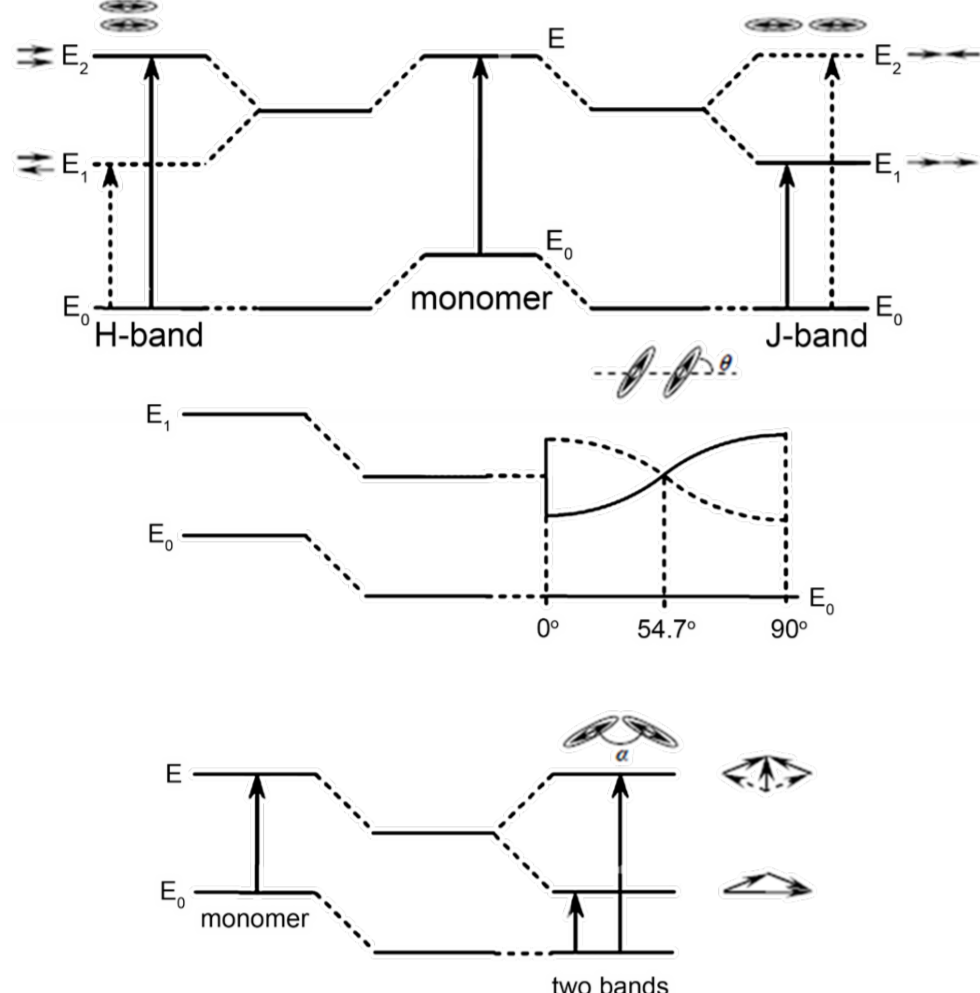


Stable Cyanine Dye J-aggregates with Plasmon Enhanced Fluorescence

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Introduction

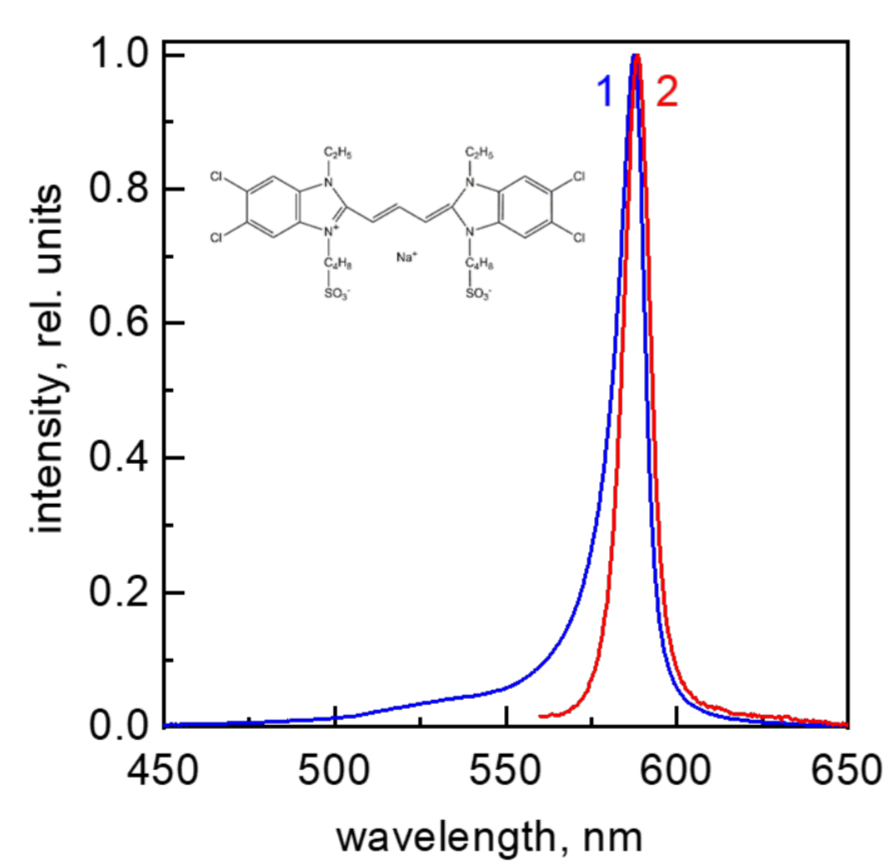
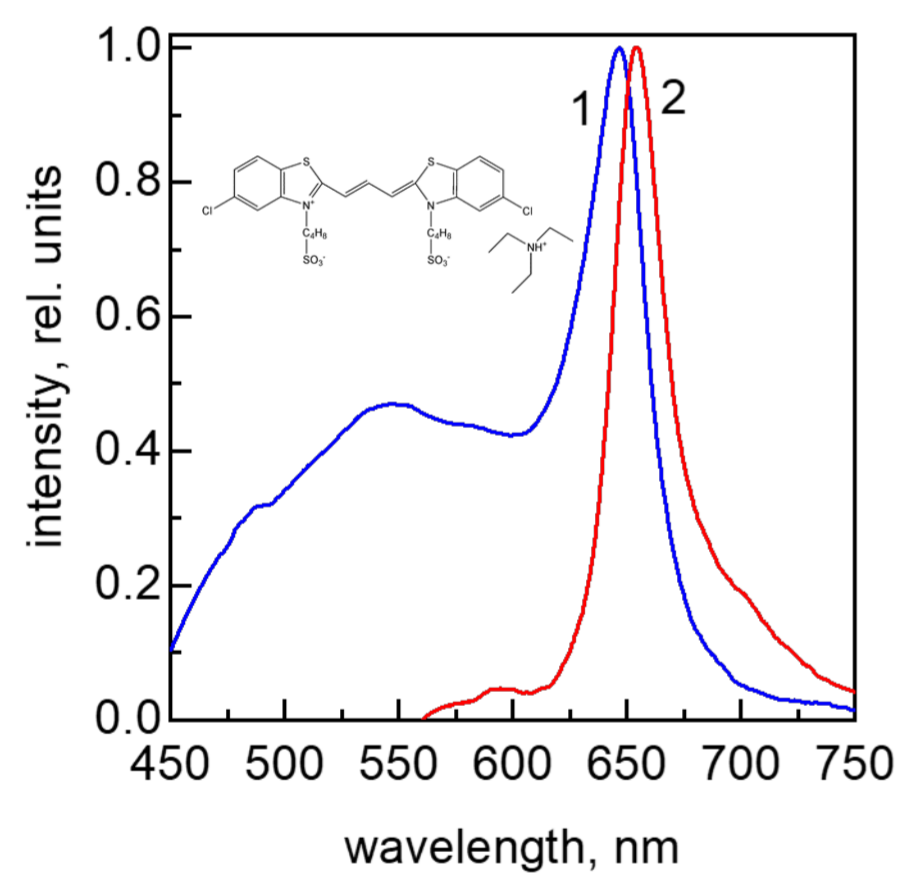
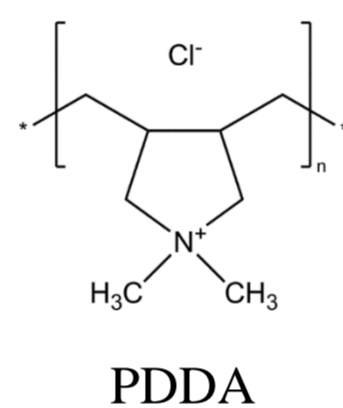
Some organic luminophores can form high-ordered molecular aggregates, called J-aggregates, which reveal unique optical properties due to the excitonic nature of electronic excitations. Depending on the molecule arrangement in the J-aggregates, the exciton band appears as a bathochromically shifted (J-band) 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 is accompanied by near-resonant fluorescence. The H-band appears at "head to head" molecule packing as the exciton band's highest energy state, which is typically non-fluorescent. Some dyes can simultaneously exhibit both the H- and J-bands in the spectra, and the corresponding structure is usually called "herringbone".

