Integrating DNA-Photonic Wires into Light-Harvesting Supramolecular Polymers

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Abstract
An approach combining DNA nanoscaffolds [1,2] with supramolecular polymers [3] for the efficient and directional propagation of light-harvesting cascades has been developed. A series of photonic wires with different arrangements of fluorophores in DNA-organized nanostructures were linked to light-harvesting supramolecular phenanthrene polymers (SPs) in a self-assembled fashion. Among them, a light harvesting complex (LHC) composed of SPs and a photonic wire of phenanthrene, Cy5, Cy5.5 and Cy7.5 chromophores reveals a remarkable energy transfer efficiency of 59%.

The phenanthrene-containing oligomers and dibutynylphenanthrene oligonucleotides used in this study are summarized in Table 1. The required 3,6-dibutynylphenanthrene phosphoramidite for the synthesis of oligomers A, B was prepared according to the published procedure [5]. All two oligomers were assembled by automated oligonucleotide synthesis. Hybridization of the phenanthrene-modified oligonucleotide B with various complementary single strands is expected to afford photonic wires with cascade energy transfer.

Self-assembly experiments were typically carried out by mixing oligomer A (0.5 μM) and an equimolar ratio of oligomer B and the cyanine-labeled oligonucleotides (15 nM) in sodium phosphate buffer (10 mM, pH 7.2) in the presence of NaCl (120 mM). Upon heating to 60 °C and cooling to room temperature over a period of 5 min, the oligomeric building blocks self-organize into DNA-assembled SPs that reach a length of several micrometers, as demonstrated by transmission electron microscopy (TEM) and atomic force microscopy (AFM). Assembly of the supramolecular nanofibers takes place in the temperature range between 60 and 50 °C.

To gain insight into the self-assembly process, the influence of increasing amounts of hybrid B’G on Cy3 emission after excitation of the phenanthrene antenna was investigated. Figure 4. Expected, Cy3 fluorescence at 570 nm grows with increasing amounts of hybrid B’G. Cy3 emission appears already in the presence of 0.47 nM B’G, which translates into 0.1% of Cy3 relative to oligomer A.

A continuous growth is observed upon further addition of B’G. Parallel to the increase in Cy3 emission, the phenanthrene fluorescence band centred at 415 nm gradually decreases up to a 15 nM concentration of B’G. This results in a plateau (Figure 4, inset) that serves as an indication that the SPs are saturated, i.e. additional B’G is not anymore integrated into the SPs.

Table 2. FRET efficiencies were calculated based on the decrease in phenanthrene fluorescence compared to the control LHC4. The obtained average efficiencies of 43% (LHC1), 49% (LHC2), and 59% (LHC3, Table 2) are significantly higher than those of the corresponding DNA photonic wires lacking SPs.

Table 2. The Configuration FRET efficiency (E) and overall AE for different LHCs.

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<thead>
<tr>
<th>Configuration</th>
<th>E (%)</th>
<th>AE (%)</th>
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<tbody>
<tr>
<td>LHC1</td>
<td>43±5%</td>
<td>22.8±(6.2)</td>
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<tr>
<td>LHC2</td>
<td>49±(11)%</td>
<td>5.6±(2.0)</td>
</tr>
<tr>
<td>LHC3</td>
<td>59±(10)%</td>
<td>1.4±(0.3)</td>
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FRET efficiency is calculated according to the equation $E = 1 - \frac{|I_0 - I|}{I_0}$, where $I_0$ and $I$ are the integrated areas of phenanthrene fluorescence emission between 355 nm and 500 nm with and without acceptor. $A_{AC}$ and $A_A$ are the absorbance of phenanthrene at 320 nm with and without acceptor. [4] Antenna effect obtained by comparing the emission of the terminal acceptor by excitation of phenanthrene to the emission of the terminal acceptor by direct excitation.

Conclusion
A novel approach combining light-harvesting, supramolecular phenanthrene polymers with DNA photonic wires has been described. DNA-derived scaffolds containing up to three fluorophores with defined inter-chromophore distances have been appended to SPs in a simple self-assembly process. A stepwise transfer of the excitation energy from the primary phenanthrene donor array to a Cy5.5 acceptor through intermediate Cy3 and/or Cy5 donors via a FRET mechanism proceeds with an efficiency of up to 59%. Antenna effects ranging from 1.4 up to 23 were observed for different LHCs. This work demonstrates that the combination of DNA-organized photonic wires with supramolecular polymers enables the assembly of artificial LHCs with excellent light-harvesting properties and high energy transfer efficiencies.

References

Figure 1. Illustration of the supramolecular assembly of a light-harvesting complex (LHC). Chromophore-modified DNA hybrids containing terminal phenanthrenes (shown in blue) are incorporated into the growing phenanthrene antenna during supramolecular polymerization.

Figure 2. Illustration of light-harvesting complex LHC1 (DNA photonic wire bearing variable acceptor dyes Cy5, Cy6 and Cy5.5 in green, yellow and red, respectively). The supramolecular antenna is composed of phenanthrene donor. Anomalous energy transfer by phenanthrene dimers is transferred along the antenna to the acceptor dyes (Cy5) and further along the DNA photonic wire via FRET.

Figure 3. Fluorescence transients of LHC2 (green), LHC3 (black) or a mixture of either oligomer A (red) or B (light blue) in combination with the Cy5-doped phenanthrene antenna.

Figure 4. Emission spectra of oligomer A (0.5 μM) in the presence of different concentrations of hybrid B’G after phenanthrene excitation (320 nm). Normalization was done by dividing the emission spectra by the absorption value of each individual sample at 320 nm.

Figure 5. Fluorescence emission spectra of LHC2 (green), LHC3 (orange), LHC4 (red) and LHC2 oligo. Concentration of oligomer A is 0.5 μM, B, C, D, E, F and H (5 μM), and deoxyribonucleic acid (DNA) concentration was maintained at 15 μM. Normalization was done by dividing the emission spectra by the absorption value of each individual sample at 320 nm.