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One-Dimensional Multichromophor Arrays Based on DNA: From Self-Assembly to Light-Harvesting

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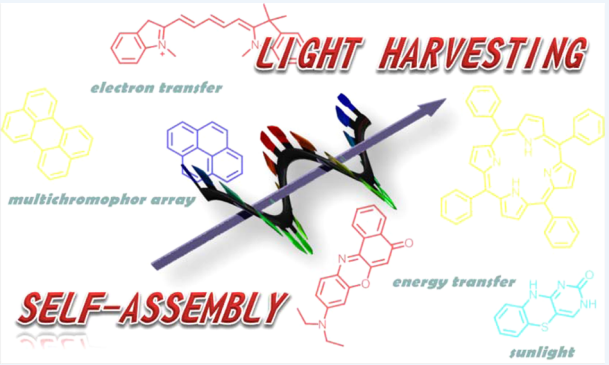
CONSPECTUS: Light-harvesting complexes collect light energy and deliver it by a cascade of energy and electron transfer processes to the reaction center where charge separation leads to storage as chemical energy. The design of artificial light-harvesting assemblies faces enormous challenges because several antenna chromophores need to be kept in close proximity but self-quenching needs to be avoided. Double stranded DNA as a supramolecular scaffold plays a promising role due to its characteristic structural properties. Automated DNA synthesis allows incorporation of artificial chromophore-modified building blocks, and sequence design allows precise control of the distances and orientations between the chromophores. The helical twist between the chromophores, which is induced by the DNA framework, controls energy and electron transfer and thereby reduces the self-quenching that is typically observed in chromophore aggregates.



This Account summarizes covalently multichromophore-modified DNA and describes how such multichromophore arrays were achieved by Watson−Crick-specific and DNA-templated self-assembly. The covalent DNA systems were prepared by incorporation of chromophores as DNA base substitutions (either as C-nucleosides or with acyclic linkers as substitutes for the 2′-deoxyribofuranoside) and as DNA base modifications.

Studies with DNA base substitutions revealed that distances but more importantly relative orientations of the chromophores govern the energy transfer efficiencies and thereby the light-harvesting properties. With DNA base substitutions, duplex stabilization was faced and could be overcome, for instance, by zipper-like placement of the chromophores in both strands.

For both principal structural approaches, DNA-based light-harvesting antenna could be realized. The major disadvantages, however, for covalent multichromophore DNA conjugates are the poor yields of synthesis and the solubility issues for oligonucleotides with more than 5−10 chromophore modifications in a row. A logical alternative approach is to leave out the phosphodiester bridges between the chromophores and let chromophore−nucleoside conjugates self-assemble specifically along single stranded DNA as template. The self-organization of chromophores along the DNA template based on canonical base pairing would be advantageous because sequence selective base pairing could provide a structural basis for programmed complexity within the chromophore assembly. The self-assembly is governed by two interactions. The chromophore−nucleoside conjugates as guest molecules are recognized via hydrogen bonds to the corresponding counter bases in the single stranded DNA template. Moreover, the $\pi-\pi$ interactions between the stacked chromophores stabilize these self-assembled constructs with increasing length. Longer DNA templates are more attractive for self-assembled antenna. The helicity in the stack of porphyrins as guest molecules assembled on the DNA template can be switched by environmental changes, such as pH variations. DNA-templated stacks of ethynyl pyrene and nile red exhibit left-handed chirality, which stands in contrast to similar covalent multichromophore−DNA conjugates with enforced right-handed helicity. With ethynyl nile red, it is possible to occupy every available binding site on the templates. Mixed assemblies of ethynyl pyrene and nile red show energy transfer and thereby provide a proof-of-principle that simple light-harvesting antennae can be obtained in a noncovalent and self-assembled fashion. With respect to the next important step, chemical storage of the absorbed light energy, future research has to focus on the coupling of sophisticated DNA-based light-harvesting antenna to reaction centers.

1. INTRODUCTION

Nature designed impressive molecular assemblies to collect sunlight and to convert it into chemical energy. These light-harvesting complexes transport the collected light energy via a cascade of energy transfer (EnT) and electron transfer (ElT) processes to the reaction center where charge separation induces formation of ATP and NADPH to store chemical energy.[1−8] It can be learned for artificial light-harvesting systems that the involved chromophores and cofactors are precisely arranged and able to generate a long-range charge separation.[9] Quantum entanglement leads to use of light energy without loss of thermal energy.[10] All EnT processes are very fast and efficient.[9] The reaction center is separated from the

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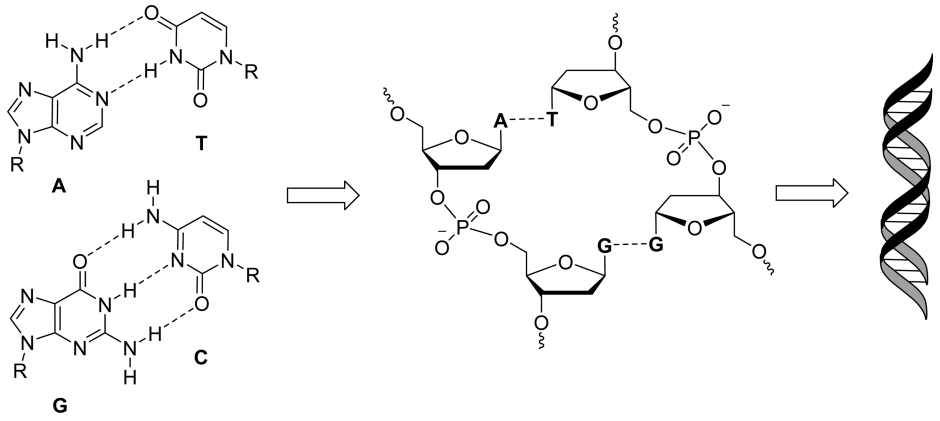

Figure 1. Canonical base pairing between A and T and G and C and stacking between base pairs controls the formation of the DNA double helix.