Objects of study

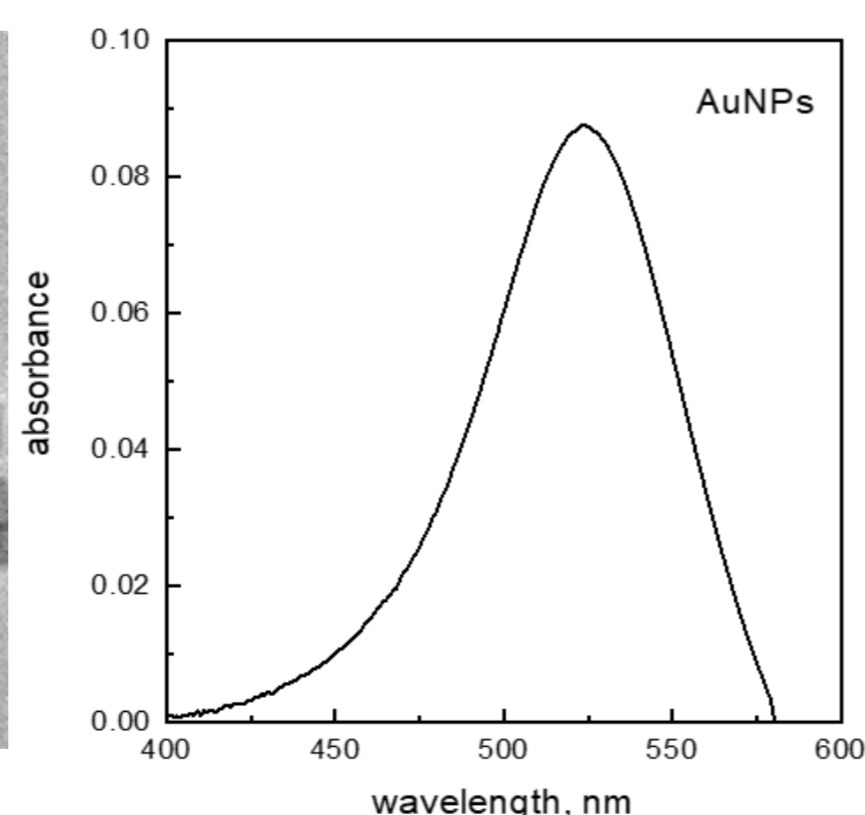
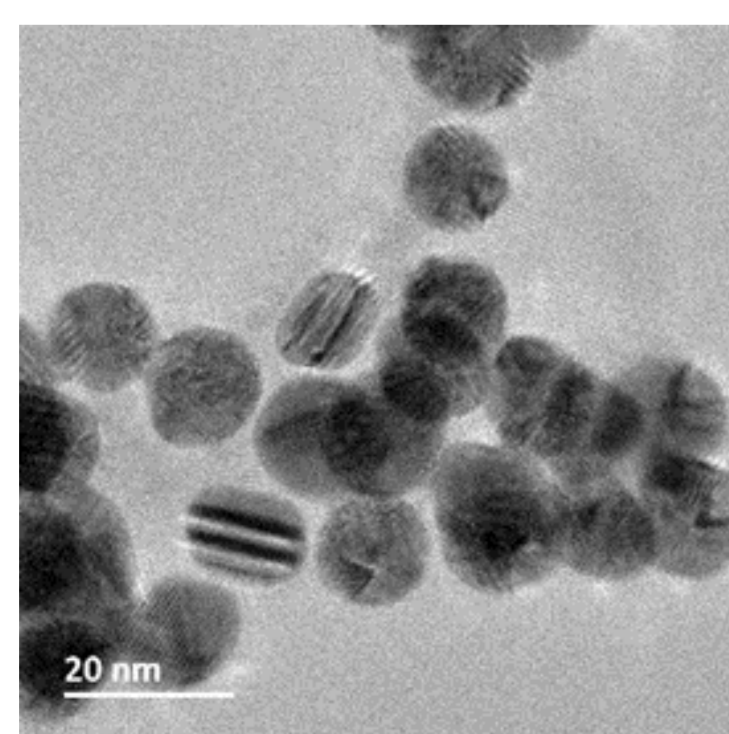
In this research, we study the fluorescence of two carbocyanine dyes, namely TCC (3,3'-disulfobutyl-5,5'-dichlorothiacyanine triethylammonium salt) and TDBC (1,1'-disulfobutyl-3,3'-diethyl-5,5',6,6'-tetrachloro-benzimidazolylcarbocyanine sodium salt), in thin polymer films, formed by polycation PDDA (poly(diallyldimethylammonium chloride)), which enhanced by positioning them at a specific distance from a layer of gold nanoparticles.



Absorption (1) and fluorescence (2, $\lambda_{exc} = 530$ nm) spectra of TCC (left) and TDBC (right) J-aggregates in a polymer film (spectra are normalized for clarity). On insets – dyes structures.

Gold nanoparticles (AuNPs)

Gold nanoparticles were synthesized using the well-known Turkevich method of water based reduction of gold salt by trisodium citrate.



The TEM image (left) and absorption spectrum (right) of AuNPs.

