



***Integrity ★ Service ★ Excellence***

# Natural Materials and Systems

**Date: 7 MAR 2013**

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**Air Force Research Laboratory**

| Report Documentation Page                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                    |                                     |                                                           | Form Approved<br>OMB No. 0704-0188                  |                                 |
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| 15. SUBJECT TERMS                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                                    |                                     |                                                           |                                                     |                                 |
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# 2013 AFOSR SPRING REVIEW PORTFOLIO OVERVIEW



**NAME:** Dr. Hugh C. De Long

## **BRIEF DESCRIPTION OF PORTFOLIO:**

The goals of this program are to: 1) study, use, mimic, or alter how biological systems accomplish a desired (from our point of view) task, and 2) enable them to task-specifically produce natural materials and systems. Both goals are to help us in our efforts to farm biology for useful science for future USAF technologies.

## **LIST SUB-AREAS IN PORTFOLIO:**

BioMimetics - Study principles, processes, designs as well as manipulate sensors/processing systems. Mimicking of sensor denial systems.

BioMaterials - Mimicking of natural materials or systems. Using organisms as natural material factories for new materials. Using existing natural materials/organisms as novel materials.

BioInterfacial Sciences - Biotic-biotic or the biotic-abiotic interface. Bionano and biomeso technology. Self-assembly.



# Scientific Challenges



- **Bio-camouflage** – Understanding the biochemistry of each element used in a pattern and how the animal controls those elements neurologically.
  - **Payoff:** Would make current camouflage ideas obsolete.
- **Peptide mediated materials synthesis** – Looking at how the peptide initiates binding and what is determining the strength of that binding
  - **Payoff:** Get to a predictive state for sequence or material.
- **Structural Coloration** – How does the animal create the hierarchical assembly; what role does each assembly play in the formation of color
  - **Payoff:** Create new paradigm for development of highly ordered biophotonic nanostructures.
- **Silk** – Trying to understand how silks can stabilize enzymes, etc
  - **Payoff:** Enable use of more sensitive biosensors by eliminating degradation issues with storage and long term usage
- **Silk** – Understand how the structure of the hierarchical assembly is changed by processing
  - **Payoff:** Enable the recovery of desirable properties in silk composites<sup>3</sup>



# Scientific Challenges - Continued



- **Chromophores** – To understand the biochemistry of a newly discovered chromophore with radically different mechanism
  - **Payoff:** New materials in desired wavelength regions
- **Cell-Directed Assembly** – Getting cell to build nanostructured architectures with engineered bio/nano interfaces w/o rejection
  - **Payoff:** Cellular factories for nano-architectures
- **Bionanocombinatorics** – Incorporation of learning into decision making of structural elements in combinatorial arrays
  - **Payoff:** Get rational design of combinatorial arrays.
- **Programmable Materials** – Make individual element properties independent of the designed materials bulk properties
  - **Payoff:** Creation of materials by design: both existing and new.



# Transformational Opportunities



- **Programmable Materials** – this is a new program with lots of opportunity with materials construction at nanometer scale for macro-molecular properties
  - will transform the way we approach materials synthesis and enable synthesis of materials that were unattainable before.
- **Silk** – biomolecular stabilization of enzymes and other biomolecules by silk in film and fiber
  - leads to new method to fabricate sensors, etc; stabilization of vaccines
- **Biocamouflage** – regeneration of coloration assemblies and their control both in pattern generation and in growth
  - Will impact the way we think about pattern construction, and control; could impact work in tissue regeneration as well.
- **Structural Coloration** – understanding the biological strategies involved in the manipulation of light, and structural color in biophotonics
  - it will produce new processing technologies to fabricate bio-inspired tunable optical architectures with optimal structure and properties at multiple length scales.



# Other Organizations That Fund Related Work



- **Chromophores** – I currently have two grants plus work in AFRL. The work of other organizations is almost exclusively on reporter technology. The interest of the AFOSR program is on wavelength, intensity, and lifetime as it pertains to marking items.
- **Silk** – DARPA has contributed to my existing program. ARO has two grantees and a joint funded effort with me. NSF has several single PI grants.
- **Structural Coloration/Bio-Camouflage** – MURI with ONR focused on vision aspect. ARO has a single grant with ICB PI. NSF has just single PI grants. AFOSR program is the largest program.
- **Biomolecular assembly** – A number of funding organizations are interested in this area, so the AFOSR program is focused on soft lithography, peptide binding, and self or directed assembly for materials. AFRL program closely tied in with this group.
- **Bionanocombinatorics and Programmable Materials** – too new for anyone else to be in. These are funded through BRI and a MURI program.
- **NSFs biomaterials** – focus on complexity, hierarchy, dynamics & adaption, healing, and morphogenesis. Focus very different from mine



# Program Trends – BRI is biggest impact



- **Chromophores/Bioluminescence** – Bio-X STT phase 1 focus. One of its discoveries are now used by AFRL TDs, Navy & several Univ PI's
- **Bio-camouflage** – FY09 PBD 709 program: iridiphores, leucophores, chromatophores, papillae, control system. Linked: FY11 AFRL/RX pgm Program under look for focusing next year.
- **Structural Coloration** –several PIs moving in and out; MURI (Harvard)
- **Biopolymers** – Mainly silk but looking at other biopolymers. The silk work is well integrated with AFRL; many exchanges of personnel & material. Narrowing silk focus to Spider and Silkworm only. Reducing cellulose footprint.
- **Biomolecular assembly/Programmable Materials** – BRI program, MURI (Northwestern), MURI (Georgia Tech), rest has remained constant.
- **Peptide Mediated Materials Synthesis** – The efforts are focused on discovering the nature of the mechanism behind this.
- **Cell-Directed Assembly** – Focused on survival and synthetic biology which includes pathway efficiency.
- **Biocombinatorics** – BRI looking at Bio based combinatorics from a bio-nano-info basis





# Transitions



- **AFRL/RX: Gold nanoparticle binding peptide – Nat Rosi (Under AFOSR MURI)**
- **AFRL/RX: Peptide functionalized Nanoparticles for Cr6 sensing (transition to 6.2/6.3 program at AMC)**
- **AFRL/RX: Peptide functionalized nanoparticles wireless sensing platform – GE GRC**
- **Northwestern: Nanoparticle Lattice Pressure Sensor, US patent disclosure 20122.**
- **Northwestern: A General Method for Achieving Nucleic Acid-Nanoparticle Conjugates, US 61/577, 419)**
- **Northwestern: “Hard-Tip Active Spring Lithography” by Keith A. Brown; Daniel J Eichelsdorfer; Xing Liao; Chad A. Mirkin; Boris Rasin; Wooyoung Shim 61/719,918.**
- **Northwestern: “Multifunctional Graphene-coated Scanning Probes Arrays” by Keith A. Brown; Xing Liao; Chad A. Mirkin; Boris Rasin; Wooyoung Shim; Xiaozhu Zhou 61/671,653.**
- **Northwestern: “A Method for Tuning the Spring Constant of Cantilever-Free Tip Arrays” by Keith A. Brown; Daniel J Eichelsdorfer; Chad A. Mirkin 61/724,760**
- **UNM: US 61/638,315 Cell-Based Composite Materials with Programmed Structures and Functions, filed 4/25/2012**
- **UNM: US 13/484,139 Living Cell-Based Biosensor Device that Outputs Signals of Differing Types when Detecting an Analyte, filed 5/30/2012**
- **UNM: US 61/682,861 Robust Process-Compatible Spin-on Ultra Low-K Mesoporous Silica, filed 8/13/2012**
- **UNM: US 61/701,575 Formation of Polypeptide Thin Film Using Atomic Layer Deposition, filed 9/14/2012**
- **Connecticut College – DNA Plasmid technology provided to 11 different university labs**
- **UCSD - Bennett Ibey, Fort Sam, Houston, TX (AFRL) (brittlestar bioluminescence for ecotoxicology)<sub>8</sub> (Deheyn DD)**





# Research



# Morphing and modeling: dynamic 3D skin and brilliant white structural coloration in cephalopods



Roger Hanlon<sup>1</sup>, L. Mäthger<sup>1</sup>, J. Allen<sup>1</sup>, A. Kuzirian<sup>1</sup>, G. Bell<sup>1</sup>, S. Senft<sup>1</sup>, P. G.-Bellido, T. Wardill<sup>1</sup>, M. Gao<sup>2</sup>, G. Kattawar<sup>2</sup>, W. Crooks-Goodson<sup>3</sup>, P. Dennis<sup>3</sup>, R. Naik<sup>3</sup>, S. Karaveli<sup>4</sup>, and R. Zia<sup>4</sup>

<sup>1</sup>Marine Biological Laboratory, Woods Hole, MA; <sup>2</sup>Texas A&M, College Station, TX; <sup>3</sup>AFRL/RX WPAFB; <sup>4</sup>, Brown University, Providence, RI

## Biologically inspired approach to development of diffuse and textured camouflage materials

### Efficient light diffusers

Commercially available diffusers rely on high-index contrast (e.g., using titania nanoparticles) and are physically abrasive.

### Adaptable 3-dimensional skin texture

3-D texture has not yet been incorporated in modern camouflage materials. Texture is added in the form of additional structures, such as “plant” materials etc.

### Cephalopod skin – inspiration for camouflage materials

**Leucophores** appear to provide both high reflectivity and near-Lambertian white scattering with a low-index contrast system. They are flexible and work under wet and dry conditions.

