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, Cy3, Cy5 and Cy5.5 chromophores reveals a remarkable energy transfer efficiency of 59%.

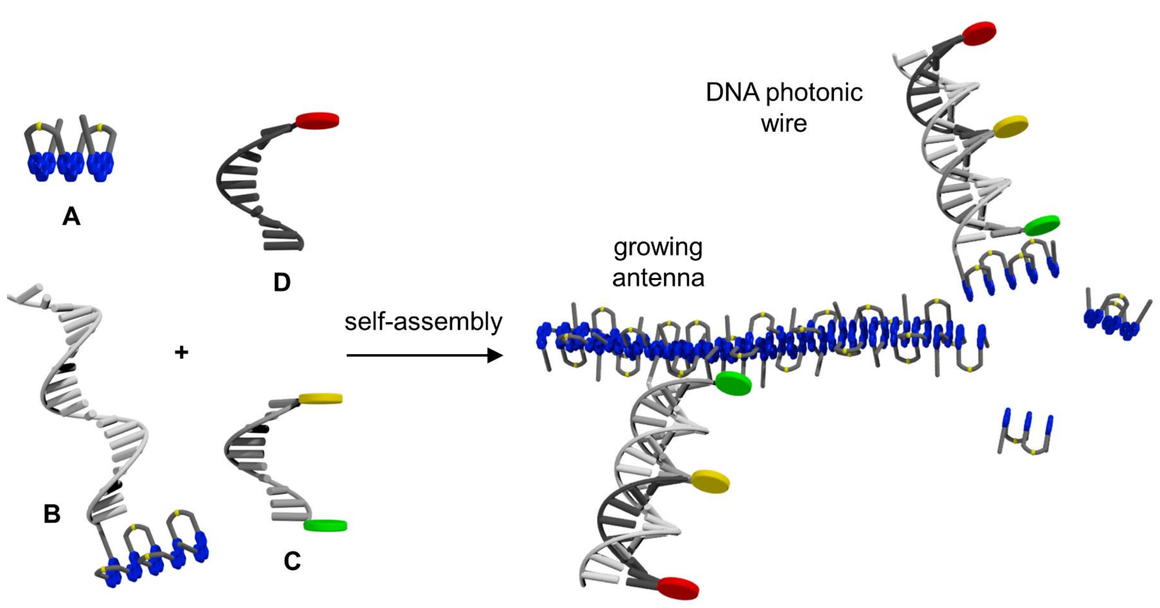

Figure 1. Illustration of the supramolecular assembly of a light-harvesting complex (**LHC3**). Chromophore-modified DNA hybrids containing terminal phenanthrenes (shown in blue) are incorporated into the growing phenanthrene antenna during supramolecular polymerization.

