Supporting Information

Photonic DNA-Chromophore Nanowire Networks: Harnessing Multiple Supramolecular Assembly Modes

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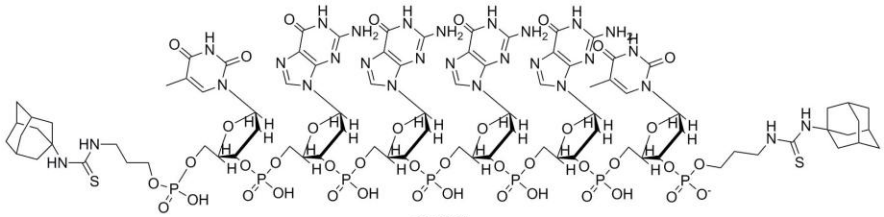
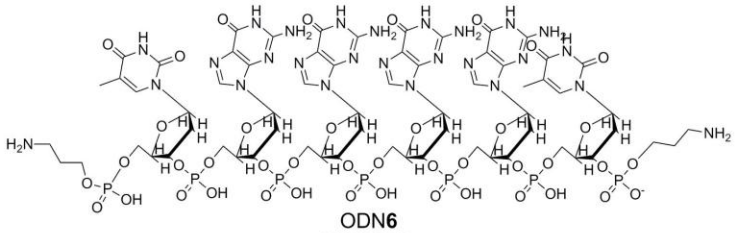
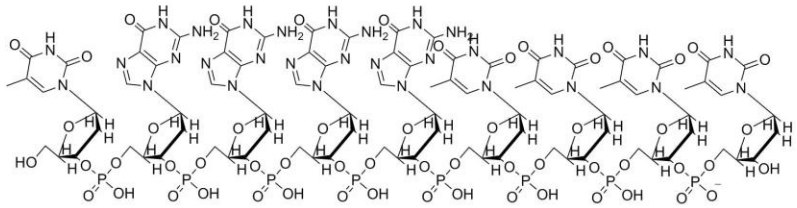
1. Structure and Characterization of ODNs



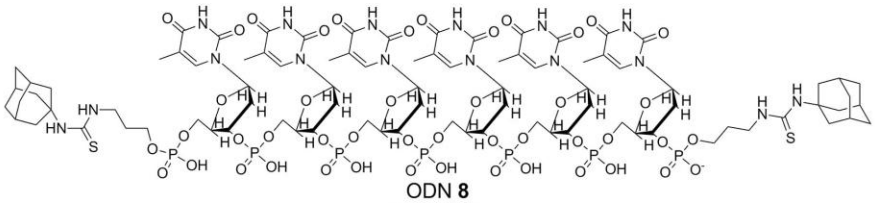
ODN**1**
MW: 2523.00



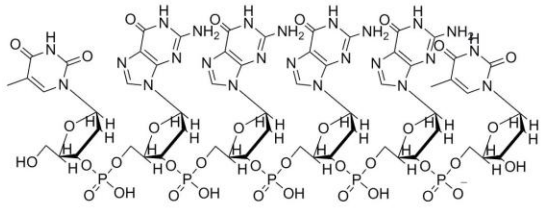
ODN**6**
MW: 2136.39



ODN**7**
MW: 2774.82



ODN **8**
MW: 2422.95



ODN **9**
MW: 1862.24

Scheme S1. Structures of ODNs **1, 6, 7, 8,** and **9.** Note**:** *Calculated mass* $[M-H]^-$ is included.

