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Self-Assembly of Hierarchical Cellular Materials from Amphiphilic Triblock Peptides

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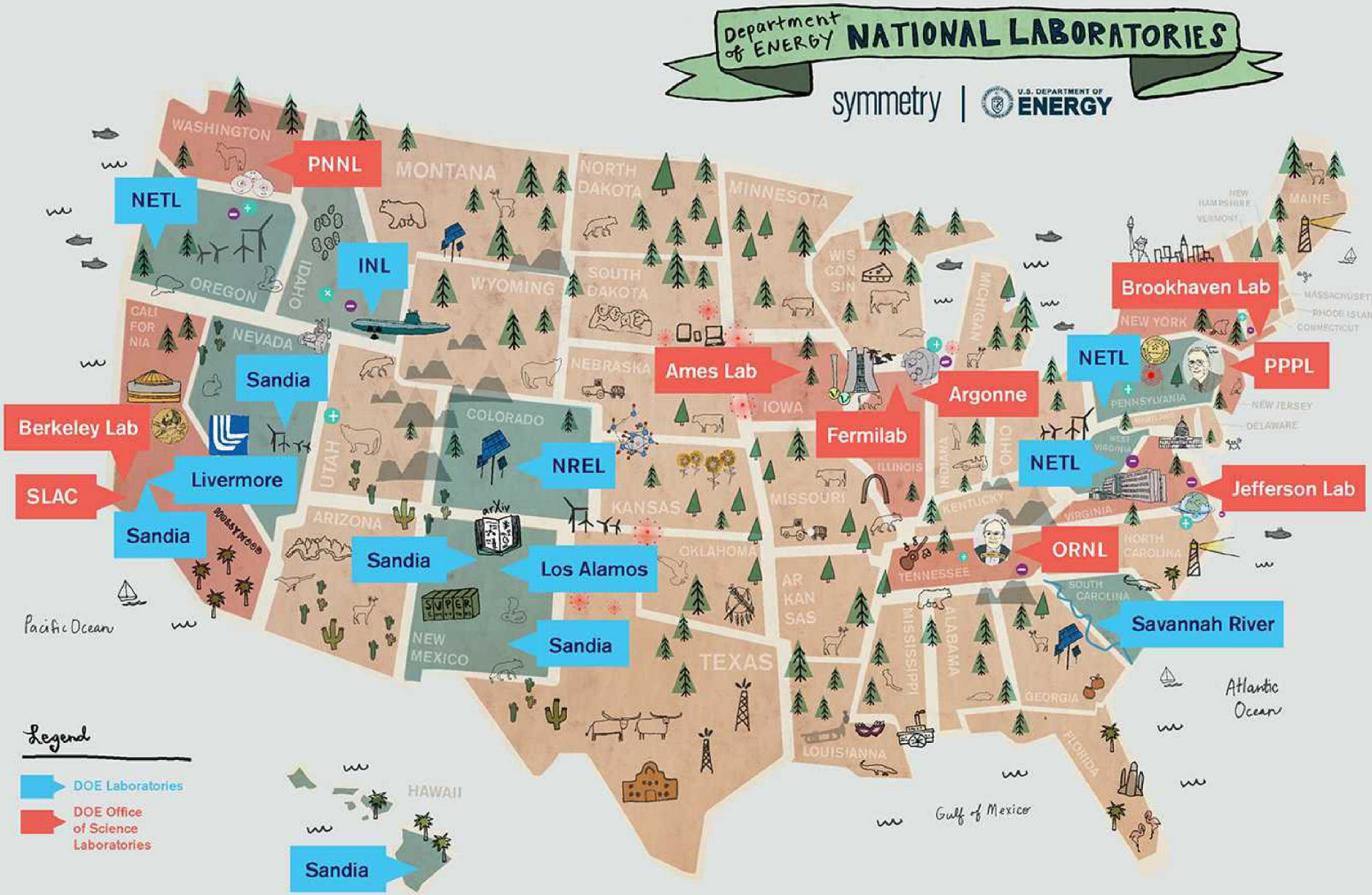
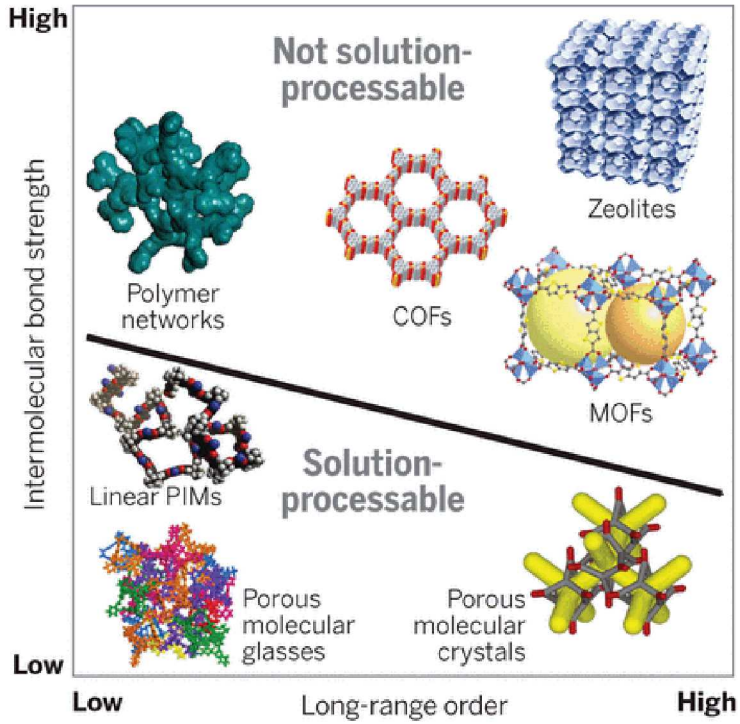
Where is Sandia?



