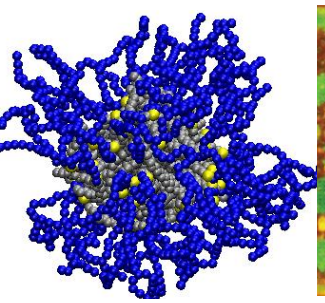
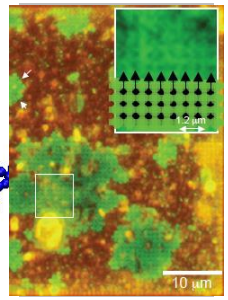
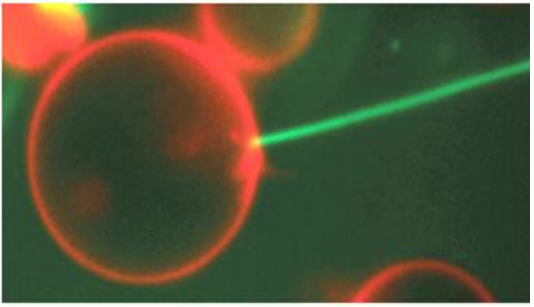
SAND2013-9147C

Alkylated PolyNIPAM Surfactants in Responsive Nanocomposites







Dale L. Huber

Principal Member of the Technical Staff

Center for Integrated Nanotechnologies

Sandia National Laboratories

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Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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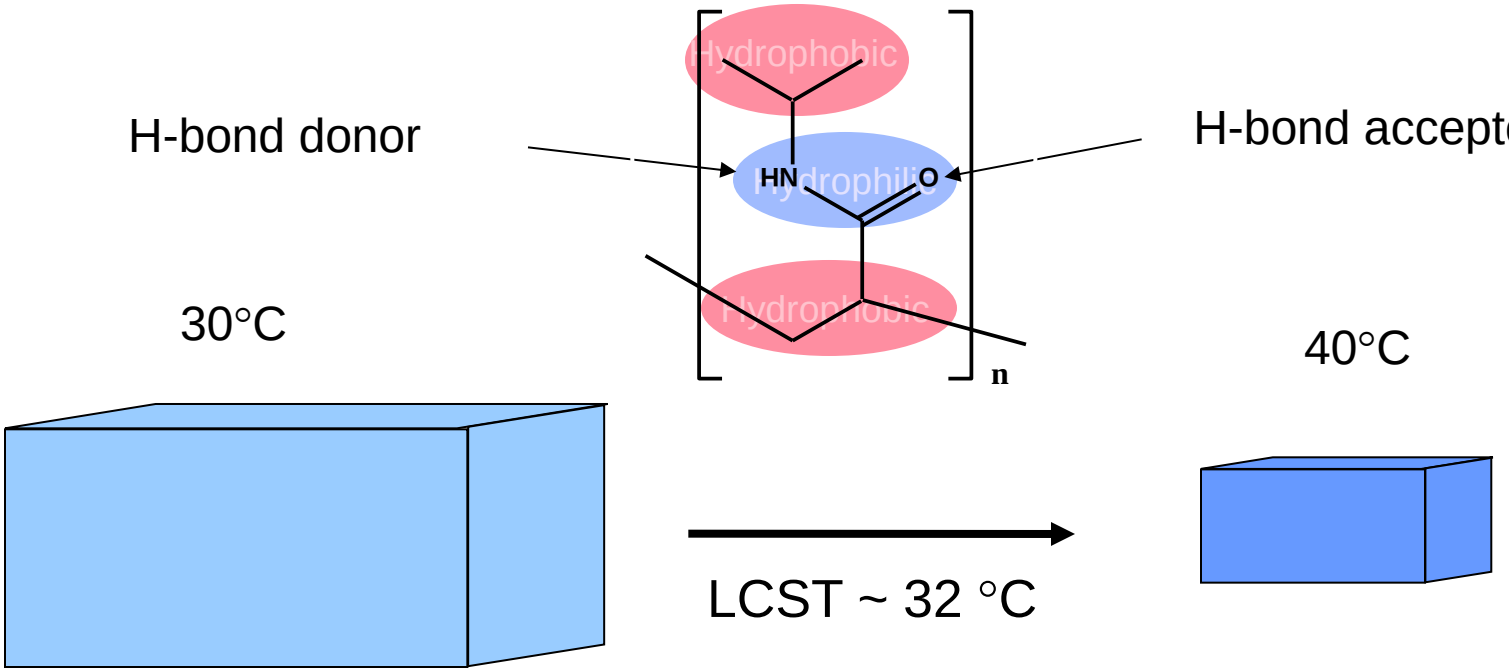
Poly(NIPAM)

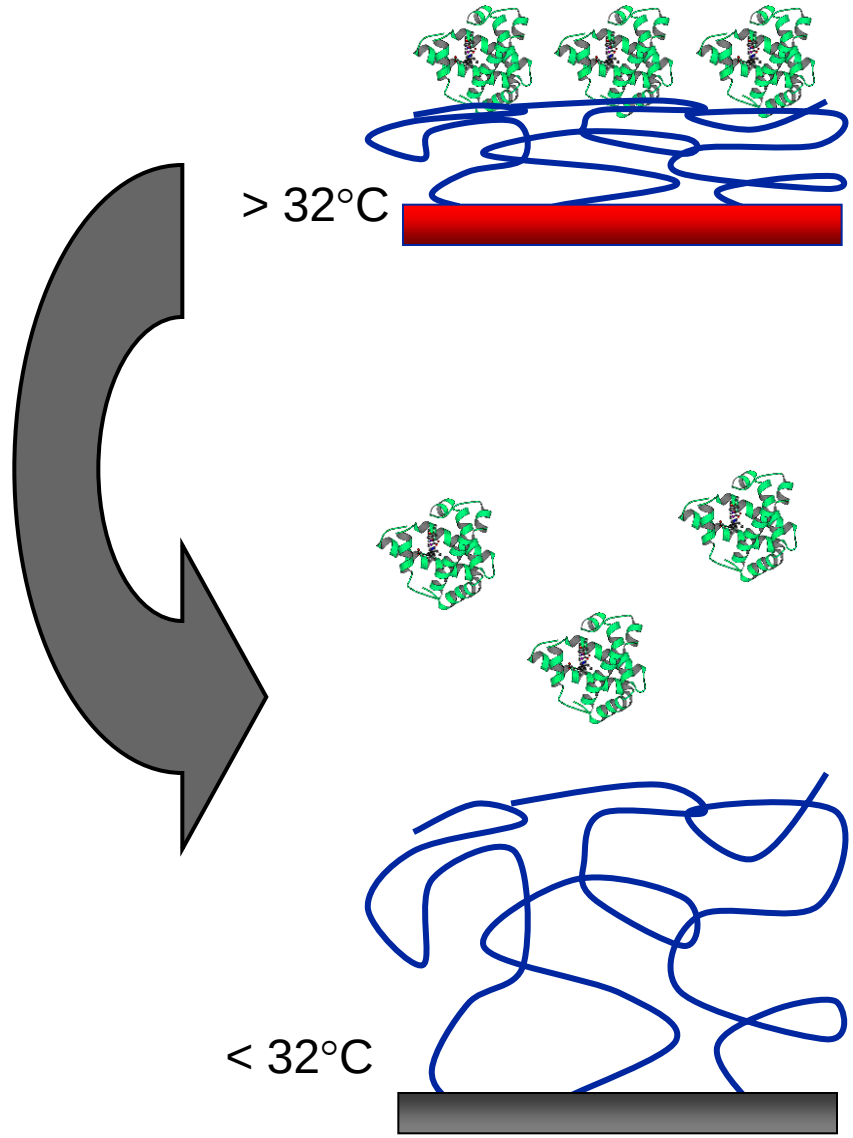


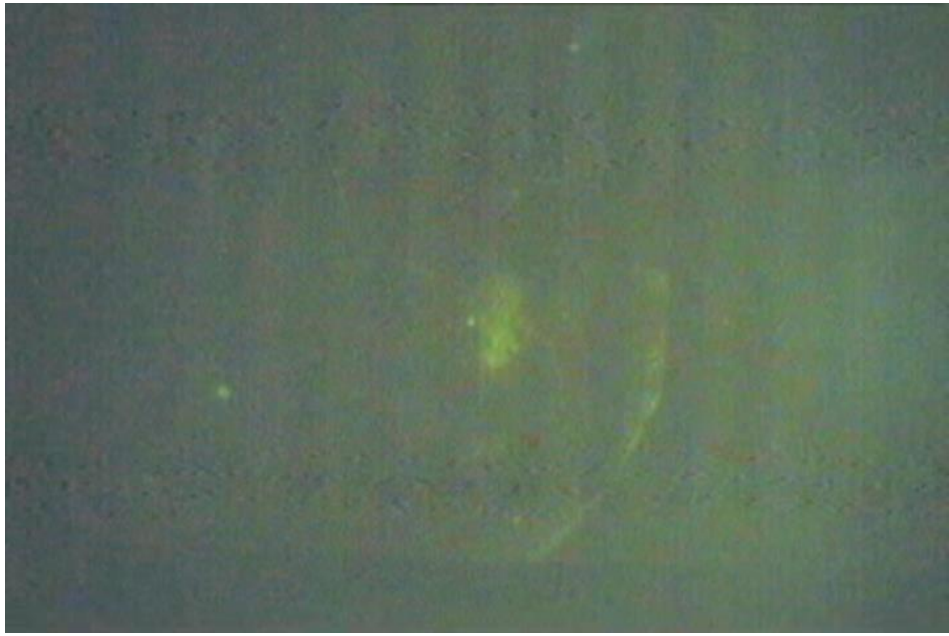
- Swollen with water--heavily hydrogen bonded
- Hydrophilic surface
- Resists protein adsorption

- Hydrogen bonding disrupted--deswelled
- More hydrophobic surface
- Does not resists protein adsorption

Applications: Drug delivery, temperature sensitive chromatography, cell culture, thermally triggered motion, immunoassays, etc.

