



Pathway Complexity in Supramolecular Polymerisation of Multidomain Peptide Amphiphiles

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Precise control over the special and temporal aspects of peptide self-assembly is fundamental to developing adaptive supramolecular materials that emulate the dynamic behavior of biological systems. Although peptide-based assemblies show great potential for applications ranging from biomaterials to synthetic protocells, achieving programmable control over formation and growth under non-equilibrium conditions remains a significant challenge. Here, we present a light-responsive strategy that couples enzymatic reaction networks with peptide self-assembly to direct supramolecular structure formation with spatiotemporal precision.

Our approach uses light-induced glucose release as an external trigger to initiate an enzymatic cascade that generates localized proton release. The resulting dynamic pH change activates the self-assembly of pH-responsive peptide building blocks, enabling temporal regulation of supramolecular organization without direct chemical intervention. By integrating a lipid bilayer interface into the system, nucleation is spatially confined to membrane surfaces, allowing peptide assembly to be selectively initiated at biologically relevant interfaces. This interfacial control provides a means to decouple nucleation from bulk assembly, resulting in localized growth of supramolecular peptide structures.

The combination of photochemical activation, enzyme-mediated proton generation, and membrane-directed nucleation establishes a versatile platform for regulating peptide self-assembly in dynamic environments.

