Interaction between Molecular Aggregates Incorporated in Layered Polymer Films

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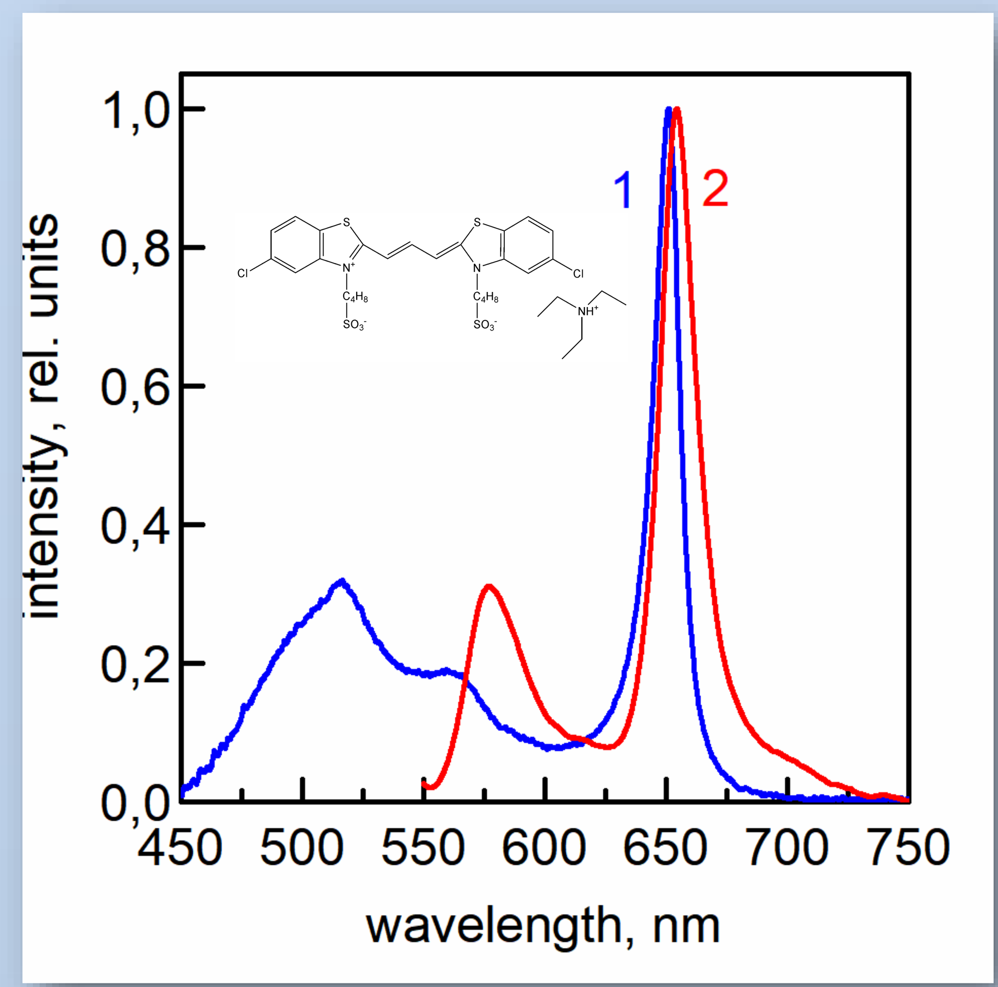
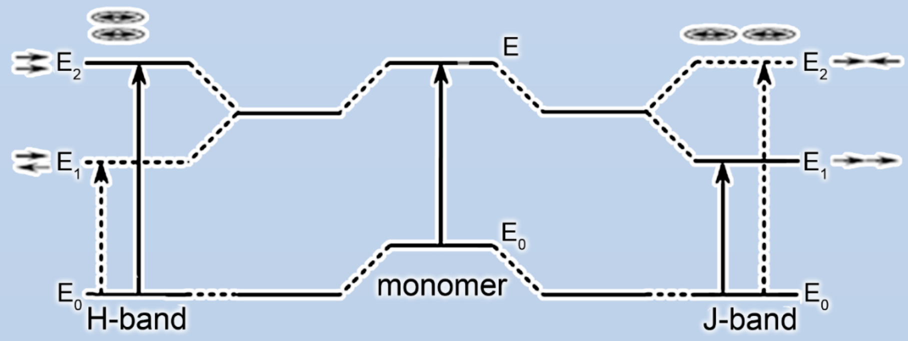