Cephalopod **papillae** produce dynamic 3-D skin texture along a broad continuum from smooth to highly rugose. The visual sensori-motor system of rapid adaptive camouflage provides novel bio-inspired approaches to materials science.

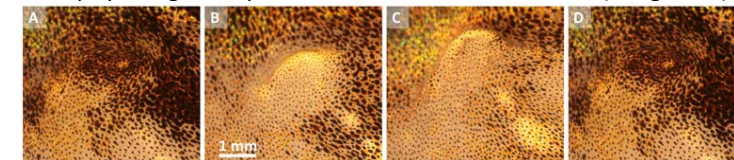
### MAIN ACHIEVEMENTS

1) Novel programming of 3D electron microscopy data enabled segregation and imaging of a single leucophore with 12,000 spheres. RI measured directly via holography. Simulation & modeling achieved.



SINGLE Leucophore fully characterized and modeled. Spheres (250-2000nm) contain reflectin proteins.

2) Detailed histology indicate papilla is a muscular hydrostat; neurophysiological expansion and retraction achieved (image A-D).



### HOW THEY WORK

The ultrastructure of passive leucophores enables nearly perfect diffusion of incident light. Papillae are under neurological control and the animal is able to achieve a range of textural states via a muscular hydrostat system.

### ASSUMPTIONS AND LIMITATIONS

The main limitation is that this bio-inspired material is restricted to the cephalopod system. While it has evolved in the marine environment, its adaptation for other uses (terrestrial, aviation) is conceivable.

### Current impact

1) Leucophores: first full characterization and modeling of a single cell; refractive index measured; reflectin proteins discovered in leucosomes. Randomly ordered system of spheres generates incoherent scattering.

2) Papillae: simple small papillae characterized by histology as muscular hydrostats. Complex musculature arrangement gives insight into compliant skin and biomechanics of extension.

### Planned Experiments

-Leucophores: quantify & explain different ratios of spheres and platelets in cuttlefish; determine how pyjama squid produces white with platelets only.

-Papillae: follow new leads on neural control; comparative histology on other papillae types to investigate different mechanisms of extension.

### Research goals

White reflection with soft nanostructures has never been achieved - leucophores may pave the way to this capability. This study also aims to elucidate the biomechanics and control of 3-D skin papillae that provide dynamic textural camouflage.

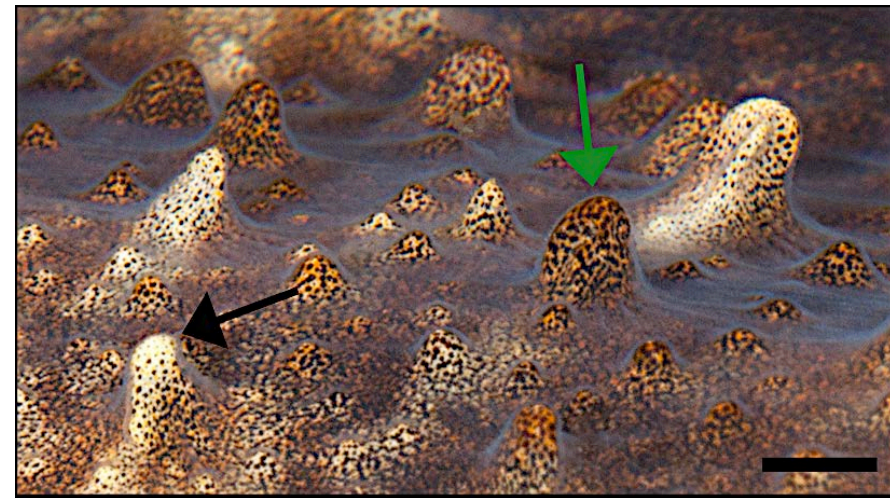
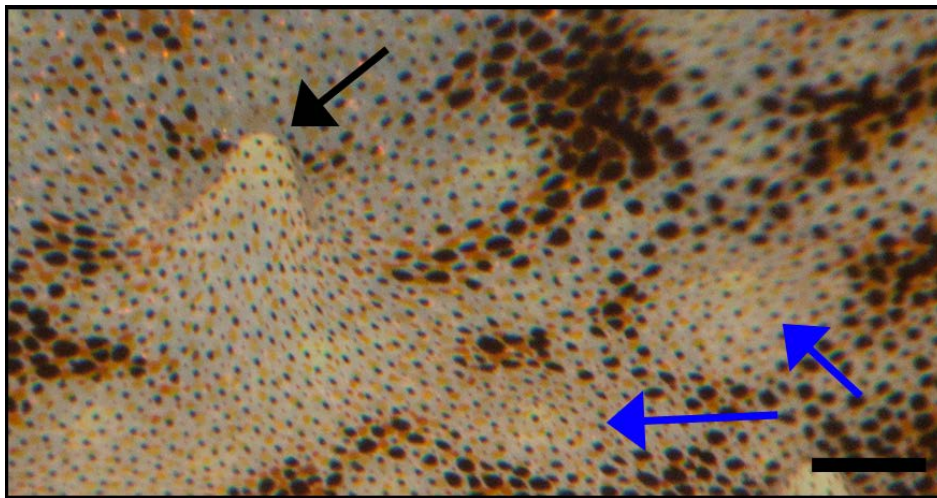
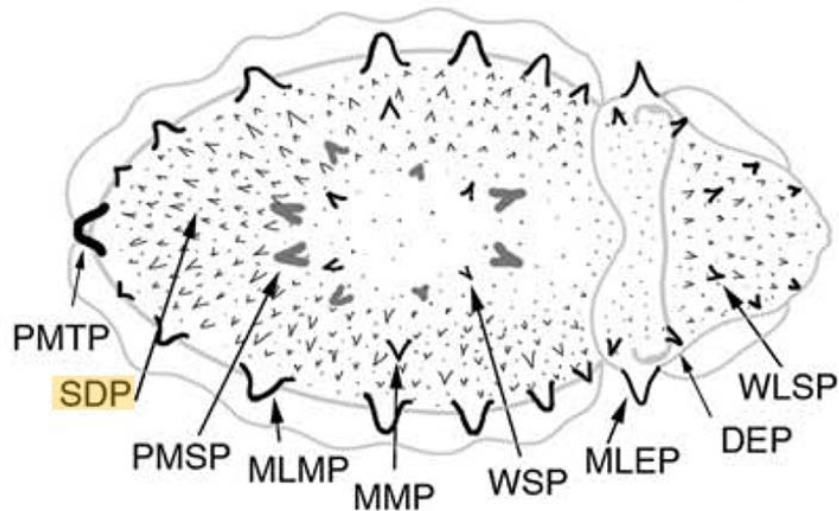
QUANTITATIVE IMPACT

END-OF-PHASE GOAL



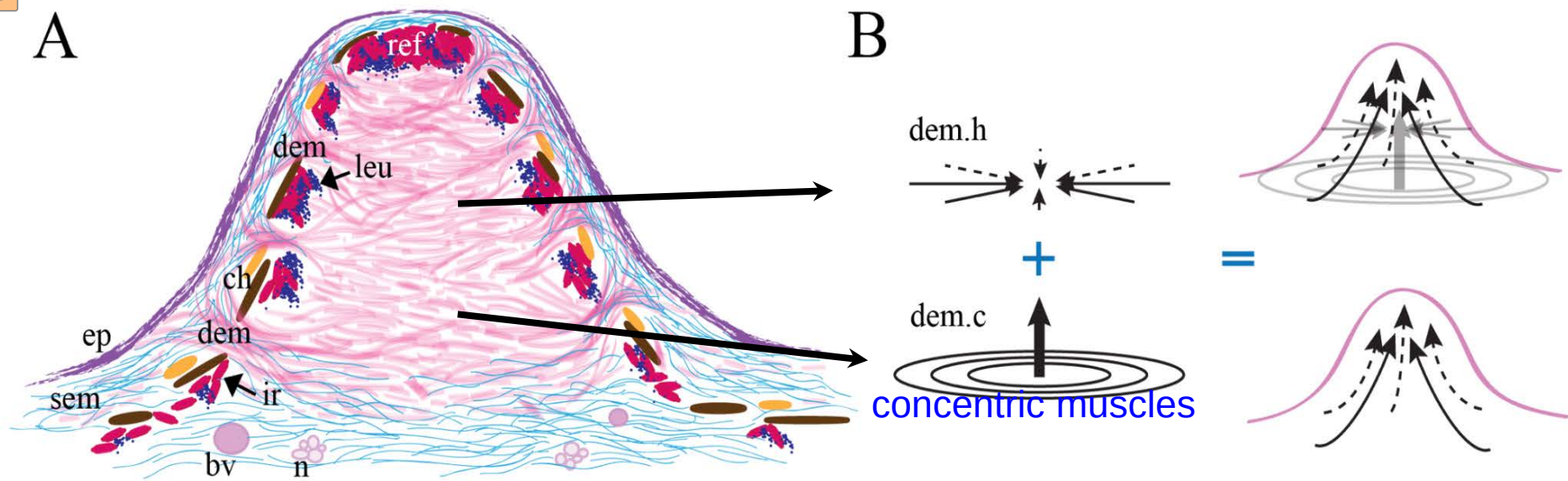


# - Aim 1: Ultrastructural analysis.



SDP = Small dorsal papillae

scale bars = 2mm



Morphology suggests **muscular hydrostatic** function:  
muscle cells do two things: (1) evoke movement (2)  
provide structural support in the absence of rigid  
elements.

