UNIVERSITY OF LATVIA
FACULTY OF PHYSICS, MATHEMATICS AND OPTOMETRY

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INVESTIGATION OF OPTICAL PROPERTIES AND AMPLIFIED SPONTANEOUS EMISSIONS OF AMORPHOUS THIN FILMS FORMING ORGANIC COMPOUNDS FOR POSSIBLE APPLICATIONS IN ORGANIC SOLID STATE LASERS

SUMMARY OF DOCTORAL THESIS

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ABSTRACT

Various 4*H*-pyran-4-ylidene (further in this work abbreviated as pyranylidene) fragment containing organic molecules as well as the guest-host systems formed by mixing those with passive polymers were investigated. All of the investigated laser dyes were synthesized at Riga Technical university, Faculty of Materials Science and Applied Chemistry, under the leadership of Dr. chem. Elmāra Zariņa and Prof. Valdis Kokars. The purpose of the dissertation was to determine the suitability of these organic light-emitting materials for organic solid-state lasers as an active medium for future use in light-amplification applications, as well as, the possibility of improving the amplified spontaneous emission (ASE) properties of the most promising molecules in the host-guest systems. Within this work, thin films of the investigated organic compounds were prepared from the solutions with a predictable low-cost spin-coating technique. The influence of molecular structure on absorption, photoluminescence, photoluminescence quantum yield (PLQY) and ASE properties was studied. It was found that, with the incorporation of stronger electron acceptor fragments within the laser dye molecules, the redshift of the absorption spectrum of the compound increased, which can be clearly observed in the case of HAPPY dyes and WK-type compounds (*mono*- and *bis*-styryl derivatives of pyranylidene with various electron acceptors). It was proved that within the neat films of *mono*-styryl pyranylidene fragment-containing compounds with 2-cyanoacetate electron acceptor moiety (= KTB-type compounds) significant reduction of intermolecular interactions in the solid state was observed. Additionally, these spin-cast neat films were acquired with a remarkable improvement in optical quality. It was determined that all KTB-type compounds show the highest PLQY values and the lowest ASE excitation energies. The most promising compound for use in organic solid-state laser is KTB with PLQY of 23% and ASE excitation threshold energy of 24 $\mu J/cm^2$. It was found that at least five times lower photoluminescence quantum yield and higher amplified spontaneous emission excitation energy values of the compounds with two electron donor groups, compared to the compounds with one electron donor group. Such differences are associated with solid-state occurred entanglement of electron-acceptor and electron-donor groups connecting molecular chains of *bis*-styryl compounds, resulting in a strong distortion of the molecule, contributing to an increase in intermolecular interactions and the formation of energy traps. As a result of the interaction of distorted molecules, previously forbidden electronic transitions become allowed - a redshift of the emission spectrum occurs and/or another ASE emission peak appears. The simultaneous presence of several allowed transitions leads to a redistribution of the excitation energy between two possible emission states, causing an increase in the excitation energy of the ASE (up to >> 2 mJ/cm^2). The incorporation (doping) of the investigated

compounds into the passive polymer matrix with a higher refractive index (for example, PVK, PSU and PS) reduces intermolecular interactions and contributes to the increase of the compounds PLQY values and a decrease of the ASE excitation energy. It has been proven that the highest PLQY values are achieved at low (> 10 wt%) concentrations of laser dye molecules in the guest-host system. In turn, lower excitation energies of ASE can be achieved at the 10 to 30 wt% laser dye concentrations range in polymer. The reason for it is, because lower concentration dye molecules in the system increased intermolecular distance between them, weakening intermolecular interactions and that in turn causes a decrease in photoluminescence quenching. It has been determined that the largest reduction of light-emitting compound amplified spontaneous emission excitation energy value can be obtained in polyvinyl carbazole matrix. In KTB:PVK guest-host system, the largest reduction of pure KTB ASE excitation energy, respectively, 9 $\mu J/cm^2$, was achieved at 20wt% KTB concentration in the PVK matrix. By changing the concentration of dye molecules in the polymer matrix from 1 to 100 wt%, the dielectric constant of the guest-host system changes too and it becomes possible to obtain a tuneable ASE emission spectrum in a tens of nanometres wide spectral range.