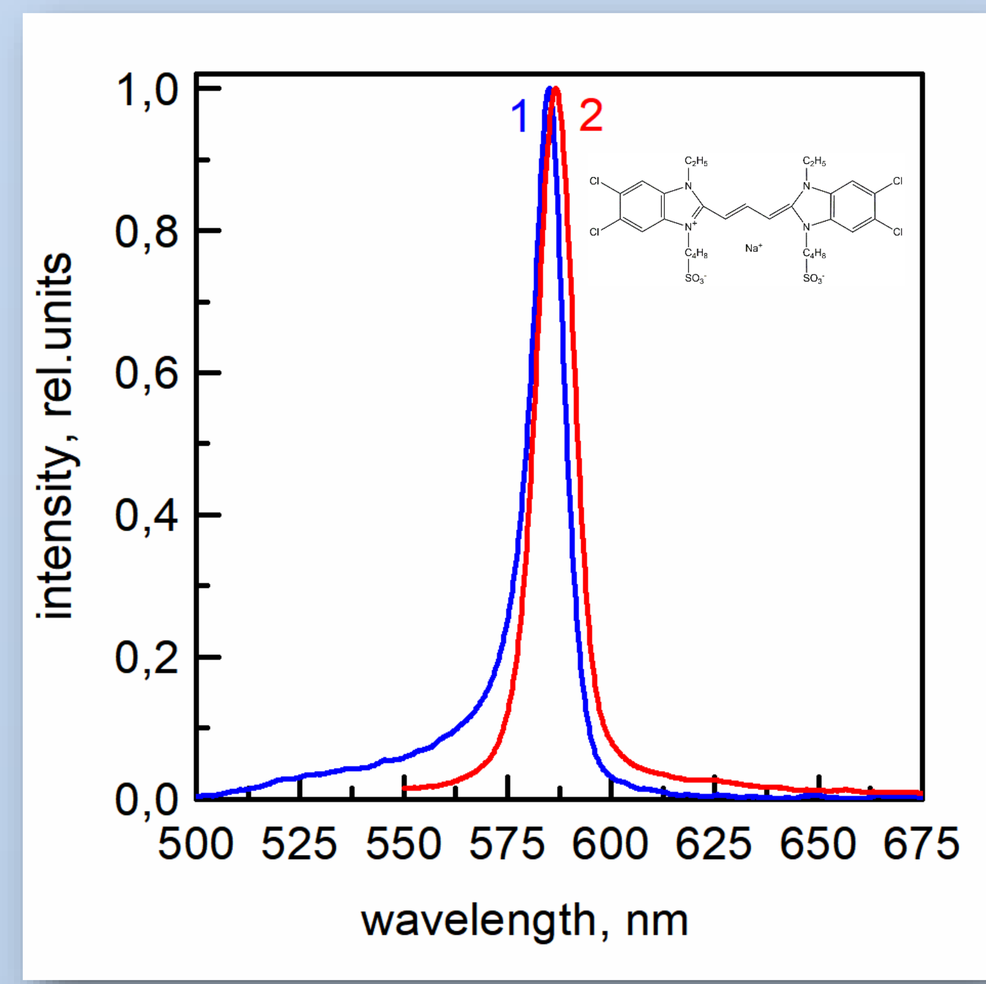
Absorption (1) and luminescence (2, λ_{exc} = 530 nm) spectra of TCC J-aggregates in aqueous solution (spectra are normalized for clarity).
On insets – the dyes structure.

Molecular aggregates of cyanine and some other dyes are nanosized luminescent clusters formed by organic molecules. They were discovered in the late thirties of the last centuries by E. Jelley and called in his honor J-aggregates.