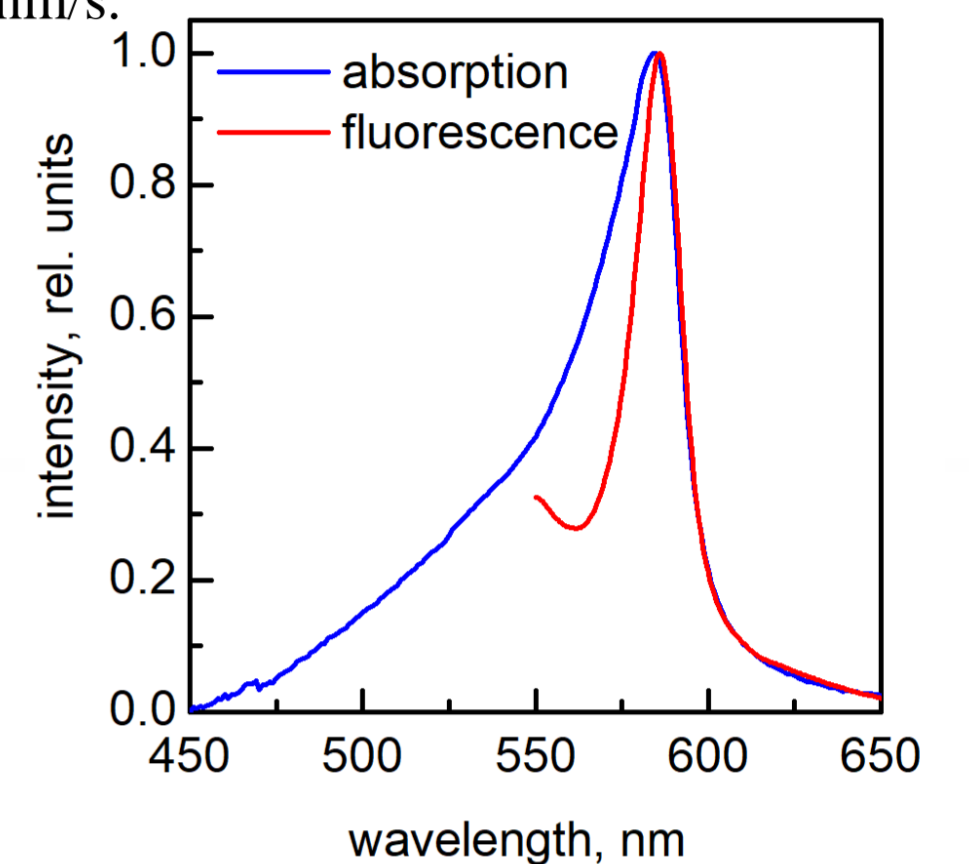
Stabilization with metal film

To stabilize the J-aggregates, the samples were coated with a thin metal film composed of 20 nm of gold and 3 nm of titanium by using a thermal and electron beam evaporation system (Edwards Auto 500). The Ti/Au were evaporated @ $\sim 2 \times 10^{-6}$ mbar of pressure and at a rate of about 0.05 nm/s.

That under a metal coating the J-band is slightly blue-shifted ($\lambda_{J}^{MF} = 584.5$ nm) and broader ($\Delta v_{FWHM}^{MF} = 490$ cm^{-1}), and the monomer band is more intense compared to the J-aggregates in water and pure LbL films.

$$N_{coh} = \frac{3 \cdot (\Delta\theta_{mon})^2}{2 \cdot (\Delta\theta_J)^2} - 1$$

