Features of cyanine dyes aggregation in TiO_2 matrices

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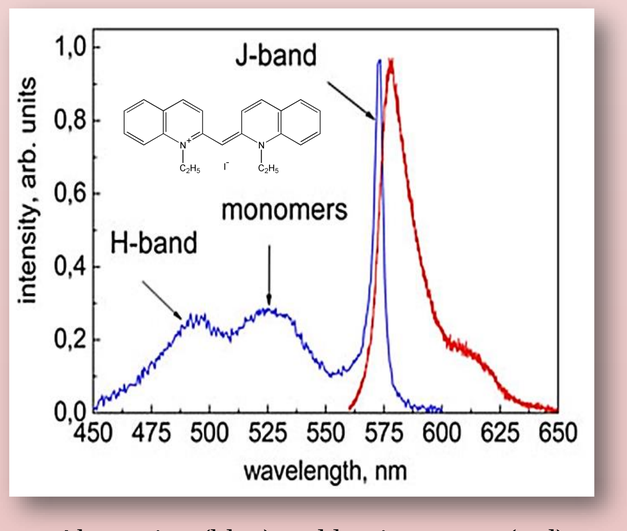
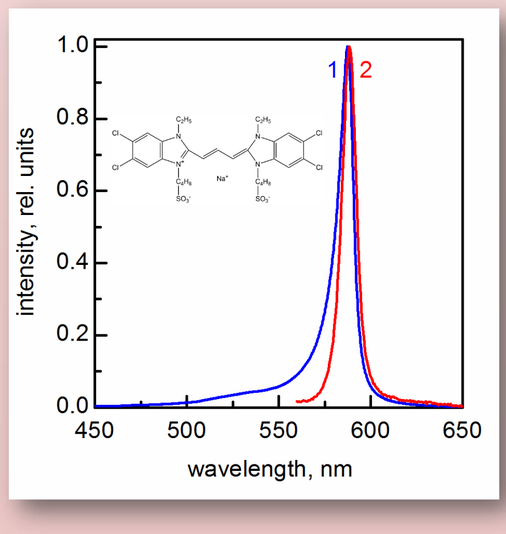
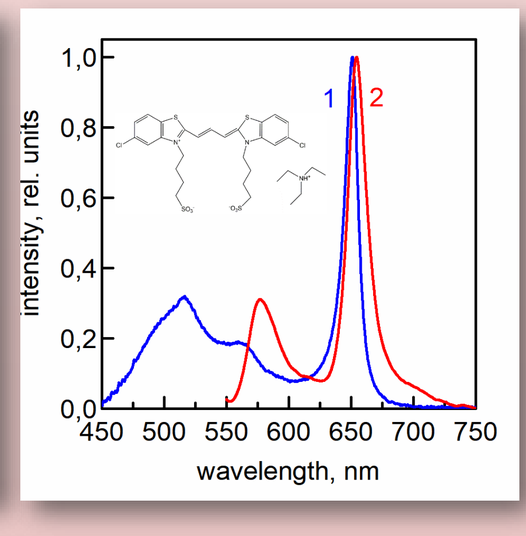


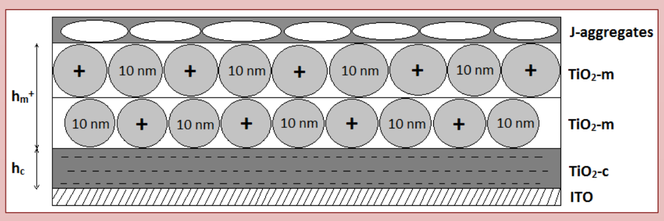
Absorption (blue) and luminescence (red) spectra of PIC J-aggregates in aqueous solution. On inset – PIC structure.