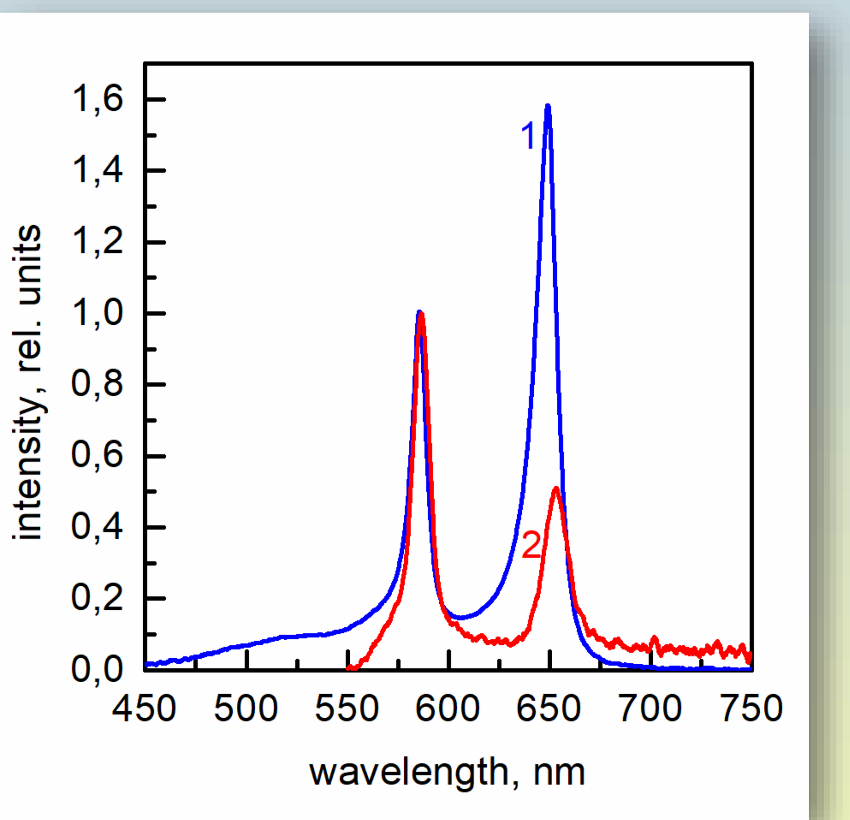
J-aggregates are characterized by a narrow absorption band (J-band) red-shifted to the monomer one, nearly resonant luminescence with a much shorter luminescence decay time than that of monomers, due to the exciton superradiation effect.

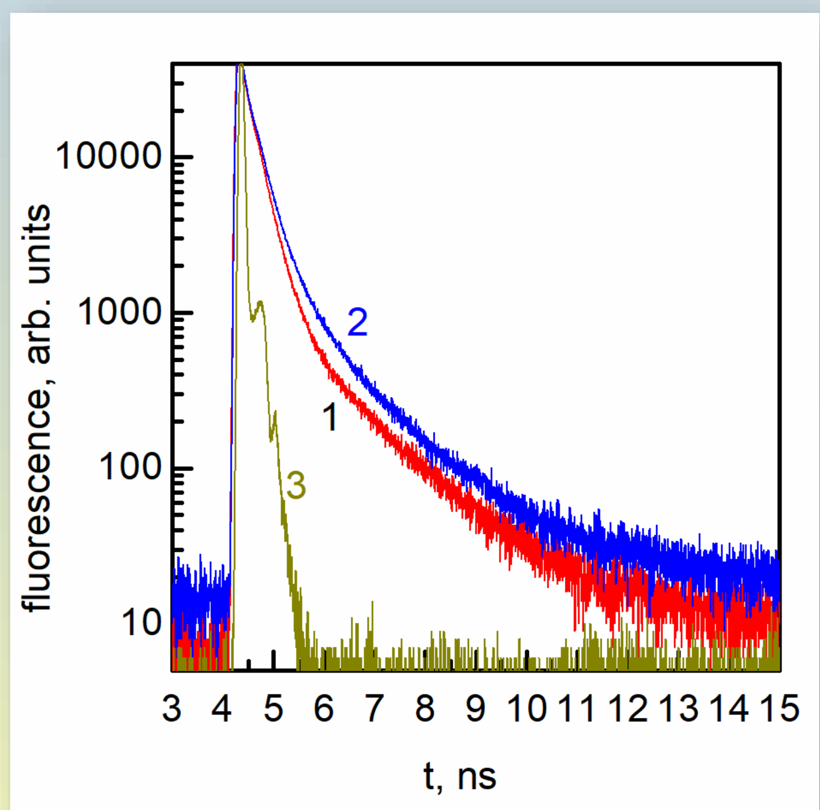
In the present work, we study the interaction between two carbocyanine dyes, namely TCC and TDBC, in aqueous solutions and thin polymer film. formed by polycation PDDA. The main purpose was to obtain the efficient energy transfer in closer packing of J-aggregates, taking into account thin film applications required for efficient light absorption in wider spectral range, like photovoltaics, etc.