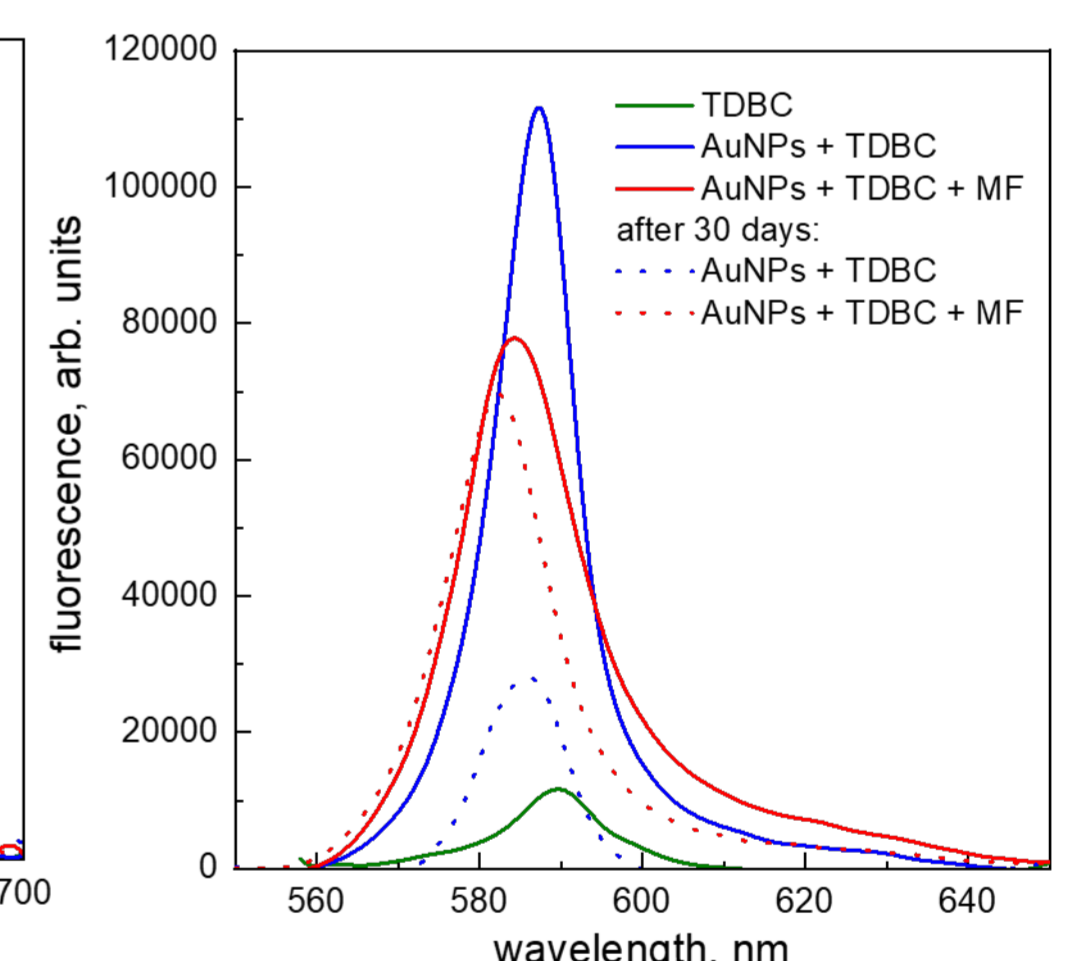
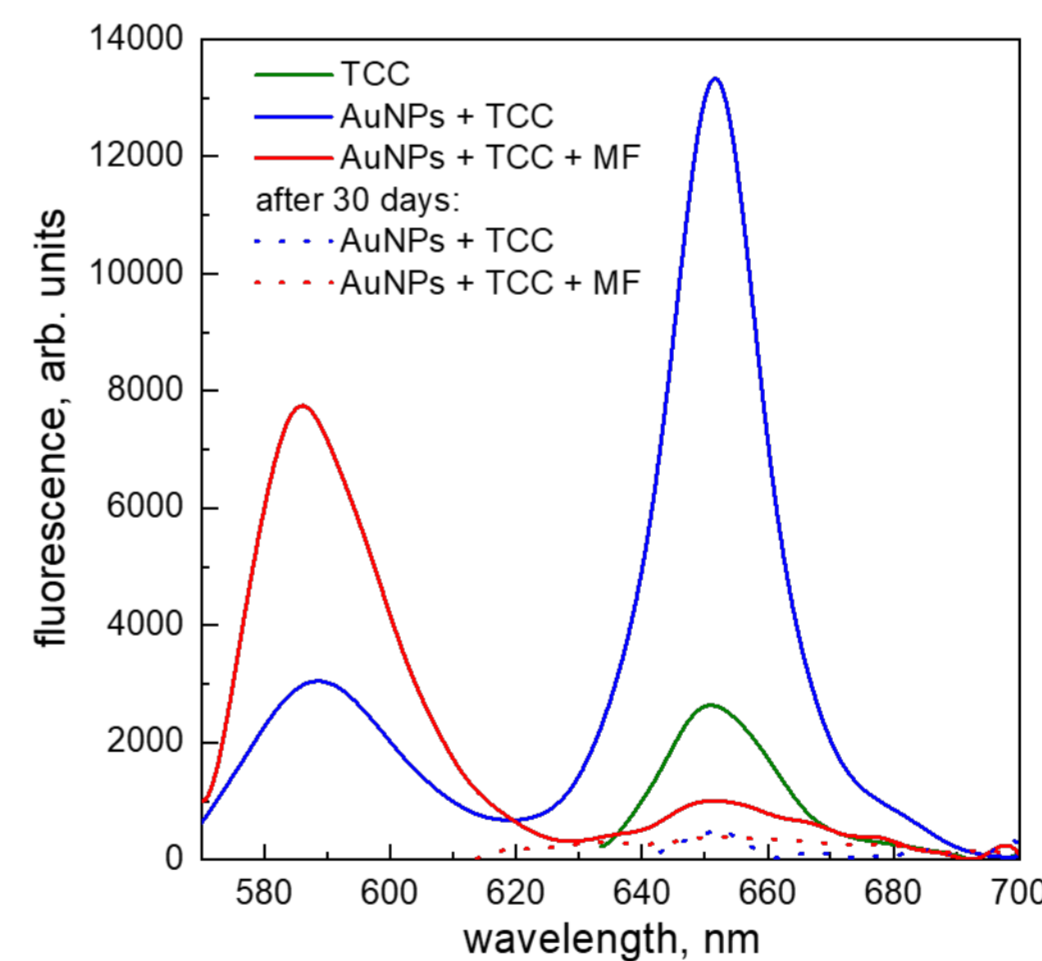
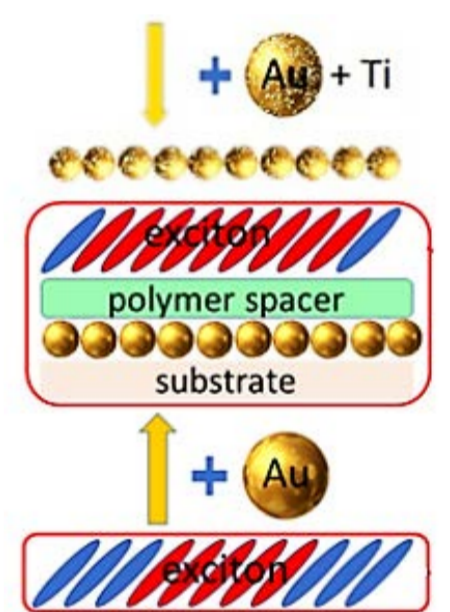
TDBC:
in water solution $N_{coh}^{sol} \sim 23$
in pure LbL $N_{coh}^{LbL} \sim 18$
in LbL cover by metal film $N_{coh}^{MF} \sim 6$