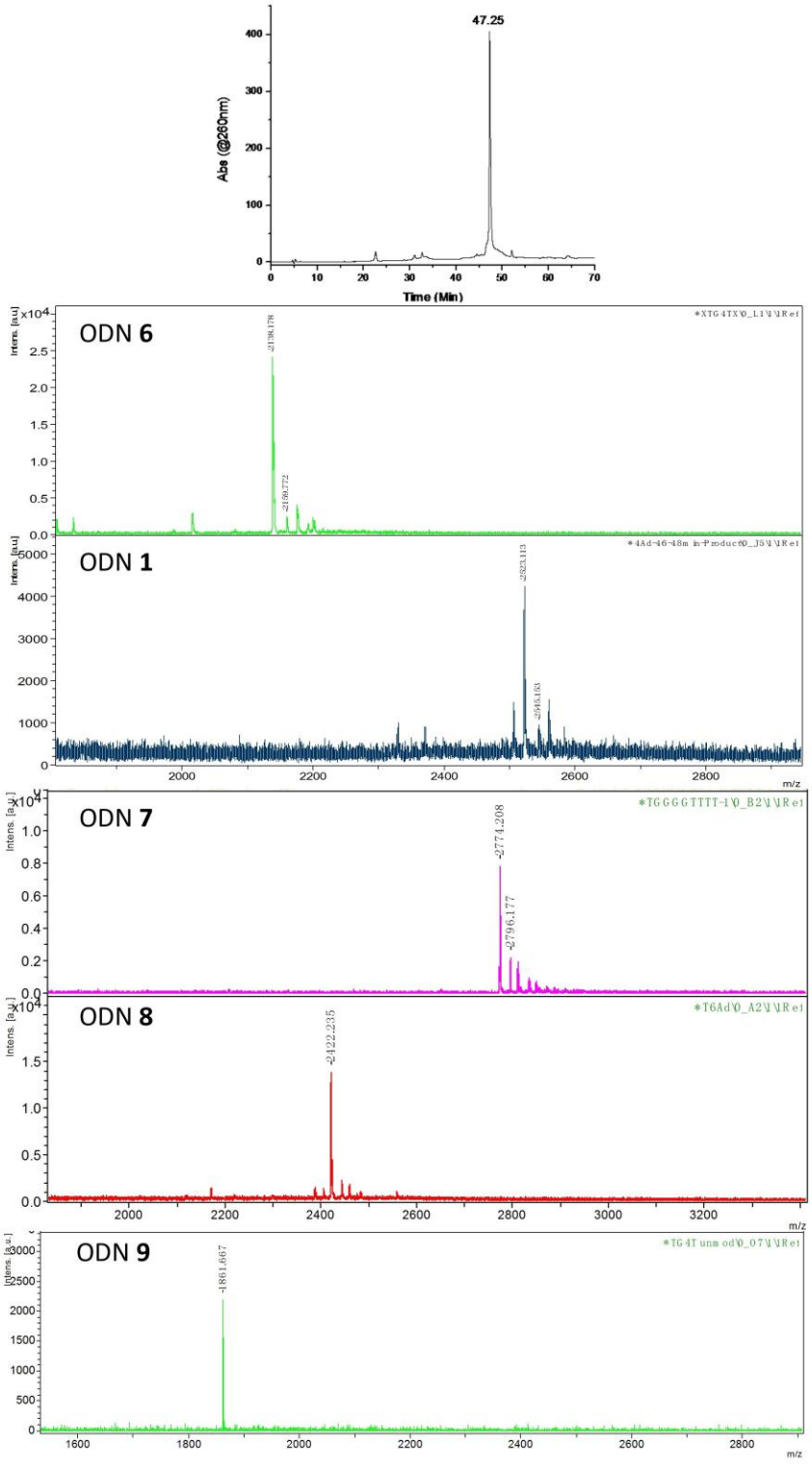
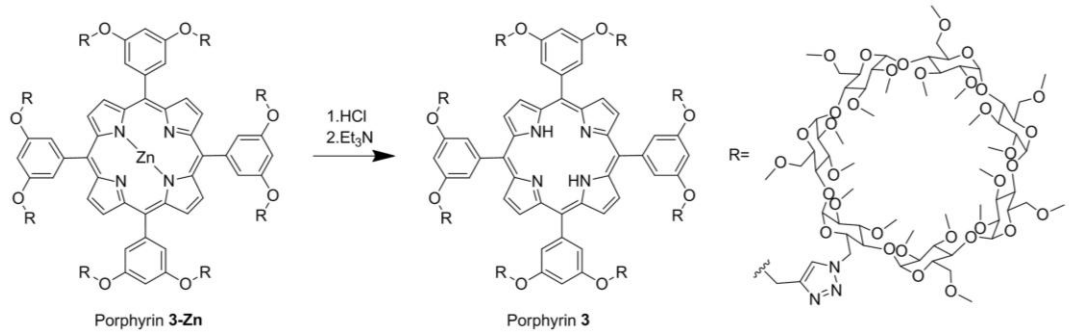


Figure S1. top: A representative RP-HPLC Trace of ODN **1**. **bottom:** MALDI-TOF mass spectra of ODNs **6**, **1**, **7**, **8**, and **9** respectively.

2. Synthetic scheme and MALDI-TOF mass spectra of Porphyrin 3



Scheme S2. Synthesis of porphyrin 3.

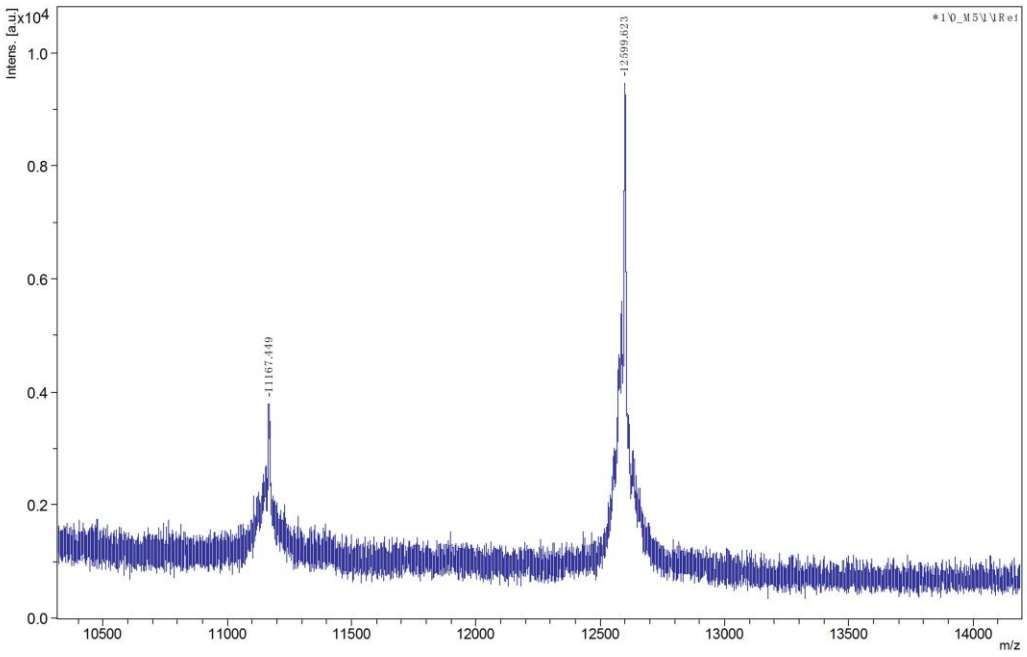


Figure S2. MALDI-TOF mass spectra of porphyrin **3**. The parent peak at 12599.6 Da ($M+K^+$) corresponds to porphyrin **3**. The less intense peak at *m/z* = 11167.4 Da corresponds to MALDI-induced fragmentation of one PM-βCD arm of **3** (possibly via cleavage of the C-N bond between the triazole nitrogen and the 6'-carbon on the glucose unit of βCD); calculated m/z of the resulting fragment = 11166.2 Da).