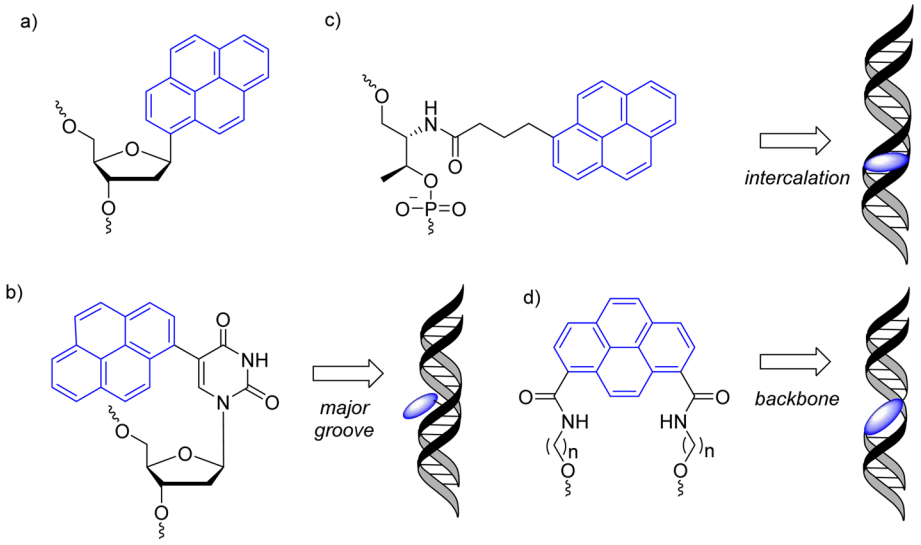

Figure 2. Artificial DNA building blocks for pyrene as representative chromophore: (a) C-nucleoside,[49] (b) attachment to the 5-position of 2′-deoxyuridine,[50] (c) D-threolinol as artificial acyclic linker,[44] and (d) achiral non-nucleosidic linker.[48]

light-harvesting complex by a distance of approximately 40 Å.[11] This is a significant advantage; even if sunlight is weak, the "dark" reactions may take place.[6,9] Over the past decade, there were synthetic antenna systems described that try to mimic the natural systems.[2,8,12−41] The requirements for such artificial systems are (i) to cover a broad range of UVA/vis absorption, (ii) to allow fast and efficient EnT between the chromophores, (iii) to generate a charge separated state, and finally (iv) to convert light energy into chemical energy. Accordingly, the construction of biomimetic light-harvesting assemblies faces enormous challenges because antenna chromophores need to be kept in close proximity but self-quenching needs to be ruled out. The rather easy and inexpensive synthesis of small molecular units can be combined with self-controlled assembly, in the ideal case, to achieve new and desired optical properties that the monomer units do not exhibit. Once the multichromophore arrays are self-assembled, it is important to understand the EnT and ElT processes therein. Properties like helical structure, well-defined distances between the base pairs, and sequence recognition encoded by canonical base pairing make DNA very attractive as a structural scaffold (Figure 1). Hence, it looks reasonable to arrange such multichromophore arrays based on DNA. Moreover, automated DNA synthesis offers the possibility to incorporate new chromophore-modified building blocks. Programmed sequence design allows precise control of the distances and orientations between the chromophores and thereby the competition between EnT and ElT processes. The helical twist between the chromophores that is induced by the DNA framework reduces self-quenching that is typically observed in chromophore aggregates. This Account summarizes covalently connected multichromophore-modified DNA and their EnT and ElT abilities on the way to light-harvesting systems and gives a perspective how such multichromophore arrays were achieved by noncovalent DNA-templated self-assembly.

2. COVALENT CHROMOPHORE ARRANGEMENTS IN DNA

2.1. Chromophores as DNA Building Blocks

The most significant advantage of DNA from the synthetic point of view is the building block chemistry.[42] The building blocks of unmodified nucleosides are commercially available, also in large quantities, and chromophores can be incorporated into DNA by providing the corresponding artificial building blocks by methods of organic synthesis. Automated synthesis allows one to program any desired sequence, mixing natural with chromophore building blocks, especially multichromo-