Keywords: organic solid state lasers, amplified spontaneous emission, active medium, organic molecules, organic laser dyes, guest-host system, amorphous thin films

CONTENTS

INTRODUCTION

Currently, one of the promising and highly perspective directions, where non crystalline structure films forming organic molecules can be used, is intensively developing organic solid-state lasers technologies [1–3]. That is highly demanded and can be used in different photonics and spectroscopy applications; medicine - lab on chip and invasive surgery technologies; telecommunications - for signal transmission; sensor technologies - for detection of IS radiation; military applications, cosmos technologies etc. [4-10]. In the case of organic solid state lasers, such as laser active, light-emitting molecules are used in the fabrication of light-emitting or/and light–amplifying laser active medium, which can be excited with the external energy source [2, 3], [11]. Optically pumped lasing action in thin films of organic light-emitting materials makes organic solid-state laser competitive with more expensive traditional inorganic laser materials. The list of organic solid-state laser advantages is quite large, among the most significant of them are: low-cost manufacturing processes, small sizes, as well as they can be much easier to process and integrate into photonic devices etc.

Nowadays the fabrication of light-amplifying medium of organic solid state lasers requires different types of low molecular weight compounds with light-emitting and light-amplification in the wide range of the visible and infrared spectra [12-19]. Meanwhile, not all light-emitting molecules are equally suitable for this purpose since the main requirement for the light-emitting materials in such lasers is high light-amplification coefficient and low amplified spontaneous emission (ASE) excitation threshold energy below a few $\mu J/cm^2$.

Motivation

One of the greatest disadvantages of organic solid-state lasers, in comparison with their inorganic precursors, is higher excitation threshold energies of amplified spontaneous emission. Until now it is still not the end of the unsolved problem that limits the use and competitiveness of organic solid state lasers with their inorganic analogues. The main reason for the impossibility of achieving such low excitation threshold values of amplified spontaneous emission in the neat thin films of the light-emitting materials suitable for commercialization is close placement of organic molecules in their solid statethat cause them to interact each other. Those intermolecular interactions induce such undesirable effects as agglomeration of neighbour molecules, singlet-singlet annihilations, and photoluminescence quenching, as a consequence of which dramatically decreases the number of potential light emitting excited states, which in turn results in the reduction of photoluminescence quantum yield (PLQY) and significant increases of the

excitation threshold energies of amplified spontaneous emission. Presently and similarly, as it occurs in highly efficient dye lasers, one of the approaches how high intermolecular interactions in organic solids can be overcomed is a separation of interacting laser dyes by increasing the distance between them by mixing them in another material matrix, which, for example, can be formed by active, energy transferring material like Alq_3 [20] or by passive - polymers [21, 22] with a high refractive index. In such way so-called host-guest systems are made, where not only a significant reduction of the ASE excitation threshold energy value can be achieved. Additionally, depending on the host and guest ratio to each other The dielectric constant of the fabricated host-guest system changes too resulting in observable and measurable solid-state solvation effect [21], [23]. Because of this physical phenomena it also becomes possible to tune emission spectrum in several nanometers wide spectral range depending on emitter concentration.

The aim of the work

The aim of the work is:

- To explore the optical and ASE properties of the original, amorphous structure forming neat films that were obtained from the solution-processable organic molecules synthesized at the Faculty of Materials Science and Applied Chemistry of Riga Technical university and to determine their suitability and perspectives for possible applications in organic solid-state lasers for laser active medium production.

To achieve the goal, the following tasks must be implemented:

- To determine the dependence of the optical and ASE properties of those organic molecule structural peculiarities: symmetry, different electron acceptor and donor groups, added spatial groups and functional fragments;
- To explore the possibilities of improving the optical and ASE properties of the studied organic molecules in the guest-host systems by mixing them in the matrix of different polymers.
- To determine the dependence of those properties on the concentration of polymer matrix and dye molecules in the system;
- To find out the most promising guest-host systems formed by organic molecules and polymers for the applications of organic solid-state laser active media creation, including organic dyes concentration in the system at which the most significant improvements can be achieved.