3. Supplementary AFM Images

As shown on the following AFM image (Fig. S3 a), 5 different height profiles of the branching points were collected. These branching points have apparent heights (Fig. S3 b) ranging from 1.25-1.87 nm, values that are close to the height of a single wire.

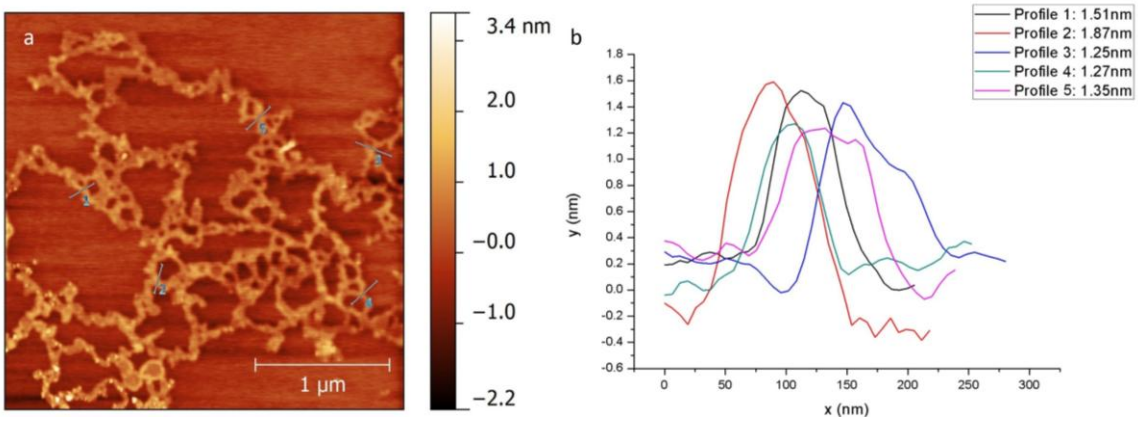


Figure S3. a) 3x3 µm^2 AFM image of assembly **4** on mica substrate. **b)** profiles 1-5 show the height profiles collected at lines 1-5 on panel a.

In an effort to insure that the nanowires and nanowire networks observed for array **4** were indeed due to the presence of quadruplex **2** and not single stranded ODN **1**, we performed control AFM studies where non-quadruplex forming control ODN **8** was incubated with porphyrin **3**. In general, these control studies showed amorphous nanostructures (see " the "dot-like" morphology shown in Figure S4a and height profile on S4c. In one case, a wire-like structure was observed (Figure S4a), however, this structure displayed apparent heights between 0.3~0.6 nm (Figure S4b). Importantly, these values are much shorter than the heights observed for nanowire **4** (height of ~1.5 nm). These studies, taken in conjunction with the thermal stability of quadruplex **2**, give evidence for the notion that

the nanowires and networks observed for array **4** are due to the self-assembly of quadruplex **2** with porphyrin **3.** In addition, a control AFM image of only quadruplex **2** (Figure S5a) collected under the same conditions does not show any discernable nanostructures.

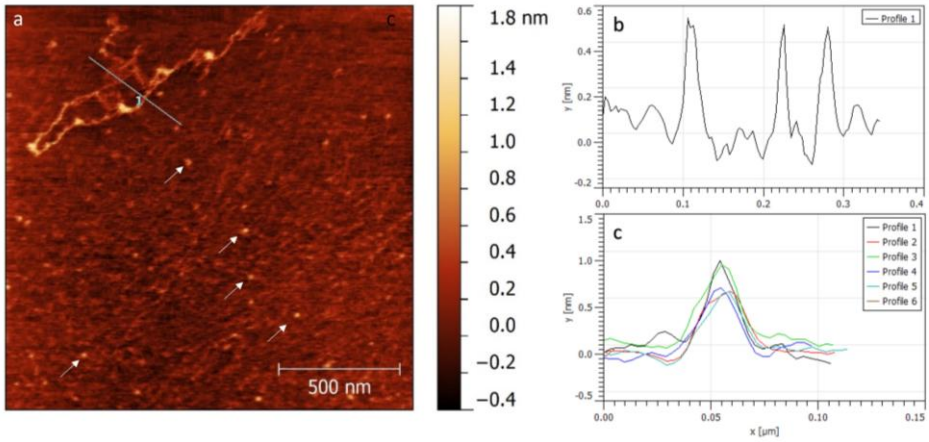


Figure S4. a) 2×2 μm^2 AFM image of mixture of ODN **8** (d(AdT_6Ad), 16 µM ssDNA) and porphyrin **3** (4 µM) on mica substrate. b) Height profile collected at line 1 on panel a. c) Height profiles collected at the indicated arrows on panel a.