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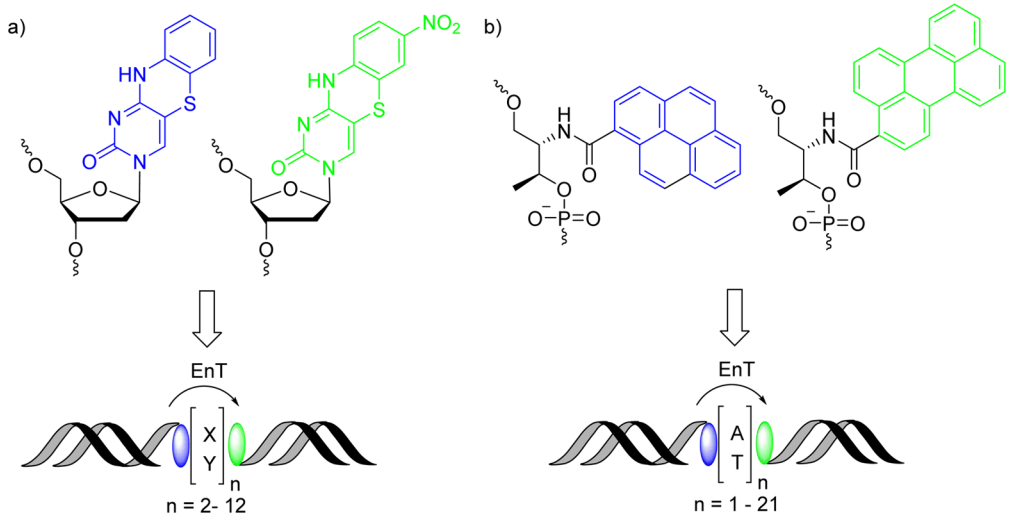

Figure 3. Phenothiazine[51] (a) as nucleosides and pyrene/perylene (b) as nucleoside analogs[53,54] to study the orientation dependence of EnT in DNA.

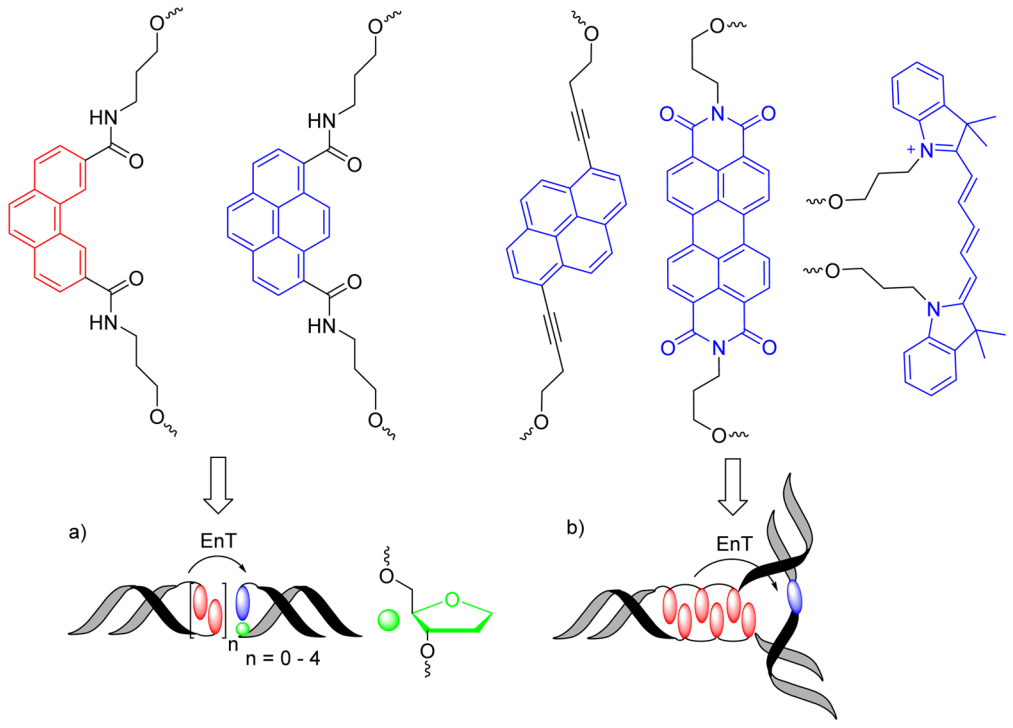

Figure 4. DNA-based light-harvesting antenna based on phenanthrene stacks in (a) DNA duplexes[37] and (b) DNA three-way junctions.[56]

phore units that are framed by natural nucleoside pairs to enable unique self-assembly. There are several principle ways for new DNA building block constructs (Figure 2).[43] The first type, the so-called C-nucleoside, carries the chromophore attached to the 2′-deoxyribofuranoside by a C−C glycosidic bond instead of a C−N bond in natural nucleosides. Thereby the chemical stability is significantly enhanced and the chromophore intercalates into the DNA base stack. The second type is the DNA base modification. The site of attachment that is routinely applied is the 5-position of pyrimidine nucleosides (dU/T and dC) and the 8-position of purine nucleosides (dA and dG) since these positions are the most reactive ones. If canonical Watson−Crick base pairing is presumed, the chromophores assemble in the major groove. The third type for chromophore incorporation uses D-threolinol,[44] D-serinol,[45] or glycole derivatives[46,47] as acyclic linkers. With these rather flexible linkers, synthetic access to new building blocks is facilitated, and chromophores intercalate very efficiently into the DNA base stack. In the last type, the chromophore itself is part of the achiral non-nucleosidic linkers.[48]

2.2. Covalently Embedded Chromophore Aggregates in DNA: From Energy Transfer to Light Harvesting Systems

The major prerequisite for the development of DNA-based light-harvesting systems is the understanding of EnT processes between chromophores that were attached covalently into the DNA base stack. Using two different phenothiazines as dC analogs, Wilhelmsson et al. studied the distance dependence of EnT along the DNA axis (Figure 2).[51] As a consequence of the