Porous and Cellular Materials

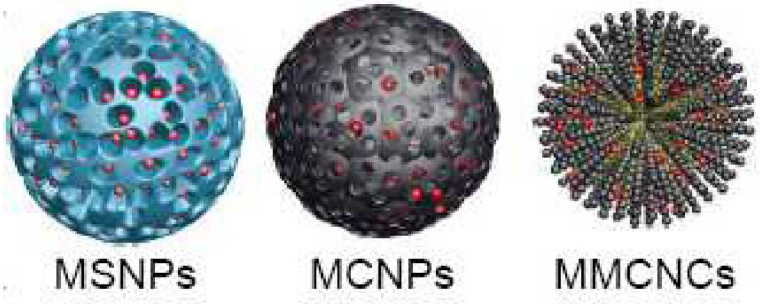
Porous and cellular materials are desirable for a range of technical applications:

- Catalysis
- Insulation
- Chemical Separations and Detection
- Drug Delivery
- Energy Storage



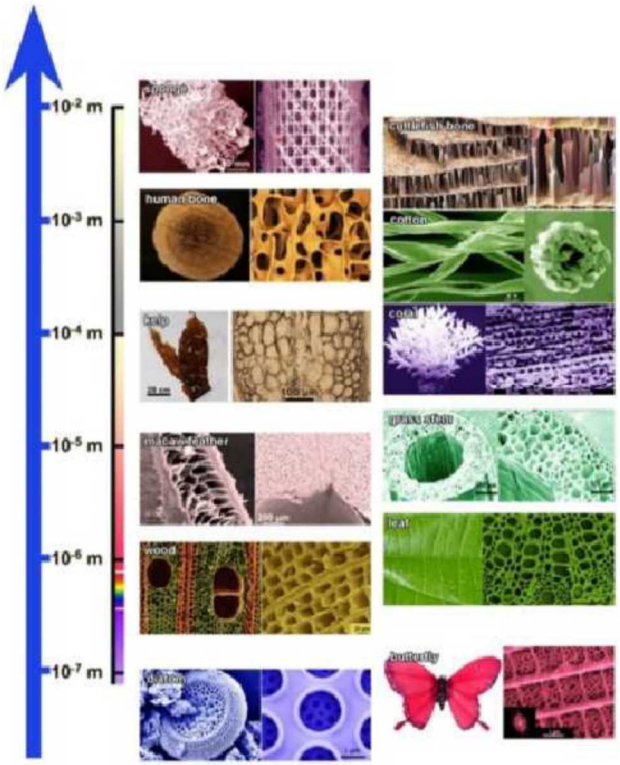
Slater and Cooper. *Science* (2015) **348** (6238) aaa8075