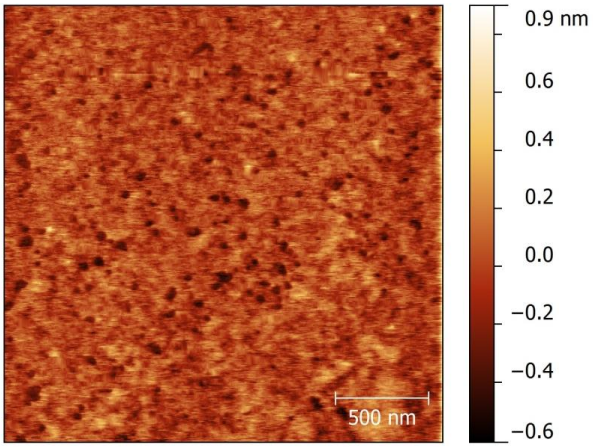


Figure S5: 2.3x2.3 μm^2 AFM image of quadruplex **2** (4 µM solution) on mica substrate.

4. Normalized UV-Vis absorption profiles of SG

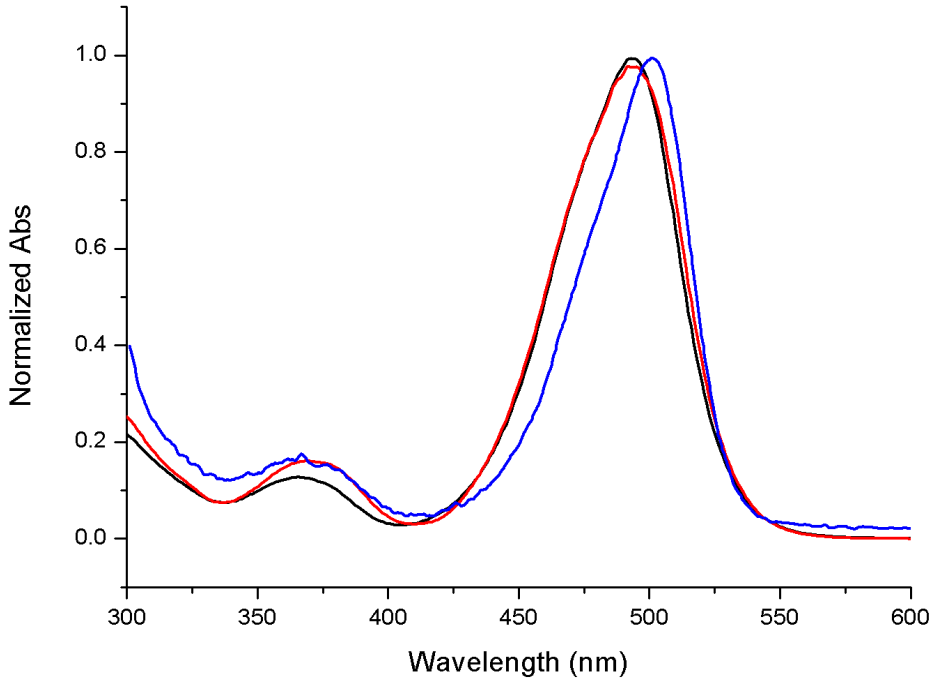


Figure S6: Normalized UV-Vis absorption profile of 4 µM SG in 80 mM KCl 10 mM TrisHCl pH 7.5 buffer (black), in EtOH (red) and a mixture of 4 µM SG, 4 µM quadruplex **2** in 80 mM KCl 10 mM TrisHCl pH 7.5 buffer (blue)

In order to determine whether SG forms dimers of higher order aggregates in aqueous buffer, UV-vis experiments were conducted in both TrisHCl buffer and in ethanol (Figure S6). The absorption profile shows no appreciable change between the high and lower polarity solvent systems suggesting that SG does not aggregate under these concentrations in aqueous buffer. Further, a slight bathochromic shift is observed when SG is mixed with quadruplex 2 indicating a binding event.

5. UV-Vis and Fluorescence Studies of Assembly 4 and 5

In order to evaluate whether the photophysical properties of porphyrin **3** were affected upon assembly formation, UV-vis and fluorescence spectra were conducted. As can be seen by inspection of Figure S7, the porphyrin Soret- and Q-absorption bands and its fluorescence emission profile do not change appreciably upon incorporation into assembly **4**. These experiments support the notion that porphyrin **3** does not self-aggregate via pi-stacking interactions and its photophysical properties are not diminished upon assembly formation.

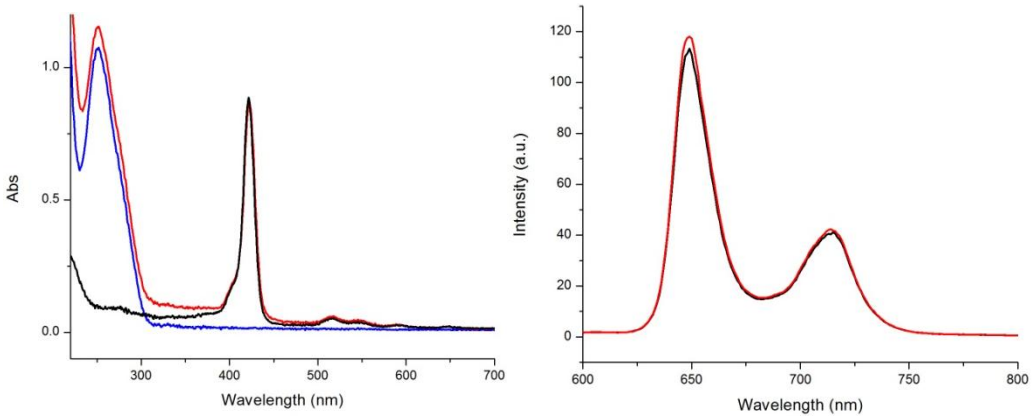


Figure S7. UV-Vis (left) and Fluorescence (right; excitation at 422 nm) spectra of quadruplex **2** (blue), porphyrin **3** (black), and assembly **4** (red). All of these samples are 4 μM (conc. of quadruplex and/or porphyrin units**)** in 10 mM Tris-HCl 80 mM KCl, pH 7.5.