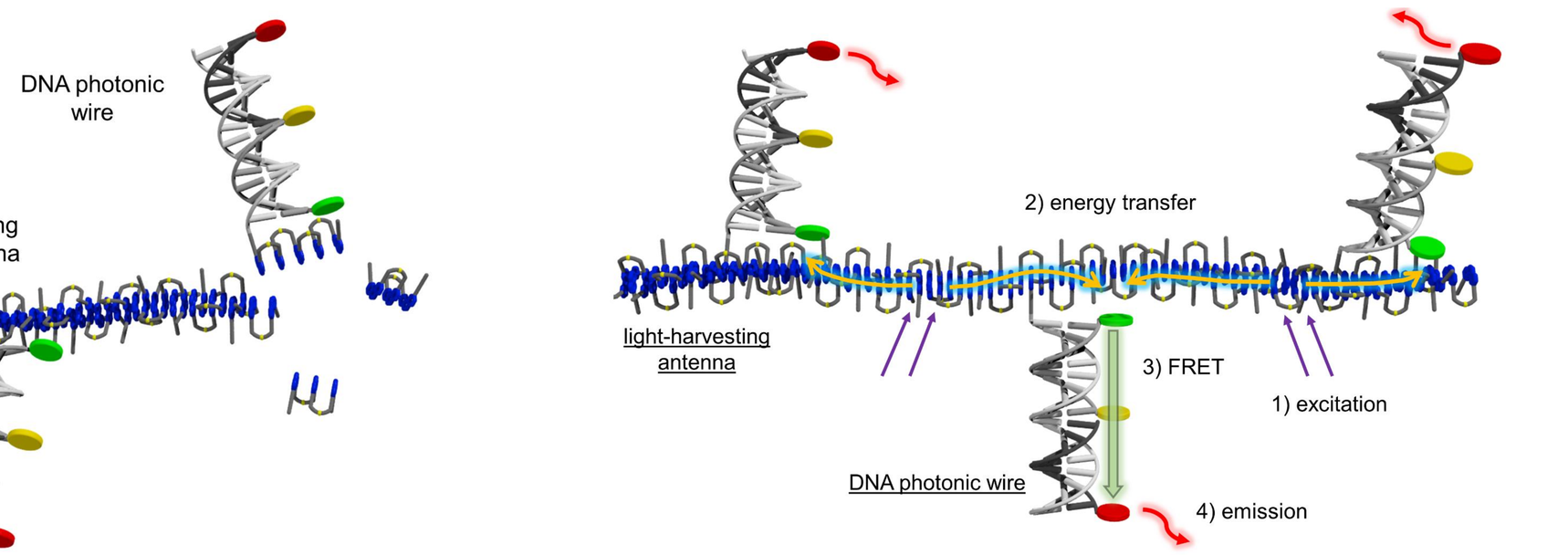

Figure 2. Illustration of light-harvesting complex **LHC3**: DNA photonic wires bearing suitable acceptor dyes (Cy3, Cy5 and Cy5.5 in green, yellow and red) are integrated into a supramolecular polymer ('antenna') composed of phenanthrenes (blue). Excitation energy absorbed by phenanthrene molecules is transferred along the antenna to the acceptor dye (Cy3) and further along the DNA photonic wire via FRET.

The phenanthrene-containing oligomers and dye-labelled 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.[3] 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.

Oligomer	Sequence
A	$(Phe)_3$
B	$(Phe)_5$ - GAA GGA ACG TAG CCT GGA AC - 5'
C	5' - Cy3 - CTT CCT TGC A - Cy5
D	5' - TCG GAC CTT G - Cy5.5
F	5' - TCG GAC CTT G
G	Cy3 - CTT CCT TGC A - 3'
H	Cy3 - CTT CCT TGC ATC GGA CCT TG - 3'
K	$(Phe)_3$ - GAA GGA ACG TAG CCT GGA AC - 5'

LHC1: (**A**,**B**,**H**) **LHC2:** (**A**,**B**,**C**,**F**) **LHC3:** (**A**,**B**,**C**,**D**) **LHC4:** (**A**,**B**,**E**,**F**)

$(Phe)_3$:

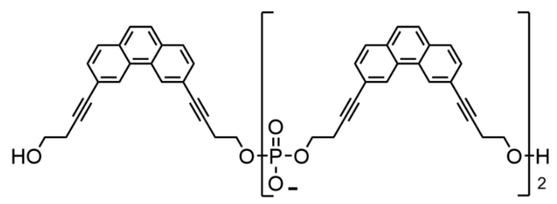

Table 1. Top: Oligomers used in this study; middle: composition of different LHCs; bottom: chemical structure of phosphodiester-linked phenanthrenes.

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 80 °C and cooling to room temperature over a period of 5 min, the oligomeric building blocks self-organize into DNA-appended 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.

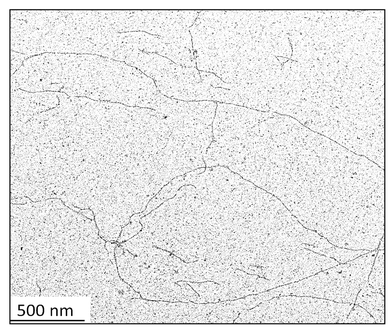

Figure 6. TEM images of **SPs** modified with DNA strands (**A**+**B**).

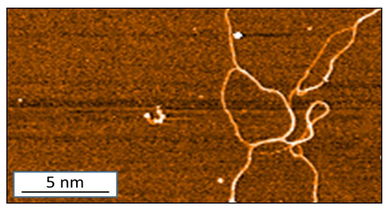

Figure 7. AFM of **SPs** modified with DNA strands (**A**+**B**+**E**+**F**) were analysed on APTES-modified mica at 20 °C.

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). 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 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.