Absorption and fluorescence ($\lambda_{exc} = 530$ nm) spectra of single-layer TDBC J-aggregates in LbL films covered by a metal film.

General research

In polymer films, the fluorescence of J-aggregates is typically highly quenched. However, it can be enhanced through exciton-plasmon interactions, which occur due to the interaction of excitons with the local field of nanoparticles. The degree of plasmon enhancement is influenced by several factors, such as the chemical structure, size, and shape of the nanostructures, as well as the distance between the nanostructures and the fluorophore molecules.



Spectra of the increase in fluorescence for TCC (left) and TDBC (right) J-aggregates in layer-by-layer films using plasmonic nanoparticles: without nanoparticles (green curve), with nanoparticles (blue curve), with an additional metal film on the top (red curve), as well as the fluorescence of the samples 30 days after film preparation (dotted curves). The samples are optically excited at 530 nm.

Conclusions

- The results demonstrated that all samples maintained stable fluorescence even after one month, indicating increased stability of the solid samples.
- This approach shows promise for the application of J-aggregates in photonic devices, particularly in thin-film configurations.

Acknowledgment

This work was partially supported by a nominal scholarship of the National Academy of Sciences of Ukraine for young scientists (from 31.10.2022 №509). The authors thank the German Science Foundation for financial support via the collaborative research center SFB 1477 "Light-Matter Interactions at Interfaces" (project number 441234705).

