Fluorescence enhancement of TCC aggregates by aggregation shifting to J-aggregates preferable formation

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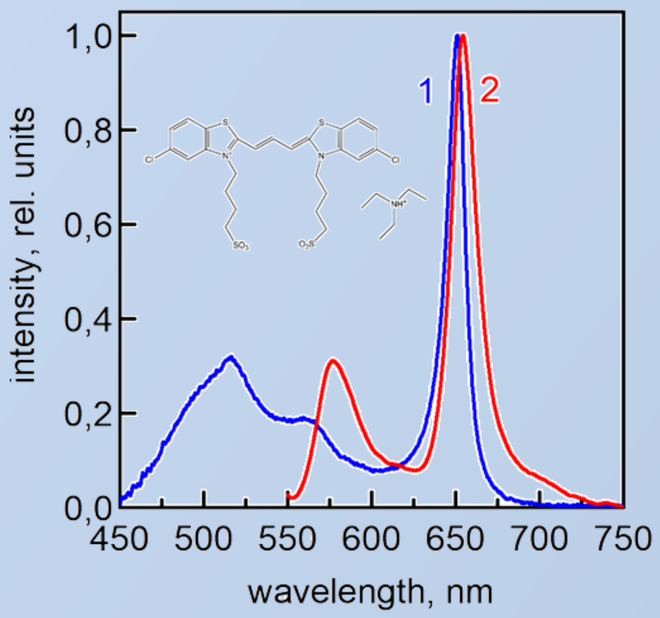


Absorption (blue) and luminescence (red) spectra of TCC J-aggregates in aqueous solution. On insets – the dyes structure.

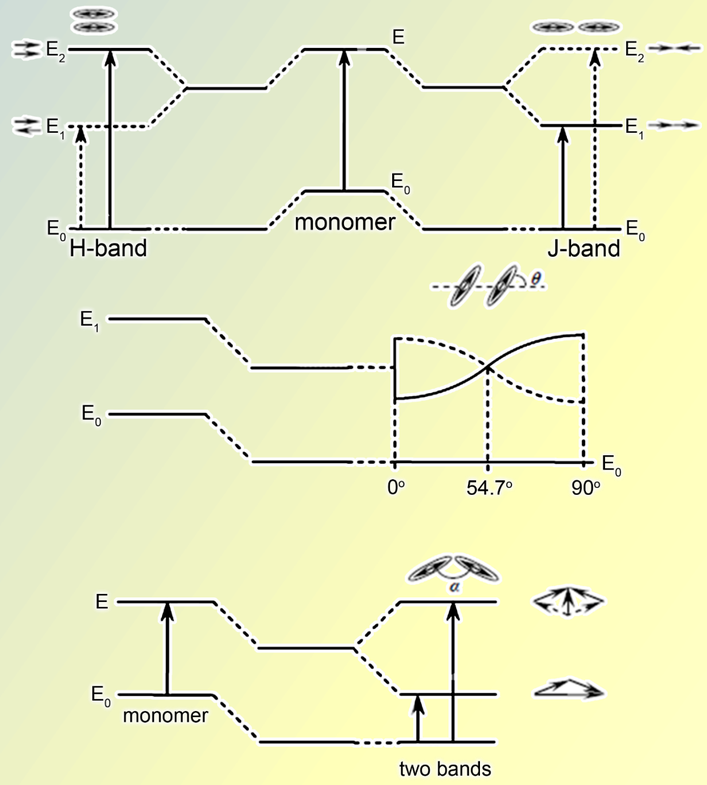
Some organic luminophores can form high-ordered molecular aggregates, called J-aggregates, which reveal unique optical properties due to excitonic nature of electronic excitations. Depending on the molecules arrangement in the J-aggregates exciton band appear as bathochromically shifted (J-band) or hypsochromically shifted (H-band) relatively monomer band.

The J-band appears at “head to tail” molecule packing as the lowest energy state of the exciton band and it accompanied by near-resonant fluorescence.