Previous Poly(NIPAM) Work

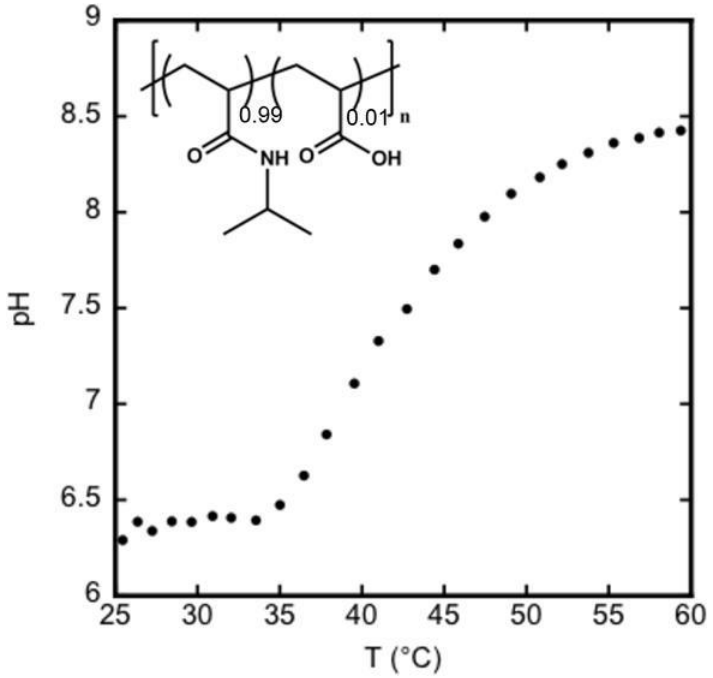




Huber et.al. *Science, 2003. 301(5631): p. 352-354.*

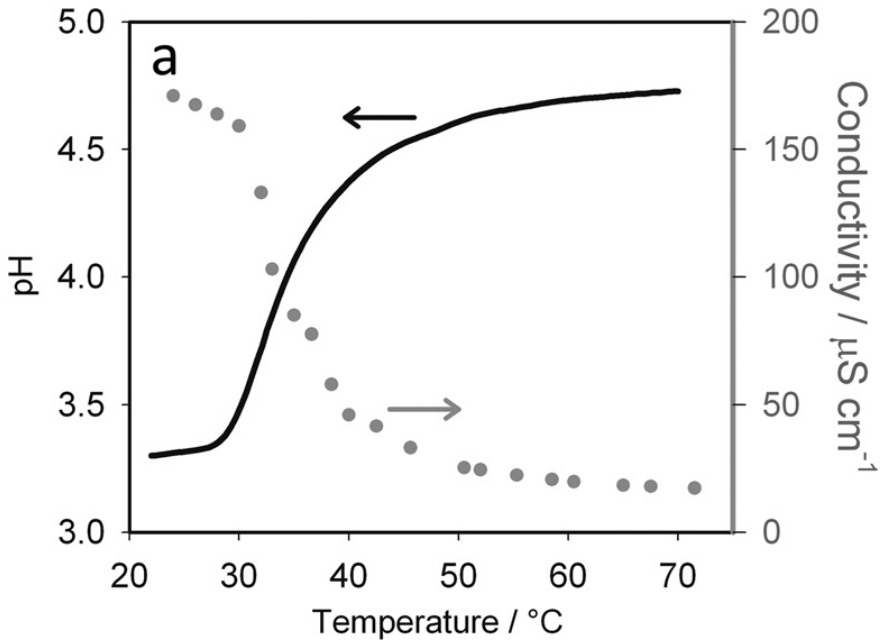
Our Recent PNIPAM Work

Thermally responsive buffers



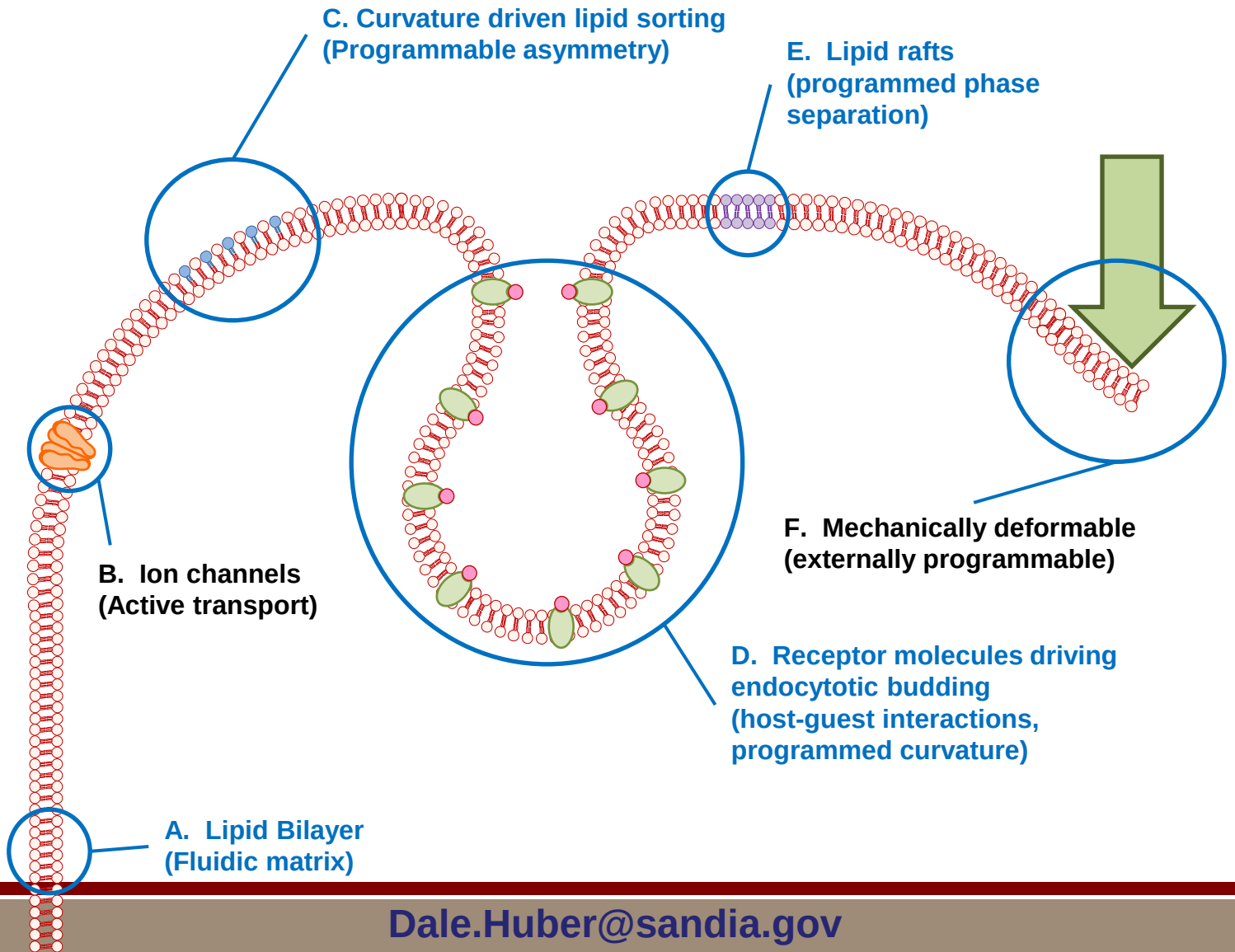
Gough, et al. *ACS Appl. Mater. Interfaces* ***2012, 4, 6247.***

Thermally responsive electrolyte

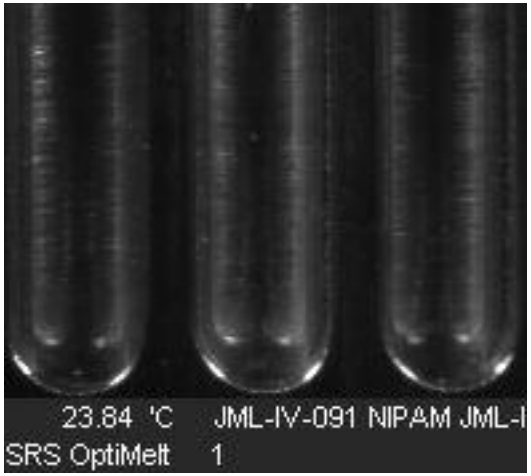


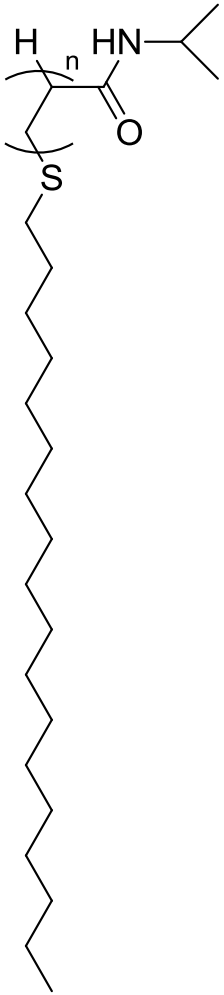
Kelly, et al. *Adv. Mater.* ***2012, 24, 886.***

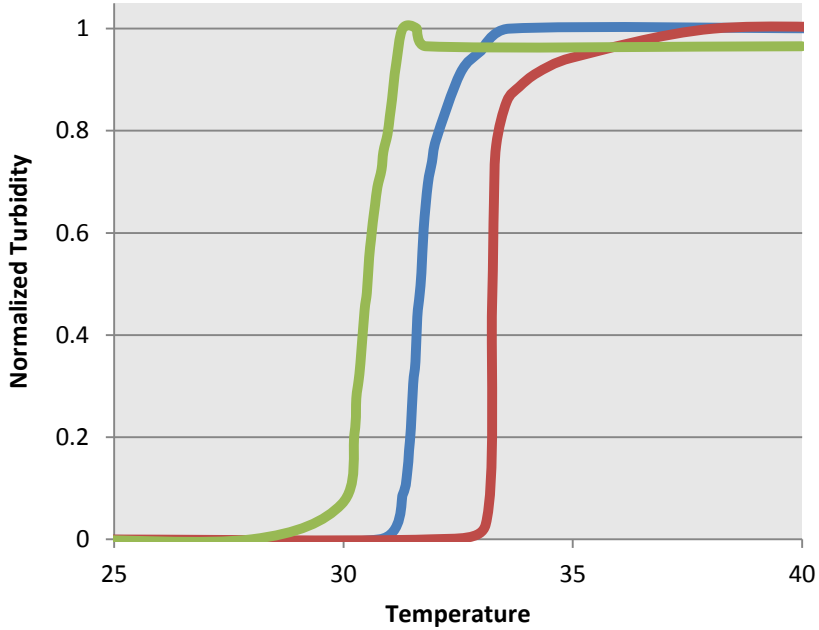
Responsive Behaviors Inspired by the Cell Membrane