The molecules of some dyes and pigments can form highly ordered structures (molecule aggregates) under certain conditions. Due to the translational symmetry of molecules within such aggregates (so called J-aggregates, named by their discoverer E. Jelley), the individual molecules electronic excitations are delocalized over aggregate chains segments with the formation of Frenkel exciton. These processes lead to unique spectral properties of aggregates, which depend on their structure and microenvironment. For example, depending on the arrangement of molecules in the chain, the excitonic band can be narrow intense red-shifted (J-band), or a broad blue-shifted (H-band). Nowadays an actual task is to create solid samples of J-aggregates that have a higher photo- and physical stability compared to solutions. In present report the optical properties of several J-aggregates (PIC, TDBC and TCC) have been studied under their formation on porous TiO_2 matrices.



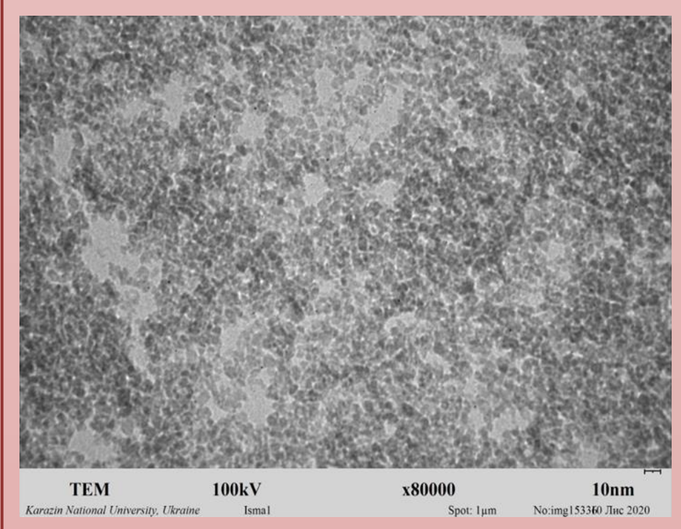


Absorption (blue) and luminescence (red) spectra of TDBC (left) and TCC (right) J-aggregates in aqueous solution. On insets – the dyes structures.



TiO_2 (+)

TiO_2-m – mesoporous layer, TiO_2-c – compact layer, ITO – conductive substrate, h_m^+ – thickness of the mesoporous layer, h_c – thickness of the compact layer.



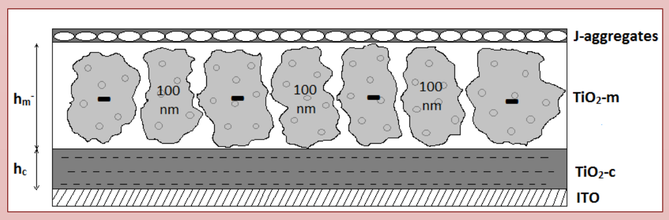
ζ=+26.8±1.9 mV

Results:

It was worked out two ways of TiO_2 nanoparticles' polycondensation procedure resulting in their different characteristics. As a result, we got two types of nanoparticles: a small one (of ~ 10 nm diameter) positively charged and a large one (of ~ 100 nm diameter) negatively charged. Therefore, the porous films, prepared using the corresponding nanoparticles, can be also referred to as positively and negatively charged ones. Different surface charges of TiO_2 porous films provide the possibility to use different dyes (namely, cationic or anionic ones), which form J-aggregates, and, hence, better opportunity to obtain the solid samples with required properties.