**Publication:**  
**Journal of Morphology**

**Cuttlefish Skin Papillae Possess Morphology  
Suggesting a Muscular Hydrostatic Function for Rapid  
Changeability**

Justine J. Allen,<sup>1,2\*</sup> George R.R. Bell,<sup>2</sup> Alan M. Kuzirian,<sup>2</sup> and Roger T. Hanlon<sup>2,3</sup>

<sup>1</sup>Department of Neuroscience, Brown University, Providence, Rhode Island 02912

<sup>2</sup>Marine Biological Laboratory, Woods Hole, Massachusetts 02543

<sup>3</sup>Department of Ecology and Evolutionary Biology, Brown University, Providence, Rhode Island 02912

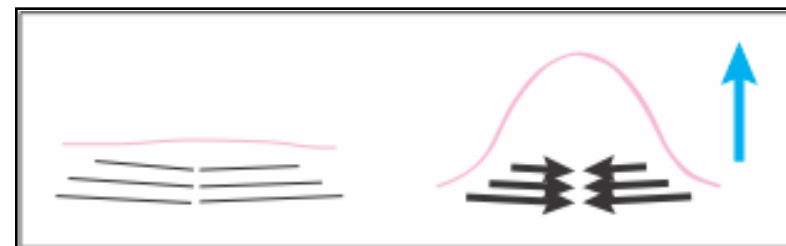
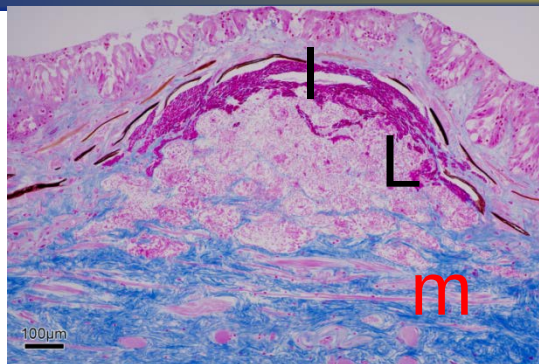




# Different Types of Muscular Mechanisms

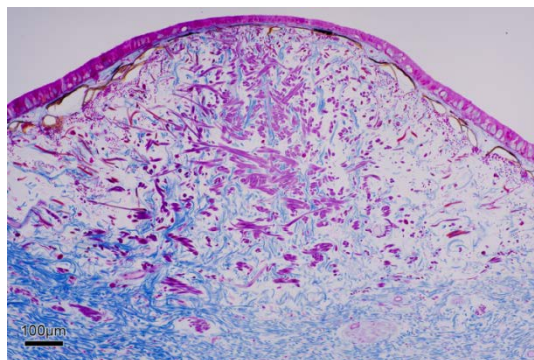


*S. apama*



buckling

*O. bimaculoides*



elastic stretching

*M. defilippi*



opposing muscle groups



**Before Stimulation**



**After Stimulation**



“On nerve”



“Off nerve”





# Spider Gland Fluids: From Protein-rich Isotropic Liquid to Insoluble Super Fiber

Gregory P. Holland and Jeffery L. Yarger, ASU



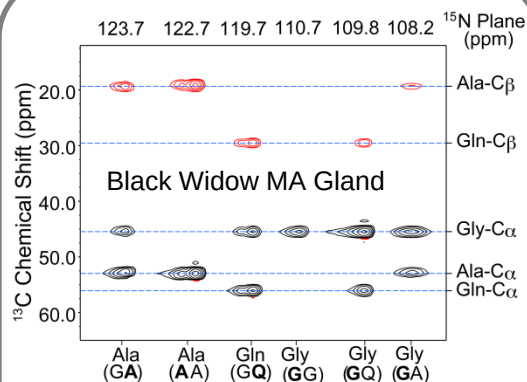
STATUS QUO

## Spider Silk

- Comprised almost entirely of protein
- Primary amino acid sequences known
- Proteins can be produced biosynthetically
- *Protein secondary structure (folding) is important for fiber mechanical properties*

### Understanding spider silk and its production at the molecular level

- Gain insight on secondary structure by studying fibers with solid-state NMR & XRD
- *Elucidate the molecular mechanisms responsible for spider silk production by studying the gland fluid with magnetic resonance (NMR/MRI) and other methods*

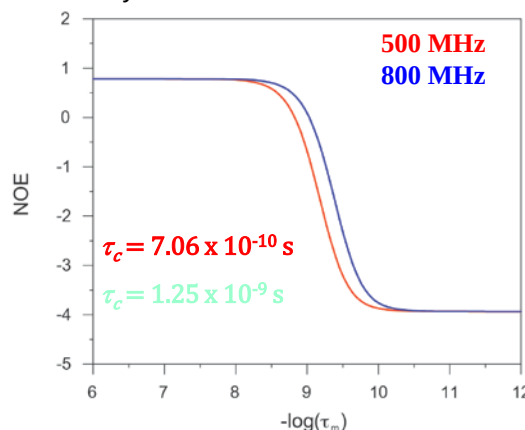


- 3D High-resolution (HR) liquid-state NMR on silk protein in the major gland
- Site specific resonance assignment for protein structure and dynamic studies

## CHARACTERIZING SPIDER GLAND FLUIDS

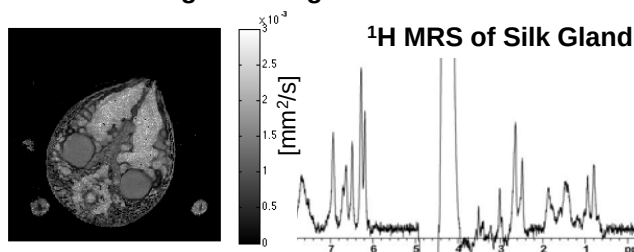
### MAIN ACHIEVEMENTS:

- We have shown with HR-MAS NMR that the two silk proteins (MaSp1 and MaSp2) in the gland are in an unstructured, random coil state
- Silk protein dynamic studied on  $^{15}\text{N}$ -labeled glands with  $^{15}\text{N}/^1\text{H}$  HSQC-NOE and relaxation measurements
- New insights into silk protein flexibility and nanosecond dynamics from these HR NMR studies



- Continued development of MRI for probing protein structure and dynamics within the silk glands of live spiders *In vivo*

### Diffusion Weighted Image of Black Widow &



QUANTITATIVE IMPACT

### IMPACT

- Understanding the conditions for converting gland fluids to fibers rich in secondary structure is the key to synthetic spider silk
- Findings regarding optimal conditions for converting the gland fluid to a  $\beta$ -sheet rich fiber are transferred to groups producing synthetic spider silks to optimize the spinning process
- Developed PDF XRD method for measuring  $\beta$ -sheet domain size in natural silk fibers, processed glands, and synthetic spider silks
- We continue to develop MRI with localized spectroscopy and diffusion weighted imaging to interrogate the spider silk producing process *In vivo*

END-OF-PHASE GOAL

### END GOAL:

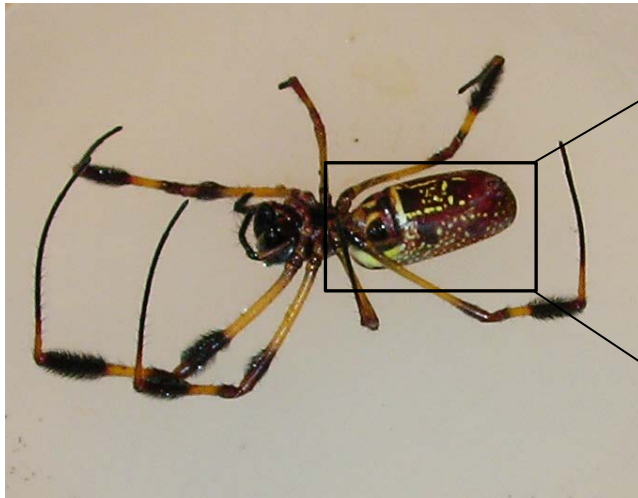
*To elucidate the molecular mechanisms and chemistries for converting spider gland fluids to high performance fibers.*

NEW INSIGHTS

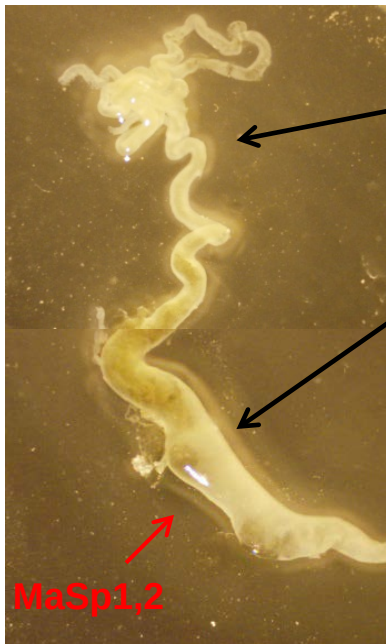
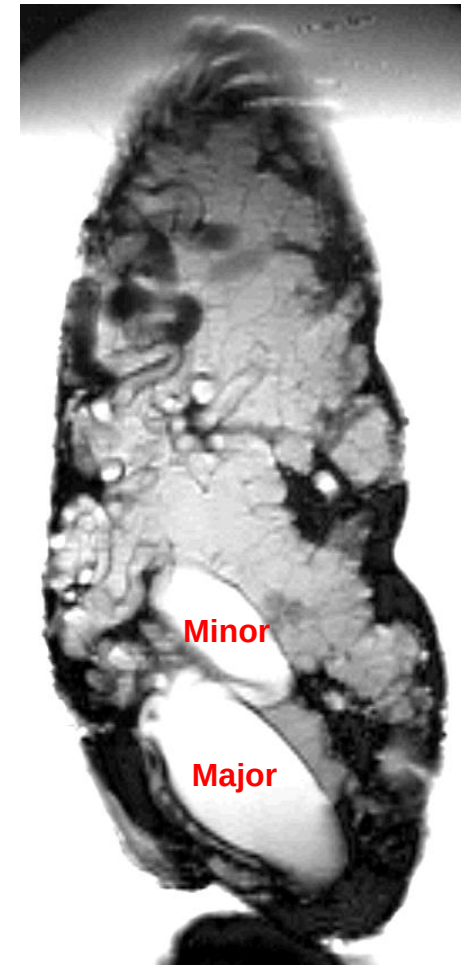