Programmable Poly(NIPAM) Based Surfactants





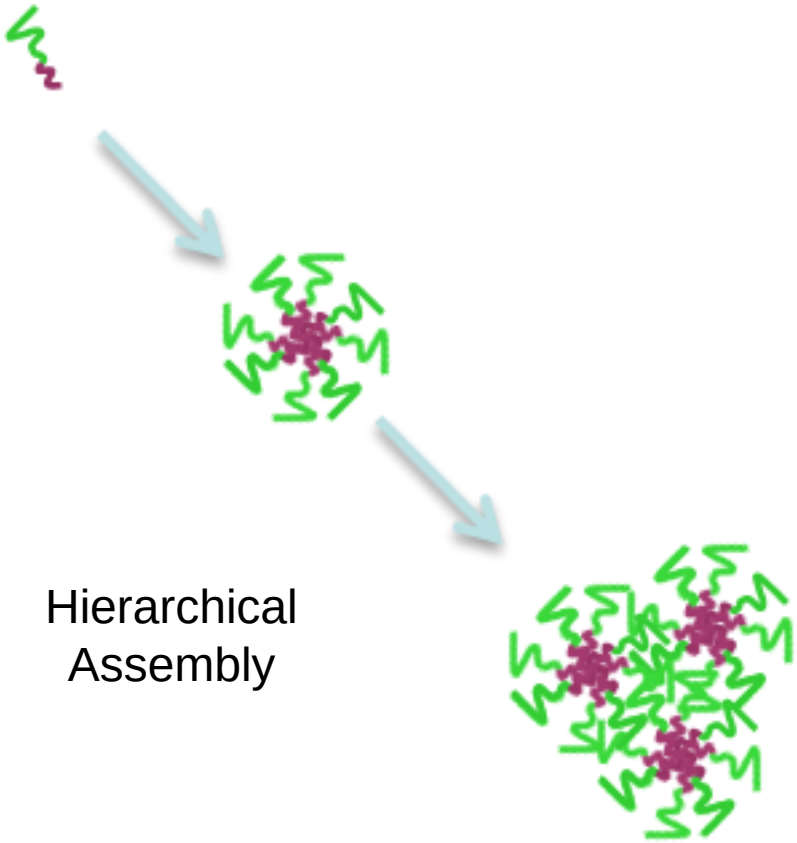


n=18

- **Phase transitions are sharp**
- **Transition temperature (LCST) depends on headgroup size (value of n).**

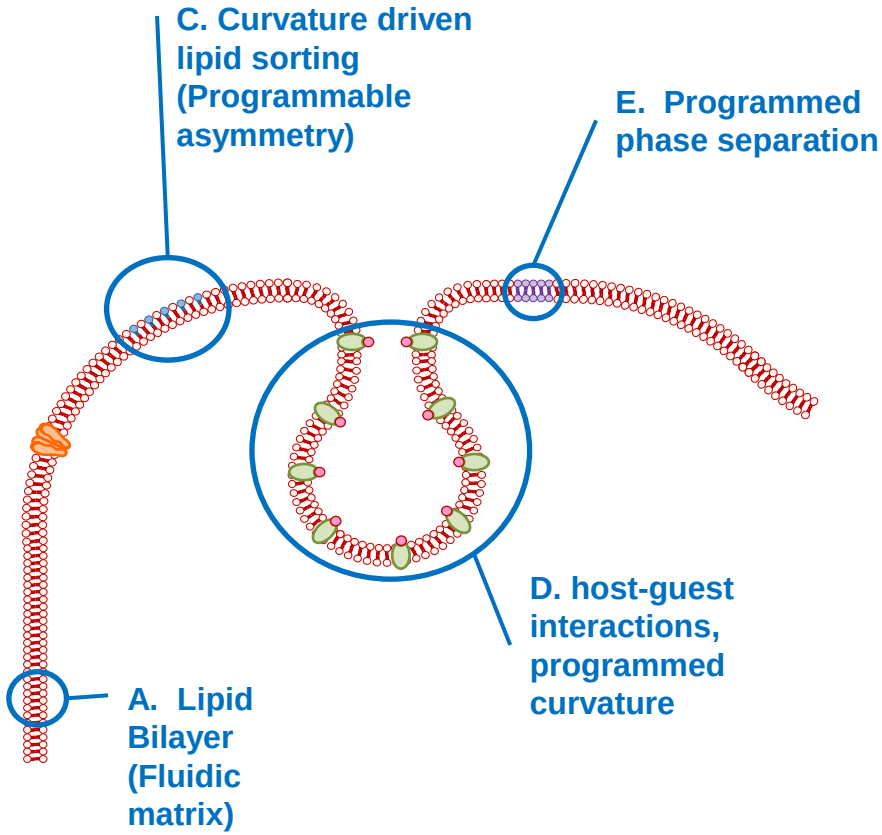
Behaviors Studied

Solution Behavior



Hierarchical Assembly

Membrane Behavior



Molecular Dynamics Simulations of Oligo-NIPAM

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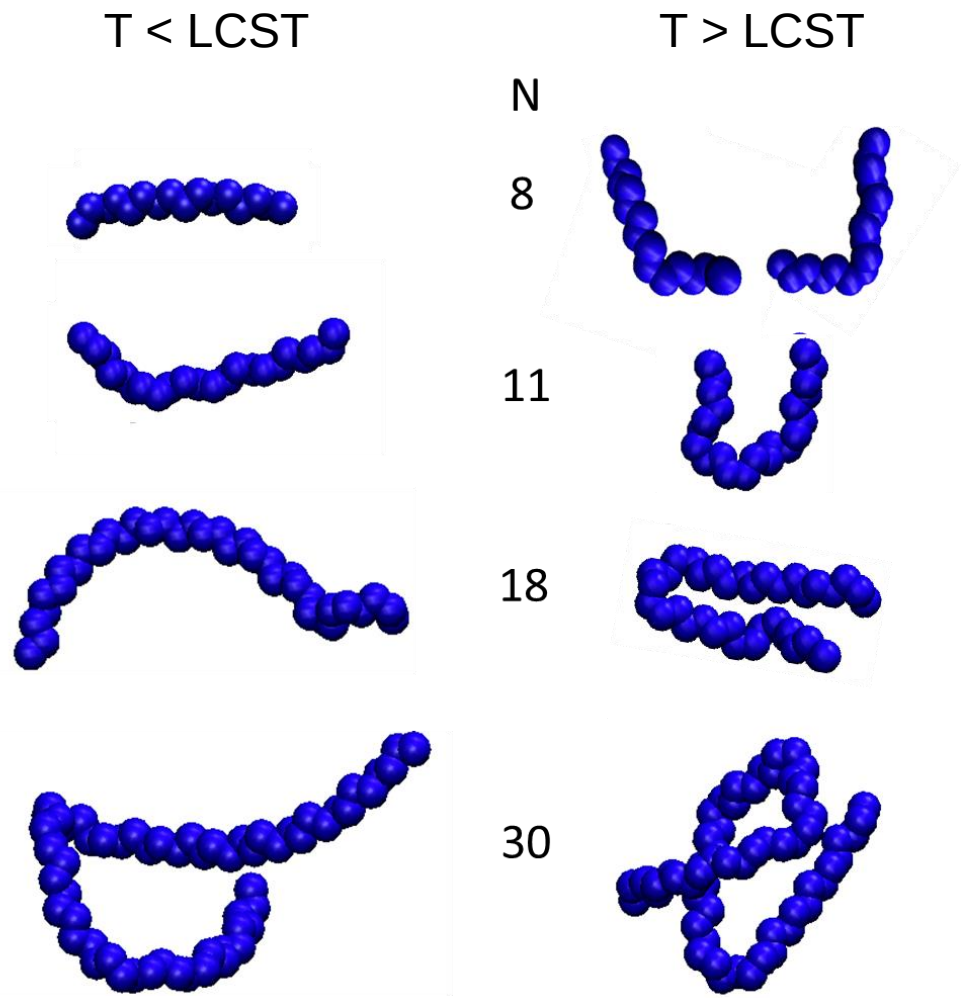
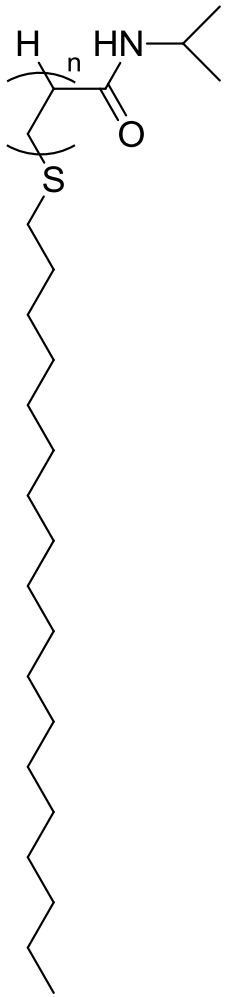


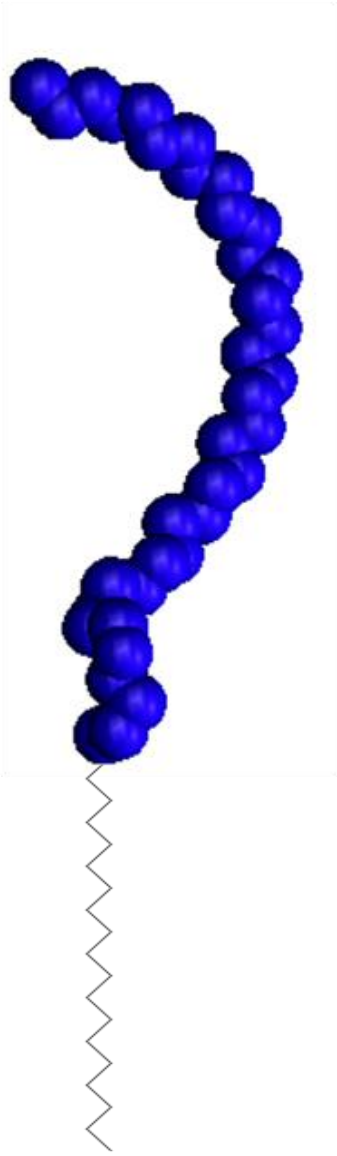
PNIPAM Surfactant



n=18

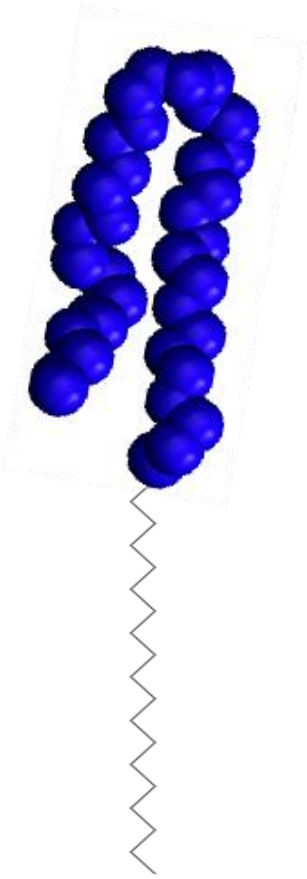
- **18 Carbon alkyl chain matches length of POPC lipid bilayer**
- **18 NIPAM repeat units (number average)**
- **36 backbone carbon chains in pNIPAM chain**
- **Hydrogen terminated**