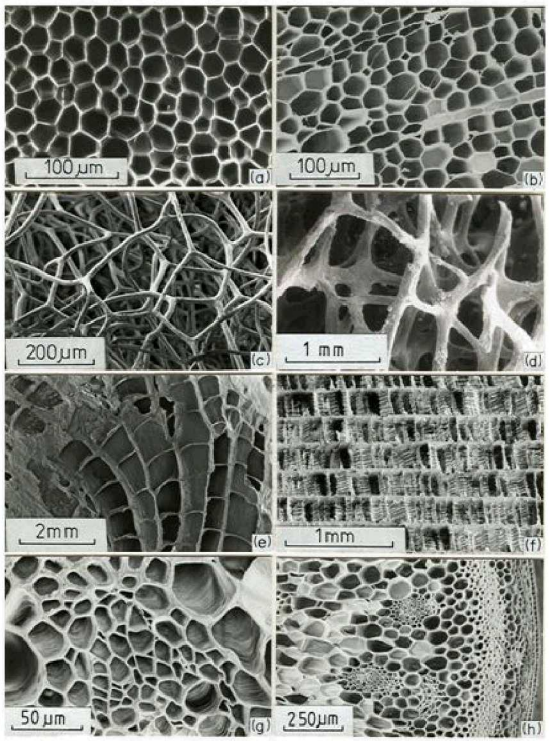
Nanoporous materials for drug delivery



Porous and Cellular Materials

In Nature, cellular materials enable diverse functions in both plants and animals, scaling across multiple length scales.

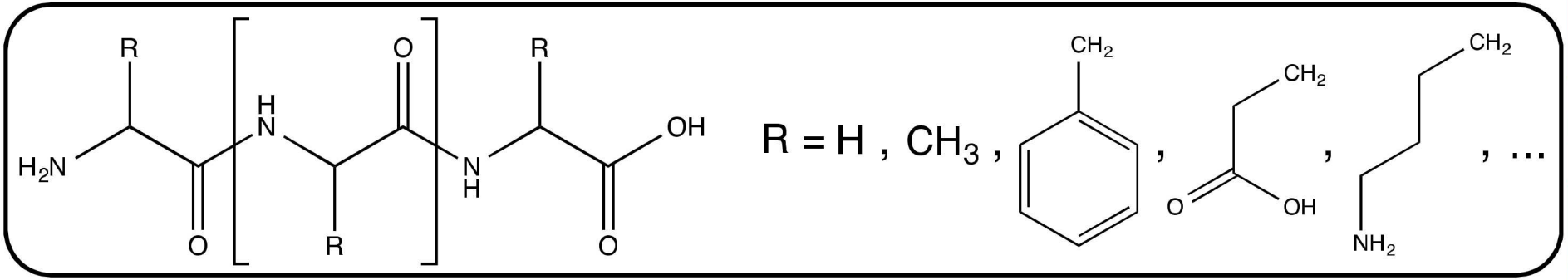




https://images.slideplayer.com/42/11424551/slides/slide_9.jpg

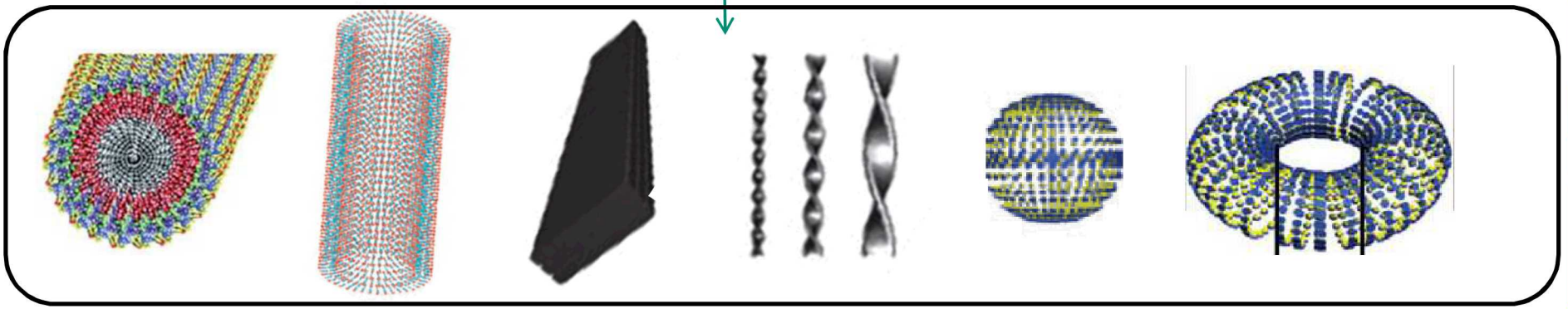
Self-Assembling Peptides Offer Potential for Diverse Molecular Morphology

A complex balance of interactions drives spontaneous self-assembly



electrostatic interactions | hydrogen bonding | aromatic stacking | hydrophobic interactions

