

pH-Controlled Chiral Packing and Self-Assembly of a Coumarin Tetrapeptide

Remy F. Lalisse, McKensie L. Mason, Tyler J. Finnegan, Jon R. Parquette, and Christopher M. Hadad

Department of Chemistry and Biochemistry, Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, United States

Self-assembled nanostructures with controllable secondary structural features is a challenging objective in supramolecular chemistry. A coumarin-tetrapeptide conjugate, **EFEK(DAC)-NH₂ (1)**, is reported to undergo a pH-dependent interconversion between nanotubes and nanoribbons. An examination of zeta potential measurements, circular dichroism (CD) spectra, and microscopy imaging (TEM and AFM) identified three different self-assembly regimes based on pH: (1) pH 2–5, positively charged, left-handed helical nanotubes; (2) pH 6–8, negatively charged, righthanded helical nanoribbons; and (3) pH 9, a monomeric/disassembled peptide. The assembly process was driven by β -sheet aggregation and π - π interactions leading to the formation of nanoribbons, which progressively wound into helical ribbons and laterally grew into smooth nanotubes as the pH decreased. Density Functional Theory (DFT) was used to predict the protonation state at the pH of 2–5, with a secondary structure of nanotubes. Several predicted starting conformations for a dimer system of **1** were used to simulate the electronic properties of the system and guide future mechanistic studies of self-assembly.