

STUDY OF SPECTRAL-LUMINESCENT AND PHOTOCHEMICAL PROPERTIES OF STYRYLSIANINE DYES

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Abstract: In this work, the relationship between the spectral-luminescent and photochemical properties of styrylcyanine homodimer dyes and the regularity of their specific electronic structure, the nature of their excited electronic state, and the processes of intermolecular interaction in solutions of the studied substances were calculated.

Keywords: wavelength, absorption, luminescence, fluorescence, aggregation, concentration.



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Annotation

Electronic absorption and fluorescence spectra of squaraine dye Sbt monomer molecules and homodimer molecules: Dbt-5 were studied in water. It was found that the form of absorption and fluorescence spectra of all studied dyes remains constant in the concentration range of 10^{-5} - 10^{-6} m. This indicates that the molecules of the studied dyes are in monomeric form.

Table 1. Spectral and fluorescent properties of the studied dyes in the water.

Bo'yoq	λ_{utmax} , (nm)	λ_{flmax} , (nm)	ϵ , ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	f_e	τ , (ns)	ν_{0-0} (cm^{-1})	SS (cm^{-1})
Sbt	511	596	23500	0,27	0,1	17480	2790
Dbt-5	502	596	12300	0,23	0,2	17450	3141

As the concentration of the dye in the aqueous solution increased, a new line located on the side of short wavelengths was observed.

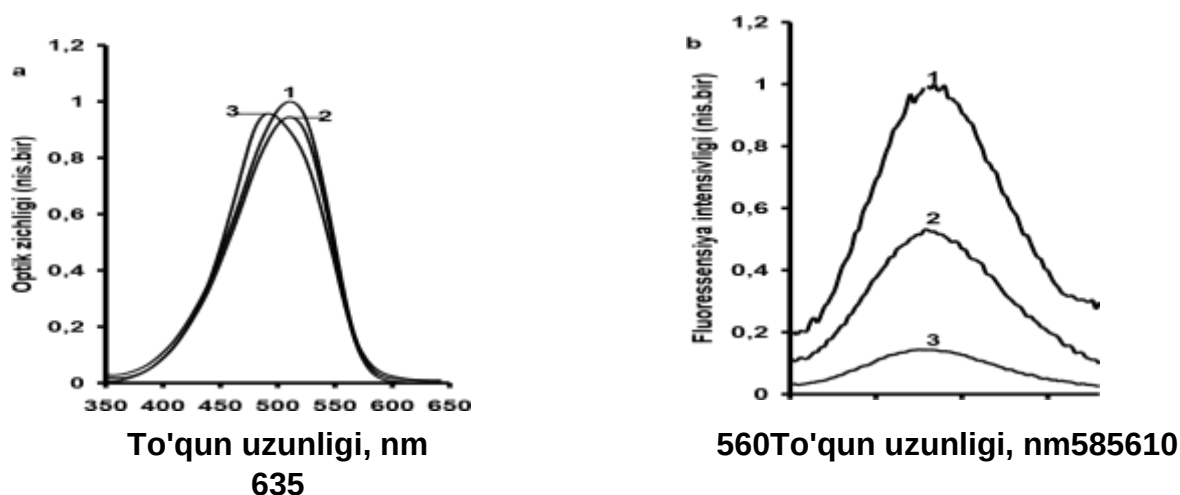


Figure 1. Concentration dependence of absorption (a) and fluorescence (b) spectra of Sbt dye in water: $1 \cdot 10^{-5}$, $2 \cdot 10^{-4}$, 10^{-3} m.

Absorption and fluorescence spectra of Sbt dye are shown. The maximum of the absorption spectrum observed with $\lambda_{\max}=511$ nm (Figure 1, curve 1) points to the monomeric form of Sbt dye. As the dye concentration increases in the absorption spectrum, the intensity of the monomeric band at $\lambda_{\max}=511$ nm decreases slightly, while a new line at $\lambda_{\max}=496$ nm appears from the side of short wavelengths (Fig. 1, curve 3). In this case, with increasing concentration, the shape of the spectrum remains constant, and KTL was observed.