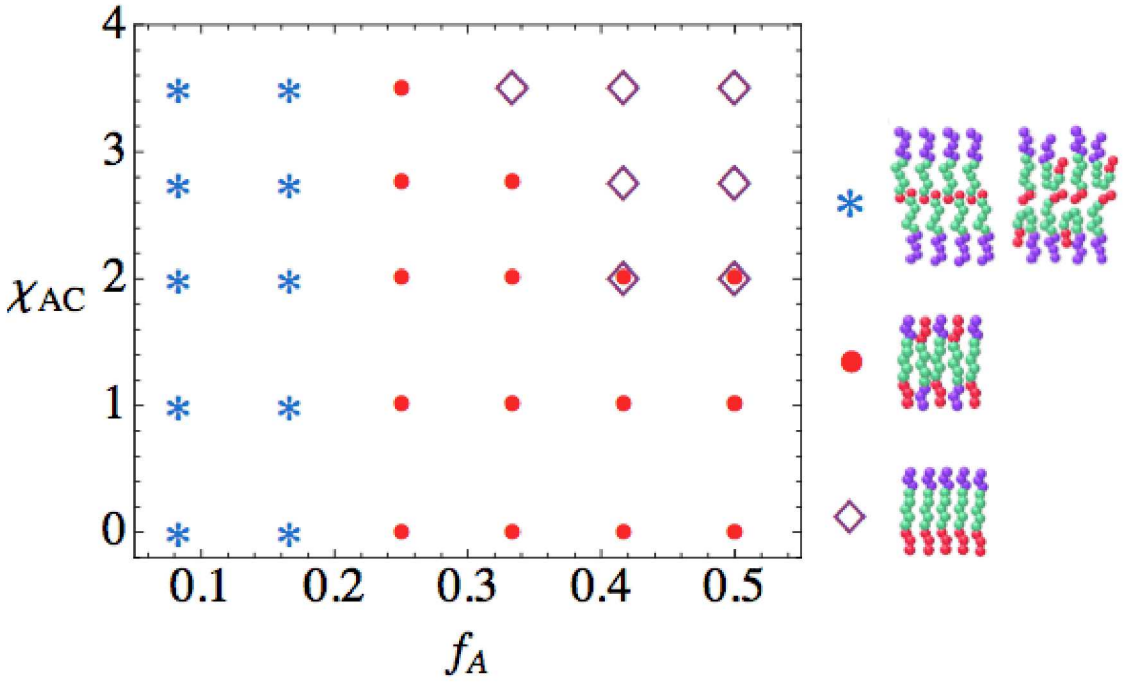
chemical environment



Hamley, I.W. *Soft Matter* **2011**, *7*, 4122; Zhao, X.; *et al. Chem. Soc. Rev.* **2010**, *39*, 3480.

Computational Inspiration for Peptide Synthesis

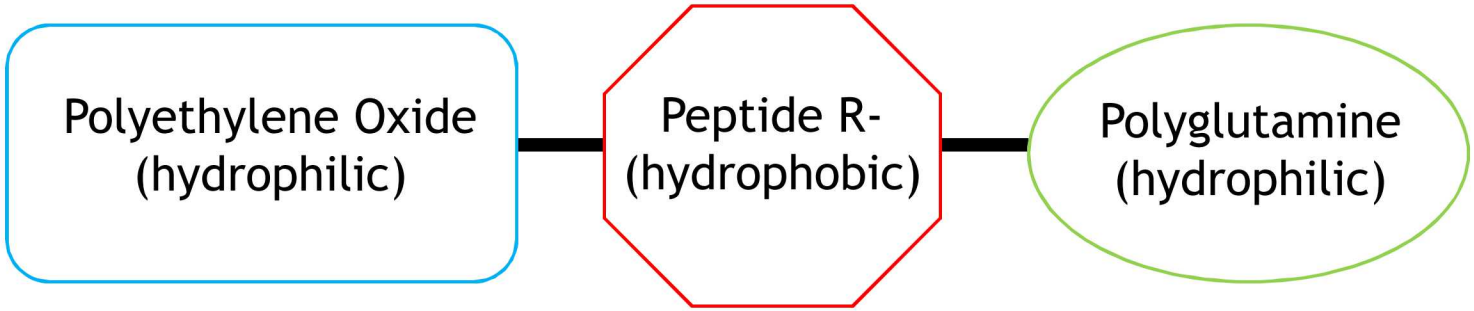
Self-Consistent Field Theory predicts how the relationships between molecular interaction asymmetry and molecular structural asymmetry can affect self assembly.

