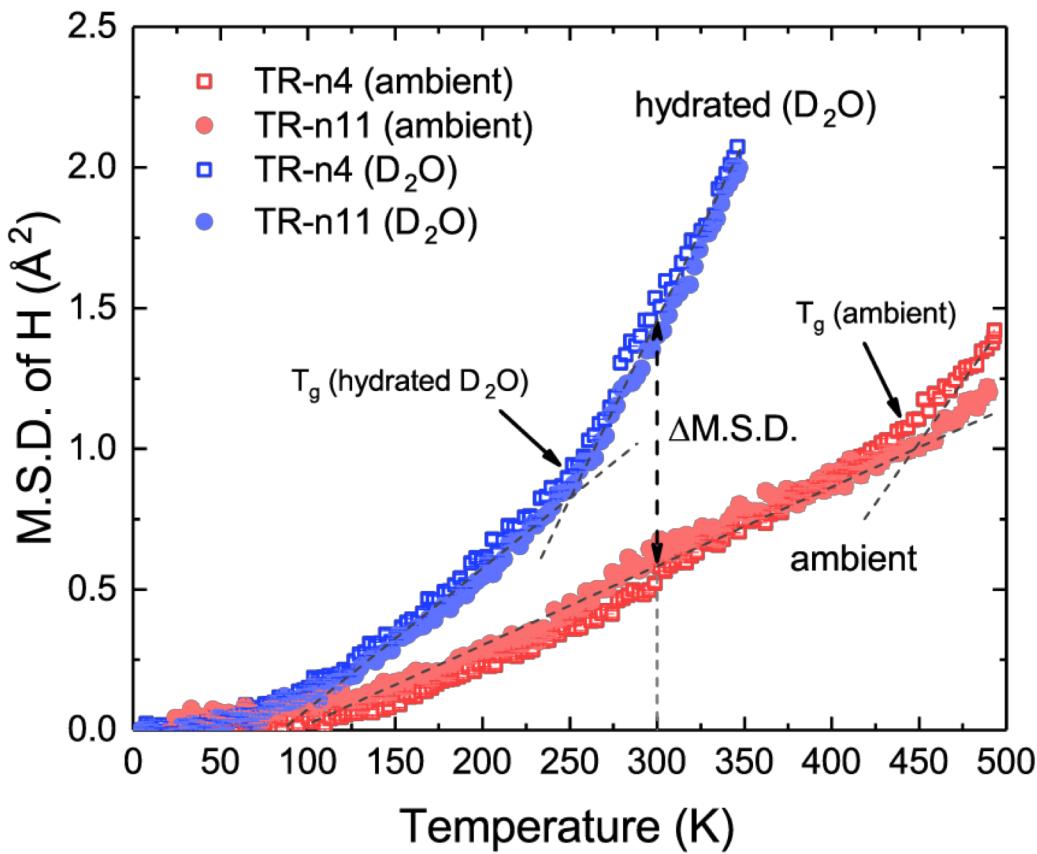


$\kappa \sim G'$

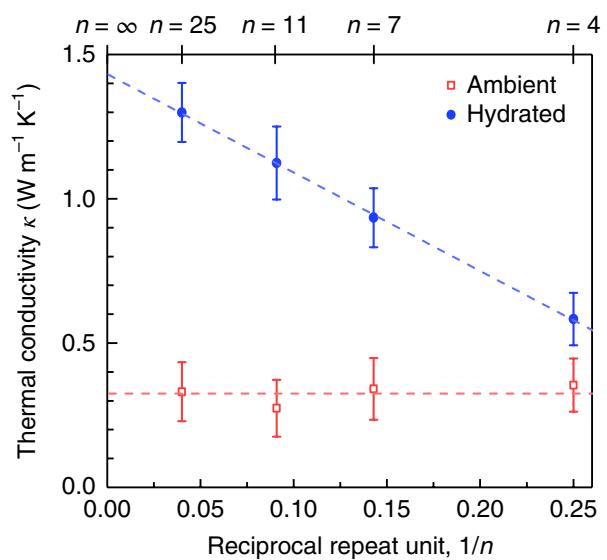
- Diamond = Strong bonds = high κ
- Polymers = weak bonds = low κ
- κ trends with $G'(1/n)$
- **Why does κ increase with hydration?**



Results – Neutron scattering (NIST)



- $\kappa \sim \text{MSD}$
- QENS in ambient and hydrated environments
- Hydration increases mean square displacement of hydrogen atoms in network



