

Synthesis and assembly of DNA-templated chromophore aggregates for light harvesting

Introduction and previous results

The hierarchical organization of dyes at the supramolecular level can be achieved if synthetic building blocks self-assemble with well-defined molecular geometries and chromophore distances. The regular geometry of DNA namely the double helical structure and the typical stacking distance of ≈ 3.4 Å between the bases offer a suitable structural scaffold. Our group has shown that the chromophores ethynyl pyrene and ethynyl nile red as conjugates with nucleosides self-assemble non-covalently and specifically along DNA templates. The mixed assemblies of both chromophores are highly ordered, show left-handed chirality and yield dual fluorescence.^[1,2] On the other hand, molecular switches provide an important tool and handle to trigger the DNA-based architectures and thereby their optical properties by light.^[3-6]

Goals

In this project we plan to develop DNA-based architectures for non-covalent arrangement of chromophores and molecular switches, both attached to nucleosides as hydrogen-binding building blocks. Statistical mixture of chromophores and molecular switches should aggregate spontaneously along a single-stranded oligonucleotide that serves as template. In the ideal case the use of molecular switches influence the chromophore arrangement in such a way that either the chiral chromophore stack is spontaneously built or completely inhibited. Thereby the optoelectronic properties of the chromophore stacks can be switched by light.

References

- [1] DNA-templated formation of fluorescent self-assembly of ethynyl pyrenes: S. Sezi, H.-A. Wagenknecht, *Chem. Commun.* **2013**, 49, 9257-9259.
- [2] Mixed non-covalent assemblies of ethynyl nile red and ethynyl pyrene along oligonucleotide templates: P. Ensslen, Y. Fritz, H.-A. Wagenknecht, *Org. Biomol. Chem.* **2015**, 13, 487-492.
- [3] Diarylethene-Modified Nucleotides for Switching Optical Properties in DNA: S. Barrois, H.-A. Wagenknecht, *Beilstein J. Org. Chem.* **2012**, 8, 905-914.
- [4] Covalent Modification of 2'-Deoxyuridine with Two Different Molecular Switches: S. Barrois, C. Beyer, H.-A. Wagenknecht, *Synlett* **2012**, 23, 711-716.
- [5] Synthesis of DNA with Spirobenzopyrans as an Internal Covalent Modification: C. Beyer, H.-A. Wagenknecht, *Synlett* **2010**, 1371-1376.
- [6] Synthesis of Spiropyranes as Building Blocks for Molecular Switches and Dyads: C. Beyer, H.-A. Wagenknecht, *J. Org. Chem.* **2010**, 75, 2752-2755.