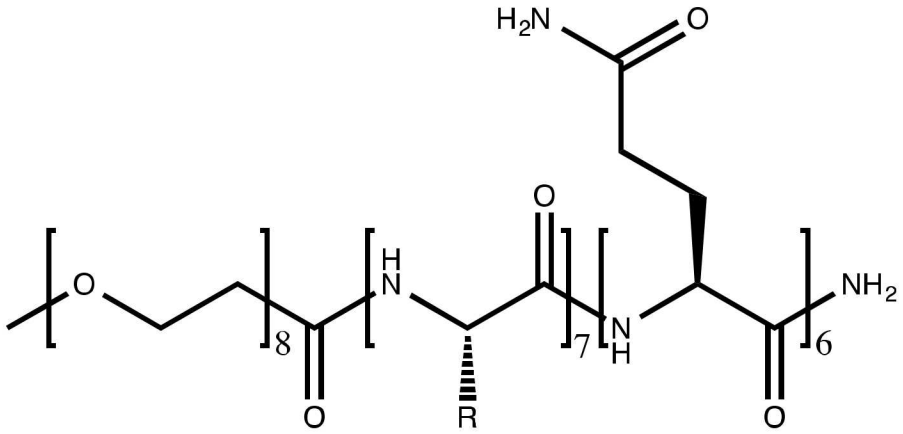


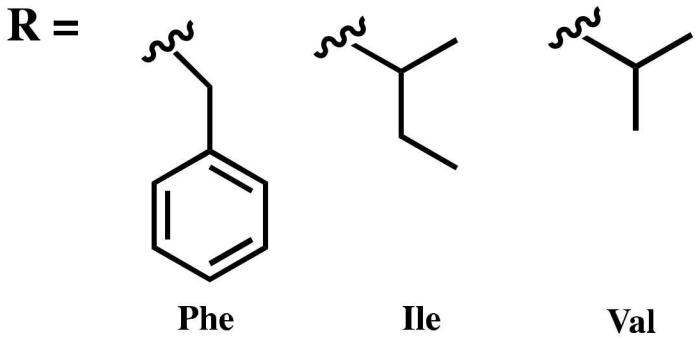
Asymmetric monolayers are desirable for the formation of sheets, which can be key aspects of a porous structure.

Phase diagram as a function of interaction asymmetry χ_{AC} and molecular asymmetry f_A. Markers correspond to symmetric bilayer (stars), symmetric monolayer (circles), and asymmetric monolayer (diamonds).