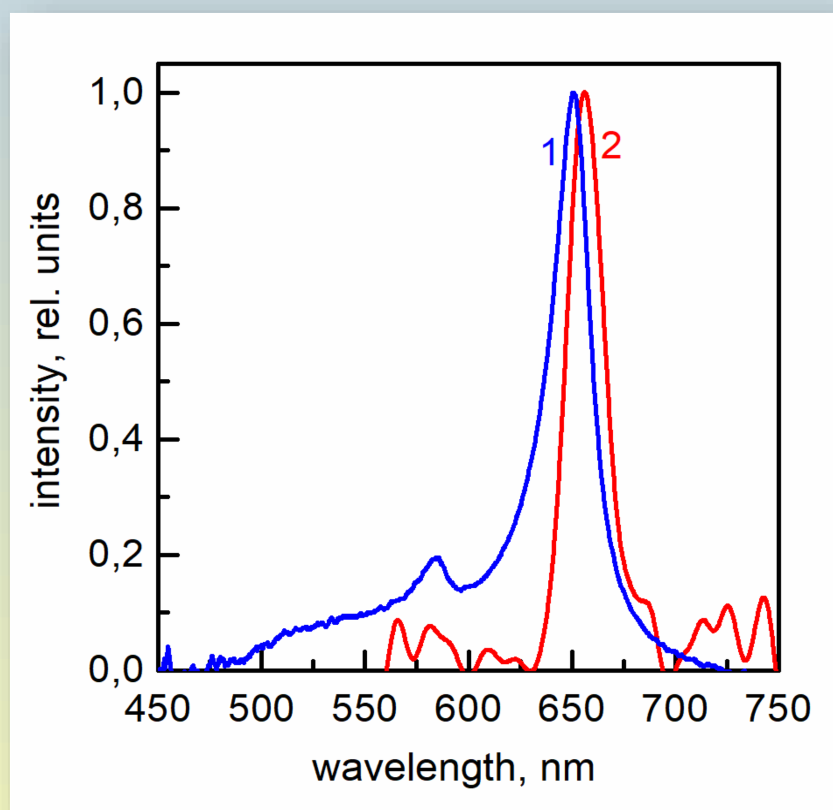
Absorption (1) and fluorescence (2, λ_{exc} = 530 nm) spectra of TDBC J-aggregates in aqueous solution (spectra are normalized for clarity).
On insets – the dyes structure.