Expected Solution Behavior

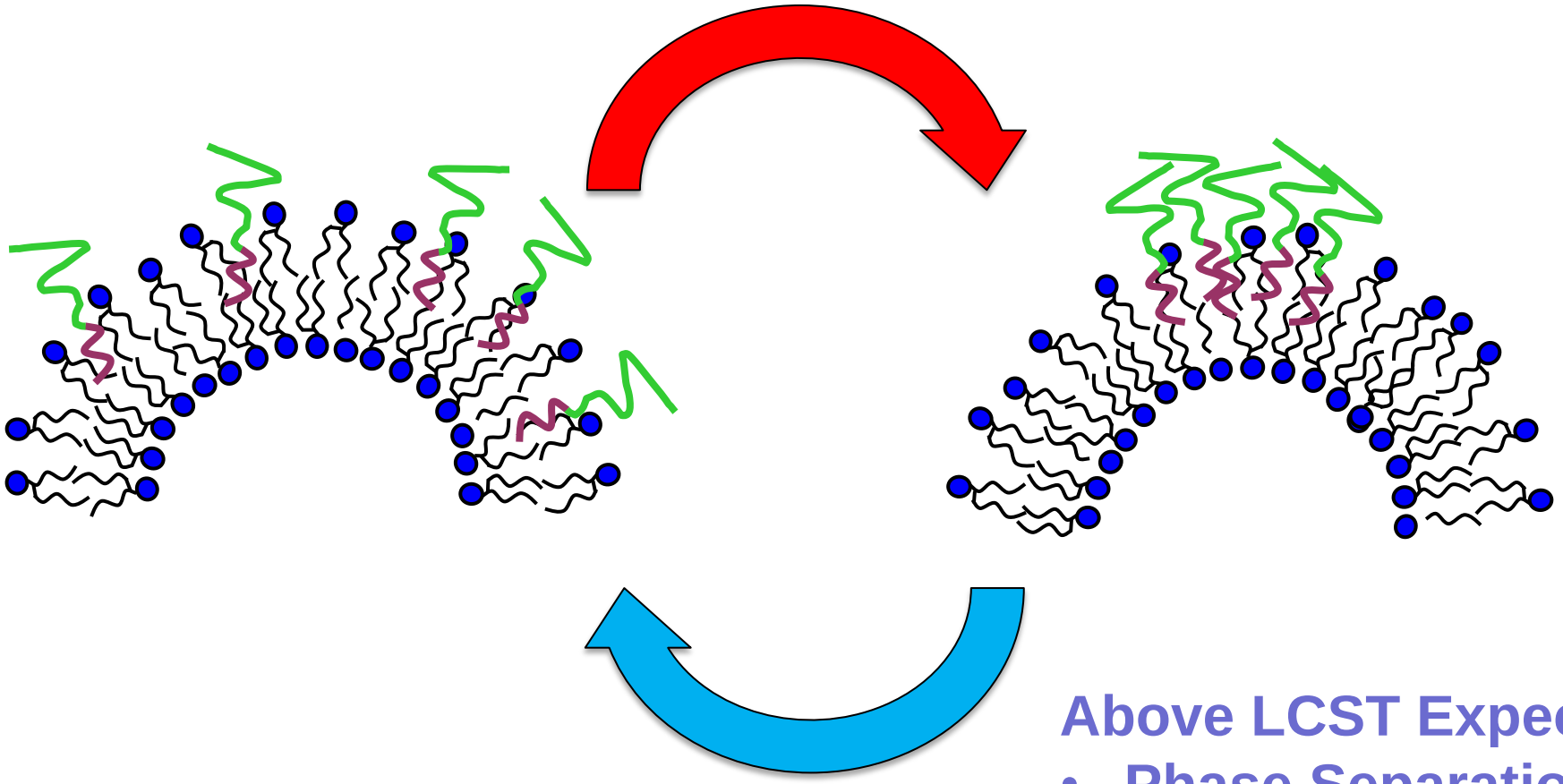


Above the LCST, the polymer is less soluble, so we expect:

- **Polymer collapse**
- **Precipitation**
- **Decrease in CMC**



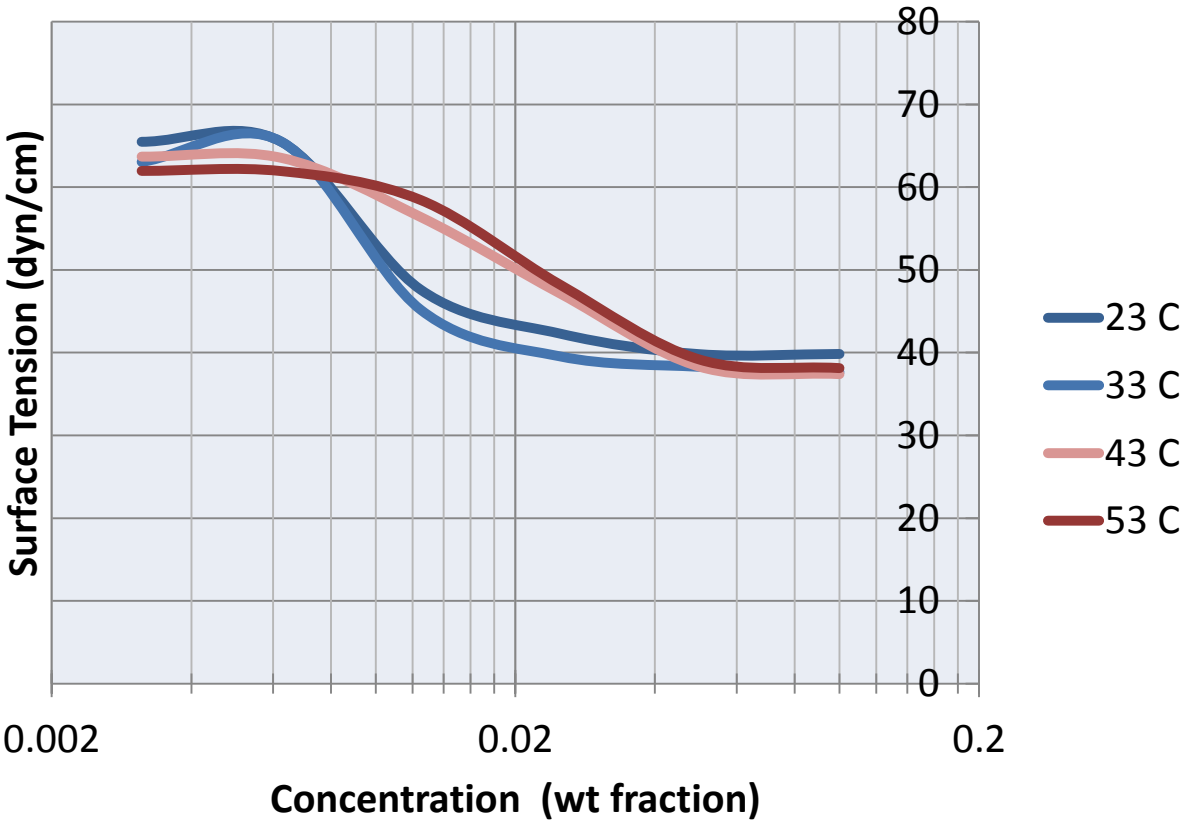
Expected Membrane Behavior



Above LCST Expect:

- **Phase Separation**
- **Induce curvature**
- **Become sticky**

CMC as a Function of Temperature



The surfactant CMC is higher above the LCST

Poly(NIPAM) Surfactant Phase Diagram

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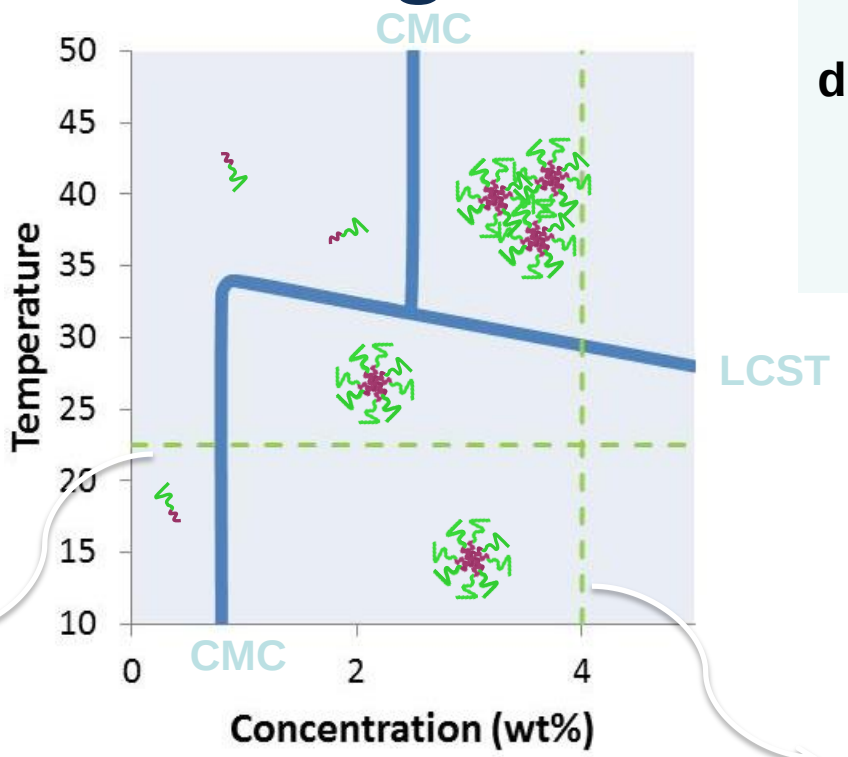
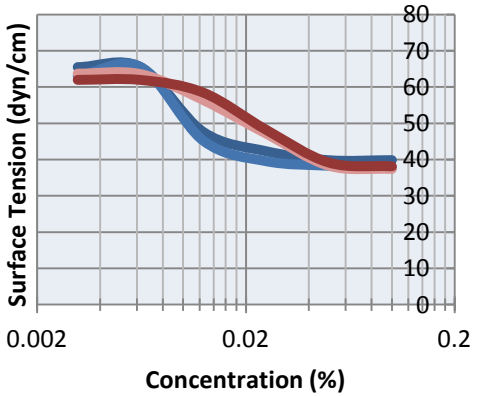
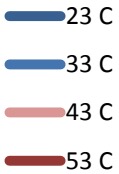
Surfactant phase diagram is perturbed by head group programming.



