Computational and theoretical modeling of pH and flow effects on the early-stage non-equilibrium self-assembly of optoelectronic peptides[1]

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Self-assembling π-conjugated peptides are attractive candidates for the fabrication of bioelectronic materials possessing optoelectronic properties due to electron delocalization over the conjugated peptide groups. We present a computational and theoretical study of an experimentally-realized optoelectronic peptide that displays triggerable assembly in low pH to resolve the microscopic effects of flow and pH on the non-equilibrium morphology and kinetics of assembly. Using a combination of molecular dynamics simulations and hydrodynamic modeling, we quantify the time and length scales at which convective flows employed in directed assembly compete with microscopic diffusion to influence assembly. We also show that there is a critical pH below which aggregation proceeds irreversibly, and quantify the relationship between pH, charge density, and aggregate size. Our work provides new fundamental understanding of pH and flow of non-equilibrium π-conjugated peptide assembly, and lays the groundwork for the rational manipulation of environmental conditions and peptide chemistry to control assembly and the attendant emergent optoelectronic properties.

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