Light Harvesting

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A DNA-Based Light-Harvesting Antenna**

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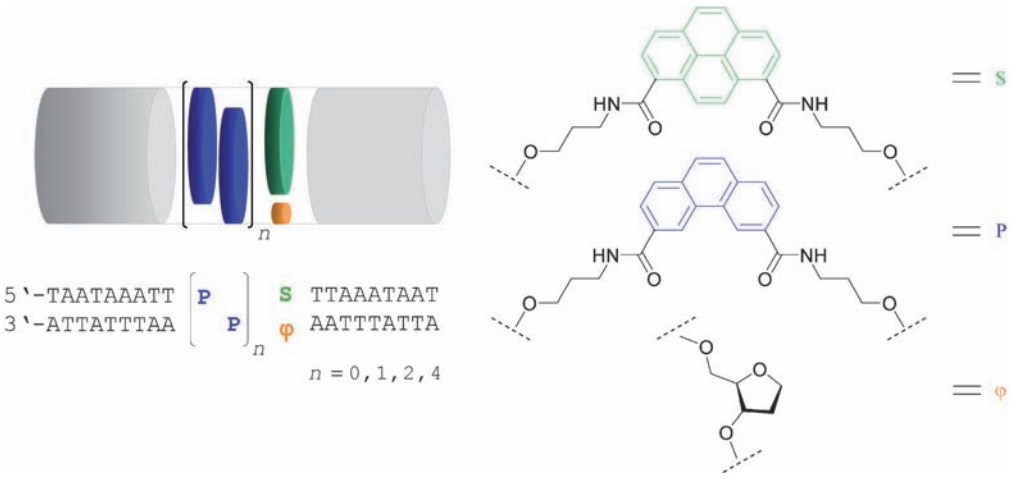
An effective mechanism for the collection of light is an essential component of natural and artificial photosynthetic systems.[1–3] After the absorption of sunlight by a light-harvesting complex (LHC), excitation energy transfer (EET) and charge separation occur.[4–6] Various types of LHCs have been described as components of artificial photosynthetic and photovoltaic systems.[7–17] As in their natural counterparts, a key aspect of LHCs is the proper arrangement of multiple light-absorbing molecules.[18–34] DNA has been used as a framework for the generation of ordered assemblies of a large variety of chromophores. Extended multichromophore arrays have electronic properties that are attractive for use in optical and electronic devices, as well as for diagnostic applications.[35–48] We have reported the DNA-assisted formation of π-stacked arrays of phenanthrene[49–51] and pyrene[52–57] building blocks. Herein, we describe the light-harvesting properties of such a DNA-organized, multichromophore array, in which light is absorbed by multiple π-stacked phenanthrenes and transferred to a phenanthrene–pyrene exciplex.

The four different oligonucleotide hybrids that were used in this study are shown in Scheme 1 and Table 1. The phenanthrene[49] (P) and pyrene[52,58] (S) building blocks (Scheme 1, right) were synthesized as previously described. The preparation of the oligomers **1**–**8** was accomplished by standard phosphoramidite chemistry (see the Supporting Information).[59] The hybrids are organized with a stack of phenanthrenes in the center of a DNA duplex, and a single pyrene at one end of the phenanthrene stack (Scheme 1). To avoid the formation of positional isomers, the position of the pyrene is fixed by placing it opposite to an abasic site analogue φ. It has been shown that non-nucleosidic aromatic residues, such as the ones used here, are well accommodated in DNA abasic sites.[58,60] The four different hybrids shown in Table 1 contain stacks of up to eight phenanthrene units. To minimize quenching of the fluorescence by the natural bases in the oligomers and the hybrids, the flanking DNA segments are composed entirely of A and T residues, to avoid the use of GC base pairs.[61]

Table 1: Oligonucleotides and the corresponding melting temperatures (T_m) of the hybrid duplexes[a].

	Oligomer	T_m [°C]
1	5′- TAATAAATT**S**TTAAATAAT	27.0
2	3′- ATTATTTAA**φ**AATTTATTA	
3	5′- TAATAAATT**PS**TTAAATAAT	34.5
4	3′- ATTATTTAA**P**φAATTTATTA	
5	5′- TAATAAATT**PPS**TTAAATAAT	36.5
6	3′- ATTATTTAA**PP**φAATTTATTA	
7	5′- TAATAAATT**PPPPS**TTAAATAAT	37.0
8	3′- ATTATTTAA**PPPP**φAATTTATTA	

[a] Conditions: 2 μM oligonucleotide (each strand), 100 mM NaCl, 10 mM sodium phosphate buffer (pH 7.0).



Scheme 1. Representation of π-stacked phenanthrenes (blue) flanked on one side by a pyrene (green); gray cylinders represent DNA duplex.

