Integrating DNA-Photonic Wires into Light-Harvesting Supramolecular Polymers

Mariusz Kownacki, Simon M. Langenegger, Shi-Xia Liu, and Robert Häner
Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland

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, Cy6 and Cy5.5 chromophores reveals a remarkable energy transfer efficiency of 59%.

The phenanthrene-containing oligomers and dye-labeled oligonucleotides used in this study are summarized in Table 1. The required 3,6-dibutyrylphenanthrene phosphoramidite for the synthesis of oligomers A, B, and C was prepared according to the published procedure. 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 mM) 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 block self-organizes into DNA-attached 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. As expected, Cy3 fluorescence at 570 nm grows with increasing amounts of hybrid B’G. Cy3 emission appears already in the presence of 0.47 mM 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 centered at 415 nm gradually decreases up to a 15 mM 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. The average FRET efficiency (E) and overall AE for different LHCs.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>E (%)</th>
<th>AE (%)</th>
</tr>
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<tbody>
<tr>
<td>LHC1</td>
<td>SP – Cy3</td>
<td>43 (±5)</td>
</tr>
<tr>
<td>LHC2</td>
<td>SP – Cy3-Cy5</td>
<td>49 (±11)</td>
</tr>
<tr>
<td>LHC3</td>
<td>SP – Cy3-Cy5-Cy5.5</td>
<td>59 (±10)</td>
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[1] FRET efficiency is calculated according to the equation E = 1 – (1 – E)² – (1 – E)³ where E1 and E2 are the integrated areas of phenanthrene fluorescence emission between 550 nm and 590 nm with and without acceptor, A1 and A2 are the absorbance of phenanthrene at 320 nm with and without acceptor, and [Cy] is the concentration of phenanthrene dyes.

[2] 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