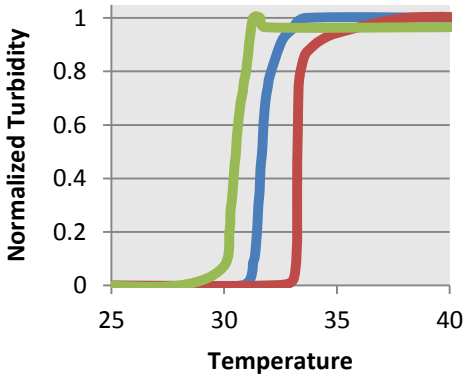
Surface Tension Measurements to Determine CMC





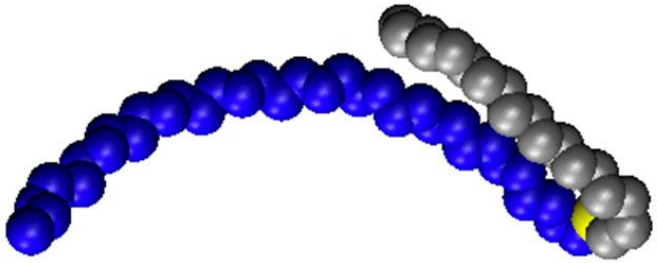
- Transition temperature depends weakly on concentration
- CMC varies above and below thermal transition

Cloud Point measurements to determine LCST



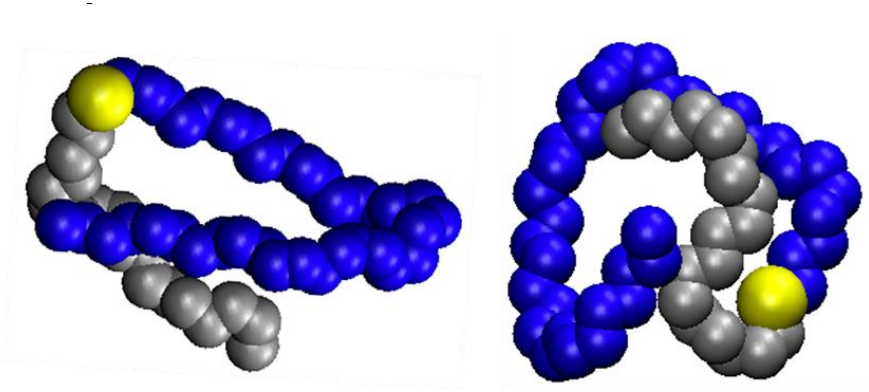
Surfactant Conformation as a Function of Temperature

T < LCST



- Hydrophobic regions of PNIPAM associate with alkyl chain
- Still looks like a micelle former

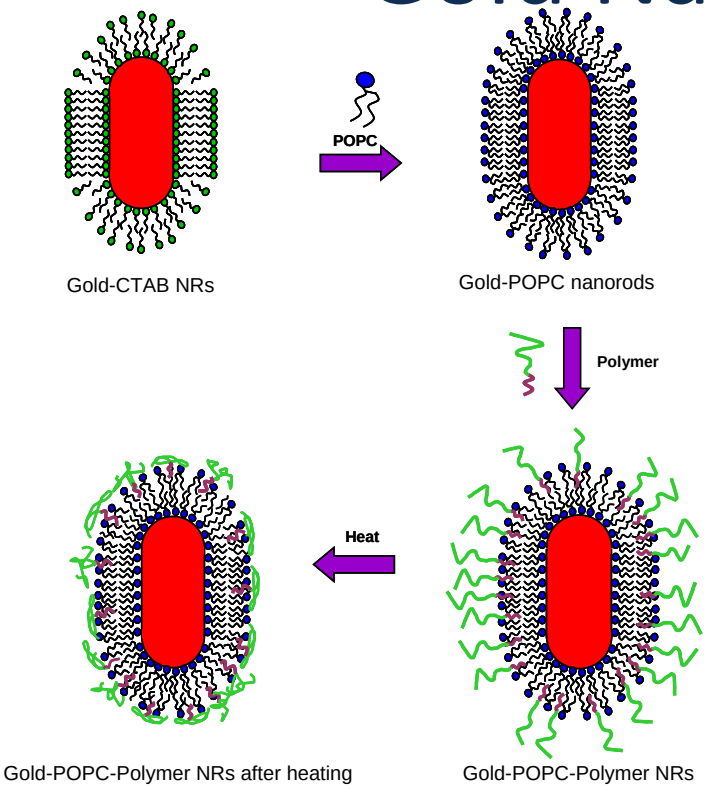
T > LCST



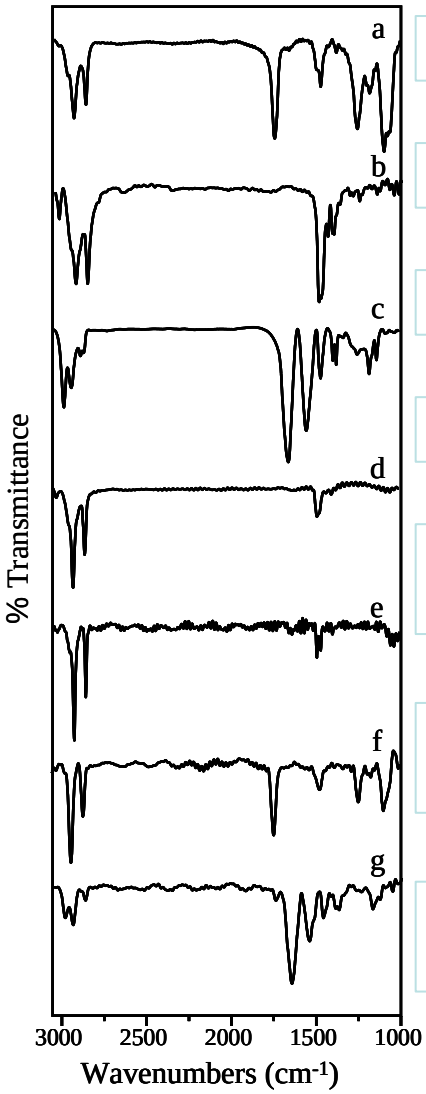
- PNIPAM collapses around alkyl chain
- Stabilizes individual monomer, destabilizes micelle

with Ashley Tucker & Mark Stevens

Poly(NIPAM) Surfactant Supported on Gold Nanoparticles



- **PNIPAM surfactant fails to insert in native capping layer (CTAB).**
- **Lipid bilayers displace native capping CTAB.**
- **Poly(NIPAM) surfactants insert into lipid films.**
- **Any active molecule with a hydrocarbon tail can insert into lipids to create programmable films.**



a) Neat POPC

b) Neat CTAB

c) Neat PNIPAM surfactant

d) CTAB rods as prepared

e) CTAB rods incubated with PNIPAM (no insertion)

f) Rods incubated with POPC (CTAB displaced)

g) POPC rods incubated with PINIPAM (insertion)

Responsive Behavior of Gold Nanocomposites

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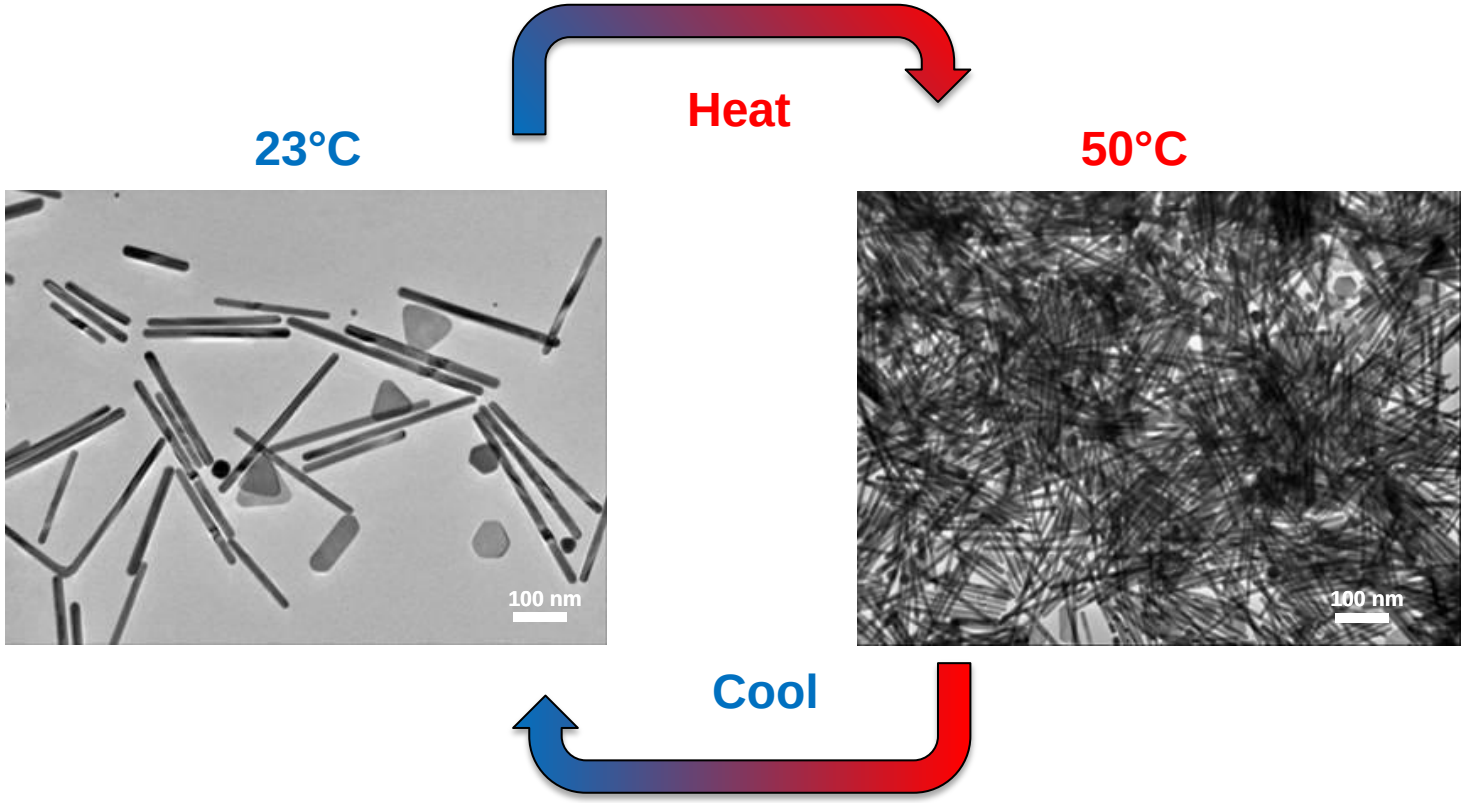
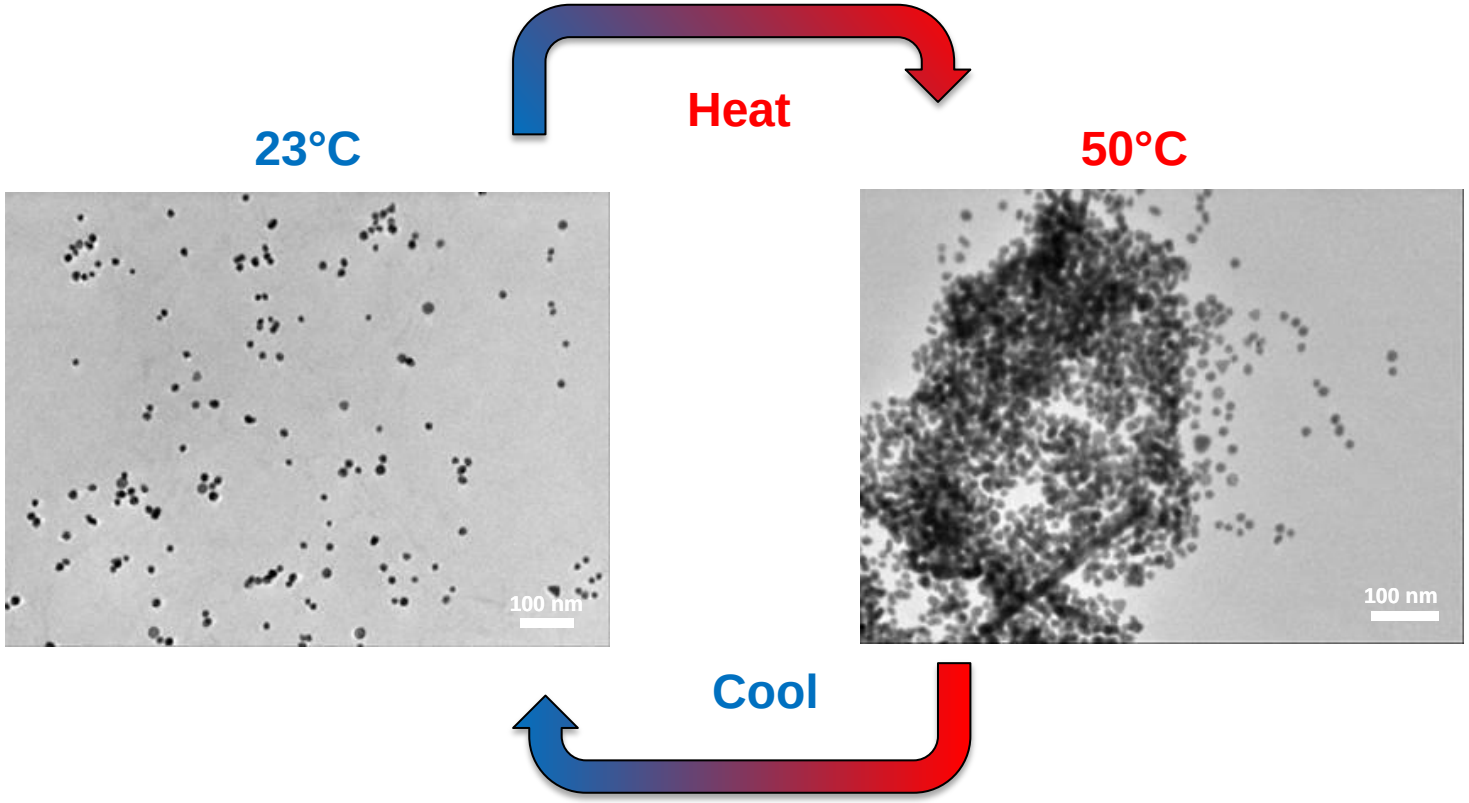


