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

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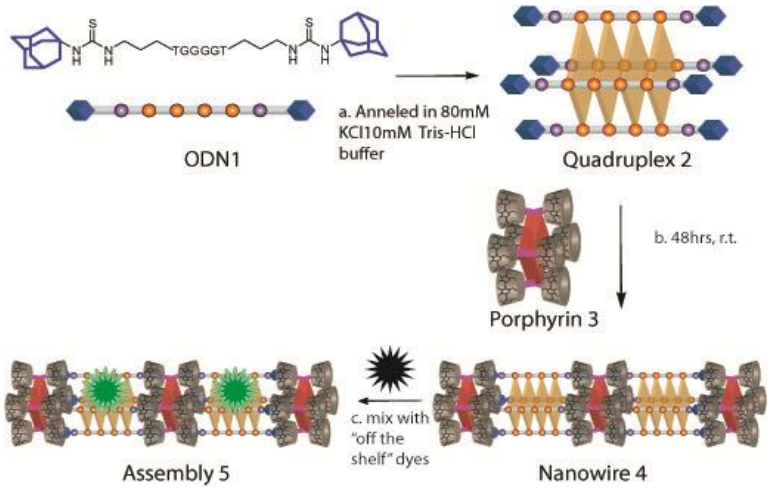

An important aim of this project is to assemble defined multi-chromophore arrays in water that show broadband absorption and interesting fluorescence emission properties. During the current funding period, ***we have designed a hierarchical assembly strategy that harnesses multiple assembly modes (including DNA base-pairing, host-guest interactions, electrostatic interactions, and metal ion coordination) to yield photonic porphyrin-DNA arrays.***

Scheme 1. Hierarchical construction of multi-chromophore containing DNA-based assembly **5**. (a) Self-assembly of bis-adamantane flanked ODN **1** into tetramolecular quadruplex **2.** (b) Host-guest interactions derived assembly of quadruplex **2** and porphyrin **3** into multi-porphyrin containing nanowire **4**. (c) Incorporation of DNA-binding chromophores to form assembly **5**.

The self-assembly starts with oligonucleotide (ODN) **1**, functionalized with two adamantane arms. ODN **1** self-assembles into a tetramolecular quadruplex **2** in the presence of templating potassium ions (Scheme 1). Second, incubation of quadruplex **2** with porphyrin **3** decorated with eight β-cyclodextrin (β-CD) arms leads to the formation of a one-dimensional porphyrin-containing DNA supramolecular nanowire as a result of multivalent β-CD-adamantane based host-guest interactions. These assemblies are then further non-covalently functionalized with off-the-shelf “signal-on” DNA-binding dyes (such as SYBR Green , SG).

The self-assembly of fluorescent array **5** can be observed in the gel study shown in Figure 1 (bottom), where a new slow moving broad band is seen (Lane 2). This band shows orange fluorescence (composed of a mixture of green fluorescence from the SG/DNA complex and red fluorescence from the porphyrin unit). The fluorescent nature of this assembly is also clearly seen in solution (see Figure 1, top)

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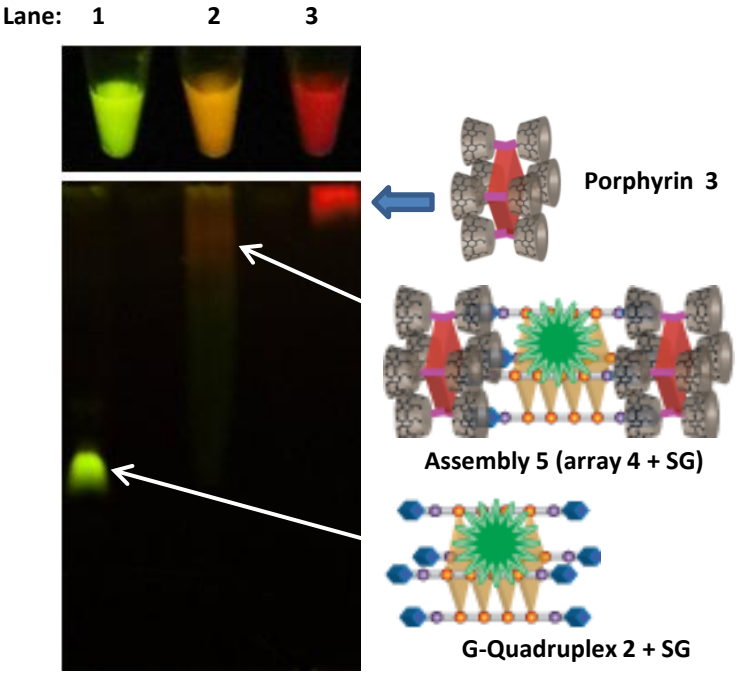

Figure 1. 15% non-denaturing PAGE. Lanes 1 through 3 correspond to SG pre-mixed with quadruplex **2**, assembly **4**, and porphyrin **3**, respectively. Gel was imaged upon excitation with a UV-lamp (λ_{max} = 365 nm).