The melting temperatures (T_m) of the hybrids ranged from 27 °C to 37 °C. To ensure the stability of the hybrids, all subsequent experiments were performed at 15 °C. The UV/Vis absorption spectra of the hybrids are shown in Figure 1. Only the phenanthrene and pyrene units, but not the nucleobases, contribute to the absorption profile in the region between 300 nm and 420 nm (Figure 1, inset). The band with a maximum at around 360 nm is the result of absorption by the pyrene, whereas the band at

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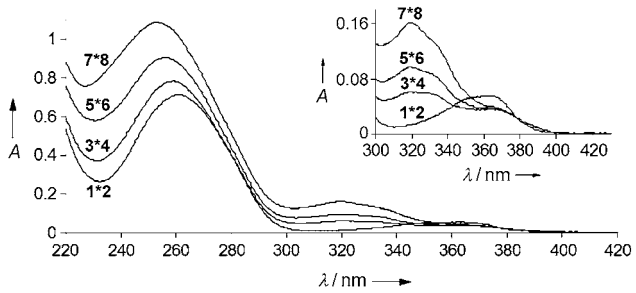

Figure 1. UV/Vis absorption spectra of hybrids; conditions: see Table 1.

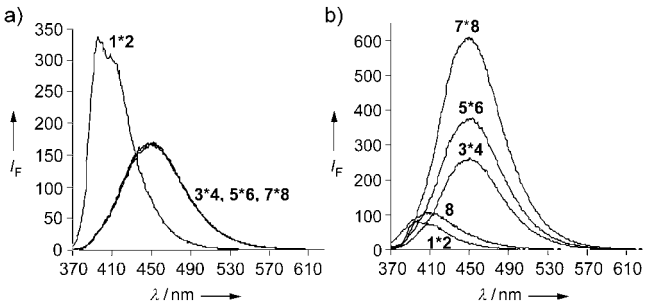

Figure 3. a) Fluorescence spectra of hybrids after pyrene excitation (365 nm). b) Fluorescence spectra of hybrids and single strand **8** after phenanthrene excitation (320 nm); conditions: see Table 1.

320 nm is the result of absorption by the phenanthrene. The intensity of the 320 nm band grows linearly with the number of phenanthrenes.

Excitation of the hybrids leads to fluorescence of either the pyrene monomer (around 400 nm, hybrid **1*****2**)[62,63] or, if phenanthrenes are present, of a phenanthrene–pyrene exciplex (450 nm, Figures 2 and 3).[64] This type of exciplex was previously observed in a triple-helical DNA construct.[65]

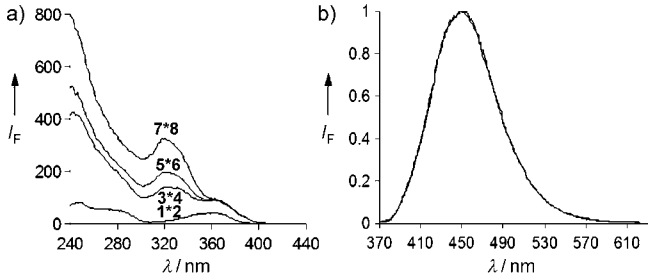

Figure 2. a) Excitation spectra of hybrids; emission: 450 nm. b) Normalized fluorescence spectra of hybrid **7*****8** after excitation at 320 nm (phenanthrene) and 365 nm (pyrene; curves are superimposed, for more details see the Supporting Information); conditions: see Table 1.

Excitation spectra recorded at the exciplex emission wavelength (450 nm, Figure 2a) reveal that the excitation of either pyrene (365 nm) or phenanthrene (320 nm) leads to the formation of this exciplex (Figure 2b). Furthermore, the absorbance and excitation spectra of hybrid **1*****2** show that the excitation of the pyrene at 320 nm is negligibly small (albeit not zero). Exciplex fluorescence can essentially be ascribed to the excitation of phenanthrene at this wavelength. Light of wavelengths 365 nm or longer, on the other hand, is exclusively absorbed by pyrene. Thus, the formation of the phenanthrene–pyrene exciplex can be accomplished through the selective excitation of either phenanthrene (320 nm) or pyrene (365 nm). The normalized fluorescence spectra of hybrid **7*****8** that were obtained by irradiation at these two wavelengths are congruent (Figure 2b).

Figure 3 shows the fluorescence spectra that result from irradiation at 365 nm (pyrene) or 320 nm (phenanthrene). Excitation of hybrid **1*****2** at 365 nm leads to pyrene monomer emission with a maximum intensity at 400 nm (Figure 3a). All other hybrids have intense phenanthrene–pyrene exciplex fluorescence. Excitation of hybrid **1*****2** at 320 nm (Figure 3b) results in weak pyrene monomer emission, which is explained by the small residual signal in the excitation spectrum at this wavelength (Figure 2a). Excitation of single strand **8**, which contains four phenanthrenes but no pyrene, induced a broad and relatively weak phenanthrene signal at 400 nm. Hybrids **3*****4**, **5*****6**, and **7*****8** have intense exciplex emissions. Importantly, the intensity of the emission increases with the number of phenanthrenes that are present in the π stack. Based on the shape of the signals, fluorescence of pyrene and/or phenanthrene monomer is negligible, if not completely absent in these hybrids.