- **Fast, dramatic, and reversible programming of the PNIPAM head group leads to switching in solubility and aggregation state.**

Responsive Behavior of Gold Nanocomposites

Sandia National Laboratories



- **Fast, dramatic, and reversible programming of the PNIPAM head group leads to switching in solubility and aggregation state.**

Ag Nanocomposites Also Show Programmable Behavior

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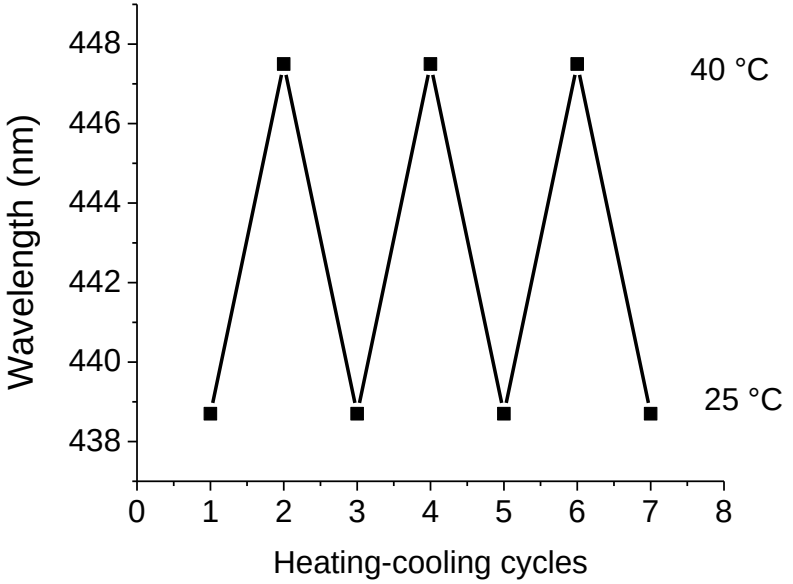
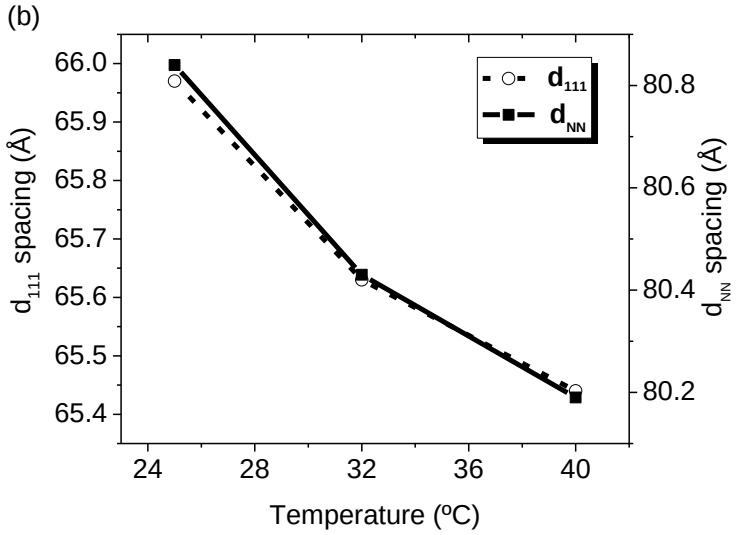
Reversible Switching of Plasmon Frequency in Aqueous Solutions



Reversible Switching of Interparticle Spacing of Bulk Nanocomposite in Humid Air (by GISAXS)



with Hongyou Fan

Mobility is a Key Attribute in Programmable Systems

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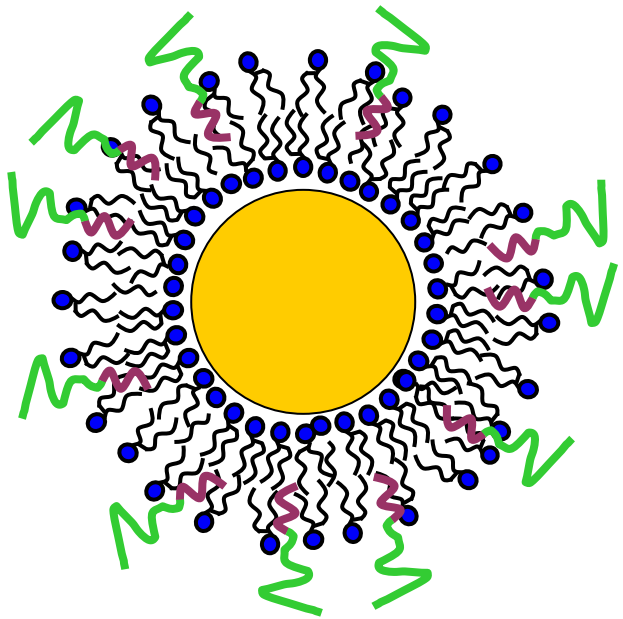
Lipid System

Fluid bilayer

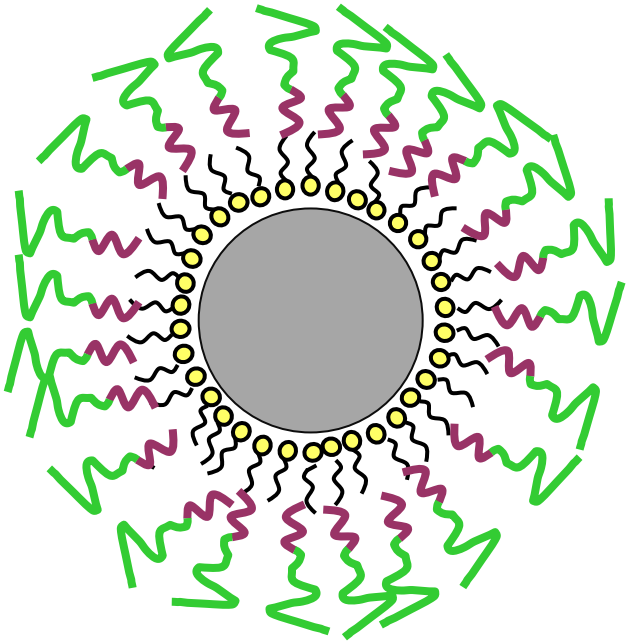
Even for <10% pNIPAM content, switching causes immediate, dramatic loss in solubility



Thiol System

Immobile bilayer

Even for 100% pNIPAM content in outer leaf, switching maintains some water solubility.