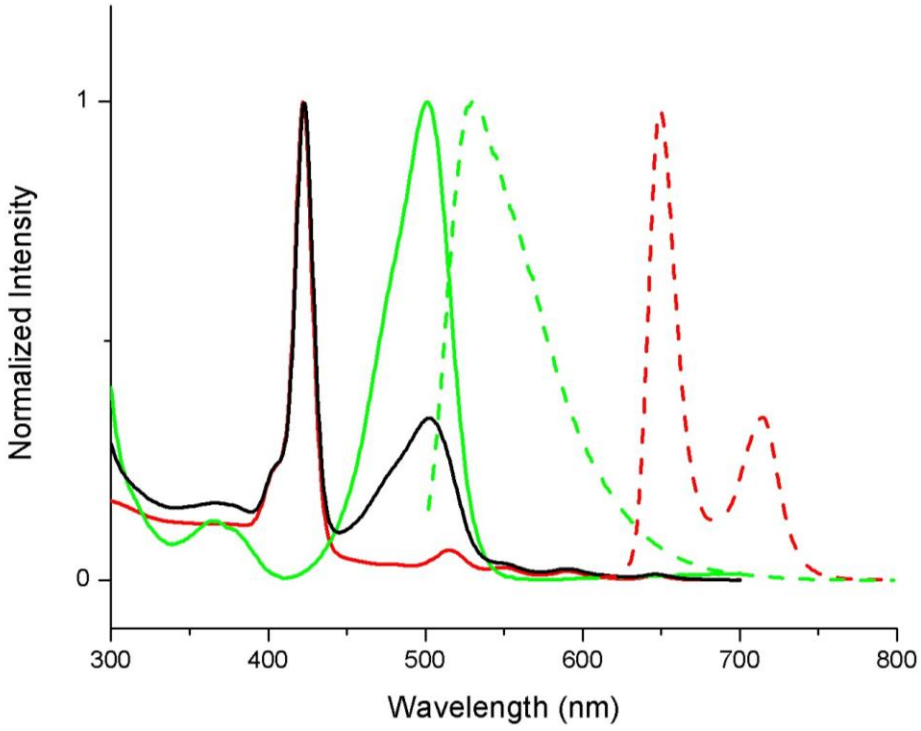


Figure S8. Normalized UV-Vis (solid lines) and fluorescence spectra (dashed lines) of porphyrin **3** (red), SG + quadruplex **2** (green) and assembly **5** (black). Note: As can be seen from Figure S8, SG bound to quadruplex **2** (solid green line) has absorption that complements the porphyrin chromophore (solid red line) since the SG absorption maxima is to the right of the porphyrin Soret band and to the left of the 2nd to 4th porphyrin Q-bands. Also, the emission spectrum of SG + quadruplex **2** (dashed green line) overlaps with all four Q-absorption bands of porphyrin **3**.

6. Absorption Data For Solutions Used in Figure 5a Main Text.

Prior to conducting the fluorescence studies (excitation at 480 nm) shown on Figure 5a in the main text, we performed UV-vis absorption experiments to ensure that excitation of (a) SG alone, (b) SG + quadruplex **2**, (c) SG + assembly **4** (i.e., assembly **5**), and (d) assembly **5** + excess β-CD (i.e., dis-assembly of assembly **5**), were all conducted under relatively matched absorbance (as shown in Figure S9).

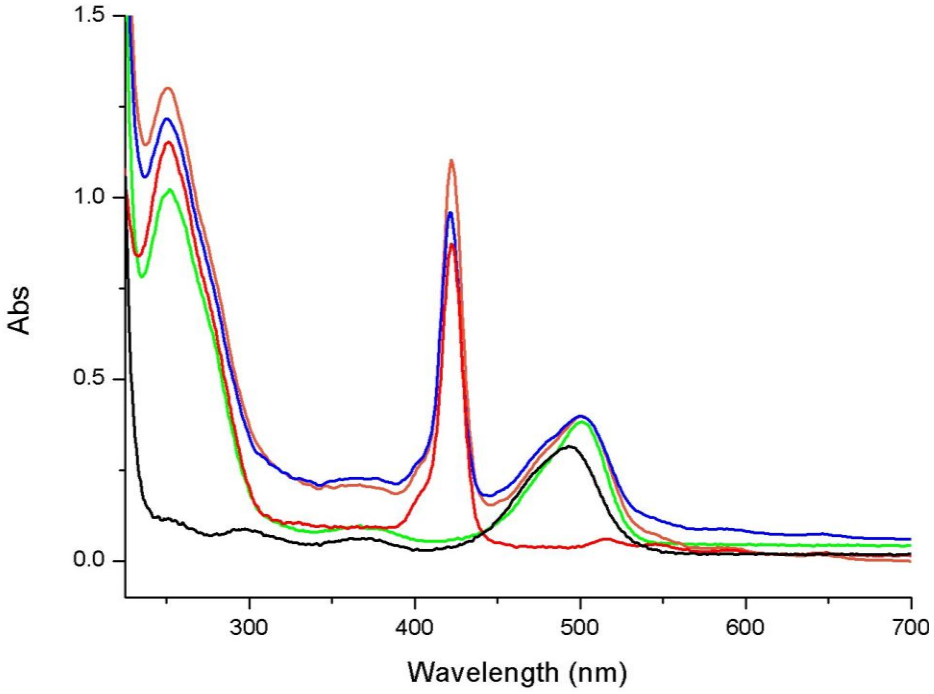


Figure S9. UV-Vis spectra of SG only (black), SG + quadruplex **2** (green), assembly **5** (orange), assembly **5** + excess β-CD (blue), and assembly **4** (red) used in fluorescence studies shown in Figure 3a. Note: All solutions were 4 μM in quadruplex DNA, porphryin **3**, and SG.