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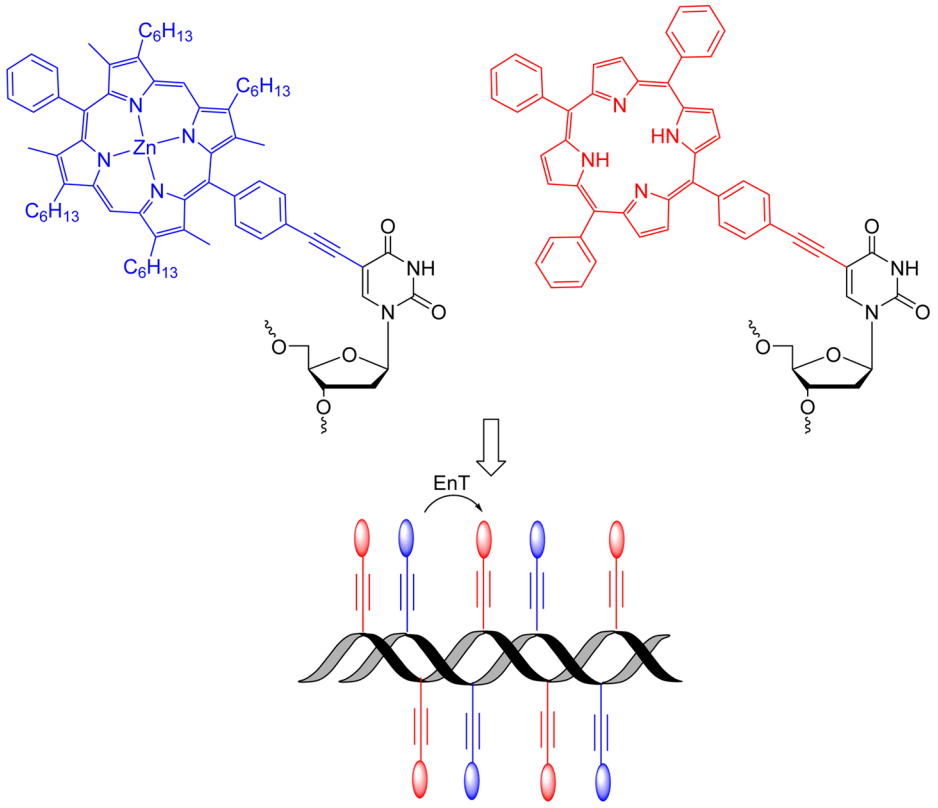

Figure 5. Tetraphenyl porphyrin for assembly of chromophores in the DNA groove.[58]

fact that both analogs were rigidly placed within the DNA base stack, the EnT between them depends not only on the distance but also on the orientation. Hence over short distances, the correct placement of the two chromophores plays a major role for efficient EnT. These results opened the way to apply EnT-based methods for studying nucleic acid conformations.[52] A very similar approach toward an EnT system was achieved by using pyrene and perylene as DNA base substitutions (Figure 3). Asanuma et al. incorporated both chromophores into DNA using the D-threoninol linker.[53] In general, the emission of pyrene overlaps nicely with the absorption of perylene in the range between 370 and 450 nm, which is a prerequisite for efficient EnT. If more pyrene units were added to the duplex, the emission of perylene at around 510 nm did not increase. This showed that the Förster radius is rather short. Similar to the previously mentioned study, Asanuma et al. investigated the distance and orientation dependence of this EnT. Astonishingly, the results were very similar to the phenothiazine−C-nucleoside system although pyrene and perylene were incorporated into DNA by the rather flexible D-threolinol. If the chromophores were placed at every half-turn of the B-type helix the EnT became very inefficient. A theoretical model of B-DNA as a rigid cylinder supported the idea that the orientation of transition dipole moments governs the EnT in DNA.[54]

In a combinatorial approach, Kool et al. investigated the stacking interactions of various chromophores that replaced the natural units of DNA by flat aromatic molecules and heterocycles, most of them as C-nucleosides. Remarkably, a multicolor set of labels was gained when excited at a single wavelength. A manifold of photophysical interactions, including excimer and exciplex formation and EnT and ElT processes were presumed, and quenching was found to be sequence dependent,[55] but the complexity of these multichromophore aggregates does not allow elucidation of these processes explicitly.

On the basis of a π-stacked array of two different chromophores, Häner et al. developed an astonishingly simple DNA-based light-harvesting antenna.[37] It contains an array of up to eight phenanthrene units in a row and one pyrene at the end (Figure 4). The stack was placed in the center of the DNA, and the pyrene was fixed on top of that stack by an abasic site analog on the opposite side. The multiple π-stacked phenanthrenes transfer energy to a phenanthrene−pyrene exciplex. Hence, the latter emission is increased with the number of phenanthrenes. This approach was transferred by Häner et al. to a DNA three-way junction. Therein, a central π-stacked phenanthrene array was also responsible for light collection, but the acceptor chromophore at the cross point was varied. Notably, the wavelength shift between excitation and emission was largest if a Cy5 chromophore was used at the mentioned position.[56]

2.3. Covalently Assembled Chromophore Aggregates along the DNA Groove

The self-organization of chromophores along the DNA double helix by DNA base modifications without significant perturbation of the canonical base pairing would be advantageous because the sequence selective recognition could provide a structural basis for programmed complexity within the assembly. This approach was recently used by Stulz et al. to yield DNA-based porphyrin arrays. The covalent attachment of several tetraphenyl porphyrins (Figure 5) in a row onto single DNA strands showed that there is virtually no limitation in the amount of substituents and, more importantly, that such porphyrin arrays were extendable to the nanometer scale.[57] Unexpectedly, no duplex stabilization could be gained by the