Reversible Curvature Changes in Giant Vesicles

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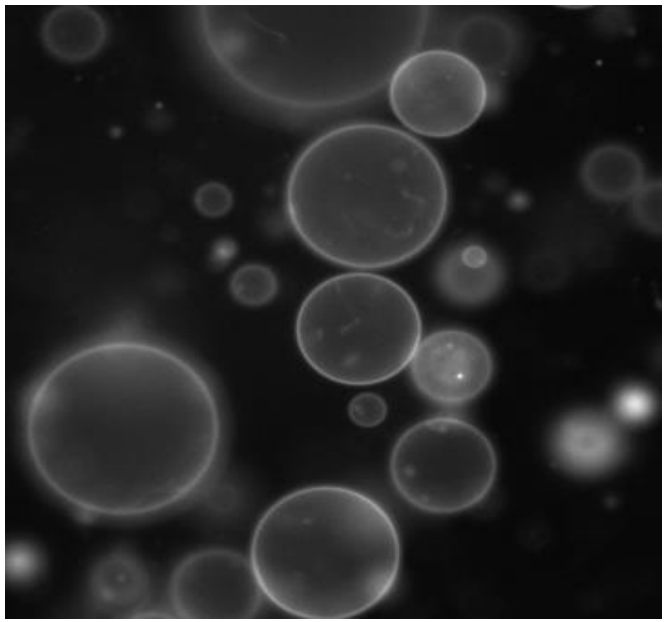
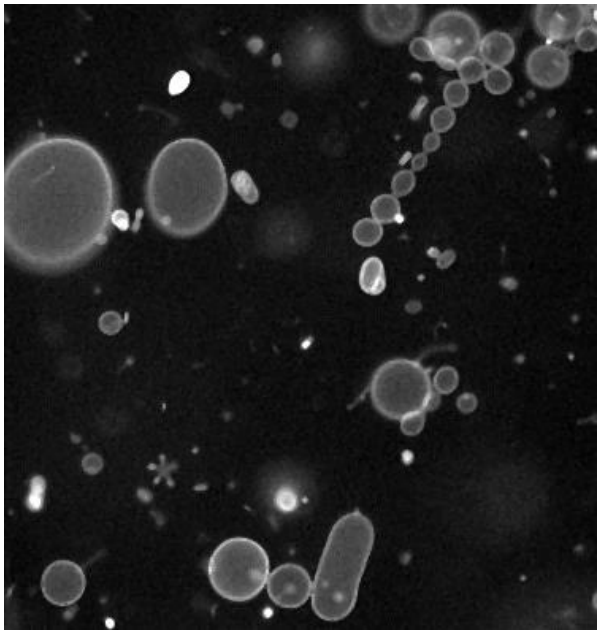
PNIPAM Surfactant Transition Induces ReversibleCurvature Changes in Giant Vesicles

25 °C

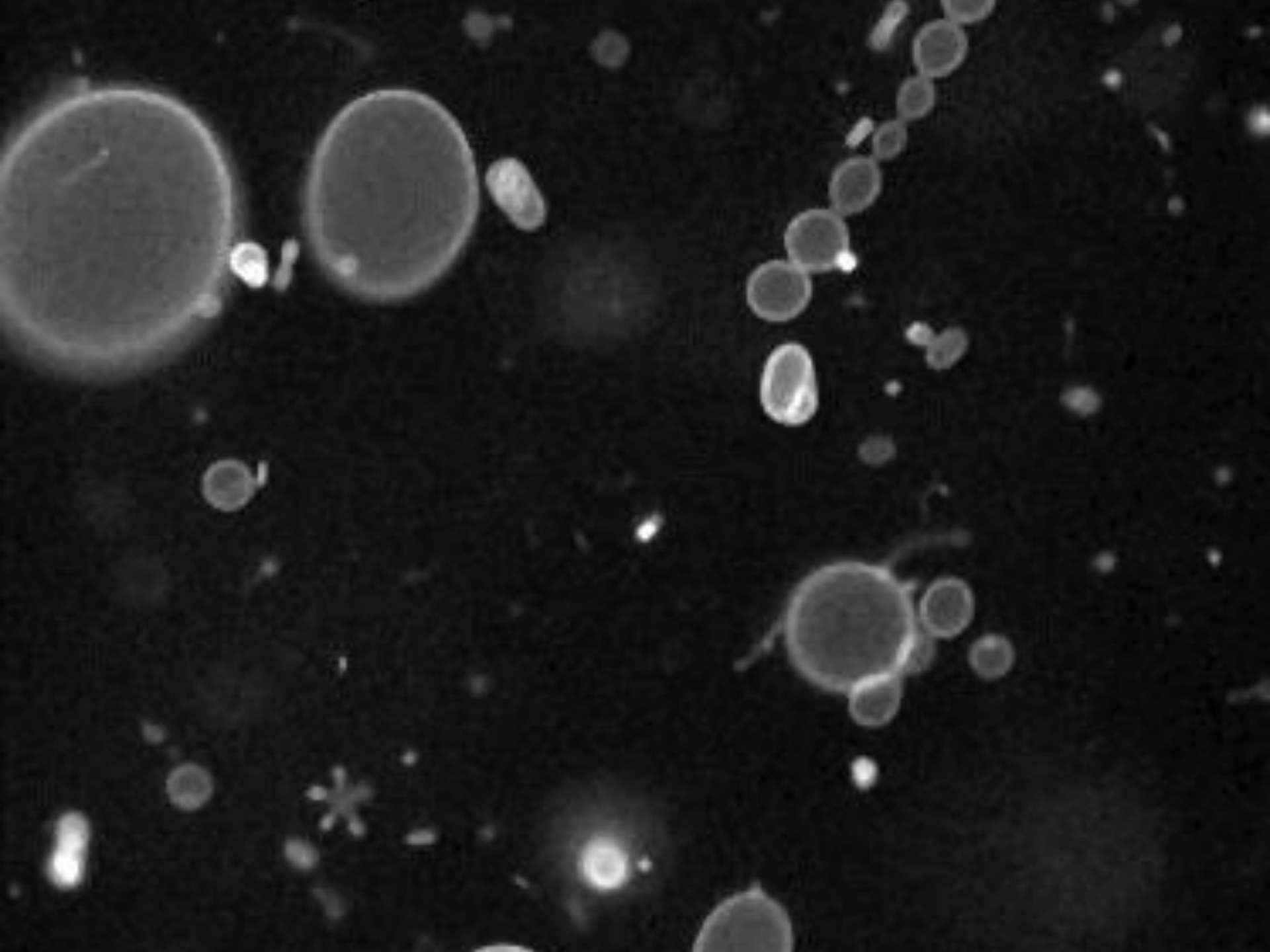


40 °C

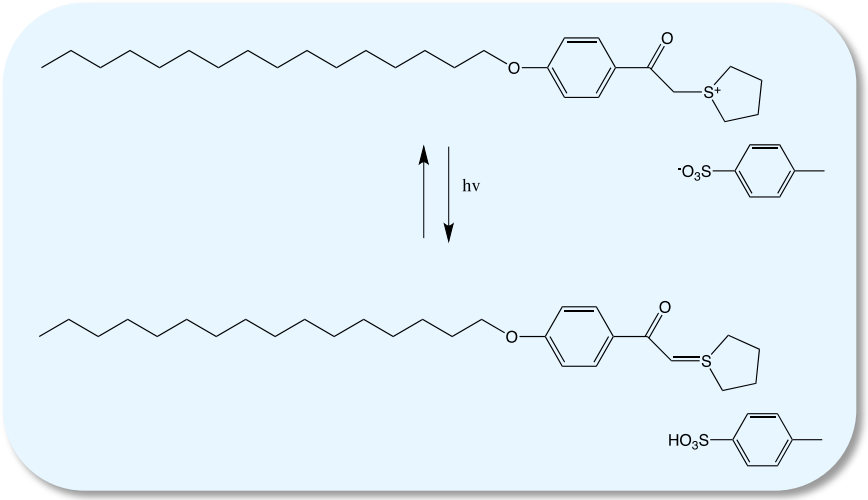


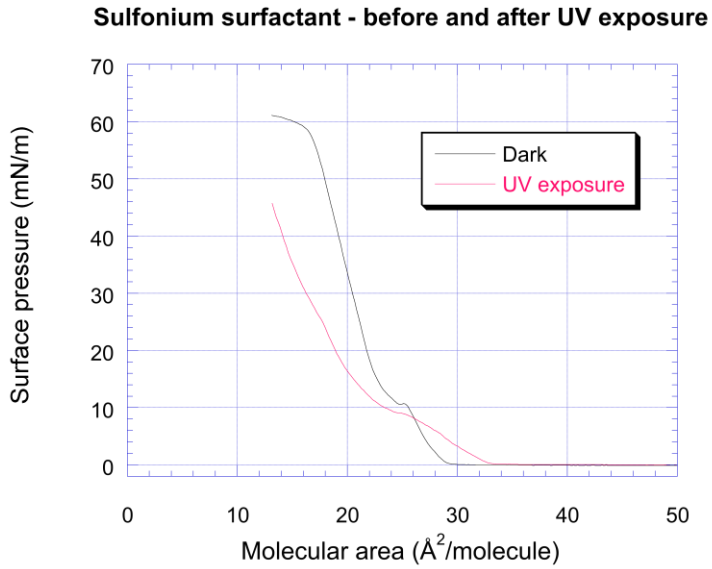
Giant vesicles of 5% PNIPAM surfactant in POPC

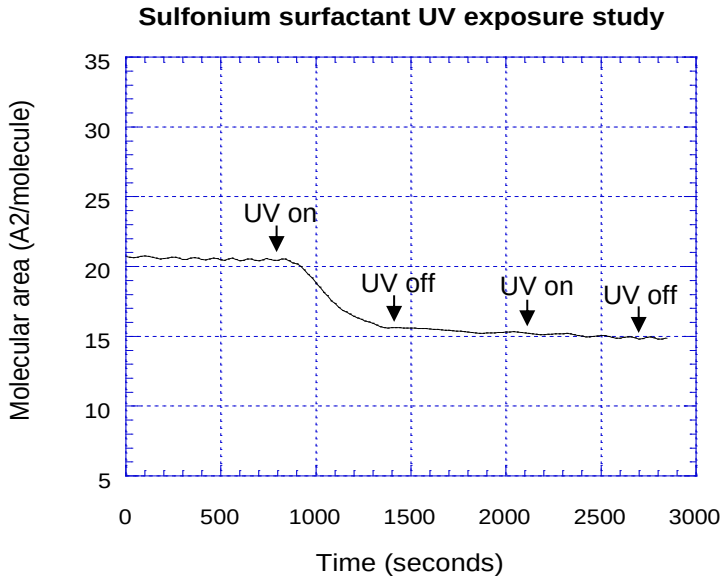
with Darryl Sasaki



Optical Stimulation Induces Volume Change







- Upon UV exposure we observe loss of ~25% of total Langmuir film area as sulfonium converts into ylide.