Mechanisms of thermal conductivity switching

Thermal conductivity of
crystalline/ordered solids

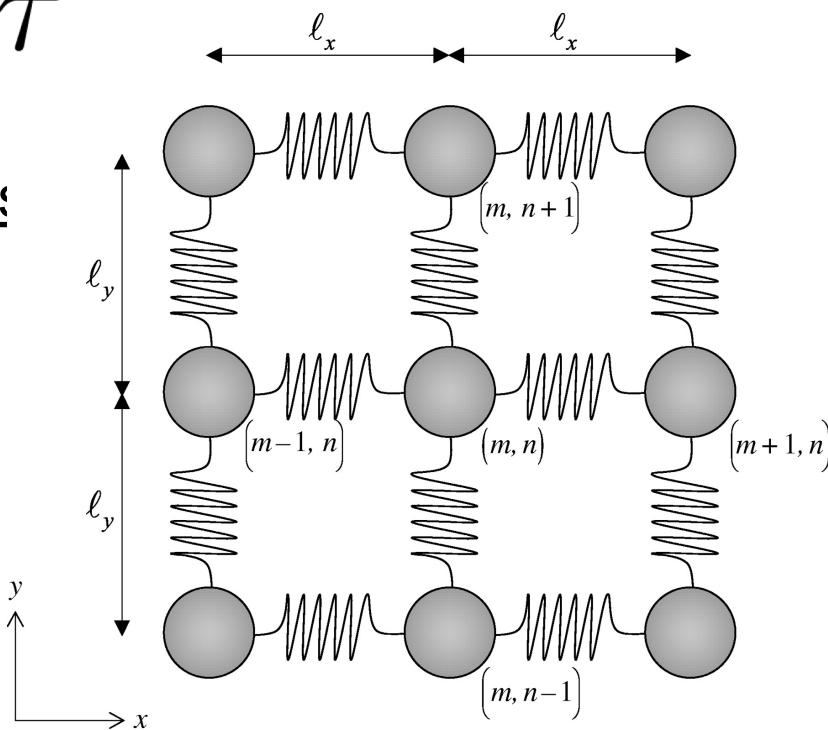
$$\kappa = \frac{1}{3} Cv \lambda = \frac{1}{3} Cv_g^2 \tau$$

Thermal conductivity of disordered solids

$$\kappa_{\text{Diffuson}} \propto \sum C_\omega D_\omega$$

D_ω = Mode Diffusivity

$$D_\omega \propto \text{MSD} \times G'^2$$



Mechanisms of thermal conductivity switching

Competing effects

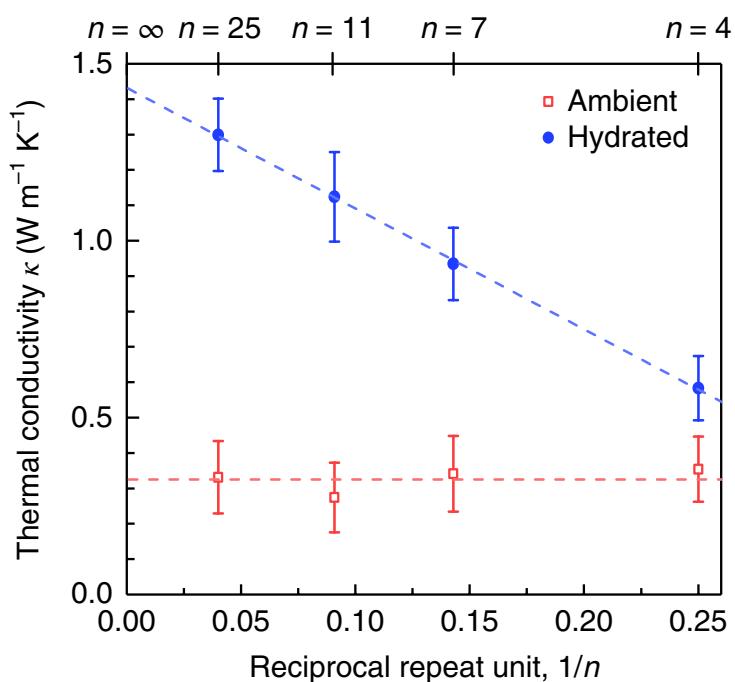
- Increase in κ due to increase in MSD
- Decrease in κ (trend in $1/n$) due to decrease in G'