The multichromophore array described here represents an artificial LHC that consists of a light-absorbing module, which contains a variable number of π-stacked phenanthrenes, and an energy-collecting phenanthrene–pyrene exciplex. The whole complex is structurally organized in a DNA framework. Transfer of the energy that is absorbed by the π-stacked phenanthrenes to the exciplex proceeds with remarkable efficiency. Figure 4 shows that the number of photons that are emitted from the exciplex grows steadily with the number of light-absorbing phenanthrenes. In contrast, the fluorescence intensity of the different hybrids remains unchanged if the exciplex is generated by excitation of pyrene (Figure 4 and Table 2). The quantum yields after

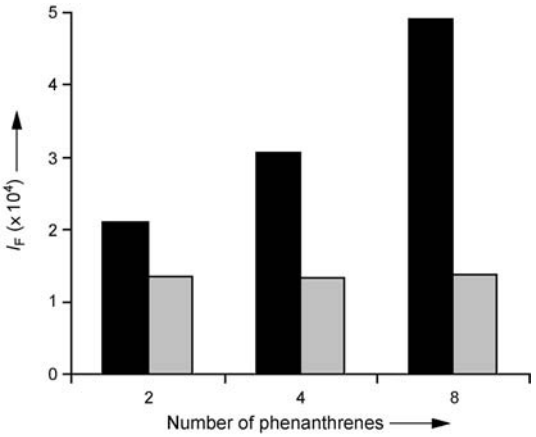

Figure 4. Fluorescence intensities (area under curve) of light-harvesting hybrids upon excitation at 320 nm (phenanthrenes, black bars) or 365 nm (pyrene, gray bars); slits: 2.5 nm; conditions: see Table 1.

Table 2: Relative fluorescence intensities and quantum yields of the different hybrids.

	1*2	3*4	5*6	7*8
$I_{365\,nm}$[a]	–	13504	13375	13699
$I_{365\,nm}$ (normalized)	–	1	1	1
$I_{320\,nm}$[a]	–	20877	30612	49038
$I_{320\,nm}$ (normalized)	–	1	1.5	2.3
Φ[b]	0.43[c]	0.46[d]	0.42[d]	0.41[d]

[a] Total fluorescence intensities (auc) after irradiation at the indicated wavelength. [b] Fluorescence quantum yield, for details see the Supporting Information. [c] Pyrene monomer fluorescence. [d] Phenanthrene–pyrene exciplex fluorescence; conditions: see Table 1.

excitation at 320 nm are fairly constant for the hybrids containing two, four, or eight phenanthrene units (46%, 42%, and 41%, respectively, Table 2), which underlines the efficiency of EET from the site of light absorption to the exciplex. The results imply that the exciplex that is formed from a pyrene and one of the phenanthrenes is an ideal acceptor of the excitation energy.

Our LHC combines two features that are relevant in the context of such systems: the absorption of light by an array of chromophores, and EET to a collection center (Figure 5).

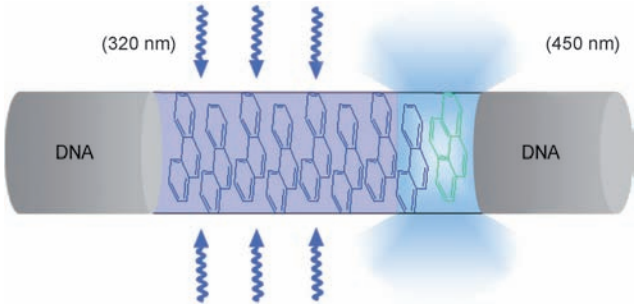

Figure 5. Illustration of a DNA-embedded, light-harvesting antenna composed of π-stacked phenanthrenes (purple block) and a fluorescent phenanthrene–pyrene exciplex (blue).

This approach resembles the use of zeolite-based dye-nanochannels for light harvesting, transport and trapping.[15,21,66] Absorption of light by the dyes that are arranged in the nanochannels[67,68] is followed by transfer of the excitation energy to acceptor fluorophores, which are located at the channel ends, by FRET.[15,69–72] In the present system, however, the light-absorbing chromophores are organized in a DNA-embedded assembly of π-stacked phenanthrenes. The importance of electronic coupling through π–π interactions for materials with optoelectronic properties,[25,73–76] and for charge-transfer processes in DNA[77–83] is well-recognized and documented. The characterization of the energy-transfer process from the phenanthrenes to the exciplex is the topic of ongoing studies.

In conclusion, a DNA-based light-harvesting antenna has been described. The system consists of an array of π-stacked phenanthrene chromophores (the light-collecting antenna), an exciplex-forming pyrene (the energy-collection center), and a DNA double helix (the supramolecular scaffold). Up to eight phenanthrenes were used for light collection. The number of photons emitted by the phenanthrene–pyrene exciplex is proportional to the number of light-absorbing chromophores. The properties of analogous systems that contain different types and different numbers of chromophores are under investigation.[84]

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