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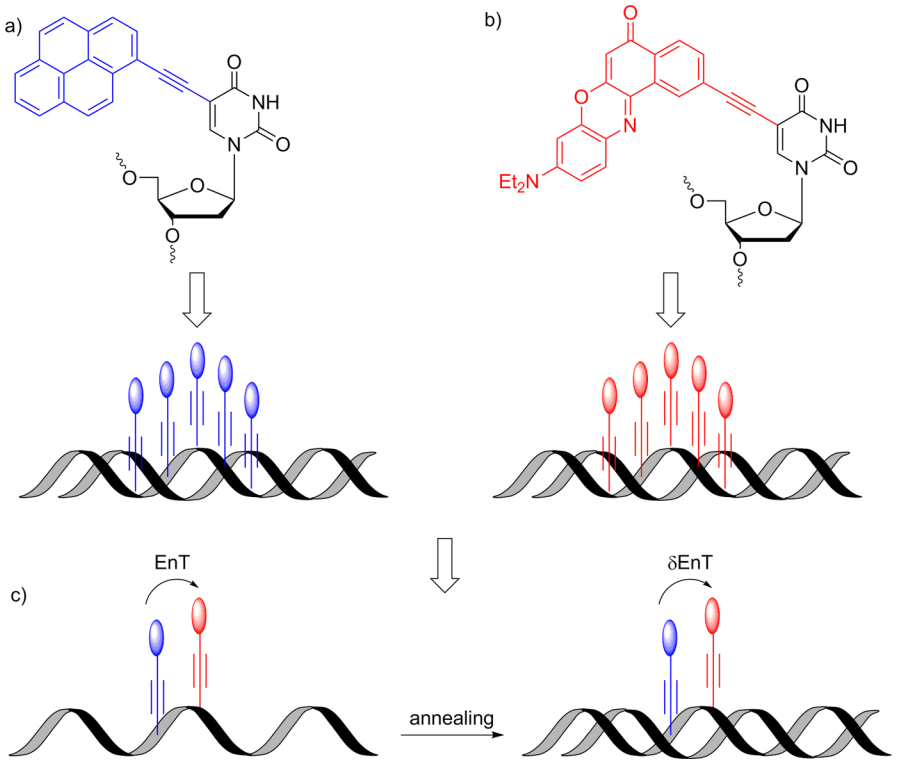

Figure 6. Chromophore assemblies based on (a) ethynyl pyrene (Py−≡−dU)[62] and (b) ethynyl nile red (Nr−≡−dU)[64] and (c) principle of efficient EnT in the DNA single strand vs inefficient EnT between Py−≡−dU and Nr−≡−dU for the development of white light-emitting DNA.[63]

interactions between the adjacent porphyrins. The key to increase duplex stabilization was an alternating sequence with porphyrins in both complementary strands of the DNA duplex.[58] Fluorescence quenching of Zn-porphyrins by metal-free porphyrins revealed an EnT in these arrays along the DNA.

We attached pyrene to the 5-position of 2′-deoxyuridine (dU)[59,60] by a single C−C bond and modified a DNA duplex with five of such units next to each other to investigate the chromophore stack along the DNA. Circular dichroism (CD) showed a strong biphasic signal in the pyrene range between 330 and 400 nm due to the right-handed helicity of the chromophore arrangement. Interestingly, the fluorescence intensity of this pyrene stack is 10-fold higher than that of a single pyrene modification and increases from the single to the double strand by a factor of 22. All results indicated a highly ordered arrangement of pyrenes along the DNA with the ability for homo-EnT processes (Figure 6).[61] Similar experiments with DNA bearing two to five ethynyl pyrene units conjugated to 2′-deoxyuridine (Py−≡−dU) showed a nonlinear rise for the pyrene absorption at 380 nm indicating excitonic interactions. This can also be seen by the strong biphasic CD signal in the pyrene absorption range between 340 and 440 nm that was observed for DNA samples with more than three Py−≡−dU units. Similar to the DNA−porphyrin conjugates described above, the highly ordered Py−≡−dU stack appears only with the right counter bases (dA). The aggregation is also visible by the fluorescence at 500 nm and, in contrast to the DNA−porphyrin stacks, by the duplex stability, since the 5-fold Py−≡−dU modification leads to a significant increase in melting temperature compared with the corresponding single DNA modification.[62]

Nile red is a very solvatochromic chromophore and shows high fluorescence quantum yield. Similar to ethynyl pyrene, ethynyl nile red was attached to the 5-position of 2′-deoxyuridine (Nr−≡−dU).[63] In covalently assemblies along DNA double strands, bearing 3 or 5 Nr−≡−dU units adjacent to each other, the fluorescence at 660 nm was quenched completely. The biphasic CD signal of the DNA with the 5-fold Nr−≡−dU modification in the range between 500 and 700 nm indicates, similar to Py−≡−dU, a highly ordered, right-handed stacked arrangement of Nr−≡−dU. Both the hypsochromic absorption shift and the fluorescent quenching are characteristic for H-type aggregation. Contradictory is the observation that the duplex is destabilized.[64] Similar to the DNA−porphyrin conjugates but in contrast to the Py−≡−dU−DNA, every additional Nr−≡−dU unit decreased the stability of the DNA duplex.[43] These results show clearly that the information that can be gained from methods of optical spectroscopy is limited with respect to elucidation of the structure of such DNA−multichromophore conjugates.