7. Job plot for SG:quadruplex 2 complex and porphyrin 3

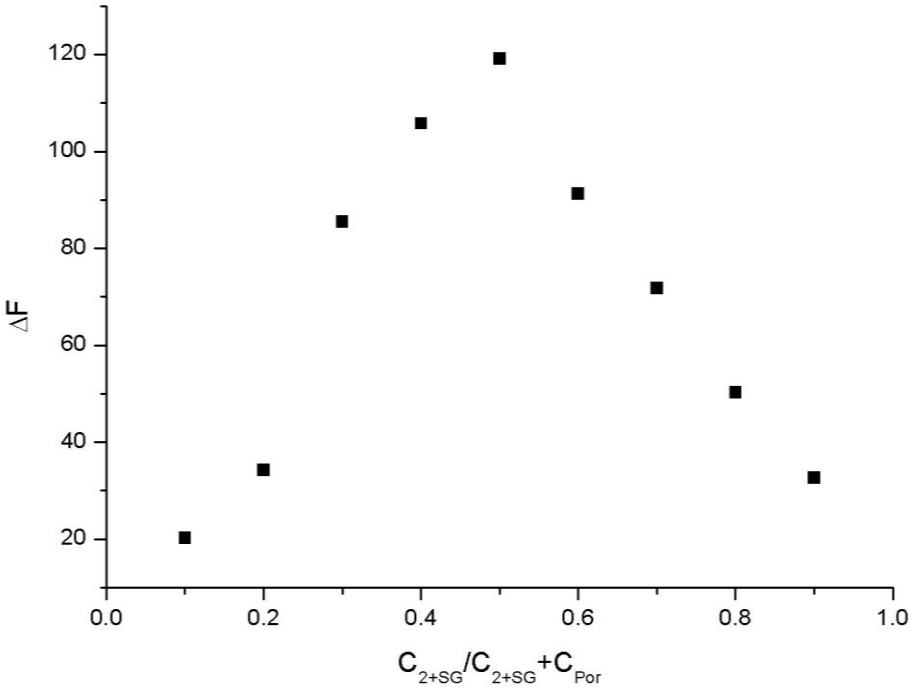


Figure S10. Job plot for binding of the SG:quadruplex **2** assembly with porphyrin **3**, based on fluorescence quenching (ΔF) of SG:quadruplex **2** assembly, when it binds to porphyrin **3**. Samples were held at 4 μM total concentration of SG:quadruplex **2** assembly and porphyrin **3** (the mixture was excited at 480 nm and emission was observed at 525 nm).

8. Calculation of the antenna effect

The antenna effect[1] ($AE = I_{5,495\ nm}/I_{5,\ Q\text{-}band\ excitation}$), is defined as the ratio of the fluorescence emission intensity of the acceptor porphyrin **3** (at 715 nm) upon selective excitation of donor SG at its λ_{max} (495 nm) to that of direct excitation of the three longer wavelength Q-bands of porphyrin **3** (at 548, 588, and 650 nm, respectively). These three Q-bands were used to measure the antenna effect since the emission spectra of SG overlaps with these three Q bands of porphyrin **3**. Based on the excitation spectra (shown in Figure 5b, main text) this antenna effect was found to be 593%, 547%, and 676%, respectively. We have also measured the antenna effect for the first Q-band at 525 nm (the antenna effect was calculated to be 188%), however, since SG chromophore also absorbs at 525 nm, we are not able to selectively excite porphyrin **3** via its first Q-band and thus the antenna effect is smaller than expected.

9. Confocal Microscopy Studies

In order to gather more detailed fluorescence data with respect to the structure of the assemblies, confocal microscopy of assembly **4** and **5** in solution phase was conducted. Assembly **4** shows the presence of red fluorescent micron-size structures (when excited at 488 nm) that are indicative of higher-order aggregation of **4** (Figure S11,top). Assembly **5**, also shows large aggregates but the emission is yellowish in color (Figure S11, bottom). The confocal microscopy derived emission spectra of these micron size structures indicate that the yellowish color is due to a combination of SG and porphyrin **3** emission peaks.