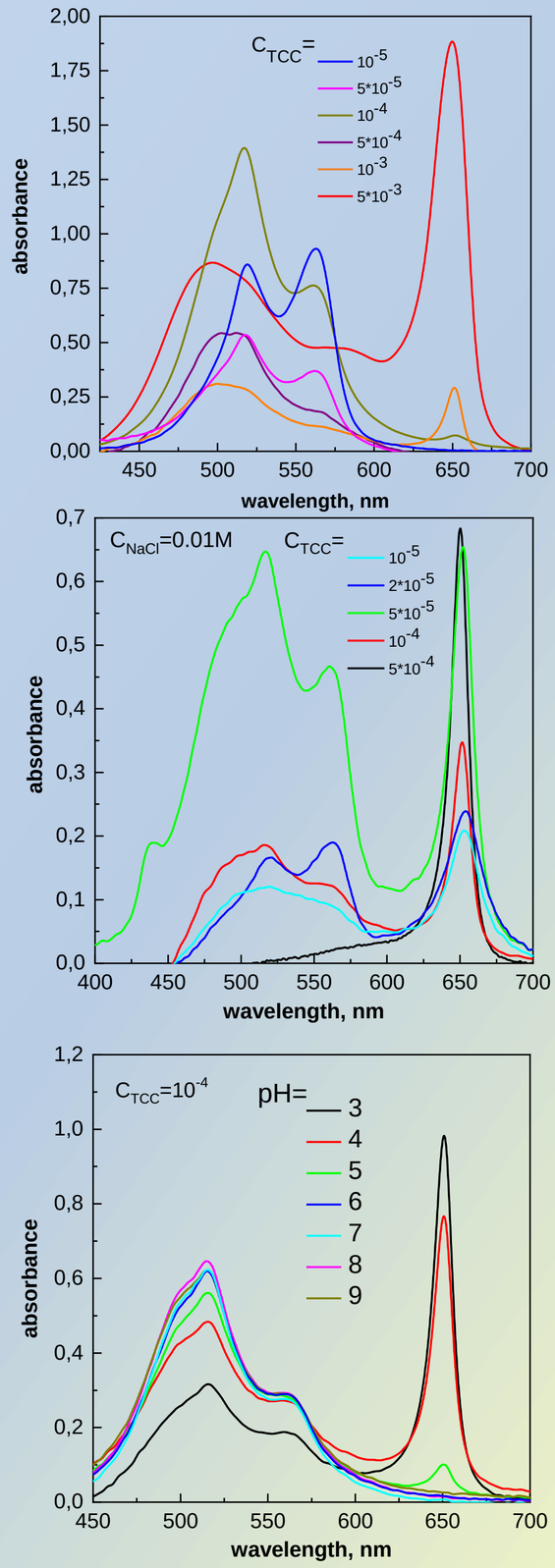
The H-band appears at “head to head” molecule packing as the highest energy state of the exciton band and this state is typically non-fluorescent one.

Some dyes are capable of simultaneously exhibiting in the spectra both the H- and J-bands, and the corresponding structure is usually called "herringbone".

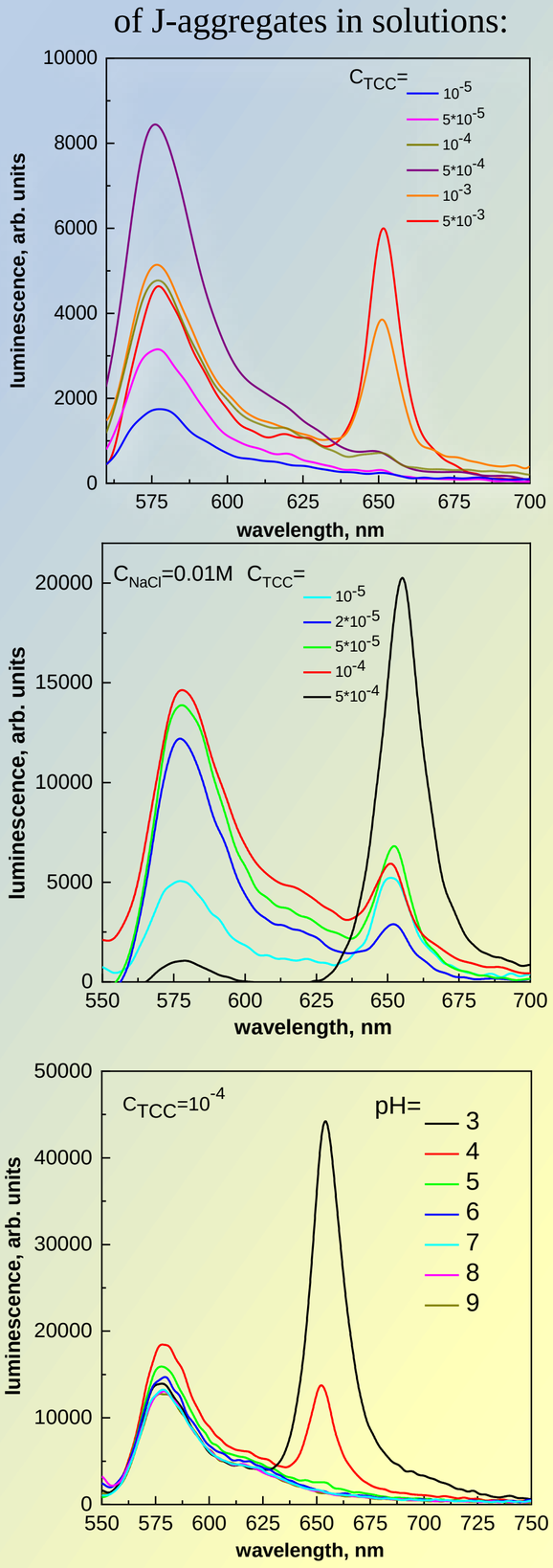
Our goal was to study the spectral properties of a dye of the thiacarbocyanine family, TCC, which is of interest to us because the band of its J-aggregates is located quite far in the long-wavelength region of the spectrum (~650 nm), almost at the border with the near-IR range.