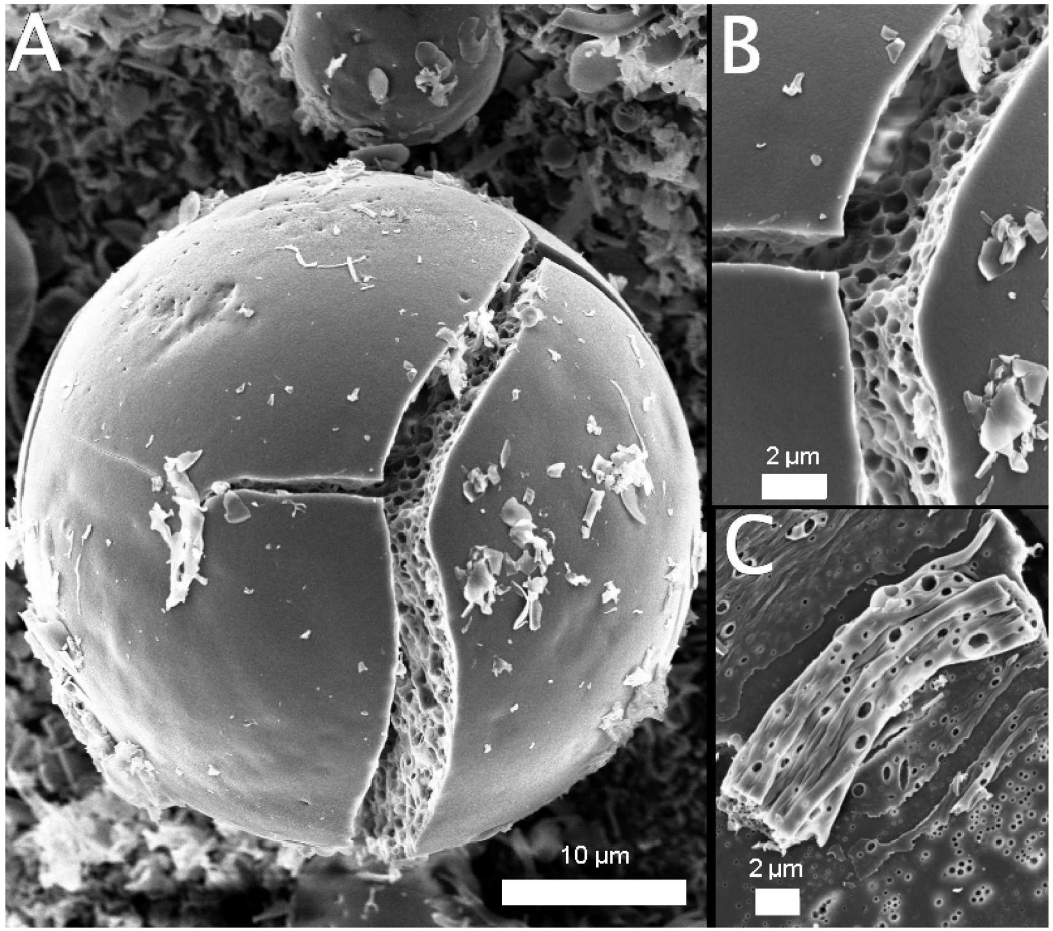
Our Basic Peptide Structure







Self-Assembly of EO_8-Ile_7-Gln_6

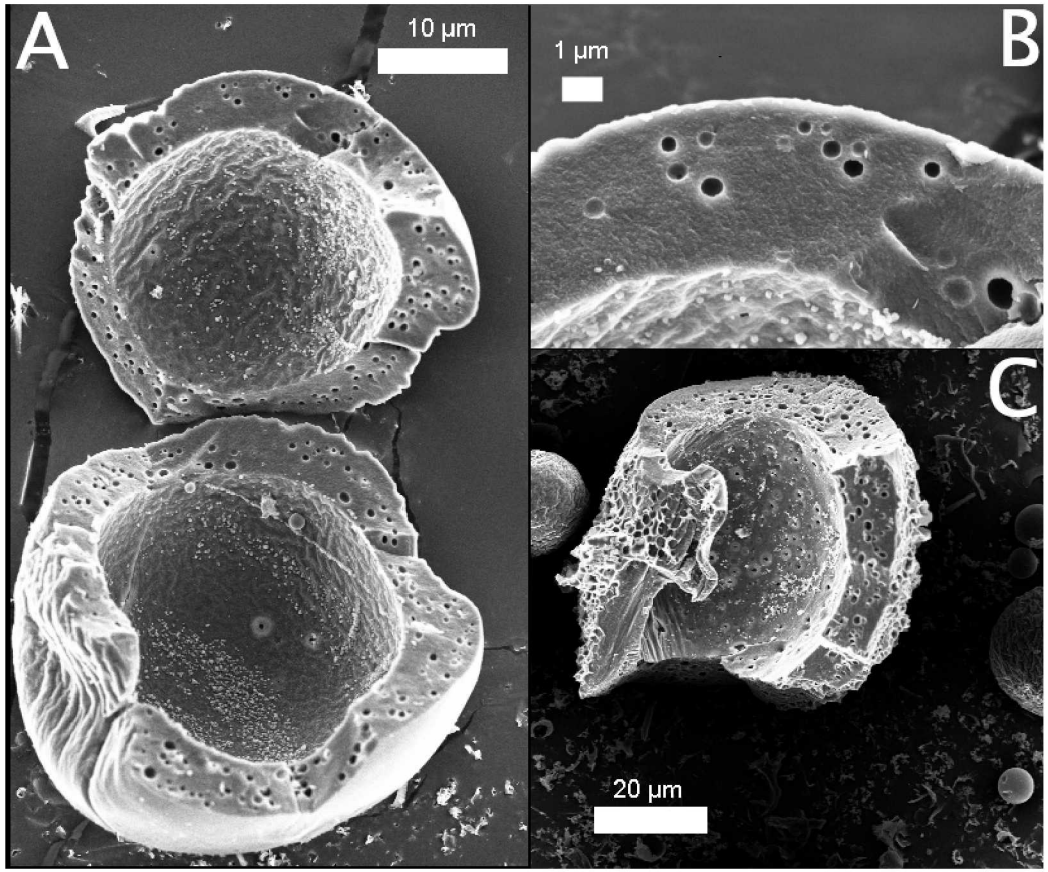


- Peptide dissolved in HFIP at 100mg/mL
- HFIP solution is rapidly diluted 100X into deionized water.
- Precipitated assemblies lyophilized and examined by SEM.

Peptide self-assembles to form large, micro-foam spheres and porous tubular structures.

Strong H-Bonding, moderate size, moderate hydrophobicity.