Other Work: Responsive Ligands and Lipids

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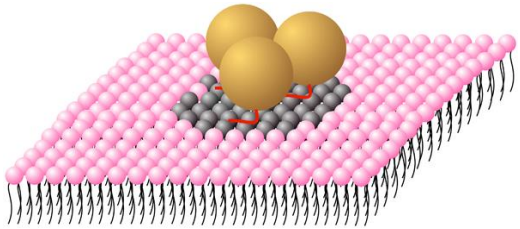
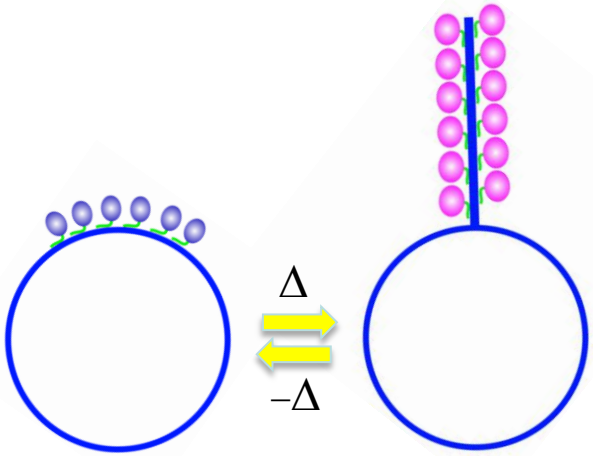
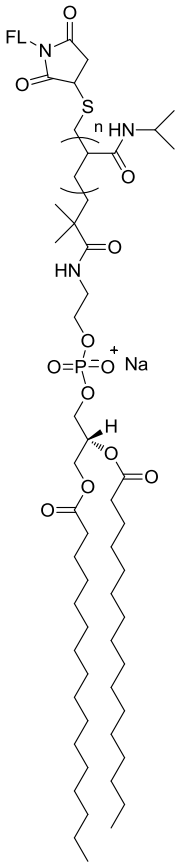
His-tagged PNIPAM





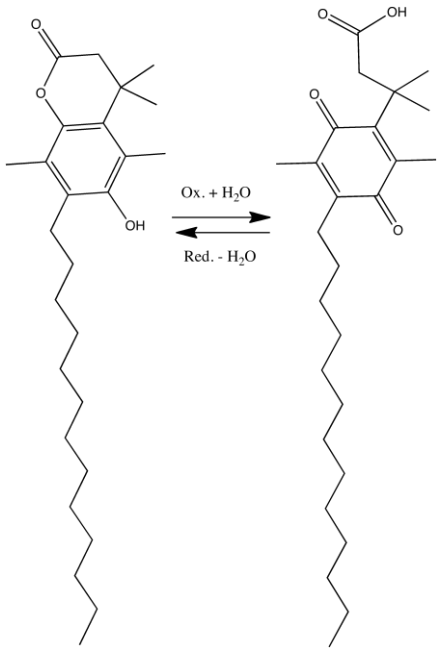
To promote interactions exclusively on the outer leaflet

Double Tail



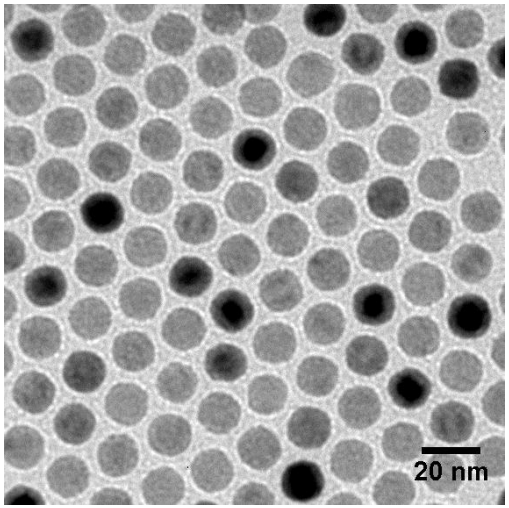
To enhance surfactant anchoring

Optical and Electrochemical Stimulation

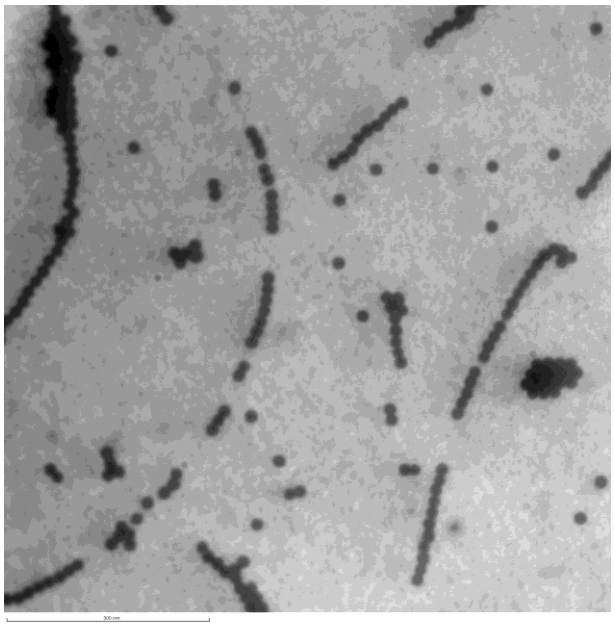


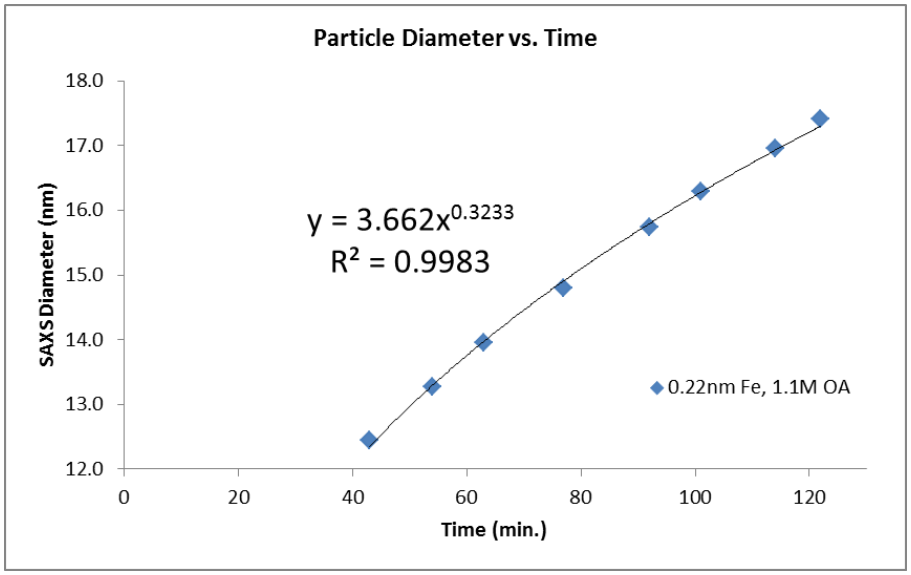
To facilitate programming in device applications

Other Work: Active Molecules on Active Particles



Designed a new magnetite nanoparticle synthesis with improved size control and reproducibility





Work will explore how magnetic particles plus active coatings yield new programmable architectures

Other Work: Simulation of Responsive Surfactant Micelles and Other Assemblies

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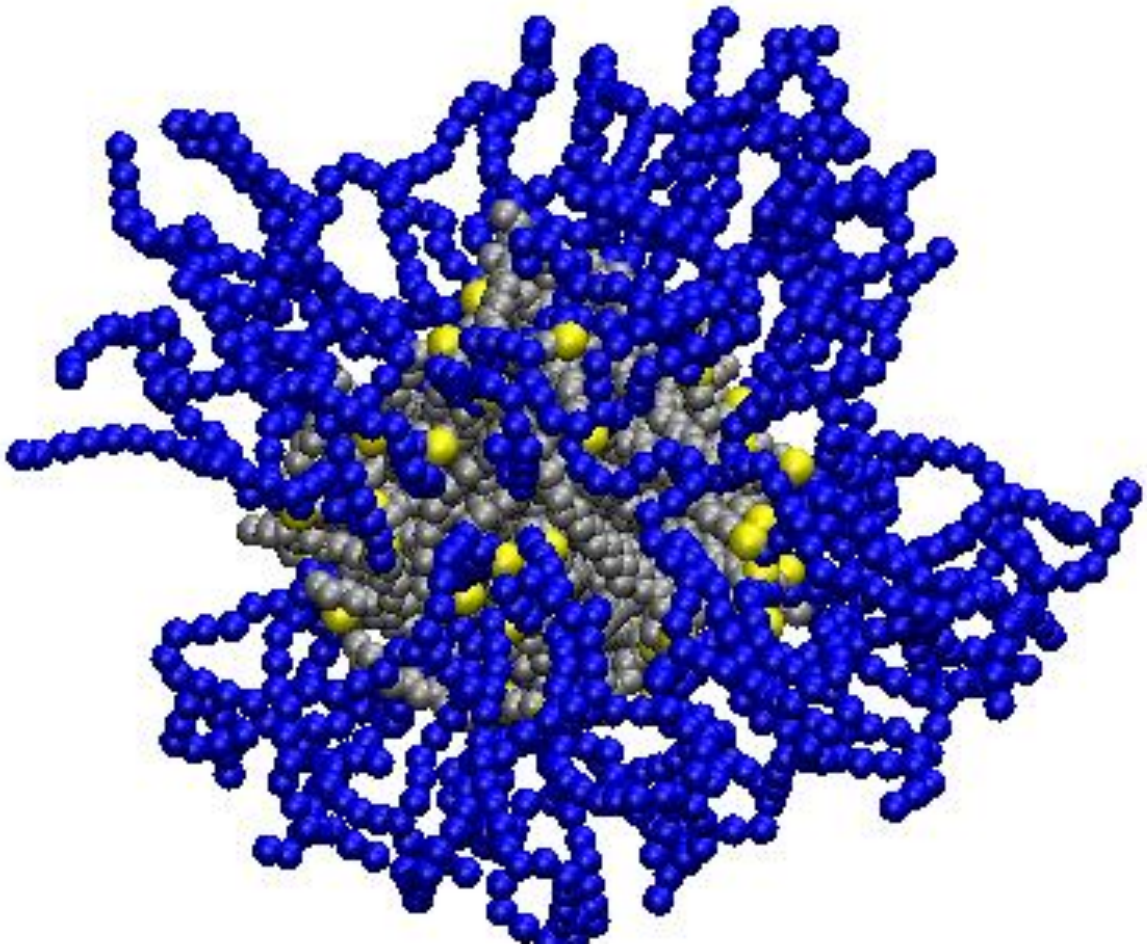

- Enormously expensiv simulations (many atoms, long times)
- Cutting edge codes
- National Lab supercomputing resources
- Mark Stevens

Acknowledgements

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UC DAVIS
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- Ben Fellows
- Dara Gough
- Margie Longo
- Maria Ogunyankin

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Center for Integrated Nanotechnologies

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