Long-wavelength supramolecular polymers based on a squaraine-nucleotide chain

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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 describe the supramolecular polymers formed by the modified oligonucleotide $(Sq)_6$-N_{10} which consists of six squaraine molecules and ten nucleotides.
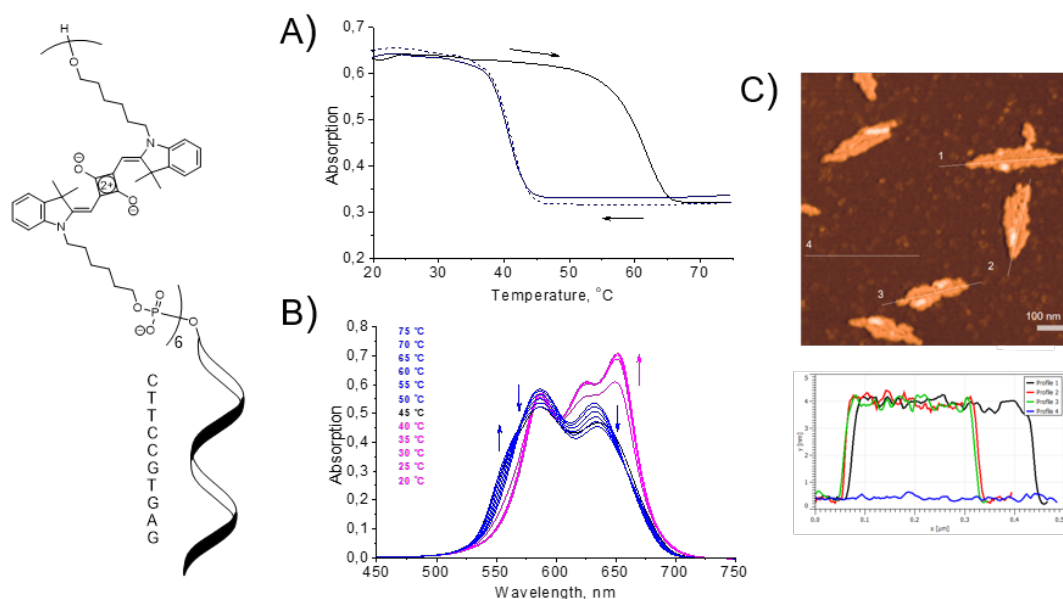
A) Cooling and heating runs for the oligomer $(Sq)_6$-N_{10} recorded at $\lambda = 660$ nm showing reversible self-assembly processes.
B) Temperature-dependent UV/Vis absorption spectra. Arrows indicate the change of spectrum on decreasing the temperature.
C) AFM image of the supramolecular polymers. Conditions: 1 µM $(Sq)_6$-N_{10}, 10 mM PB, 300 mM NaCl, 15% EtOH.

In aqueous medium, the oligomer $(Sq)_6$-N_{10} can form both H-type (blue shifted absorption band) and oblique (splitting of the absorption band) aggregates depending on the conditions of preparation. The oblique aggregates exhibit the signs of the supramolecular polymers, in which the squaraine-nucleotide oligomers are arranged in a helical fashion. AFM and TEM investigations of the $(Sq)_6$-N_{10} sample reveal well-defined objects with a height about 4 nm, a width between 50-100 nm, and a length of up to 550 nm. Based on the Kasha and Davydov theories [1, 2], it was calculated the angle between the transition dipole moments of the individual squaraine molecules ($\alpha \approx 90°$) and the center-to-center distance between the molecules ($R = 11.9$ Å).

[1] M. Kasha, H.R. Rawls, M.A. El-Bayoumi, *Pure Appl. Chem.*, **1965**, *11*, 371–392.
[2] A.S. Davydov. McGraw-Hill, New York, 1962.