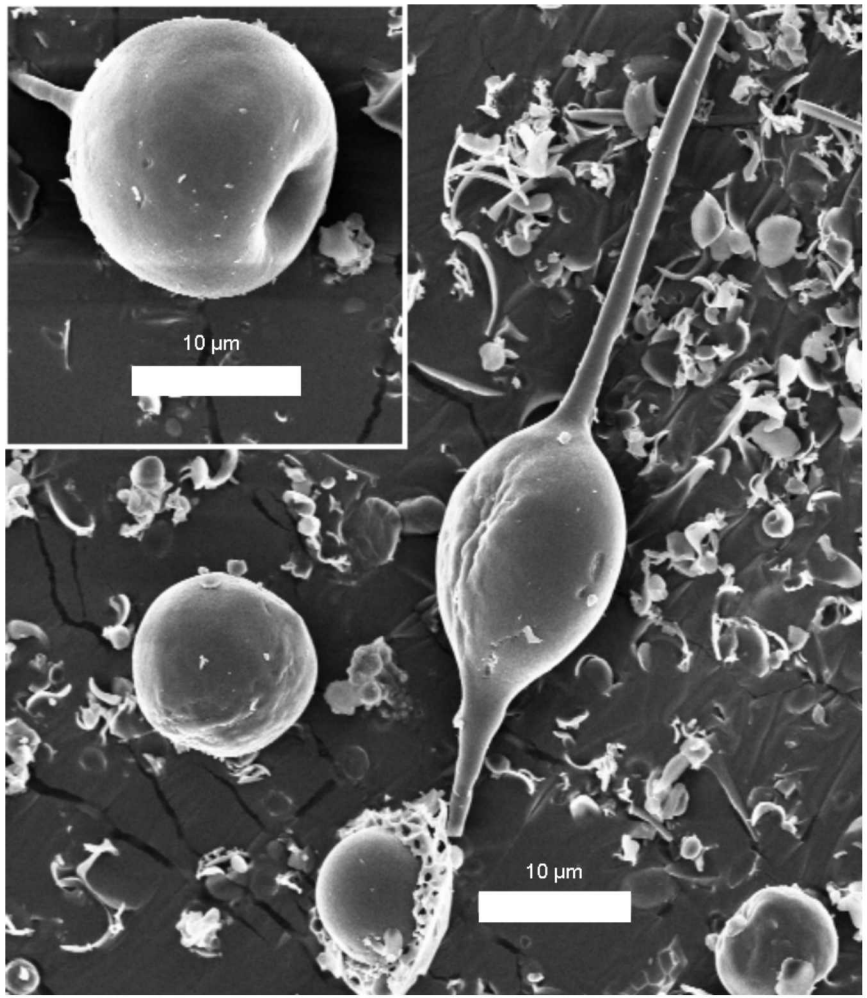
Self-Assembly of EO_8-Phe_7-Gln_6



- Peptide dissolved in HFIP at 100mg/mL
- HFIP solution is rapidly diluted 100X into deionized water.
- Precipitated assemblies lyophilized and examined by SEM.

Strong H-Bonding, large size, strong hydrophobicity.

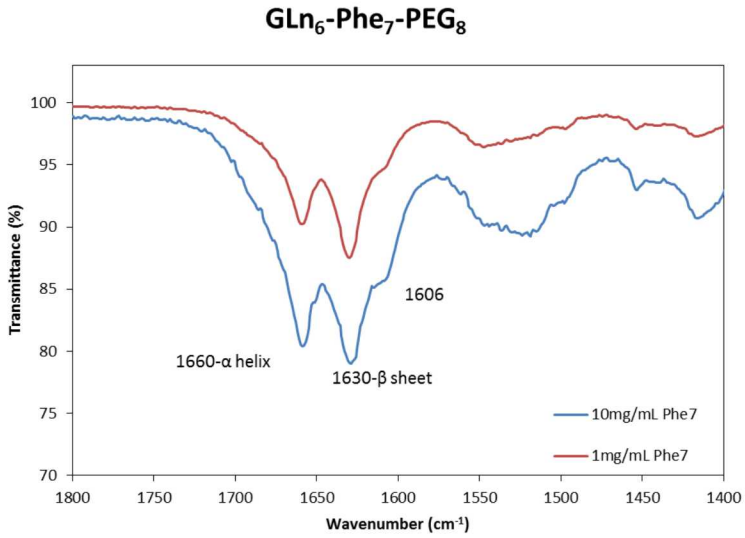
Self-Assembly of EO_8-Val_7-Gln_6



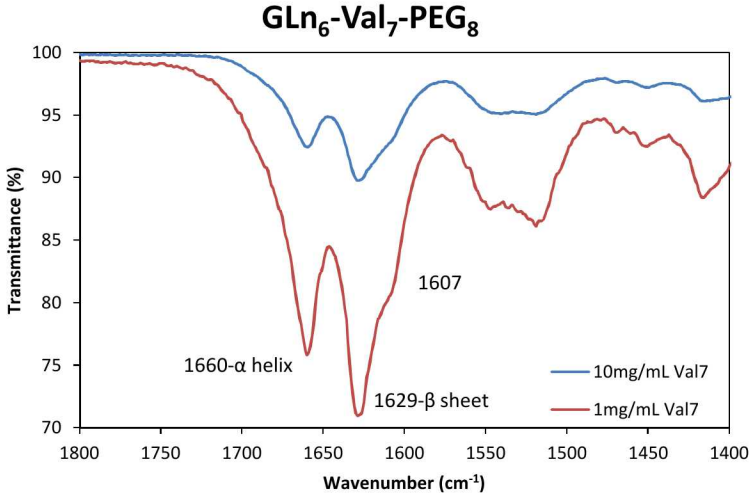
- Peptide dissolved in HFIP at 100mg/mL
- HFIP solution is rapidly diluted 100X into deionized water.
- Precipitated assemblies lyophilized and examined by SEM.

