



Photoinduced Morphological Transformation in the Azobenzene-Cored Hybrid Peptides

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The discovery of template-directed peptide self-replication has opened a new perspective on the origin of life research. It has opened up the innumerable avenues for the design of peptide-based molecules as potential progenitors of the present DNA-based world. Herein, we present stimuli-responsive pseudopeptides that undergo reversible morphological transition upon photoirradiation. We designed and synthesized simple photo-responsive designer azobenzene-cored pseudopeptides that self-assemble to vesicles and fibers. The tryptophan (Trp)-appended azobenzene-cored pseudopeptide assembles to vesicles in its *trans* form, while irradiation with light causes isomerization to *cis* form, leading to a larger number of vesicles. This apparent increase in the number of vesicles has a striking similarity to biological self-replication. In addition, we also report the light-induced transformation of right-handed helical fibers into vesicles in a Phenylalanine (Phe)-appended pseudopeptide and spherical aggregates into vesicles in a Leucine (Leu)-appended pseudopeptide. Detailed high resolution microscopic imaging (scanning electron, transmission electron, atomic force and confocal microscopies), and spectroscopic studies are utilized for probing the self-assembly. Confocal imaging without any external probe, utilizing the autofluorescence of the self-assembled state, stemming from the aggregation of chromophores, enabled us to probe the morphological transformation. SEM and Confocal microscopic imaging of vesicles illustrated the fission and fusion of vesicles in case of the Trp-appended pseudopeptide. The self-assembly of azobenzene-cored pseudopeptides to vesicles and fibers arises from its intrinsic property to associate. The hydrogen-bond-directed self-assembly is evident from the single crystal X-ray structure analysis of leu-appended azobenzene-cored pseudopeptides.