So far, only one type of modification (Nr−≡−dU *or* Py−≡−dU) was assembled along DNA. Remarkably, if both chromophores were placed adjacent to each other in a single DNA duplex, a white-light-emitting DNA was obtained (Figure 6).[63] The characteristic absorption of both chromophores at 400 and 615 nm, respectively, ruled out the possibility of significant ground-state interaction between them. An EnT is possible due to the overlap of Py−≡−dU fluorescence and Nr−≡−dU absorption and occurs with a rate constant of approximately 5.2×10^9 s^{-1} in the single strand and significantly more slowly in the double strand (1.7×10^9 s^{-1}). The concomitant Nr−≡−dU fluorescence increase and Py−≡−dU fluorescence decrease (compared with the single strand) yielded a white emission with almost equal intensity for the blue-green (440 nm) and red (660 nm) contributions. Similar to the work of Wilhelmsson et al.[51] and Asanuma et

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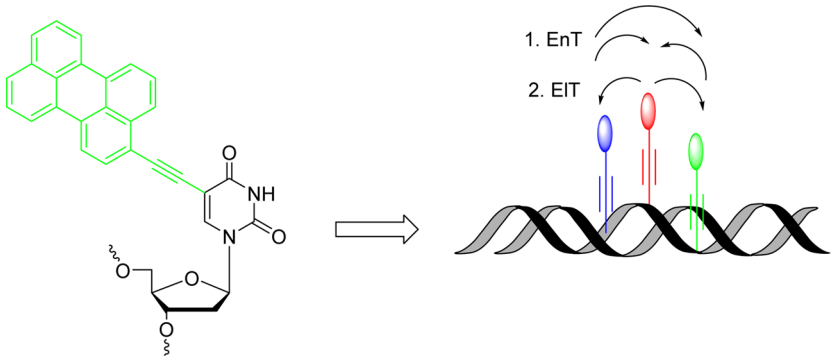

Figure 7. DNA-based light-harvesting system based on Py−≡−dU (blue), Pe−≡−dU (green), and Nr−≡−dU (red), for structures of Py−≡−dU and Nr−≡−dU, see Figure 5.[66]

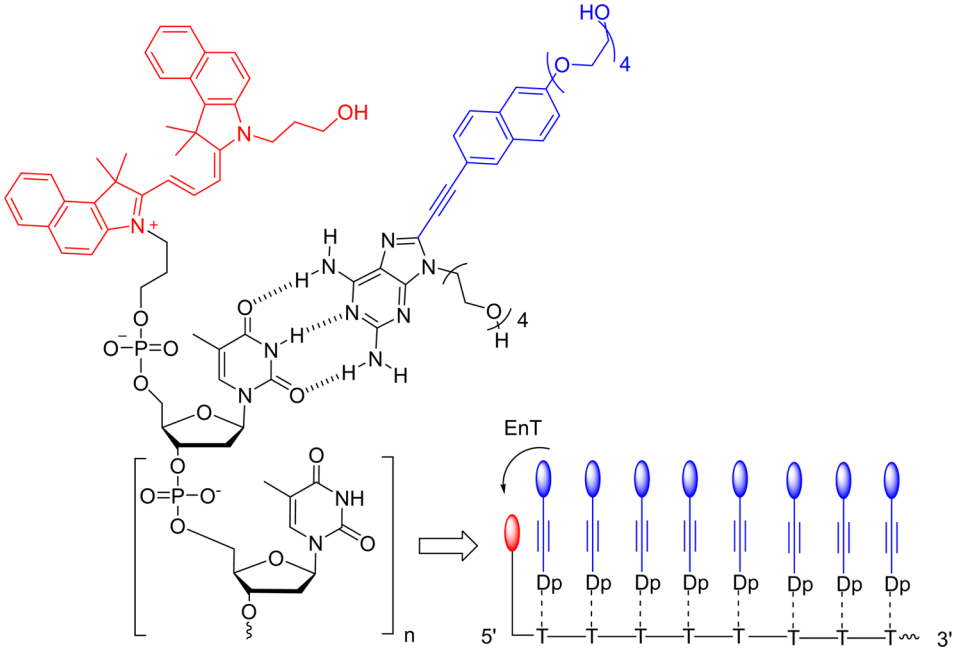

Figure 8. Self-assembly of naphthalene−diaminopurine (Dp) conjugates along oligothymidine as DNA template and EnT to Cy3.5 at the 5′-terminus.[71]

al.[65] described above, the EnT is highly dependent on the relative orientation of the chromophores. Hence, the observed difference of the EnT rates and efficiencies in the single strand vs the double strand is likely due to the change in the relative orientation of the chromophores since duplex formation induces a helical twist between them. An additionally interesting feature of this white light-emitting DNA is that the EnT efficiency can be controlled by association and dissociation of the duplex and that means by temperature.

If ethynyl perylene, also attached to the 5-position of 2′-desoxyuridine (Pe−≡−dU), is combined with Py−≡−dU and Nr−≡−dU in one DNA double helix (Figure 7), nearly the whole UV/vis- absorption range between 350 and 700 nm is covered, which is a perfect prerequisite to develop a DNA-based light-harvesting system.[66] Some ground state interactions between the three different chromophores can be seen by small absorption shifts and by appearance of CD signals for the three building blocks. If the chromophores are separated by two intervening dA−T base-pairs, the absorption is similar to the monomeric units, the CD signals disappear, and a strong Nr−≡−dU fluorescence at 660 nm appears upon excitation of the Py−≡−dU due to an EnT cascade from Py−≡−dU → Pe−≡−dU → Nr−≡−dU. This fluorescence is completely quenched when the chromophores are placed directly next to each other due to the occurrence of ElT processes from Nr−≡−dU → Pe−≡−dU and Nr−≡−dU → Py−≡−dU yielding a charge separated state. This interplay of EnT processes in one direction and ElT processes in the opposite direction was elucidated by time-resolved fluorescence spectroscopy. This adjustable three-chromophore system is a very promising DNA-based light-harvesting antenna because charge separation can be achieved by excitation at every wavelength between 400 and 700 nm and can potentially be used for chemical photocatalysis or other optochemical applications. In conclusion, light-harvesting systems can be designed astonishingly simply by helical arrangement of covalently attached chromophores in DNA-based architectures.