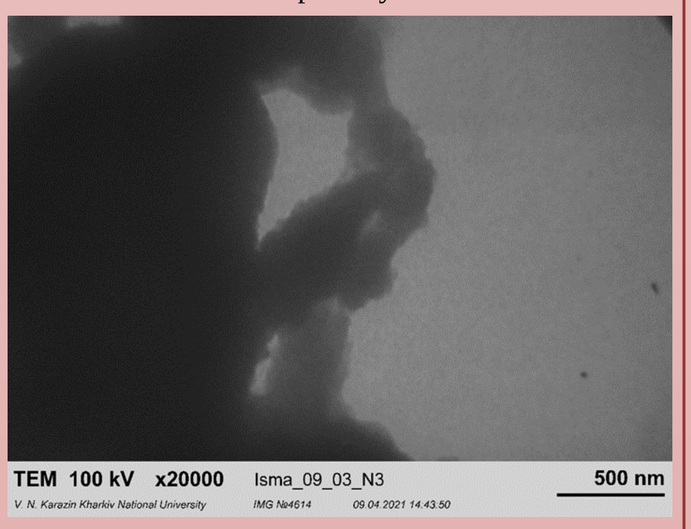
Indeed, J-aggregates anionic dyes TDBC and TCC can be easily formed on positively charged films, while J-aggregates of cationic dye PIC were formed on negatively charged TiO_2 surface. For all J-aggregates the excitonic bands widening and decreasing the luminescence quantum yields were found demonstrating the significant disorder increasing and various exciton localization effects realizing. A similar situation could be often revealed for J-aggregates formed as the solid samples, like polymer films of other porous matrices.

Importantly, the J-aggregates combinations can be realized on both types of TiO_2 films. On the graphs below the TDBC-TCC and PIC-TCC films are shown. In both cases, only longer wavelength luminescence of TCC J-aggregates is seen, assuming the energy transfer between J-aggregates.

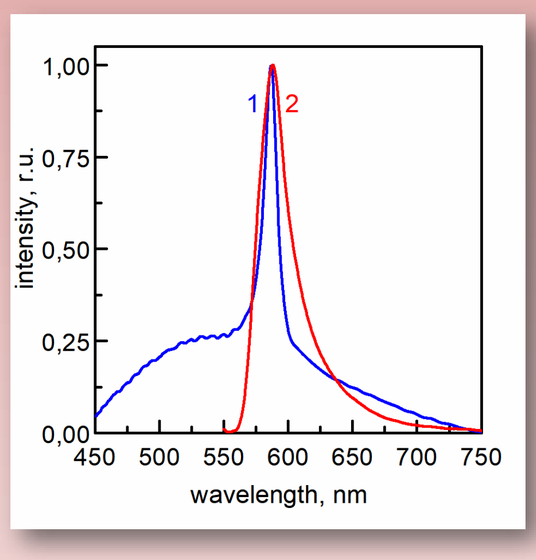


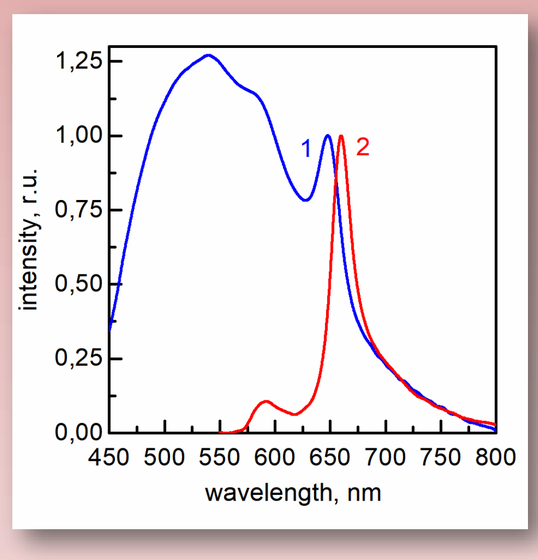
TiO_2 (-)

TiO_2-m – mesoporous layer, TiO_2-c – compact layer, ITO – conductive substrate, h_m^- – thickness of the mesoporous layer, h_c – thickness of the compact layer.