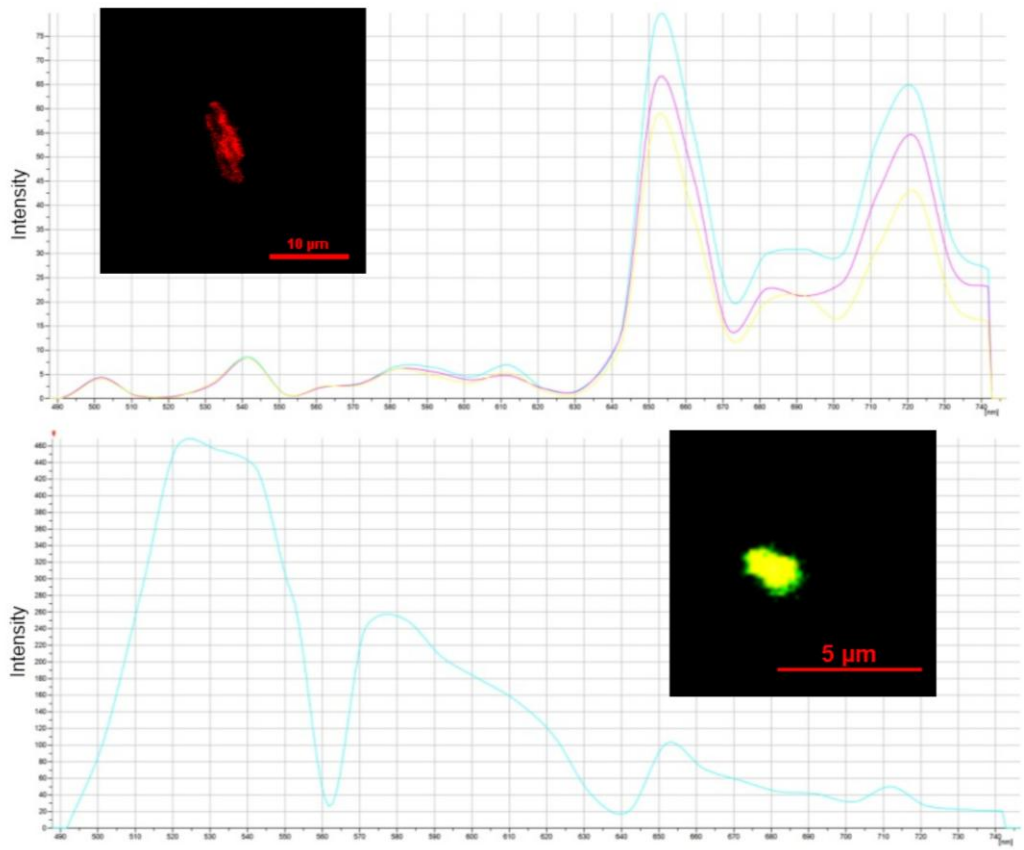


Figure S11. Fluorescence emission spectra collected on a Nikon A1 confocal microscope using 26 PMT channels from 492-742 nm. Excitation λ = 488 nm. **Top:** Fluorescence emission spectra collected on the microscopic particle of assembly **4** (shown in inset). Three different regions of the same particle (shown in different colors) were probed. This spectra clearly shows the fluorescence emission from porphyrin **3** (at 655 nm, and 715 nm). **Bottom:** Fluorescence emission spectra collected on the microscopic particle of assembly **5** (shown in inset). Here, the emission peaks are found at 530 nm, 655 nm, and 715 nm indicating the existence of both SG and porphyrin **3** units. Note: the negative peak at 561 nm is due to the laser blocking filter which protects the detector from direct exposure to the 561 nm excitation laser.

10. Dis-Assembly of Assembly 5 Probed by PAGE

PAGE studies were also used to show that supramolecular assembly **5** could be dis-assembled upon addition of excess free β-CD. As shown in Figure S12**,** the characteristic fast migrating quadruplex **2** band (shown in control lane 1) is clearly observed after assembly **5** (prepared by mixing assembly **4** and SG for 5 minutes) was exposed to 250 eq. of free β-CD (per each CD unit on Porphyrin **3**) for 20 minutes (see lane 2). Also observed in lane 2 is a slow migrating reddish band that is moving slightly slower than expected for free porphyrin **3** (control shown in lane 3). The reason for this difference in migration may be due to the large excess of free β-CD present in lane 2.

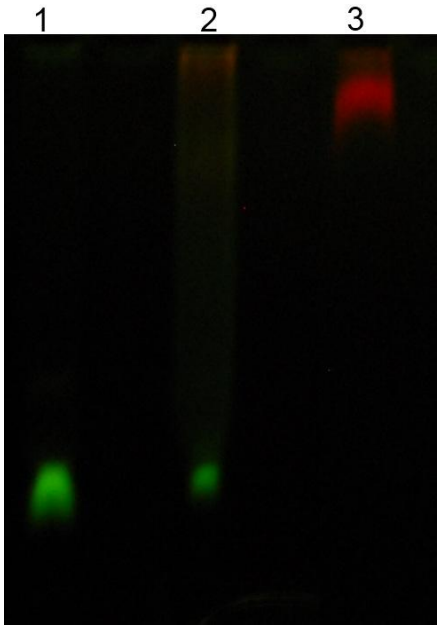


Figure S12. 15% PAGE. Lanes 1 through 3 correspond to quadruplex **2** + SG, assembly **4** + SG + free β-CD (250 equiv. per each PM-β-CD unit on porphyrin **3**), and porphyrin **3** + SG, respectively.