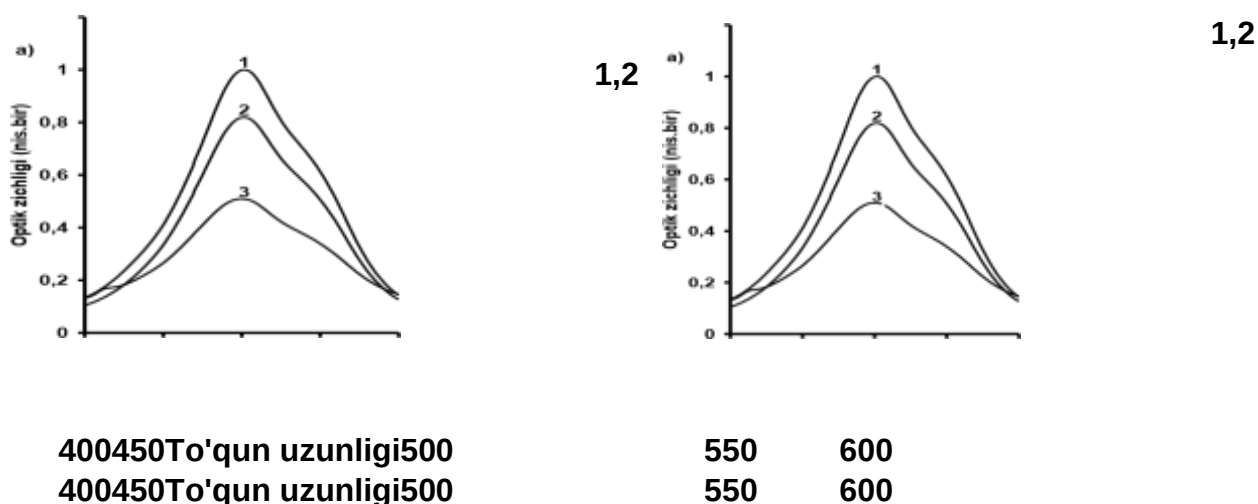


Figure 2. Concentration dependence of absorption (a) and fluorescence (b) spectra of Dbt-5 dye in water: $1 \cdot 5 \cdot 10^{-6}$, $2 \cdot 5 \cdot 10^{-5}$, $3 \cdot 5 \cdot 10^{-4}$ m.

As the dye concentration in aqueous solution increases, Dbt-5 homodimeric dye appears in the absorption and fluorescence spectra. Figure 2 shows that a twoorder increase in Dbt-5 dye concentration causes a decrease in the absorption intensity of the monomer band at $\lambda_{\max}=502$ nm (Figure 2a, curve 3). The fluorescence intensity of aqueous solutions of the homodimeric dye decreases with increasing concentration (Figure 2). The phenomena observed in the absorption and fluorescence spectra of aqueous solutions of Sbt are explained by the formation of non-luminescent aggregates of dye molecules with the help of molecules. Water solvent molecules act as a bridge between paint molecules due to the formation of hydrogen bonds. From Fig. 2.a, an increase in the concentration of Dbt-5 in an aqueous solution leads to a decrease in absorbance (hypochromic effect).

In such cases, the hypochromic effect in the absorption spectra is accompanied by long and short wavelength broadening (Fig. 2a, curves 2 and 3). The aggregation process for Dbt-5 dye molecules occurs in aqueous solutions as well as for Sbt dye, where a water molecule acts as a bridge between two dye molecules. The ability to form different aggregates depends on the structure of their chromophores, i.e. important dipole moments, exchange of opposite charges and planar structure of the chromophore, which determines the high energy of MMV.

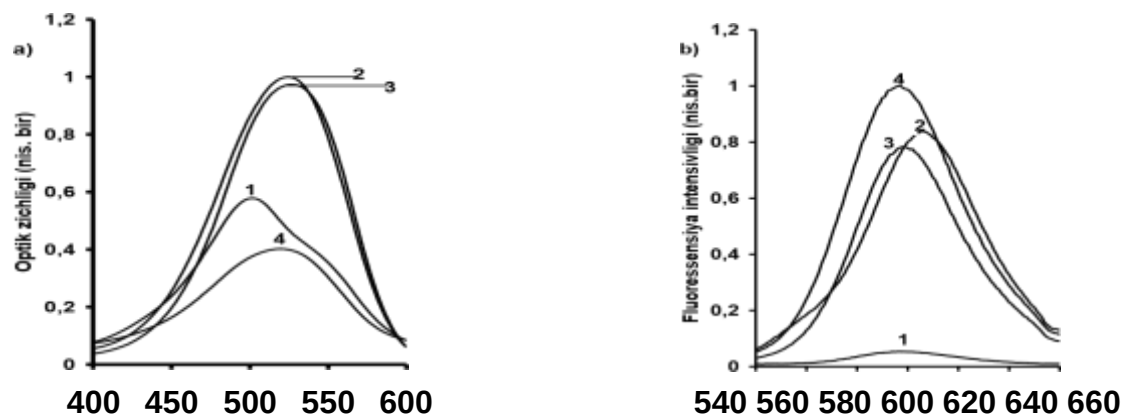


Figure 3. Absorption (a) and fluorescence (b) spectra of Dbt-5 dye ($c=4 \times 10^{-6}$ M) as different solvents are added: 1-aqueous solution, 2-1% water + 99% ethanol, 31% water + 99% DMF, 4-1% water + 99% dioxane.