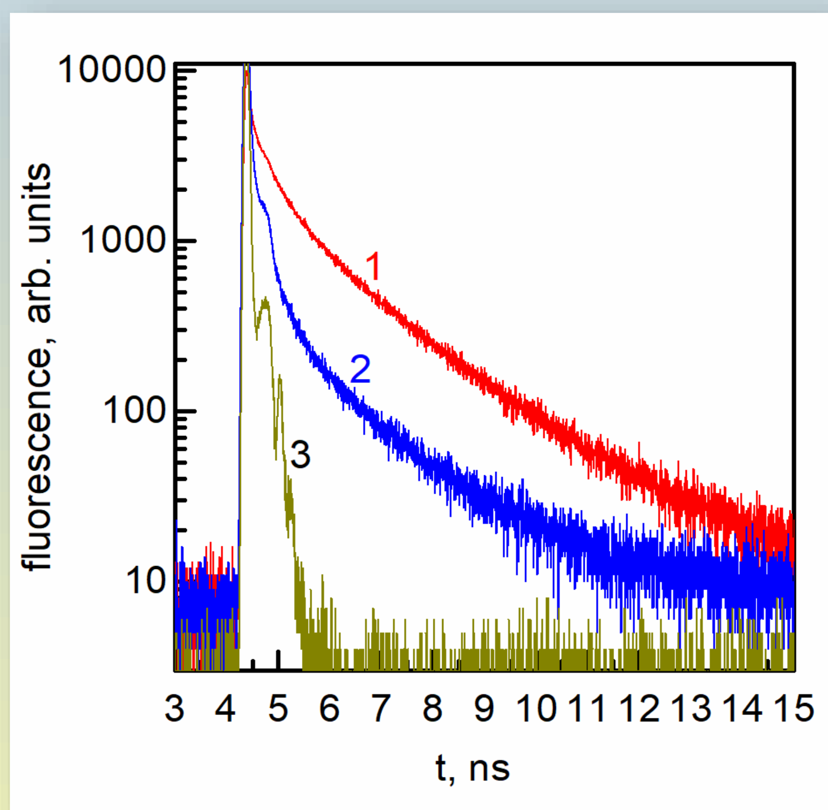
Results:



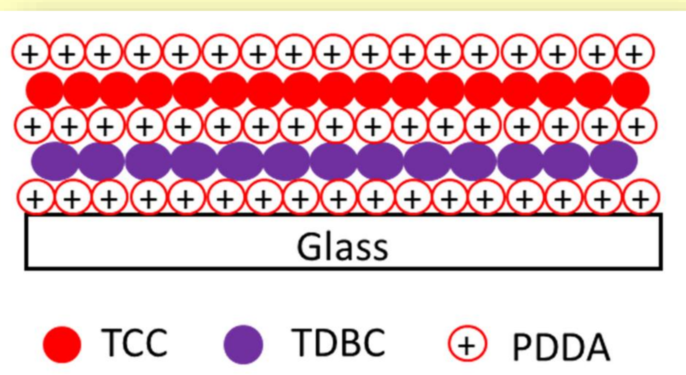


Absorption (1) and fluorescence (2, λ_{exc} = 530 nm) spectra of the mixture of TDBC and TCC J-aggregates in aqueous solution (spectra are normalized by TDBC J-aggregate bands for clarity); the fluorescence (λ_{exc} = 531 nm) decay curves: 1 – λ_{reg} = 586 nm, 2 – λ_{reg} = 655 nm, 3 – IRF.