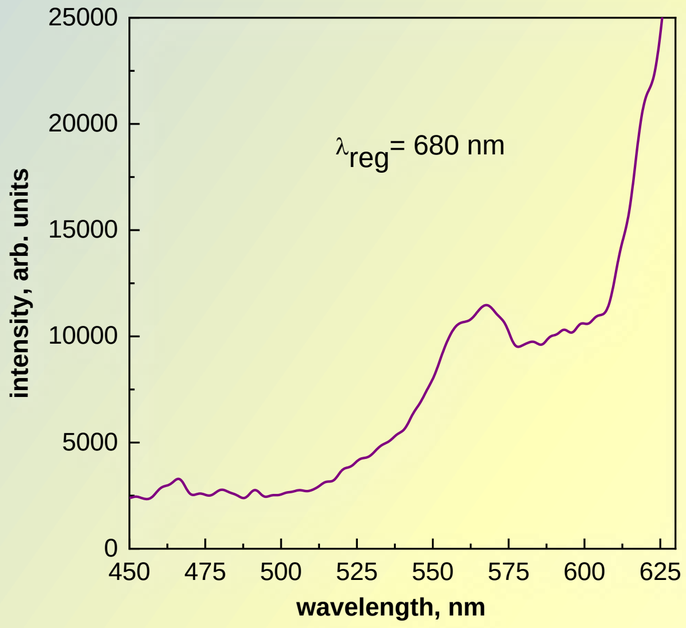


Absorption spectra of J-aggregates in solutions:

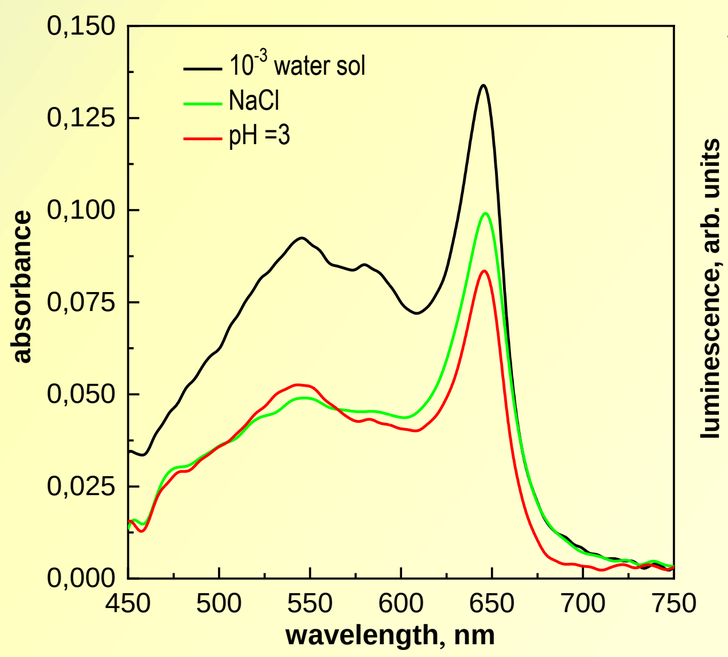


Luminescence spectra of J-aggregates in solutions:





Luminescence excitation spectrum of the solution containing both types of aggregates with registration in the band of J-aggregates.



Absorption and luminescence spectra of J-aggregates in LbL films.

Summary:

- The thiacarbocyanine dye TCC in an aqueous solution forms separate H- and J-type aggregates that do not interact with each other.
- It is possible to shift the equilibrium towards the preferential formation of J-aggregates by adding salt, or shifting the pH of the solution towards higher acidity.
- The preferential formation of TCC J-aggregates can be achieved in polymer films.
- In aqueous solutions TCC aggregates have a rod-like morphology, while in polymer films they can have a two-dimensional island-like morphology.

References:

- G. Busse, et al. Structure determination of thiacyanine dye J-aggregates in thin films: Comparison between spectroscopy and wide angle X-ray scattering // Phys. Chem. Chem. Phys. – 2004. – 6. – P. 3309-3314.
- A.V. Sorokin, et al. Unusual Enhancement of Dye Luminescence by Exciton Resonance of J-aggregates // Optical Materials. – 2019. – 96. – P. 109263.

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