Spectral and fluorescent properties of styrylcyanine dyes in different solvents ($c=10^{-5}$ M).

BO•YOQ	λ_{max} (nm)	λ_{fmax} (nm)	ϵ ($\text{l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$)	f_e	τ (ns)	ν_{0-0} (cm^{-1})	SS (cm^{-1})	I _{etanol} /I _{uv}
2% WATER +98% ETHANOL								
Sbt	525	597	22700	0,42	0,1	17370	2297	1,6
Dbt-5	524	598	21300	0,56	7,9	17390	2361	14,6
2% WATER +98% DMF								
Sbt	522	606	27600	0,50	8,7	17310	2655	1,7
Dbt-5	526	606	20800	0,36	0,1	17360	2509	15,7
2% WATER+98% DIOXANE								
Sbt	520	599	27400	0,55	8,0	17430	2536	1,3
Dbt-5	520	597	8600	0,17	0,2	17450	2480	18,7

When using dye solutions in various fields of science and technology, along with spectral and fluorescent properties, an important parameter that determines their service life is photostability. In order to use dyes effectively and rationally, it is necessary to have information about the photostability of the studied dyes, as well as changes depending on the nature of the solvent, the concentration of the solution, etc. Considering the above, the photostability of Sbt and Dbt-5 dyes depending on the nature of the organic solvent was studied in detail. The solution irradiation technique is presented in paragraph 2.2 of this dissertation. Studying the photostability of aqueous and binary solutions: water + ethanol, water + DMF, and water dioxane showed that for all solutions, a decrease in the intensity of the monomer absorption band is observed, as is the light emission of the solutions. In the case of a binary solution of water + dioxane, a dark color change is observed for Dbt-5 dye. As an example, in Fig. Figure 3.5 shows the absorption and fluorescence spectra of an aqueous solution of Dbt-5 dye. As can be seen from the figures, when the aqueous solution is irradiated, the absorption spectra show a decrease in the absorption intensity of the main band with $\lambda_{\max}=502$ nm.