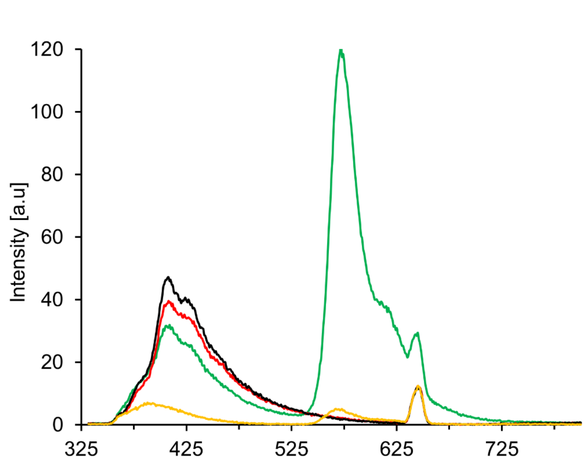

Figure 3. Fluorescence intensities of **LHC1** (green), **LHC4** (black) or a mixture of either oligomer **A** (red) or **B** (light brown) in combination with the Cy3-derived oligonucleotide **H.**

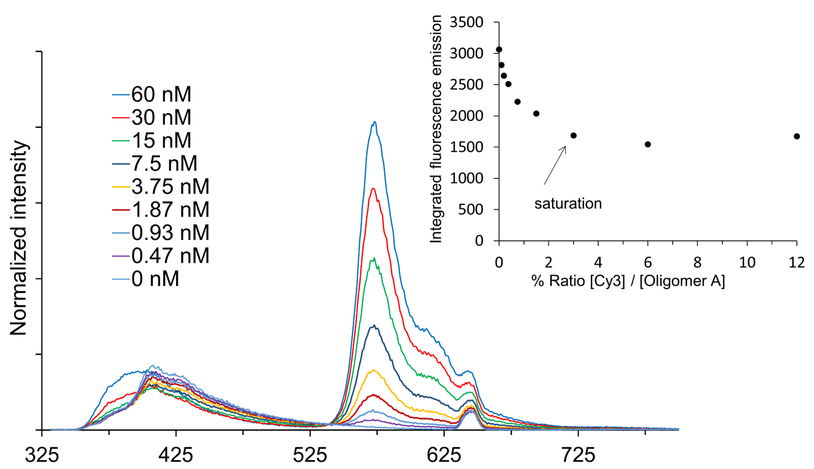

Figure 4. Emission spectra of oligomer **A** (0.5 µM) in the presence of different concentrations of hybrid **B*G** after phenanthrene excitation (322 nm). Normalization was done by dividing the emission spectra by the absorption value of each individual sample at 322 nm.

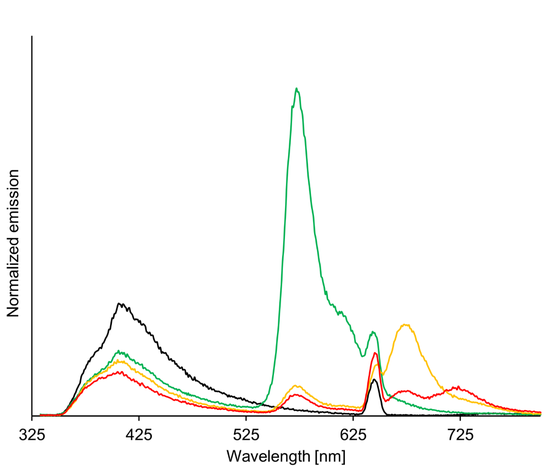

Figure 5. Fluorescence emission spectra of **LHC1** (green), **LHC2** (orange), **LHC3** (red) and **LHC4** (black). Concentration of oligomers: **A** (0.5 µM), **B**, **C**, **D**, **E**, **F** and **H** (15 nM); conditions as in Fig. 3. Normalization was done by dividing the emission spectra by the absorption value of each individual sample at 322 nm.

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 average FRET efficiency (*E*) and overall AE for different LHCs.

	Configuration	*E*[a]	AE[b]
LHC1	SP – Cy3	43 (±5)%	22.8 (±6.2)
LHC2	SP – Cy3-Cy5	49 (±11)%	5.6 (±2.0)
LHC3	SP – Cy3-Cy5-Cy5.5	59 (±10)%	1.4 (±0.3)

[a] FRET efficiency is calculated according to the equation $E = 1 - \frac{I_{DA}/A_{DA}}{I_D/A_D}$ where I_{DA} and I_D are the integrated areas of phenanthrene fluorescence emission between 335 nm and 520 nm with and without acceptors. A_{DA} and A_D are the absorbance of phenanthrene at 322 nm with and without acceptors. [b] 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

[1] K. Boeneman, D. E. Prasuhn, J. B. Blanco-Canosa, P. E. Dawson, J. S. Melinger, M. Ancona, M. H. Stewart, K. Susumu, A. Huston, I. L. Medintz, *J. Am. Chem. Soc.* **2010**, *132*, 18177-18190

[2] P. K. Dutta, R. Varghese, J. Nangreave, S. Lin, H. Yan, Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 11985-11993

[3] C. B. Winiger, S. Li, G. R. Kumar, S. M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.* **2014**, *53*, 13609-13613