3. NONCOVALENT AND DNA-TEMPLATED SELF-ASSEMBLY OF CHROMOPHORES

The major disadvantages of solid-phase DNA synthesis for the multichromophore conjugates described in the previous paragraphs are the poor yields for longer conjugates and the

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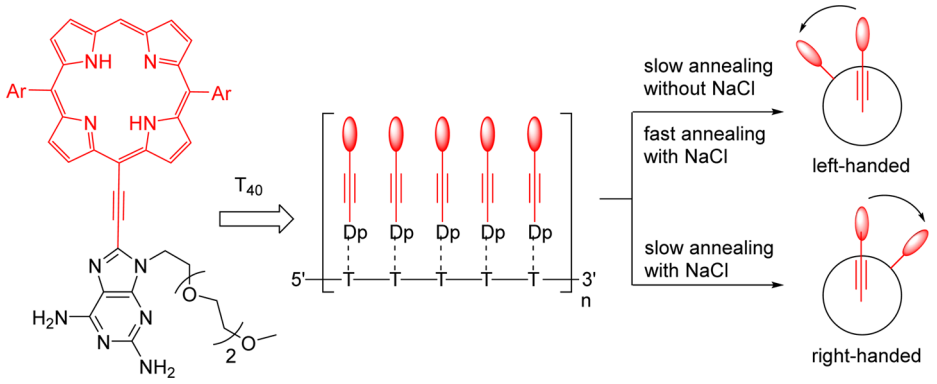

Figure 9. Self-assembly of porphyrin−diaminopurine conjugates along oligothymidine as template and control of supramolecular helicity.[74,75]

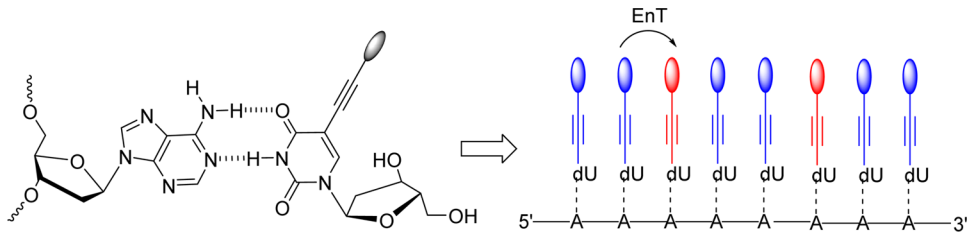

Figure 10. Self-assembly of Py−≡−dU and Nr−≡−dU along $(dA)_n$ templates,[76,77] for structures of Py−≡−dU and Nr−≡−dU, see Figure 5.

solubility issues for oligonucleotides with more than 5−10 chromophore modifications in a row. There are various examples of DNA-based nanoscale architectures reported by Albinsson et al.,[67] Kumar et al.,[68] Yan et al.,[69] and Roelfes et al.[70] where organic dyes were self-assembled along duplex or quadruplex DNA, for example, by intercalation, to achieve promising light-harvesting antenna. The specific and thereby sequence-controlled supramolecular oligomerization of chromophores into multichromophore stacks in water requires the application of single stranded DNA as template for self-assembly of chromophore-nucleoside conjugates. Schenning et al. were among the first who discovered that naphthalene-2,4-diaminopurine conjugates as guest molecules are recognized via hydrogen bonds to oligothymidine as single stranded DNA template. Moreover, the $\pi-\pi$ interactions between the stacked chromophores stabilize these self-assembled constructs with increasing length (Figure 8).[71]

The theoretical model to describe the DNA-templated self-assembly supported the experimental observations that both host−guest (hydrogen-bonding) and guest−guest interactions (π-stacking) regulate this process. Hence, longer DNA templates are more attractive for self-assembly. In combination with thermodynamic calculations, a correlation length of eight units was determined at the supramolecular polymerization temperature. This value could potentially be further improved by increasing the attractive interactions between the chromophores. The helicity in the stack of guest molecules assembled on the DNA template can be switched by changing the pH value as a result of protonation of the guest. At pH = 3 left-handed and at pH = 7 right-handed chirality was observed.[72] If this type of assembly is equipped with a Cy3.5 dye at the 5′-end (T_{40}−Cy3.5), a directed EnT to this dye was observed since the naphthalene emission overlaps with the Cy3.5 absorption between 500 and 600 nm.[73] This result is very similar to the covalent DNA−chromophore assembly consisting of phenanthrenes and pyrenes as described in section 2.2 and thereby clearly shows that this kind of light-harvesting antenna can also be achieved in a completely noncovalent but specifically self-assembled fashion.