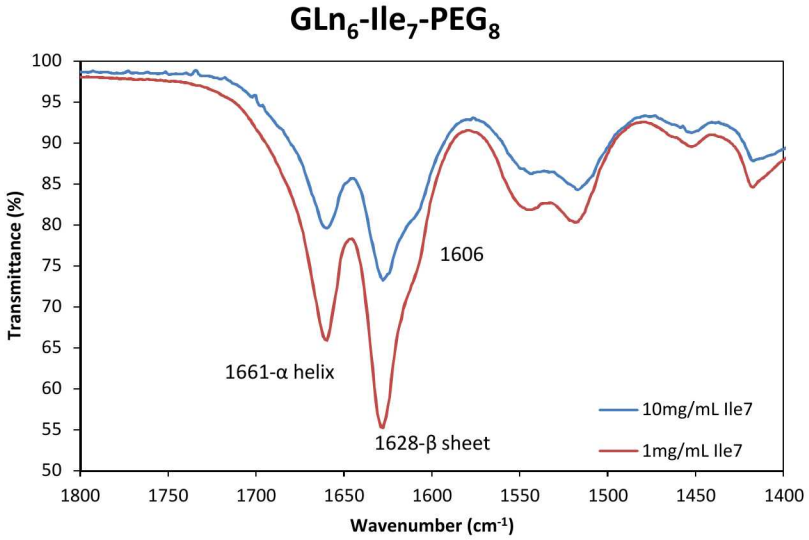
Moderate H-Bonding, smaller size, modest hydrophobicity.

Spectroscopic Characterization of Triblock Assemblies



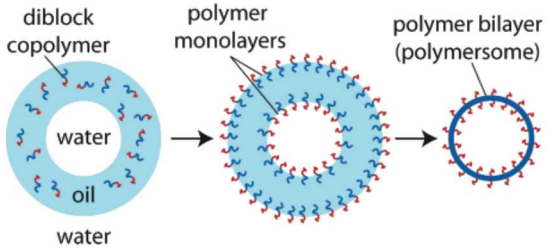
FTIR analysis of the self-assembled peptide triblocks shows strong β-sheet formation.





A Proposed Mechanism for Structure Formation

These structurally diverse, assembled structures are believed to be formed through a collaboration of molecular self-assembly, double micelle formation, and osmotic pressure.



1) Rapid mixing of the HFIP/peptide forms a stabilized double emulsion.

2) HFIP begins to diffuse out of the peptide layer, driving molecular assembly.

- Rapid, strong assembly of the Ile-variant leads to entrapment of smaller HFIP-emulsions within the peptide layer that eventually manifest as porosity.
- Strong assembly, slowed by the steric bulk of the Phe-variant allows for rearrange at the molecular level, allowing entrapped HFIP to escape, reducing secondary porosity.
- With relatively weaker, slower self-assembly in the Val-variant, there is little entrapment of the HFIP within the polymer layer, but significant HFIP entrapment within the larger micelle. Rapid escape of the HFIP from the outermost layer of the peptide layer forms a "skin" on the peptide layer.

3) Osmotic pressure from HFIP trapped within the micelle leads to deformation of weaker structures or perforation/breakage of more robust micelles.

Take Away Messages

- ✓ Guided by SCFT modeling, systematically-varied ABC triblock peptides were prepared.
- ✓ By varying the size, hydrogen bonding affinity, and hydrophobicity of the B-block in these triblock molecules, distinctive self-assembled morphologies were obtained during aqueous dilution of HFIP-peptide solutions.
- ✓ Structures demonstrated unusual, hierarchical porosity with nanopores forming in the walls of microscale micelles.
- ✓ The mechanisms behind the formation of these unique structures is believed to involve a collaboration of molecular self-assembly, double micelle formation, and osmotic pressure.

Applications of the diverse functionality imparted by peptide chemistry to create multi-component molecular building blocks holds promise in using self-assembly to create new hierarchical cellular materials.

Acknowledgements and Thanks

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