



Control Over Peptide Based Nanostructures for Biomedical Applications

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Received: May 28, 2021

Published: June 01, 2021

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Programming the supramolecular polymerization of building blocks in aqueous medium is a prerequisite to create tunable and well-ordered nanomaterials with multiple functionalities for potential applications in biomedical field. The most sophisticated structures in Nature are often obtained by highly ordered and controlled self-assembly of molecular units in all dimensions, in which the interplay between various weak non-covalent interactions, including hydrogen bonds, ionic bonds, hydrophobic interactions, and van der Waals interactions play a key role. The exploration of bioinspired assemblies not only allows for mimicking the structures of living systems, but it also leads to functions for applications in different fields that benefit mankind. In the past decades, efforts to understand thermodynamically controlled self-assembly of artificial small molecules have produced a large library of candidates for various biomedical and materials-based applications. More recent investigations, however, have shown that kinetically favored metastable species can also exist in competition with the thermodynamic product, which strongly influences the outcome of the self-assembly process and, ultimately, the nanoscale morphology. Control over the dimensions of self-assembled nanostructures by different processing methodologies has important implications for the performance of functional devices. In order to furnish functional synthetic supramolecular biomaterials, it is now unexceptional to combine self-assembling building blocks with molecules possessing coveted functional property, such as selective recognition of a cell surface receptor, antigenicity or enzymatic activity. A recent bias in supramolecular chemistry has focused on examining the interactions between nanomaterials and biological systems that rely on the size and shape of nanostructures. However, it remains challenging to program the self-assembly of building blocks into nanostructures with specific size and shape. Among all the

renowned building blocks, peptides are especially desirable candidates for biomaterials applications because of their unique facets such as: a) they are built on naturally occurring amino acids that are biocompatible and biodegradable; b) they can be synthesized using versatile and cost-effective methods; c) they are highly responsive to the environmental conditions; d) based on the amino acid sequence, they self-assemble into a wide variety of nano- and mesoscopic structures such as micelles, vesicles, fibrils, nanosheets, ribbons and nanotubes as well as numerous secondary structures such as β -sheet, α -helix, coiled coils, etc. Generally, self-assembly of peptides follows a spontaneous thermodynamic pathway based on the synergistic effect of different intermolecular non-covalent interactions. The energy landscape of the finally organized nanostructures not only builds upon the fine adjustment of weak non-covalent interactions but can also be regulated by tuning of external variables such as pH, temperature, counterions, concentration, solvent, and thermo-, redox-, photo-responses. Fine tuning of selected experimental parameters allows the isolation of metastable self-assembled structures and ultimately controls the kinetics of the transformation into the thermodynamic product. Kinetic control of peptide assembly is necessary not only for gaining insights into the mechanistic pathways, but also to create dynamic materials. Currently, these harmonizable nanostructures have gained rigorous attention due to their wide variety of applications in biomedicine such as for drug-delivery, tissue engineering, antimicrobial coating and bioinspired nanotechnology (hybrid materials for optoelectronics, nanocatalysis, biosensing etc).

Volume 5 Issue 7 July 2021

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