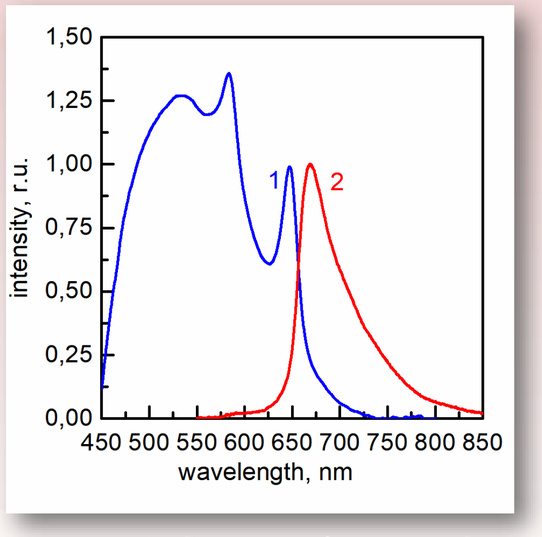


ζ=-23.6±3.7 mV

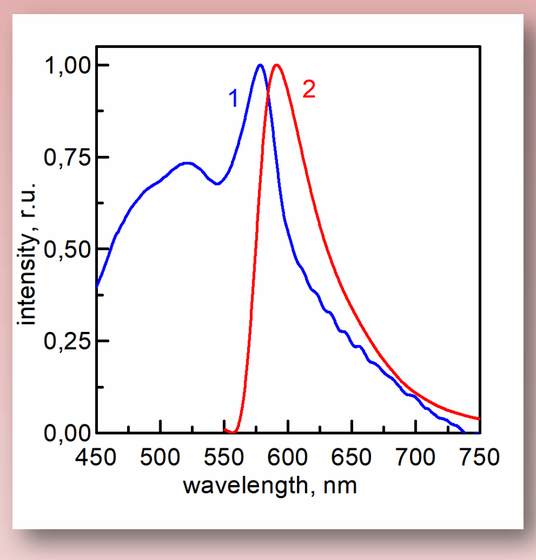


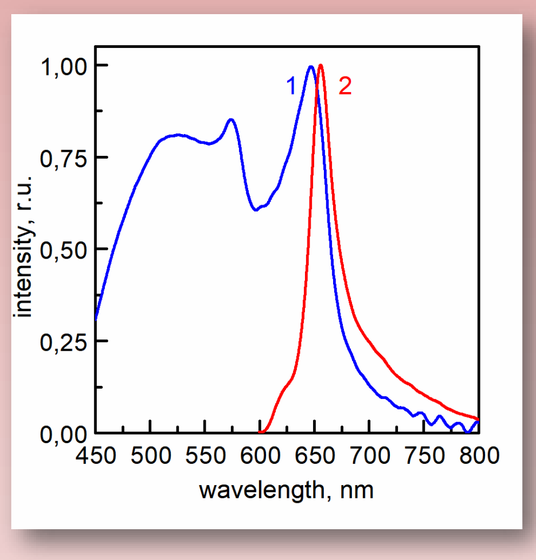


Absorption (blue) and luminescence (red) spectra of TDBC (left) and TCC (right) J-aggregates on porous positively charged TiO_2 matrices.



Absorption (blue) and luminescence (red) spectra of successively applied J-aggregates of two dyes (first TDBC, and after TCC) on porous on porous positively charged TiO_2 matrices.





Absorption (blue) and luminescence (red) spectra of PIC (left) and [PIC+TCC] mixes (right) J-aggregates on porous on porous negatively charged TiO_2 matrices.

Conclusions:

1. This work demonstrates the features of several cyanine dyes aggregation in TiO_2 matrices as separate or combined thin films.
2. It has been revealed, that depending on the charge of the titanium dioxide matrices, aggregates of different types could be formed.
3. It has been shown, that using the different J-aggregate combinations the optical response of the sample can be improved.

References:

- Song X. M. A dual-layer titania film with enhanced photocatalytic activity // Journal of Physical Chemistry C.-2009.-113.-P. 10681-10688.
- Sorokin A.V. Using cyanine dye J-aggregates as luminescence probe for nanostructured media / A.V. Sorokin et al. // Functional Materials.-2017.-24.-P. 388-392.