# Spider Silk Glands



Spider MRI



**Tail** – Protein Synthesis Secretion

**Gland** – Accumulation/Storage

**Duct** – Shear/Dehydration/pH/Salt

**Spinneret** – Final fiber

MaSp1,2

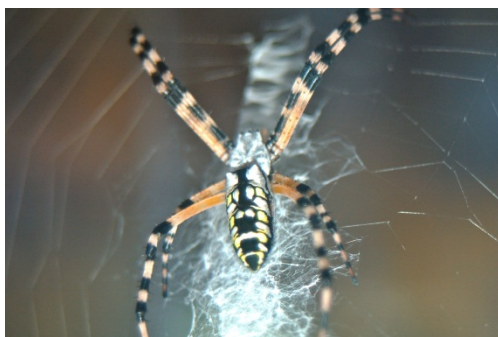


# $^{13}\text{C}$ HR-MAS NMR of Major Ampullate Glands



## *Argiope aurantia*

U- $^{13}\text{C}$  $^{15}\text{N}$ -Alanine



MaSp1 : MaSp2

40%:60%

## *Nephila clavipes*

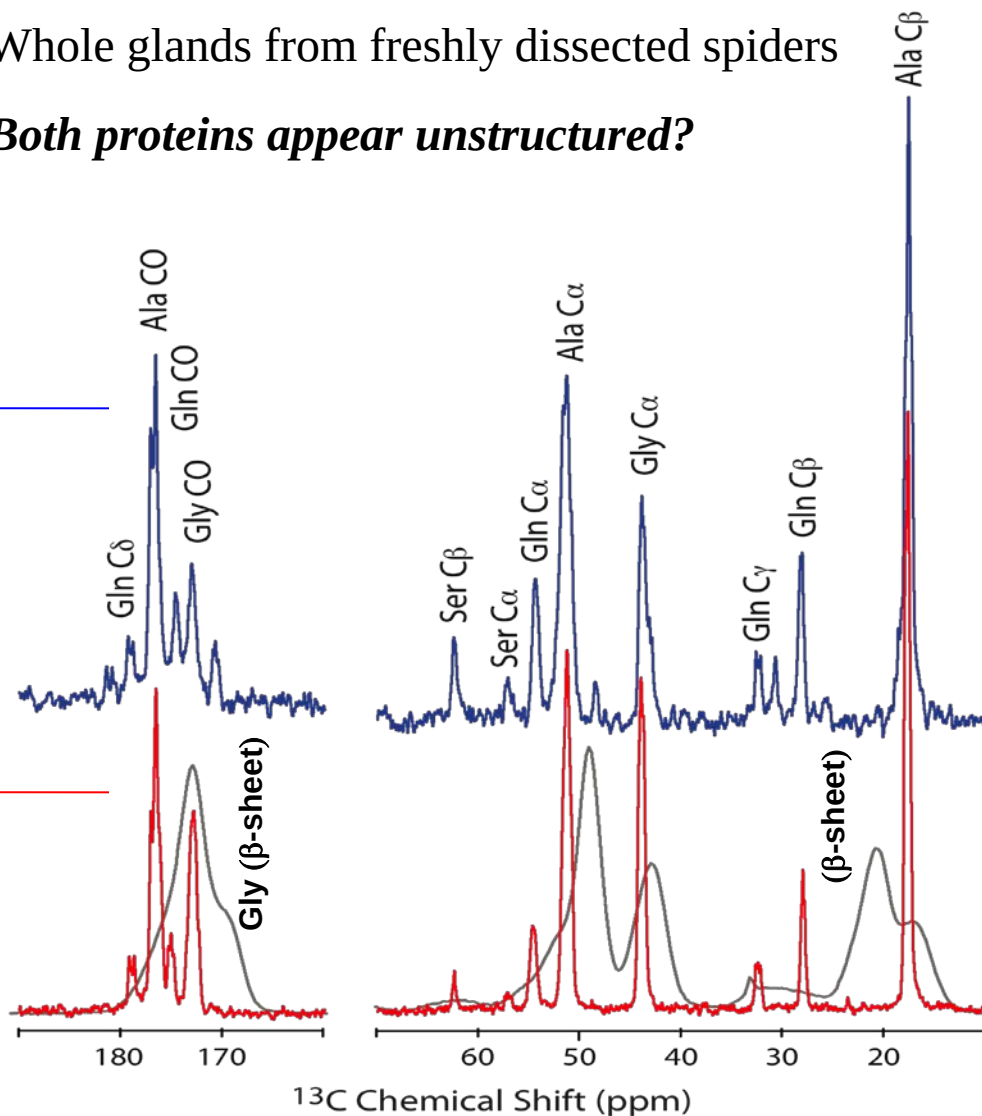
U- $^{13}\text{C}$  $^{15}\text{N}$ -Alanine



MaSp1 : MaSp2

80%:20%

- Whole glands from freshly dissected spiders
- ***Both proteins appear unstructured?***

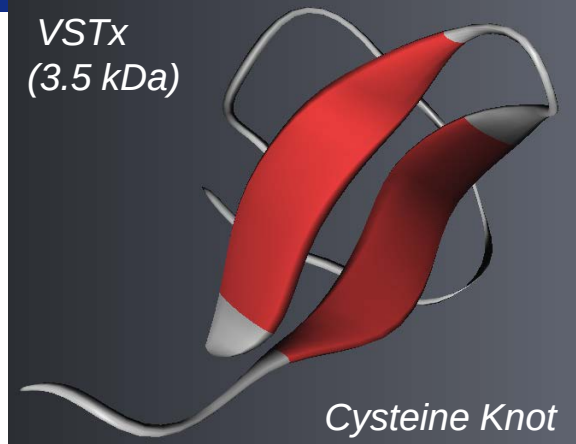




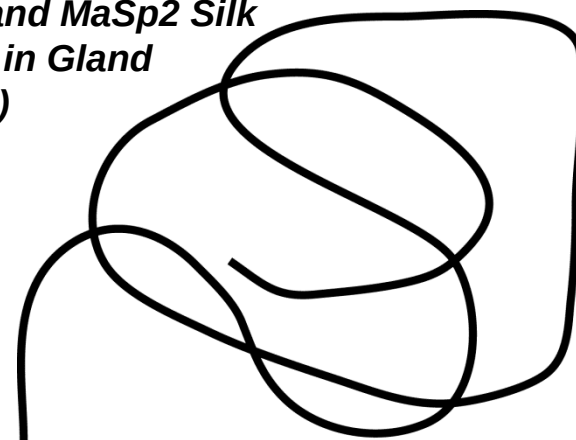
# $^1\text{H}$ , $^{13}\text{C}$ Chemical Shifts Indicate Random Coil<sup>1</sup>



VSTx  
(3.5 kDa)

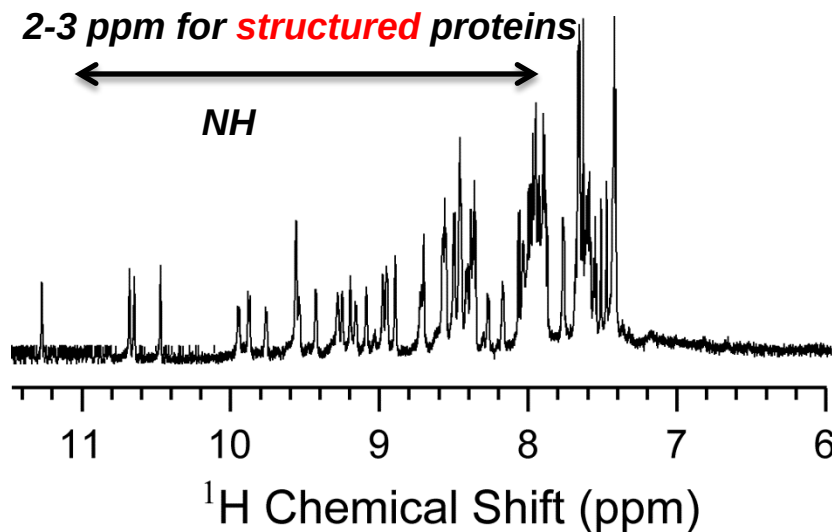


MaSp1 and MaSp2 Silk  
Proteins in Gland  
(300 kDa)

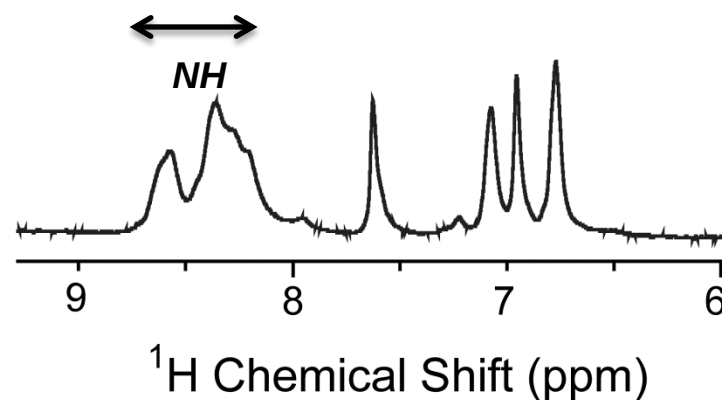


Random Coil

2-3 ppm for **structured** proteins



0.5 ppm for **unstructured** proteins



[1] Jenkins et al. *Soft Matter*, 2012, 8, 1974.

