DNA single strands and duplexes with two sequentially incorporated squaraine molecules

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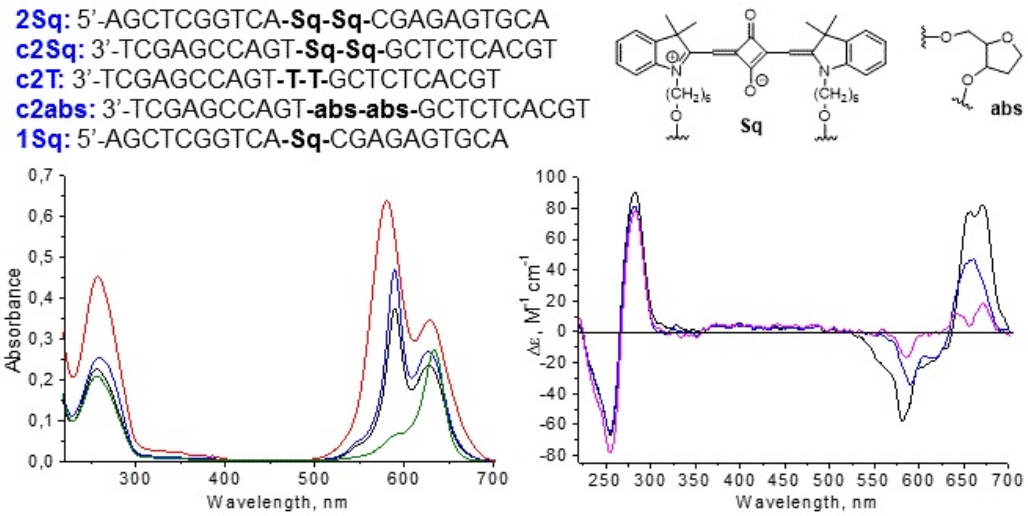
DNA´s remarkable self-recognition properties make it one of the most promising systems for studying interactions between synthetic molecules precisely incorporated into duplexes. Sequence-defined oligonucleotides modified with target molecules can be obtained by solid-phase synthesis using readily available reagents.

In this work, oligonucleotides **2Sq** and **c2Sq** with two squaraine molecules sequentially incorporated in the backbone were synthesized by phosphoramidite approach and their absorption, fluorescence, circular dichroism (CD) spectra and quantum yields (Q.Y.) were studied before and after hybridization. The same spectral properties were investigated for duplexes **2Sq*c2T** and **2Sq*c2abs** where deoxythymidine (**T**) or abasic site (**abs**), correspondingly, were placed opposite squaraine (**Sq**) molecules. Melting temperatures (Tm) of the duplexes were also studied.



Left: absorption spectra of the squaraine-modified oligonucleotides **2Sq** (black), **c2Sq** (blue) and **1Sq** (green) and duplex **2Sq*c2Sq** (red). Right: CD spectra of the duplexes **2Sq*c2Sq** (black), **2Sq*c2T** (magenta) and **2Sq*c2abs** (blue). Conditions: 1 μM of each strand, phosphate buffer 10 mM, NaCl 100 mM.

The incorporation of two **Sq** units into single DNA chain results in the appearance of a new absorption band at shorter wavelength (588 nm *vs*. 633 nm for **1Sq**). Additionally, the quenching of fluorescence is observed (3.1% *vs*. 29% for **1Sq**). These effects are attributed to the dimerization of squaraines by H-type. The hybridization of **2Sq** leads to more pronounced quenching of the fluorescence.

Oligonucleotides **2Sq** and **c2Sq** do not show noticeable CD signals in the spectral range 500-700 nm. However, the CD spectra of the duplexes exhibits the signals with amplitude A = +141 (**2Sq*c2Sq**), +81 (**2Sq*c2abs**) and +36 (**2Sq*c2T**).