Thermal conductivity of disordered solids

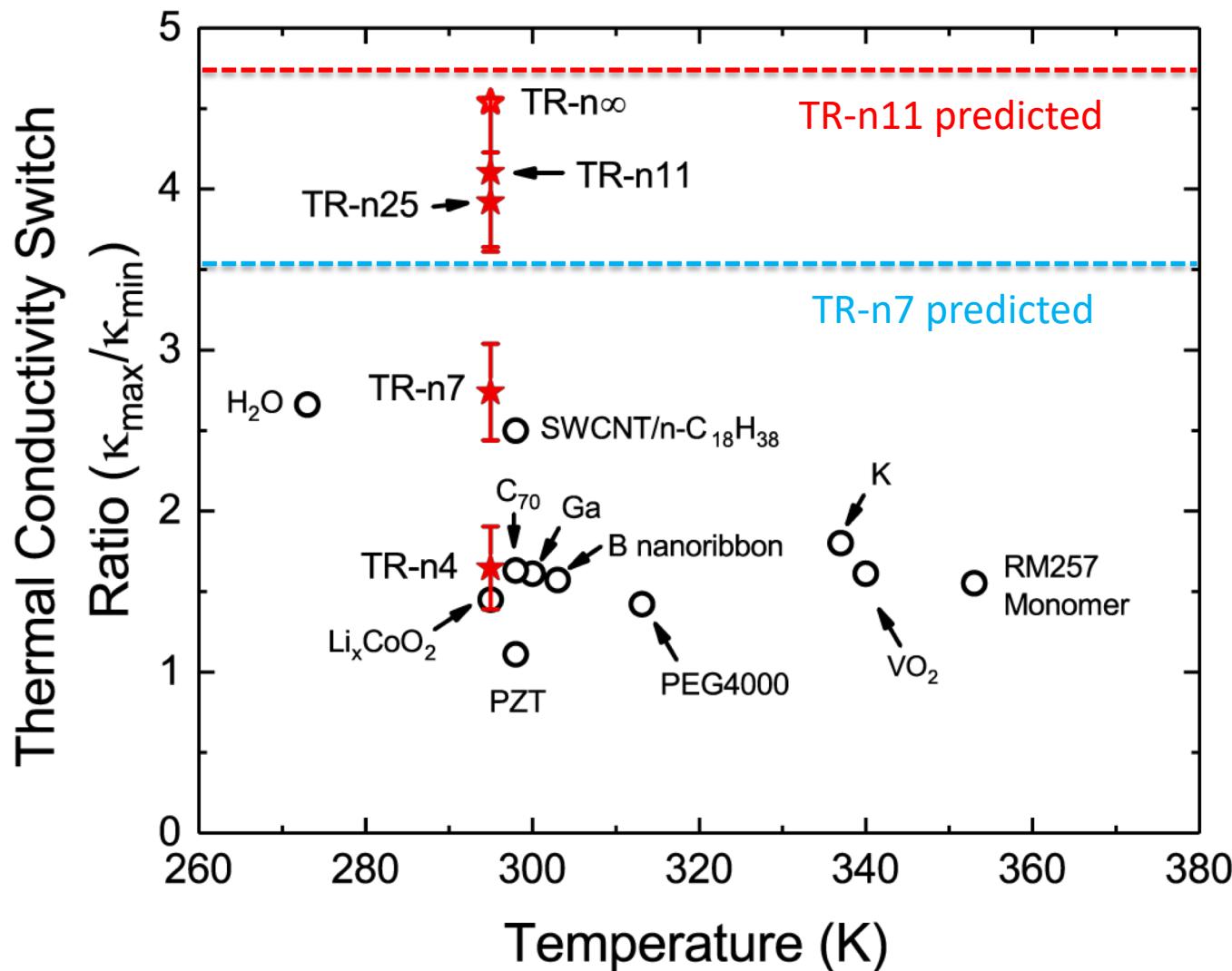
$$\kappa_{\text{Diffuson}} \propto \sum C_\omega D_\omega$$

D_ω = Mode Diffusivity

$$D_\omega \propto \text{MSD} \times G'^2$$



Redefining the SOA of κ switches with SRT



Summary



nature
nanotechnology

ARTICLES

<https://doi.org/10.1038/s41565-018-0227-7>

Tunable thermal transport and reversible thermal conductivity switching in topologically networked bio-inspired materials

John A. Tomko^{1,10}, Abdon Pena-Francesch^{2,3,10}, Huihun Jung^{2,3}, Madhusudan Tyagi^{4,5}, Benjamin D. Allen^{6,7},
Melik C. Demirel^{1,2,3,7*} and Patrick E. Hopkins^{1,8,9*}