The question of helicity was further elucidated with conjugates of porphyrins and 2,4-diaminopurine along a oligothymidine (T_{40}) template by Balaz et al. (Figure 9).[74] Remarkably, they reported that it is possible to control the supramolecular helicity by the ionic strength and the cooling rate. A red shift of the Soret band in the UV/vis absorption spectra to 491 nm and a strong CD signal in the porphyrin range between 400 and 500 nm supported a strong excitonic coupling of the porphyrins in the self-assembled stack. DFT calculations were used to assign the helicity of the assemblies.[75] This was the first example of a DNA-templated self-assembly where the helicity could be switched by environmental conditions.

The questions that we asked ourselves were (i) whether it is possible to specifically assemble a Py−≡−dU stack along a complementary DNA single strand and (ii) how the optical properties would potentially differ from the DNA double strand that was covalently labeled with up to five Py−≡−dU chromophores adjacent to each other (see section 2.3). Py−≡−dU was only soluble in aqueous solution in the presence of an oligo-2′-deoxyadenosine strand (dA_{17}). That means that the precipitation of Py−≡−dU in water observed both in the absence of DNA and in the presence of the "wrong template", oligothymidine (T_{17}), ruled out that unselective binding of Py−≡−dU may occur. Notably, only the Py−≡−dU_x/dA_{17} assembly is soluble in water, and the optical properties are very similar to the covalent DNA system. The strong CD signal in the pyrene absorption range between 350 and 450 nm, however, evidenced a self-assembled helical Py−≡−dU stack along the dA_{17} template but showed left-handed chirality. This stands in contrast to the DNA system with five covalently connected Py−≡−dU units where right-handed chirality was observed.[76] Nr−≡−dU behaved very similarly when self-assembled along dA_{20}. Again, left-handed chirality was observed. Obviously, both chromophore−-nucleo-

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side conjugates, Py−≡−dU and Nr−≡−dU (Figure 10), exhibit an intrinsic property to assemble with left-handed chirality, which was also observed in nanoparticles that were formed of Nr−≡−dU without any template.[64] Remarkably, DNA templates are not able to overrule this intrinsic behavior. Only the covalent connection via phosphodiester bonds in double-stranded DNA forced the chromophores to stack with right-handed helicity.[62]

Carefully performed titration experiments revealed the complete occupation of all available binding sides on the template strands $(dA)_n$ by Nr−≡−dU units. As expected from H-aggregates, and in contrast to the Py−≡−dU assembly, the emission at 660 nm is completely quenched and the absorption is shifted hypsochromically. The interesting next question is how the optical properties vary if Py−≡−dU and Nr−≡−dU are mixed in different ratios and assembled along the $(dA)_{20}$ template.[77] It became clear that large Py−≡−dU stacks can be interrupted by small amounts of Nr−≡−dU and vice versa. This is astonishing because it indicates that mixed assemblies are formed spontaneously. Fluorescence showed primarily quenching in these mixed assemblies but revealed dual emission in assemblies with ratios of Py−≡−dU/Nr−≡−dU = 10:10 to 2:18. This reveals experimental evidence for an EnT between the two chromophores, which was also verified by excitation spectra. These noncovalently assembled and mixed chromophore stacks represent promising examples for DNA-based light-harvesting antenna. It is a simple approach to build large multichromophore assemblies with absorption that covers the main parts of the UVA/vis range between 350 and 600 nm and with tunability of EnT and ElT by different mixing ratios.

4. CONCLUSION

The multichromophore systems presented herein showed that the design and preparation of light-harvesting assemblies based on DNA can be achieved both by the covalent modification of DNA using artificial chromophore building blocks for solid phase synthesis and by specific self-assembly of chromophore-nucleoside conjugates along single-stranded DNA as templates. Current research is focused on the elucidation of EnT and ElT processes in these multichromophore stacks. With respect to the correct placement of different chromophores as energy donors and energy acceptors and the appropriate distances between them (the requirement that is impressively demonstrated by the natural light-harvesting complexes) the covalent DNA systems are one step further than the noncovalent assemblies since the DNA building block chemistry allows the sequential design by programmed synthesis. It is clear that the self-assembly approach has to be significantly improved by providing different nucleoside conjugates that exhibit different hydrogen-bonding patterns and that are specifically recognized by corresponding complementary units in the template strand. In the ideal case small molecular chromophore units assemble in a complex but completely self-controlled way to materials with new optoelectronic properties. It is clear that, in principle and shown by the presented examples herein, such multichromophore arrays can be arranged based on DNA. There are very few reports that go beyond the design and spectroscopic elucidation of chromophore arrangements: Yan et al. showed that a three-arm DNA nanostructure labeled with fluorophores can be coupled by energy transfer to a bacterial reaction center;[78] Sotzing et al. reported on dye-doped DNA nanofibers that were applied in white LEDs.[79] But with respect to the next and equally important step, chemical storage of the absorbed light energy, we are not yet there and, in fact, far away from the goal. Future efforts have to focus on the coupling of sophisticating DNA-based light-harvesting antenna to reaction centers, for example, for hydrogen production or chemical photocatalysis.

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Notes

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Hans-Achim Wagenknecht studied chemistry in Freiburg (Germany), got his Ph.D. in 1998 in bioorganic chemistry in Basel (Switzerland) and worked as a postdoctoral researcher at Caltech (USA). His independent career started in 2000 in Munich (Germany). In 2005, he got a professorship at Regensburg, and since 2010, he holds the chair for organic chemistry at KIT. His research is focused on bioorganic chemistry with nucleic acids and peptides, fluorescent imaging, DNA architectonics, and chemical photocatalysis.

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