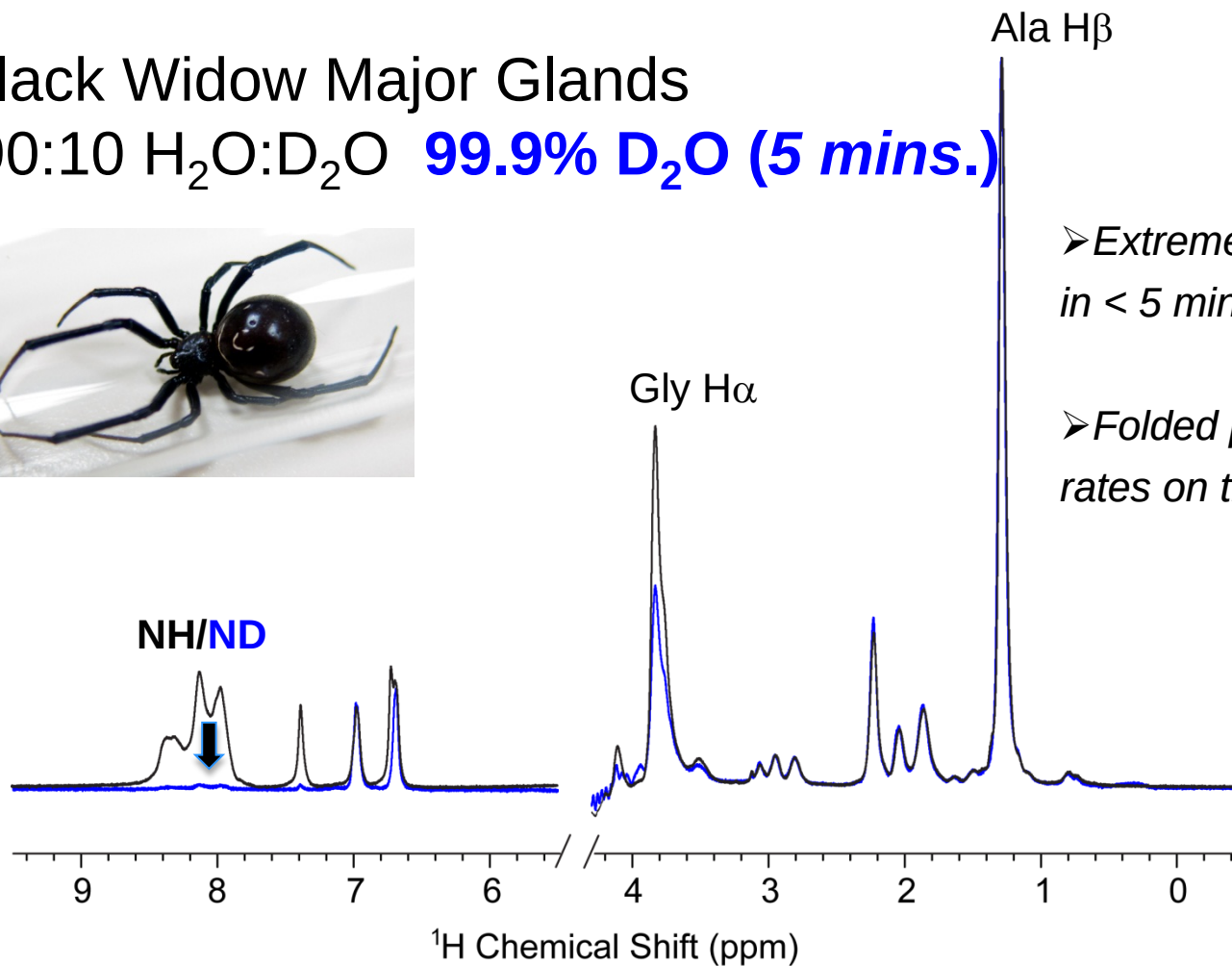


# H/D Amide Exchange: Black Widow Major Glands



## Black Widow Major Glands

90:10 H<sub>2</sub>O:D<sub>2</sub>O **99.9% D<sub>2</sub>O (5 mins.)**



➤ *Extremely rapid H/D amide exchange in < 5 mins*

➤ *Folded proteins exhibit exchange rates on the order of hours to days*





# Silk Quality and Spin-ability

## STATUS QUO

**(A)** Confused understanding of the properties of natural silk fibres: **WHY?**

= Poor modeling and limited understanding of native/natural silks

**(B)** Lacking ability to spin quality fibres using natural extrusion technology: **WHY?**  
= need to better understand the relationships between protein phase-transitions and the spinning ducts.



## NEW INSIGHTS

**(A1)** New link established between silk properties and filament dimensions.

**(A2)** Novel insights into differences between live and dead silk proteins.

**(B1)** Rheology, Thermo Mechanical and a range of Spectroscopies are providing key data.

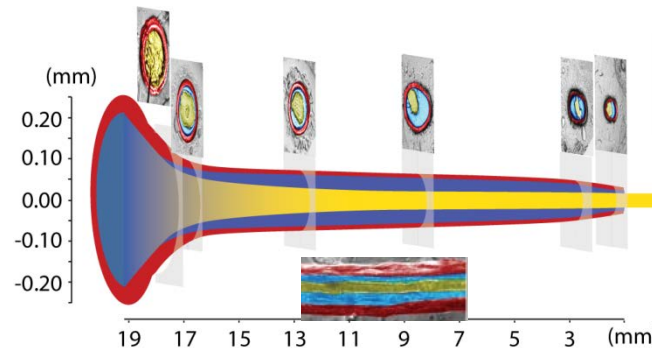
**(B2)** A novel *Aquamelt* hypothesis tests for generic principles of silk spinning.



## SCIENTIFIC ACHIEVEMENTS

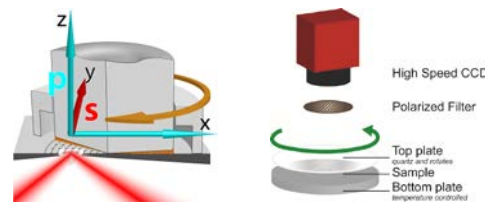
(a) Novel insights into fibre properties (published).

(b) Novel insights into fibre spinning (submitted)



(c) Further progress towards reliable reconstitution of silk materials (unpublished).

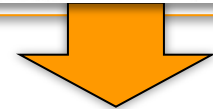
(d) Novel insights into silk nanoscale ribbon-films



**Other Achievements:** (a) Vollrath, Porter and Holland gave invited key-note lectures at major conferences, (b) Three PhD theses submitted/awarded, (c) Chris Holland was awarded a prestigious Career Advancement Grant and also assumed Lectureship in Materials at Sheffield University

## QUANTITATIVE IMPACT

- (a) Scientific Citations
- (b) Press Publicity
- (c) New Silk Dope
- (d) Silk Film Research
- (e) Uptake of Model

