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MAINZ. GERMANY
FROM DYNAMIC STRUCTURES TO FUNCTIONAL MATERIALS

From Nanofibers to Nanotoroids: Visible-Light-Regulated Pathway Selection in Fluoroazobenzene–Peptide Self-Assembly

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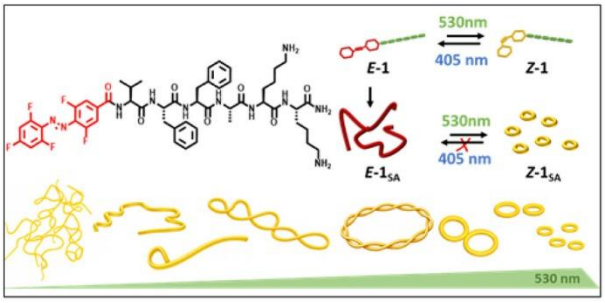
Controlling supramolecular pathway selection is crucial for understanding and designing adaptive peptide-based materials. Here, we report a visible-light-responsive fluoroazobenzene-peptide conjugate that exhibits topology-dependent self-assembly, providing insights into pathway complexity and structural memory in peptide systems. The molecular design consists of a pentafluorinated azobenzene photoswitch conjugated to the amyloidogenic peptide sequence VFFAKK. In aqueous media, the linear E-isomer self-assembles into β-sheet-rich nanofibers through a cooperative nucleation–elongation mechanism. Upon irradiation with visible light, photoisomerization introduces a conformational change that redirects the assembly pathway toward discrete nanotoroidal architectures. Microscopic and spectroscopic investigations reveal a remarkable nanofiber-to-nanotoroid transformation accompanied by reorganization of the supramolecular packing. Unlike the fibrillar state, the nanotoroidal assemblies are kinetically trapped and exhibit persistent structural memory, highlighting the role of molecular geometry in governing access to distinct regions of the supramolecular energy landscape. Computational studies suggest that the bent geometry of the Z-isomer, together with fluorine-mediated interactions, promotes curvature and stabilizes the toroidal topology. More broadly, this work establishes a strategy for navigating complex self-assembly landscapes and accessing nonequilibrium states through external stimuli, offering new opportunities for the development of adaptive and responsive peptide-based materials.



[1] D. Gupta, *et al*., *Chem. Mater.* **34**, 4456 (2022).
[2] G. Hooda, *et al*., *Chem. Mater.* **xx**, xxxx (2026).