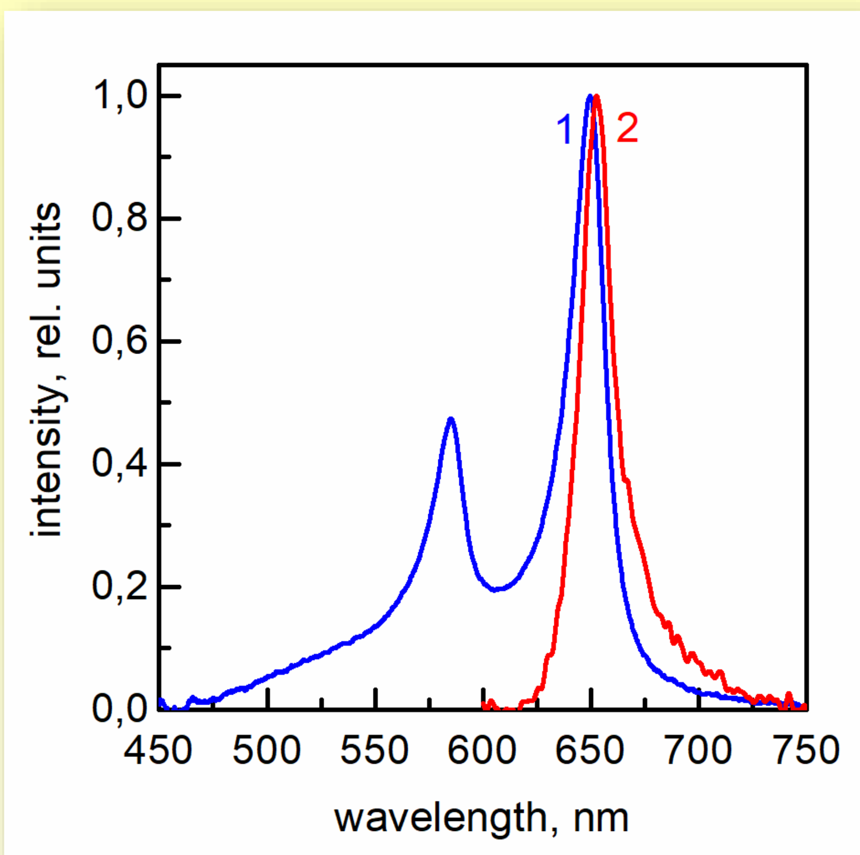


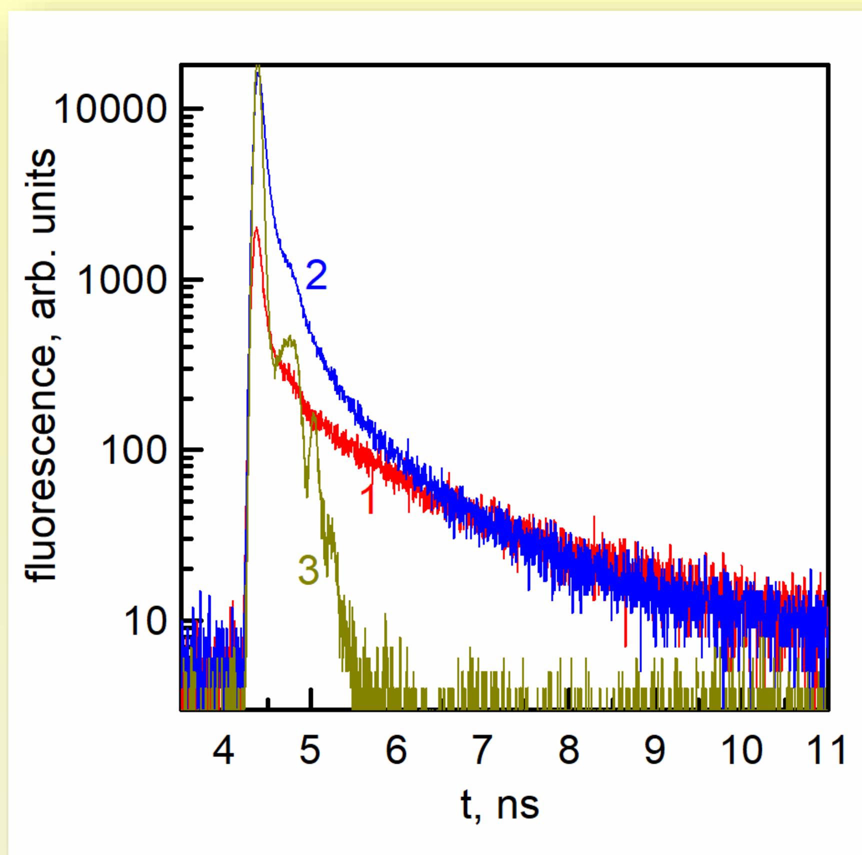


Absorption (1) and fluorescence (2, λ_{exc} = 530 nm) spectra of the mixture of TDBC and TCC J-aggregates in thin polymer film (spectra are normalized by TCC J-aggregate bands for clarity); the fluorescence (λ_{exc} = 531 nm) decay curves: 1 – λ_{reg} = 586 nm, 2 – λ_{reg} = 655 nm, 3 – IRF.