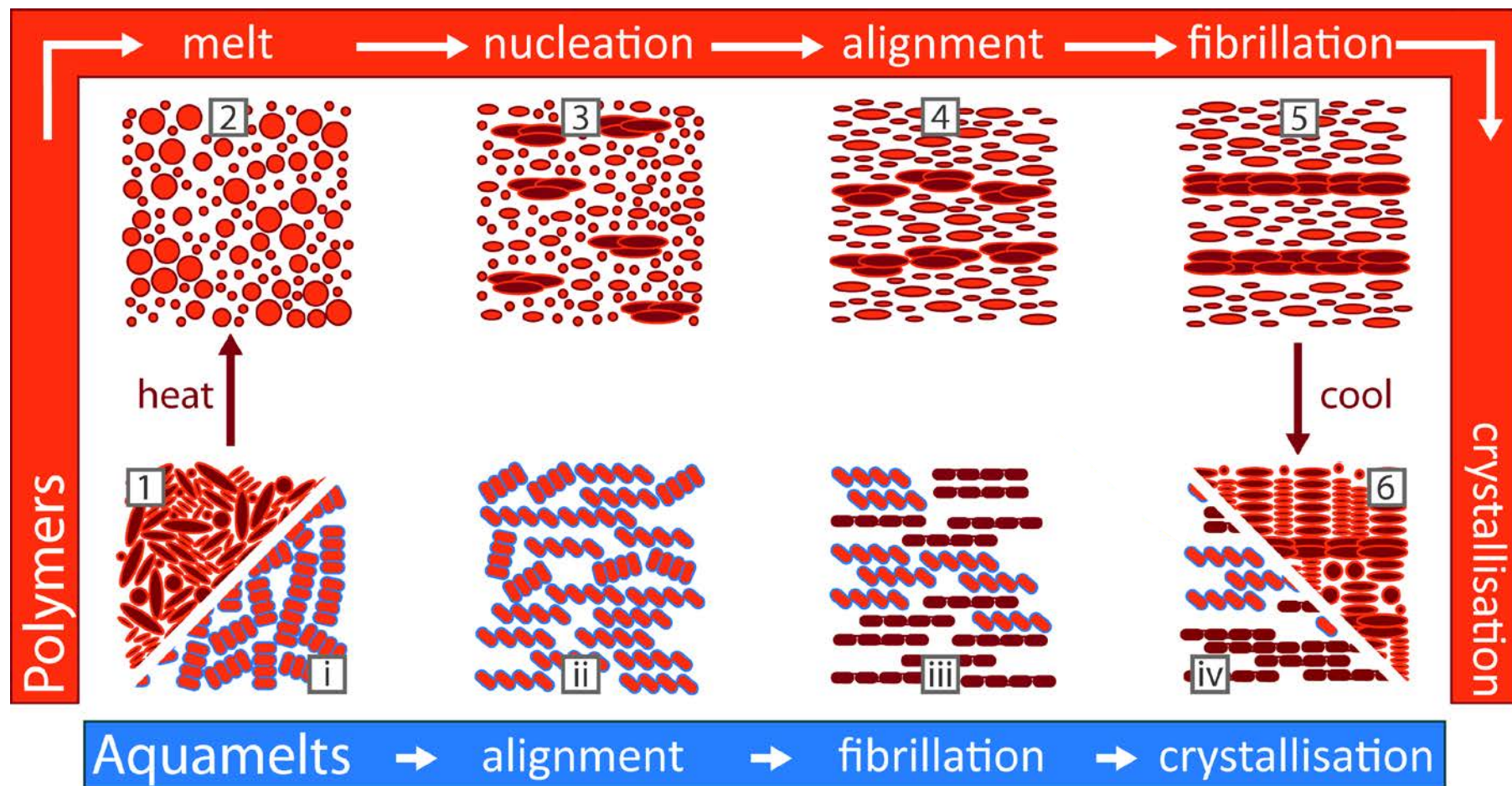


## END-OF-PHASE GOAL

- (a) To create/prepare novel silks for experimental evaluation.
- (b) To overcome the differences between native and reconstituted silks.
- (c) To integrate natural silk composites into hybrid synthetic/silk composites.



# Aquamelts: A transformative hypothesis



Aquamelt: a naturally hydrated polymeric material able to solidify at environmental temperatures through a controlled stress input



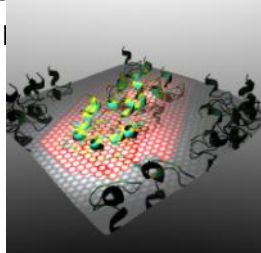
# Understanding Biotic-Abiotic Interactions

## Rajesh R. Naik AFRL/RXBN



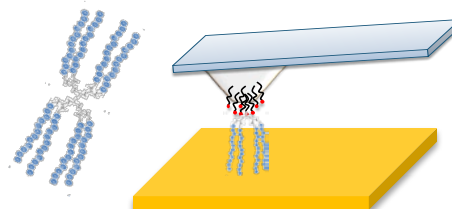
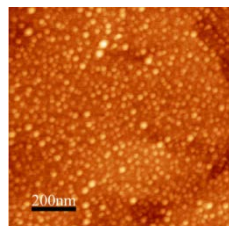
STATUS QUO

- Understanding the interaction of biomolecules with inorganic surfaces
- Directed supramolecular assembly of nanostructures to give rise to unique physical properties
- Control nanoparticle inter

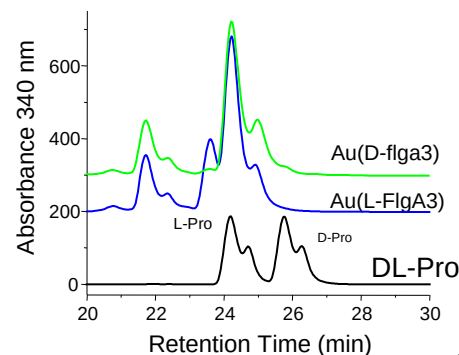
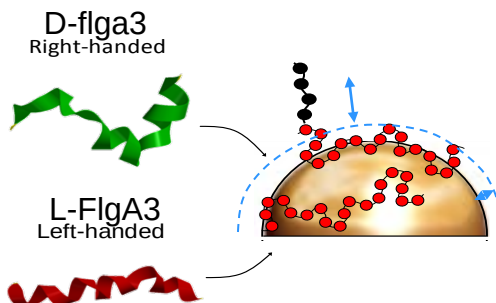


### MAIN ACHIEVEMENTS

- Understanding the role of peptide multi-valency on metal interaction

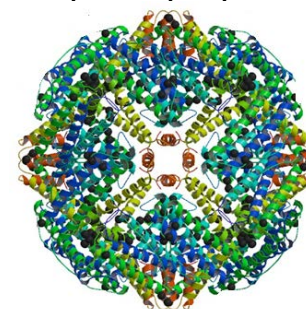


- Gold nanoparticles that exhibit peptides isomerase-like activity – HPLC for chiral separation



### IMPACT ACHIEVED

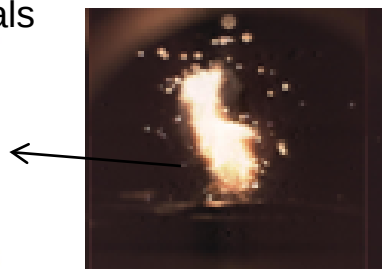
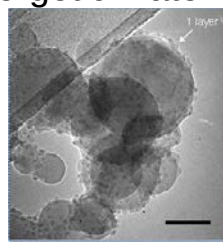
- Better understanding of biotic-abiotic interactions to create materials with tailored properties
- Selective functionalization of graphene
- Biofunctionalized nanoparticles exhibit unique optical properties



NEW INSIGHTS

- Understanding biotic-abiotic interactions
- Developing modeling and experimental tools to
- Bioenabled assembly of nanomaterials with unique properties
- Rational design of biomolecules with desired inorganic interactions

- Protein cages for tuning the reactivity of energetic materials

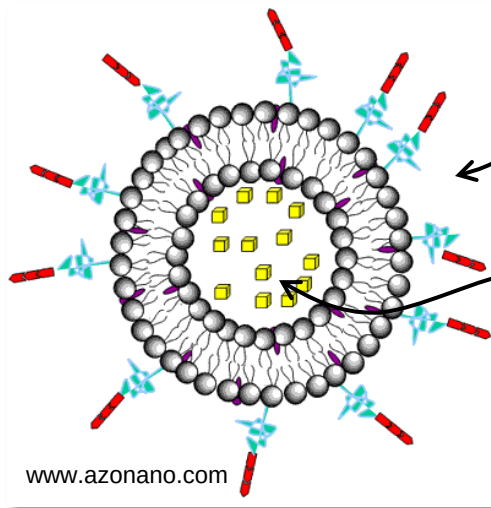


- Demonstrate the use of biomolecules to recognize, organize, and assemble materials
- Understand biotic-abiotic interaction using experimental and computational tools

QUANTITATIVE  
IMPACT

END OF PHASE GOAL

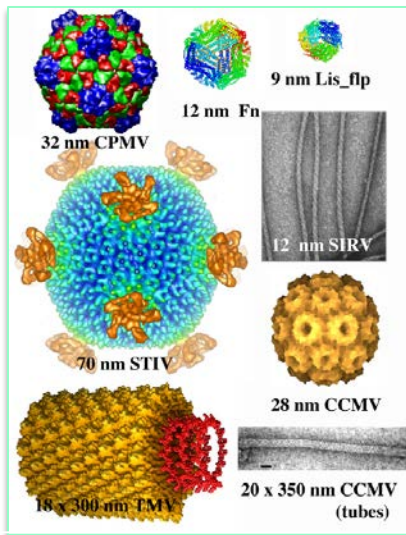
# Protein Cages as Agent Carriers



Targeting tag

Agent (drug, contrast agents, nanomaterials)

- Protein cages tailored as carriers
- Facile modification of internal or external surfaces (addressable molecular components)
- Monodispersed
- Attachment of targeting ligands for localized delivery (recombinant engineering)
- Loading of cargo (internally or surface)