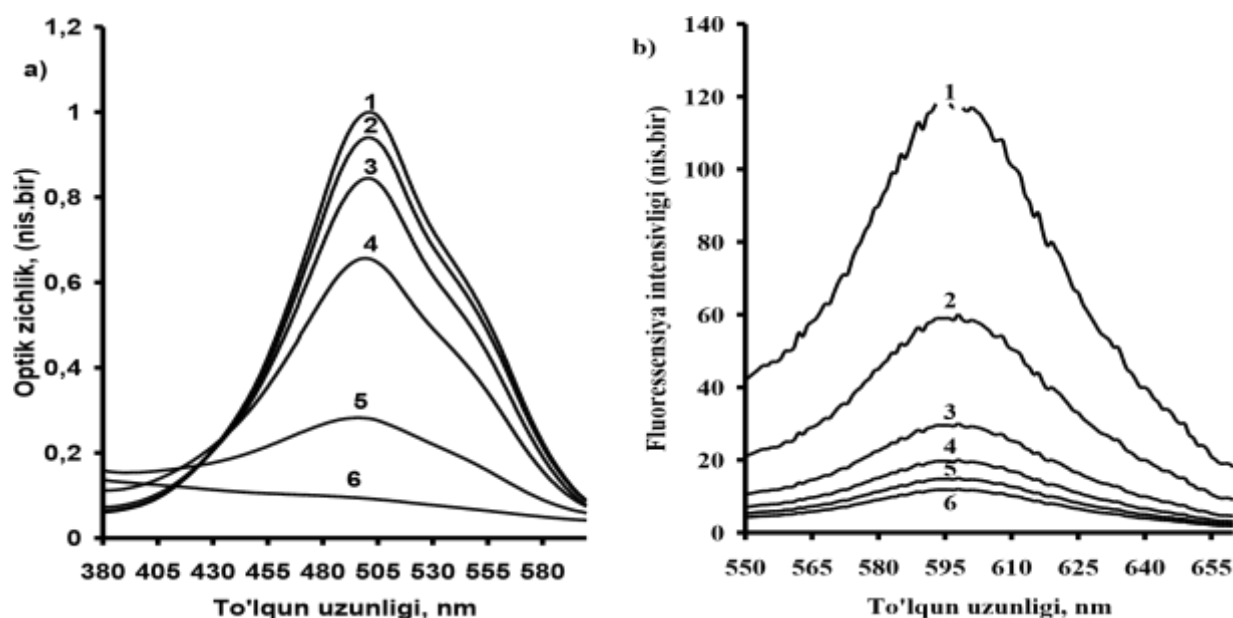


Figure 3.5. Absorption (a) and fluorescence (b) spectra of Dbt-5 dye in water ($c = 10^{-5}$ M) under irradiation: 1-0.2-300, 3-1320, 4-3000, 5-6000, 6-8700 seconds.

Table 3.3.

This phenomenon increases with increasing irradiation time. There are no significant changes in the form of fluorescence spectra and a decrease in the luminescence intensity is observed. Similar phenomena occur in absorption and fluorescence spectra of binary solutions of Dbt-5 dye and aqueous and binary solutions of Sbt dye under light irradiation (Table 3.3).

Light irradiation time (in seconds) required for complete photobleaching of the solutions of the studied dyes.

Paint	water	2% water+ 98% ethanol	2% + water 98% DMF	2% water+ 98% dioxane
Sbt	1800	5400	4200	Dark whitening
Dbt-5	4800	22800	22800	4200

The phenomena observed in the absorption and fluorescence spectra can be explained by the fact that the photolysis of organic solvents occurs according to the

□ following scheme

during irradiation: $H_2O \xrightarrow{h\nu} H \cdot OH \cdot$ for water,

□

$C_2H_5OH \xrightarrow{h\nu} C_2H_5(C_2H_4 \cdot H) \cdot OH$ For ethanol, in the case of DMF:

□

$NCON(C_2H_5)_2 \xrightarrow{h\nu} C_2H_5 \cdot CH_2CONH$ in the case of dioxane:

$C_2H_4OOC_2H_4 \xrightarrow{h\nu} C_2H_4(CH_2O \cdot CH) \cdot OH$.

In the process of photolysis, the solvent molecule is first split into separate parts, then the resulting decomposition products of the solvent interact with the dye molecule and cause their separation into separate parts. The proposed mechanism of the process of photodecomposition of the studied dyes in organic solvents confirms the following experimental fact: lack of photodegradation process when the studied dyes are dissolved in organic solvents and occurrence of this phenomenon when the same dyes are dissolved in previously irradiated solvent. It should be noted that the photobleaching process increases when the solution is diluted. Photobleaching of the studied dyes is irreversible, that is, the solutions are not dyed, and accordingly, the absorption and fluorescence spectra are not restored with time. From the table. As can be seen from 3.4, the addition of ethanol or DMF to the aqueous solution of the studied dyes increases the photostability of the aqueous dye solution.

As for dioxane, it should be taken into account that dioxane itself is an unstable compound and can easily form peroxides, which are strong oxidizing agents: , This confirms the accelerated kinetics and TO of water-dioxane solutions of the studied dyes compared to Dbt-5 dye in other binary solvents (Table 3.3)

Conclusion

Thus, as can be seen from the above results, depending on the concentration and nature of the solvent, under the influence of light, different processes can occur in the solutions of the studied dyes, each of which has its own spectral appearance.

Absorption and fluorescence electronic spectra of water-soluble Sbt and Dbt-5 styrylcyanine dyes were studied. Based on the experimental data obtained for molecules in the monomer state, the following are determined: absorption (λ_{max}^{yt}) and fluorescence (λ_{max}^{fl}) maxima, existence coefficient (ϵ), oscillator strength (f), quantum yield (B), excited state residence time (t), transition frequency () and Stokes shift (SS).

The process of transition from aqueous solutions to binary solutions was studied: a bathochromic or hypsochromic shift was observed in absorption and fluorescence spectra when transitioning to water+ethanol, water+dioxane and water+DFM. This observed spectral manifestation was explained by the breaking of the shell of dye molecules. 18-22 nm bathochromic shift of lines in absorption and fluorescence spectra when passing from water solutions to water+ethanol, water+dioxane and water+DFM solutions. The observed spectral features are explained by the change of solvate shells of dye molecules.

As the solutions of the studied dyes were irradiated with light in water+DMF, water+ethanol and water+dioxane mixtures, absorption and fluorescence power decreased without changing the shape of the spectrum. The observed phenomena were explained by the photodestruction of dye molecules.

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