11. CD Profile of Na^+ Stabilized Quadruplex of ODN 1

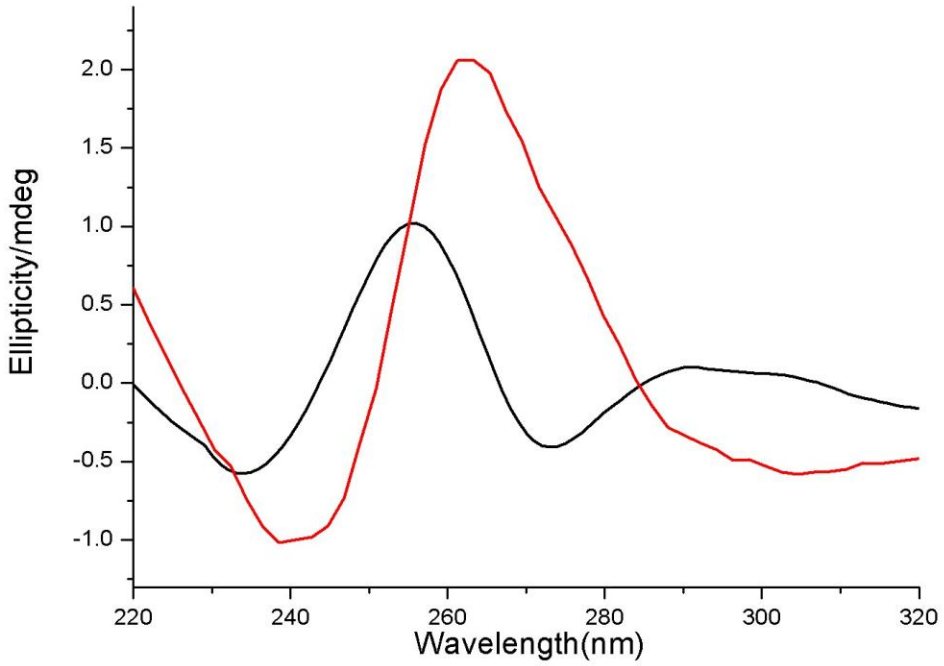


Figure S13. Circular dichroism spectra of quadruplexes formed by ODN **1** (16 μM single strand concentration) in sodium containing buffer (black, in 80 mM NaCl, 10 mM Tris-HCl, pH 7.5) and in potassium containing buffer (red, in 80 mM KCl, 10 mM Tris-HCl, pH 7.5)

The CD profile of the ODN **1** incubated in Na^+ containing buffer was also collected. In contrast to the CD profile of K^+ stabilized quadruplex **2**, the CD profile of ODN **1** incubated with Na^+ shows two negative peaks at 235 nm and 272 nm and also shows two positive peaks at 255 nm and 292 nm. This profile suggests the presence of a mixture of parallel and anti-parallel quadruplex structures in Na^+ containing buffer. [2]

12. CD Profile of K^+ Stabilized Quadruplex of ODN 9

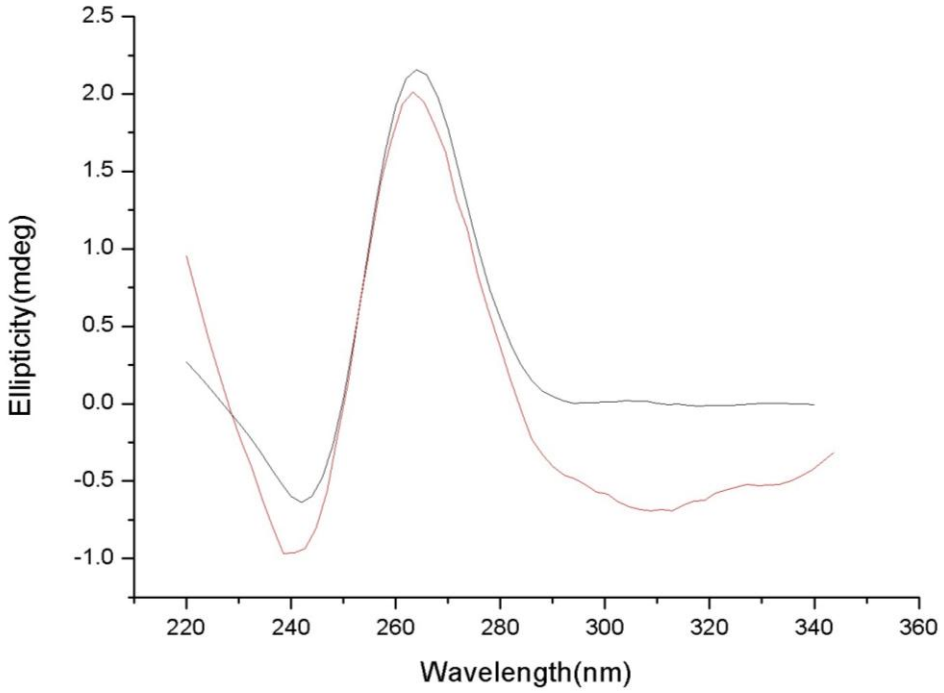


Figure S14. Circular dichroism spectra of quadruplexes formed by ODN **9** (black) and quadruplex **2** (red) in potassium containing buffer (80 mM KCl, 10 mM Tris-HCl, pH 7.5)

The CD spectra of quadruplex **2** was also compared with a control sequence ODN **9** (TGGGGT, structure shown in SI-Scheme 1) that does not have the adamantane head-groups. The quadruplex of ODN **9** also shows a similar CD profile as quadruplex **2** when exposed to standard quadruplex forming buffer conditions (80 mM KCl, 10 mM Tris-HCl, pH 7.5).

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[1] Dutta, P. K.; Varghese, R.; Nangreave, J.; Lin, S.; Yan, H.; Liu, Y. *J. Am. Chem. Soc.* **2010**, *133*, 11985-11993.

[2] Ambrus, A.; Chen, D.; Dai, J.; Bialis, T.; Jones, R. A.; Yang, D. *Nucleic Acids Research*, **2006**, *34*, 2723–2735