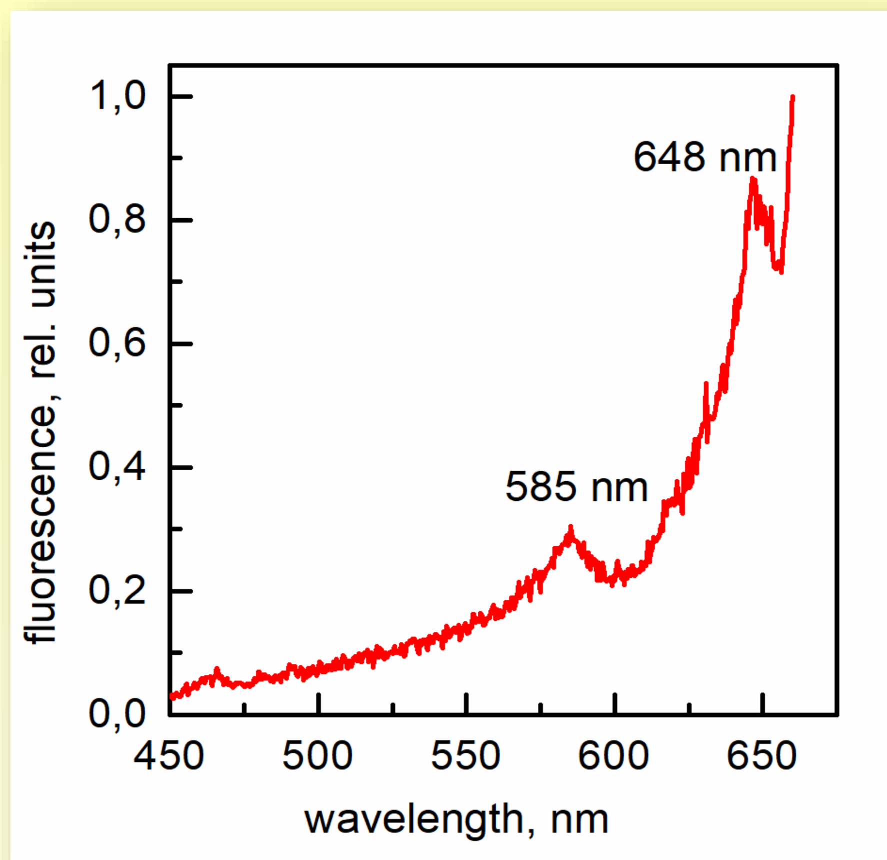


Scheme of the layered polymer film with TDBC and TCC J-aggregates layers separated by PDDA polymer layer.





Absorption (1) and fluorescence (2, λ_{exc} = 530 nm) spectra of the film shown on scheme (spectra are normalized by TCC J-aggregate bands for clarity); the fluorescence (λ_{exc} = 531 nm) decay curves: 1 – λ_{reg} = 586 nm, 2 – λ_{reg} = 655 nm, 3 – IRF.



Fluorescence excitation spectrum (λ_{reg} = 670 nm) of the film shown on scheme (spectrum is normalized for clarity).

Conclusions:

This work demonstrates the features of the interaction of two types of J-aggregates in different media, one of which can be used as an energy donor, and the other as an energy acceptor. It has been shown that it is impossible to provide TCC and TDBC J-aggregates, interaction in their mixture both in aqueous solution and polymer film. However, it has been found that layer-by-layer deposition of TCC and TDBC J-aggregates as separate layers creates a system with efficient energy transfer. Such an approach can be used for the development of composite systems with efficient light absorption in a wide spectral range and energy or electron transfer.

References:

- F. Würthner, et al. J-Aggregates: From Serendipitous Discovery to Supramolecular Engineering of Functional Dye Materials // Angew. Chemie Int. Ed. – 2011. – 50. – P. 3376–3410.
- 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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