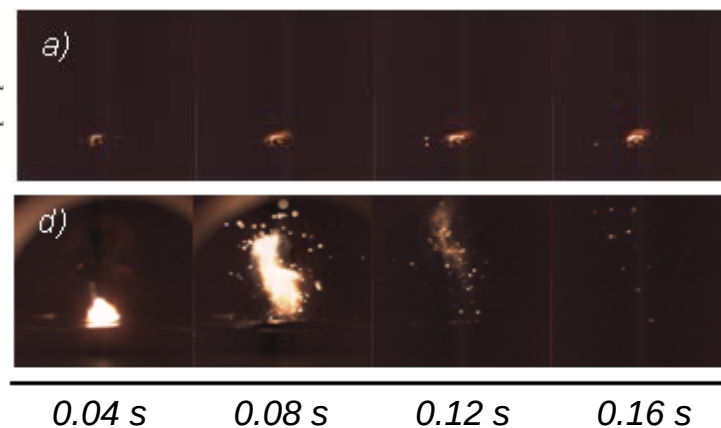
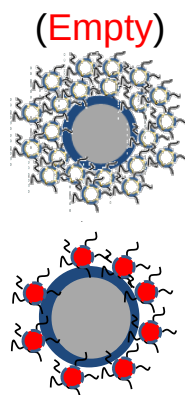
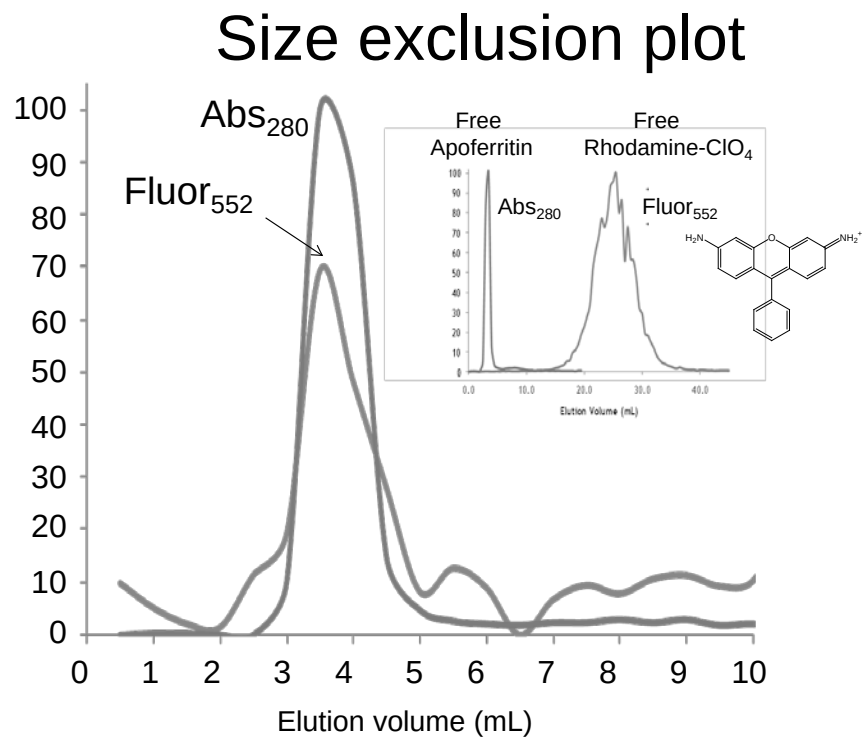
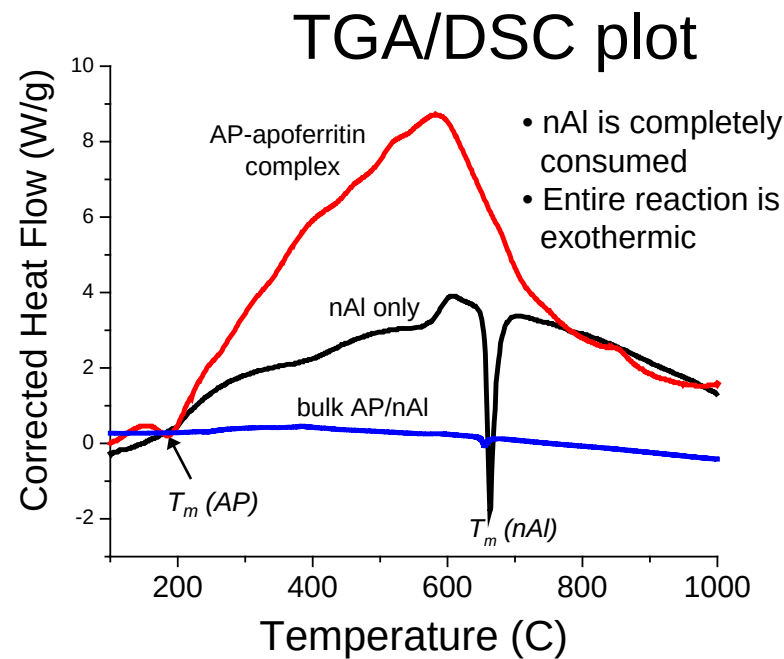
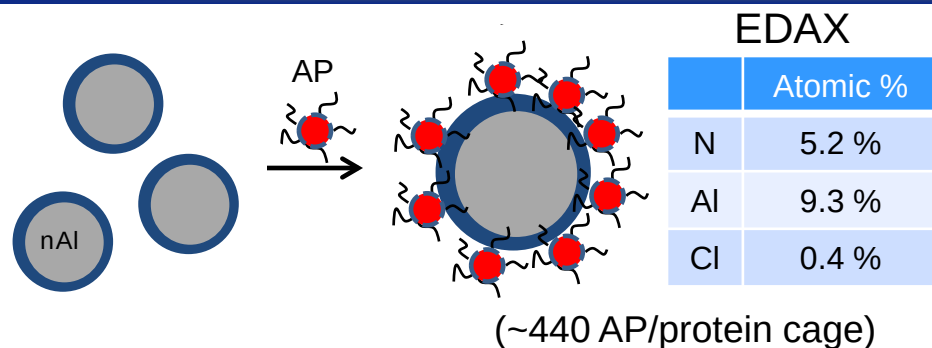


- Constrained synthesis of nanoparticles
- Decontamination: Heavy metal sequestration
- Catalysts: Photoreduction capabilities of Cr, Ti.
- Magnetic separation: CoPt nanoparticles
- Biomedicine: drug delivery



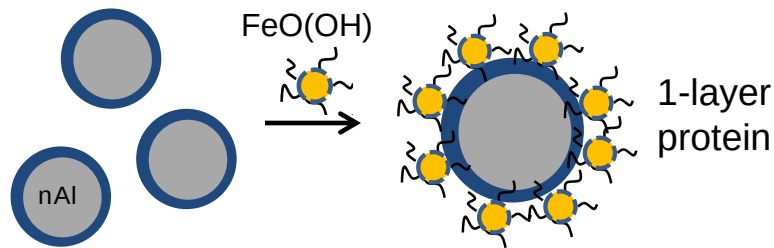


# Ammonium Perchlorate Loaded Apoferritin-nAl Hybrid

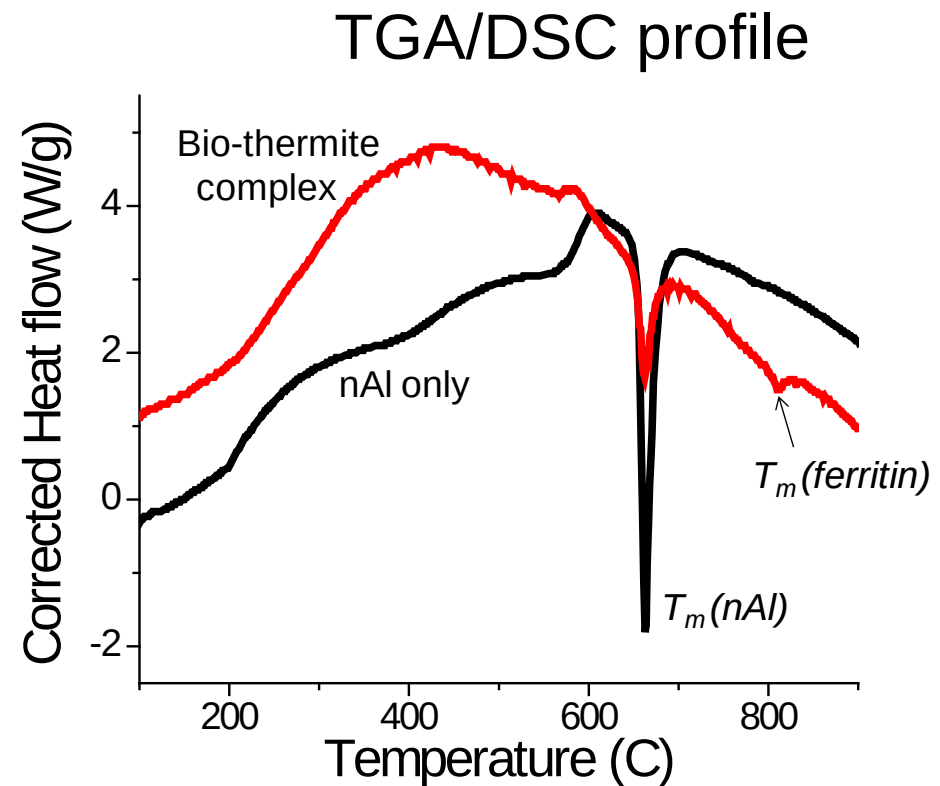
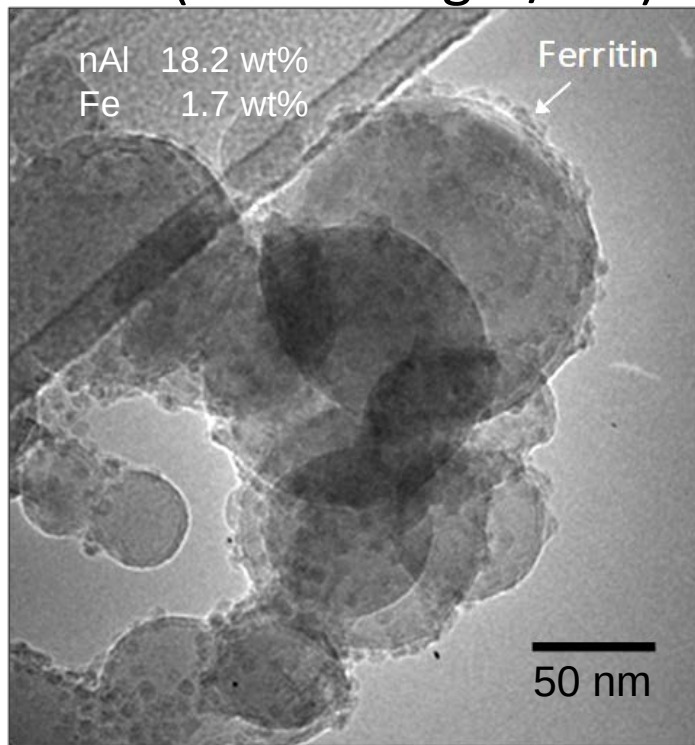




