Aggregation of a squaraine-modified oligonucleotide in aqueous solution

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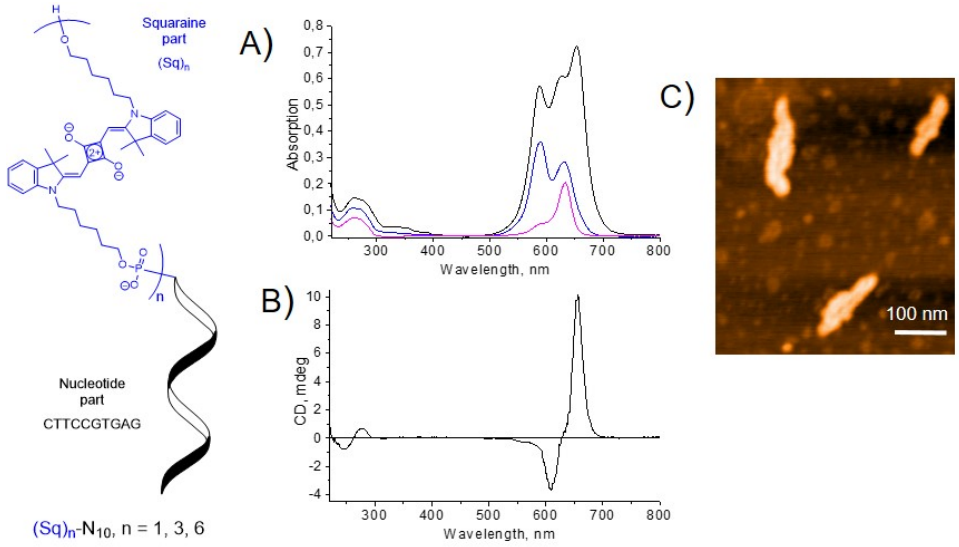
Squaraine-based compounds are promising chromophores for the creation of new materials for biomedical or diagnostic applications through the methods of supramolecular chemistry. Squaraine dyes exhibit a molar absorptivity of up to 260 000 $M^{-1}cm^{-1}$. They absorb and emit light in the long-wavelength region of the visible spectrum. Furthermore, they tend to form well-ordered aggregates in organic and aqueous solutions.

In this work, we study the aggregation properties of oligomers which consist of squaraines (1, 3, or 6 molecules) and nucleotides (10 units). Their aggregation properties are studied by spectroscopic (UV-Vis and CD) and microscopic (AFM and TEM) methods in water/ethanol solutions (see Figure below).



A) UV-Vis spectra of the oligomers: (**Sq)$_1$-N$_{10}$** (magenta, no aggregation), (**Sq)$_3$-N$_{10}$** (blue, H-aggregation), and (**Sq)$_6$-N$_{10}$** (black, oblique aggregation) B) CD spectrum and C) AFM image of the (**Sq)$_6$-N$_{10}$** oblique aggregates

Based on UV/vis spectroscopy, oligomer (**Sq)$_1$-N$_{10}$** with one squaraine molecule shows no well-defined type of aggregation. Oligomer (**Sq)$_3$-N$_{10}$** containing three squaraine units, however, reveals stacking of the chromophores in H-type fashion (blue shifted absorption band). Finally, oligomer (**Sq)$_6$-N$_{10}$** can form both H-type and oblique (splitting of the absorption band) aggregates depending on the conditions of preparation. The oblique aggregates of the (**Sq)$_6$-N$_{10}$** exhibit the signs of the supramolecular polymers, in which the squaraine-nucleotide oligomers are arranged in a helical fashion.