Self-Assembly of Directional Porphyrin Arrays in Water via Cyclodextrin-Based Host-Guest Interactions

Janarthanan Jayawickramarajah, Department of Chemistry, Tulane University

Modulating Inter-Porphyrin Spacing via Guanine Quadruplex Assembly*:** One goal of this project is to self-assemble water-soluble porphyrin arrays wherein the inter-porphyrin distances can be readily modulated. ***We have developed a straightforward strategy that harnesses β-cyclodextrin/adamantane host-guest interactions and guanine quadruplex formation to prepare water-soluble porphyrin nanowires with controlled porphyrin spacing

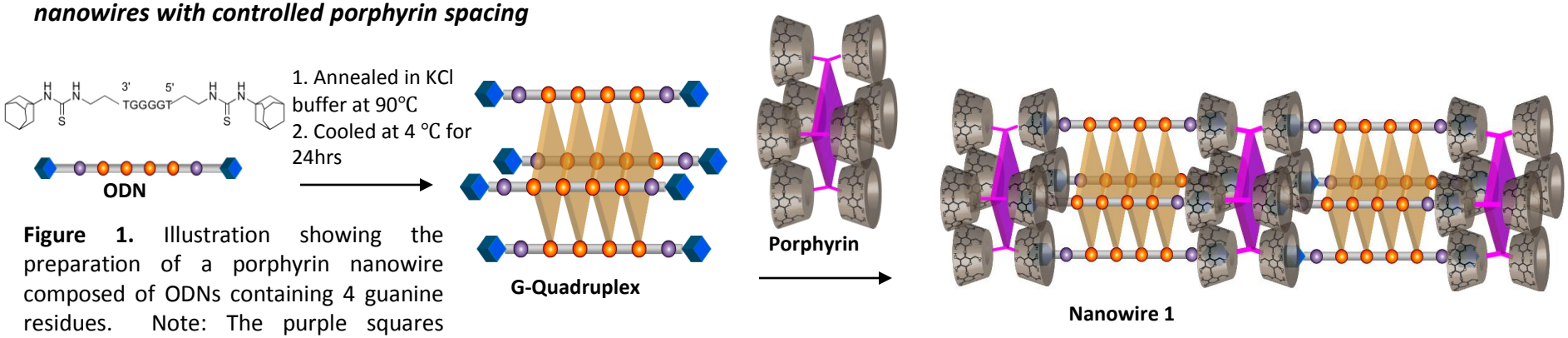

Figure 1. Illustration showing the preparation of a porphyrin nanowire composed of ODNs containing 4 guanine residues. Note: The purple squares represent the porphyrin core, and light brown squares represent the G-quartets.

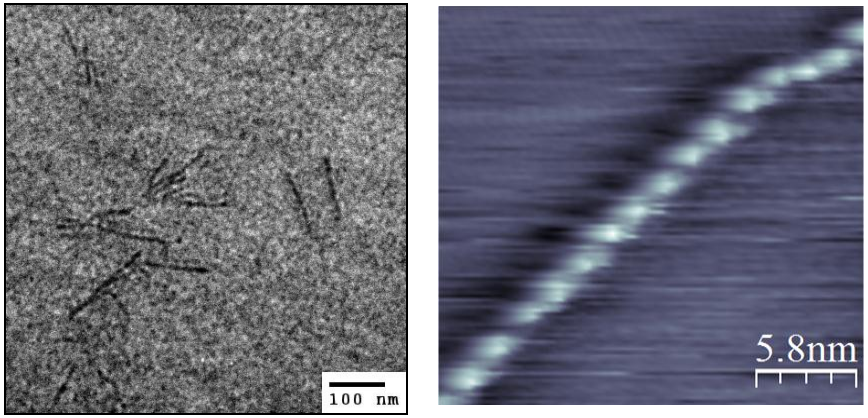

Figure 2. Cryo-TEM (left) and STM (right) images of nanowire **1** (5μM).

Specifically, a guanine rich oligonucleotide (ODN) strand containing adamantane head-groups assembles into a tetramolecular quadruplex in the presence of potassium cations (KCl buffer), resulting in the projection of four adamantane guests from each face. The quadruplex is then exposed to a porphyrin that projects four cyclodextrin hosts from each face. The resultant array has been probed via circular dichroism, STM, and TEM studies.

Importantly, the number of guanine residues in the parent ODN sequence dictates the inter-porphyrin spacing, with each guanine extending the spacing by 0.34 nm. Further, the number of guanines also has an influence on the linearity of the nanowires. For instance, ODN strands with only 2 guanines form serpentine like nanoarrays while strands with 4 guanines are more linear.

Our next goal will be to synthesize quadruplexes that only project adamantane arms from one termini and use these and other end-capping agents to modulate the length of the self-assembled nanowires.