# Bio-thermite Reaction



(~40-44 cages/nAl)



- Exotherm appears at 300°C
- Unreacted nAl present with 1-layer

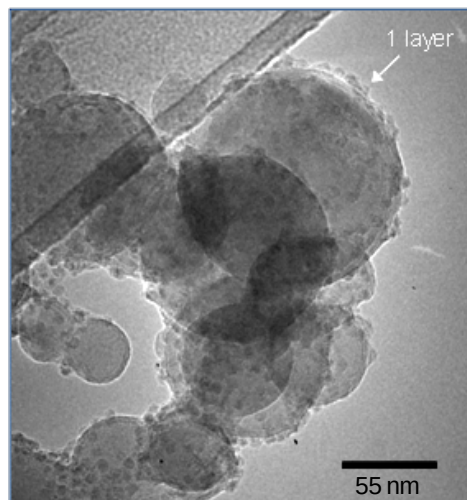




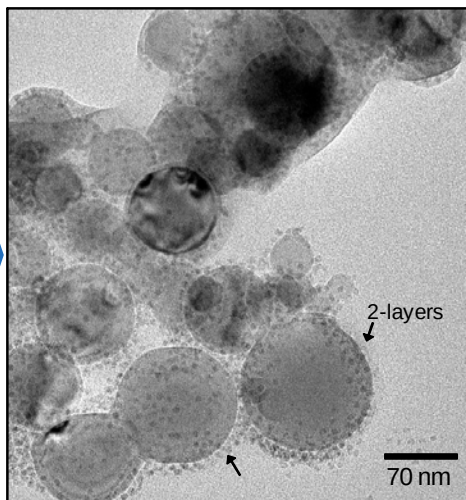
# LBL Assembled Protein Cages on nAl



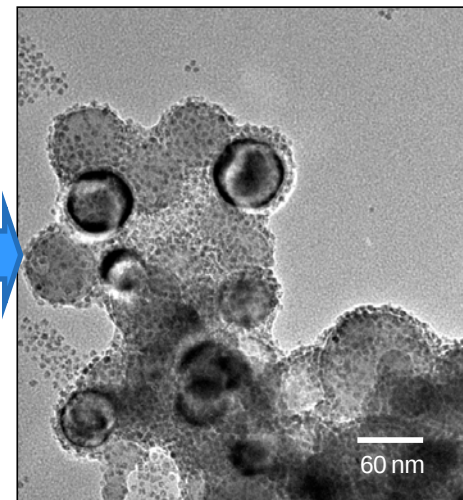
1-Layer



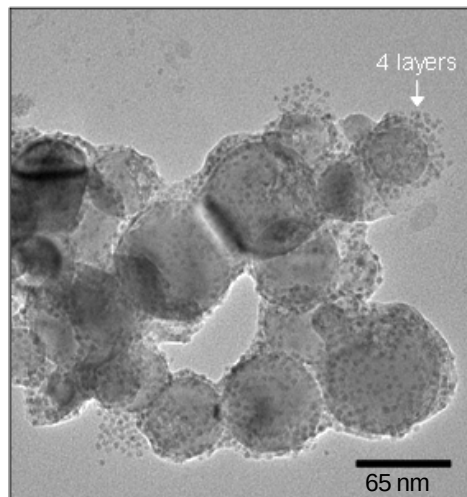
2-Layers



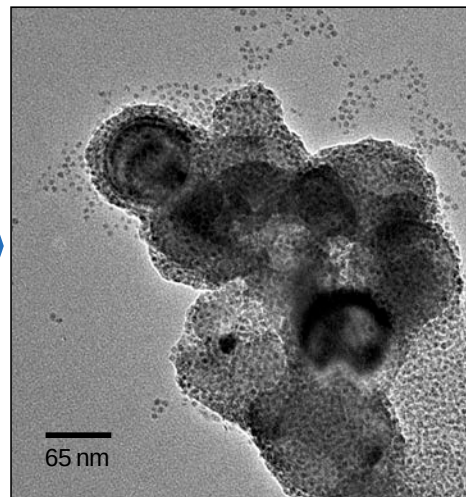
3-Layers



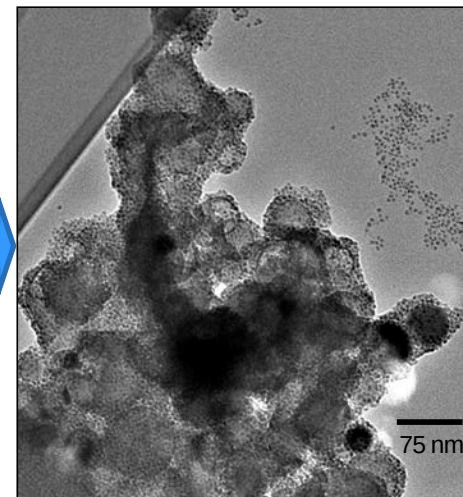
4-Layers



5-Layers

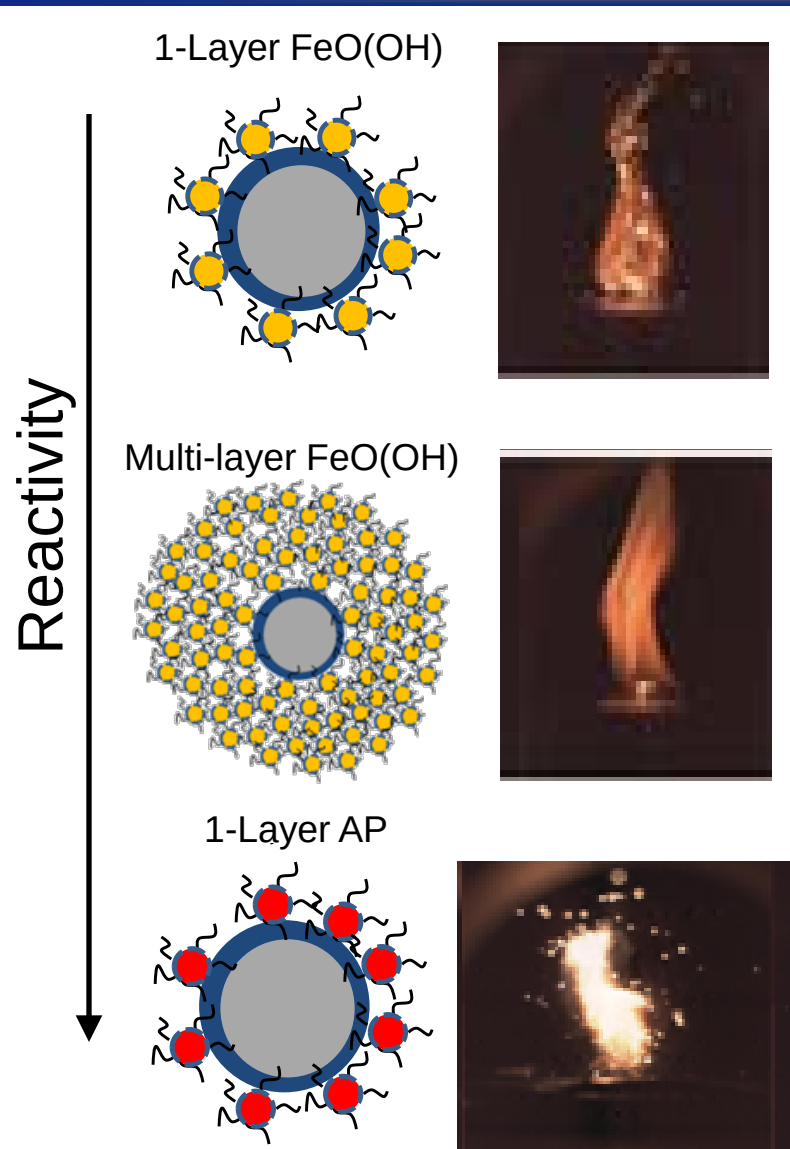


6-Layers





# Summary Energetics



- Protein cages offer the ability to encapsulate and stabilize reactive components, interact with nAl, and quickly deliver components to the surface.
- Ferritin used in a single or multi-layer structure leads to greater energy release and enhanced kinetics.
- Reactivity can be controlled by dialing in the number of protein layers added on nAl or by changing the protein contents.
- Each protein layers can be customized with inorganic materials, oxidizing agents, and/or explosive materials on demand.



# SUMMARY



- This represents basic research support for a broad range of biological science initiatives to provide the background and innovation necessary for the future development of biomaterials, devices and biosensors and their incorporation into future Air Force weapons systems.
- To accomplish this, an increasing emphasis will be placed on research that supports the following areas: biooptics, composites, biocombinatorics, directed self-assembly, and programmability.
- Program Impacts:
  - Understanding structure and mechanism of Leucophore and papillae
  - Investigation of silk structure and function
  - Bio-assembly of catalytic subunits