Author's contribution

The author of the work herself has prepared all thin film samples, measured their thicknesses, absorption and photoluminescence spectra and taken optical images of the surface The author has improved and modified the existing set-up for ASE measurements and performed measurements of the amplified spontaneous emission excitation in the prepared sample layers. The

author herself has processed all the obtained experimental data, the necessary calculations, graphical approximations and analysis of the results. The results obtained during the development of the doctoral thesis: (1) presented at local and international conferences and (2) published the obtained results in international scientific journals together with colleagues who have studied non-physical properties of investigated compounds.

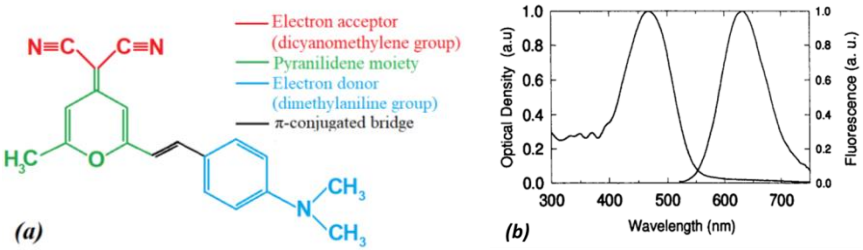
Scientific novelty

Optical and amplified spontaneous emission properties of molecules containing pyranylidene moieties, 2-cyanoacetic acid derivatives, 4*H*-pyran and 1*H*-pyridine derivatives have been studied. In the research, statements and conclusions about the effect of the structure (symmetry) of the studied organic molecules and their different elements (added/substituted electron acceptor and donor groups, spatial groups and functional moieties) on the optical properties of compounds were made: (1) depending on the addition to the electron donor or acceptor part of the molecule and (2) its affects the resulting interaction with other structural elements of the molecule and neighbouring molecules. Explaining in detail the changes in optical properties with the effect of the respective groups on the optical transitions in the molecule and the specific interactions of the molecules in the solid layer caused by the modified structure. Possibilities for improving the optical, PLQY and ASE properties of organic compounds in guest-host systems are shown and explained. The changes in the electron transitions in the emitter molecule caused by the concentration of the organic compound and the polymer matrix and the resulting switching between different radiation states - ASE emission maxima - have been studied. The effect of the 2-cyanoacetate fragment added to the *mono*-styryl pyranylidene moiety-containing compound on the reduction of intermolecular interactions in the solid layer and on the improvements in the optical quality of the amorphous thin films prepared from the solution was investigated. The incorporation of 2-cyanoacetate moiety within the KTB-type compounds contributes to the highest PLQY and lowest ASE excitation energy values in their neat films. For the first time in a guest-host system formed by a compound containing a ylidene moiety (KTB) and a polymer polyvinyl carbazole (PVK), the lowest excitation energy of 9 $\mu J/cm^2$ ASE is achieved at 20wt% dye concentration compared to similar previously studied compounds in the PVK matrix. The suitability of the studied compounds, guest-host systems and their perspectives for the applications as organic solid-state laser active medium production have been summarized and evaluated, nominating KTB: PVK host-host system as the most appropriate and promising designed system.

2. LITERATURE REVIEW

2.1. Organic molecules containing pyranylidene moieties and their optical properties

One of the first and most widely studied laser dyes, which has proven itself in liquid active media lasers is 4-dicyanomethylene-2-methyl-6-(4-N,N-dimethylaminostyryl)-4*H*-pyran DCM *(see Figure 2.1. part a)*: organic molecules that contain pyranylidene moiety. At one time, the great interest in DCM and the high demand for the use of the dye in lasers was explained by its high photoluminescence quantum yield in solutions, where it can be up to 80% [3], [24-28]. DCM is a low molecular weight organic compound with an asymmetric structure, consisting of one electron acceptor (dicyanomethylene group) and one electron donor (dimethylaniline group). In turn, the transfer of electrons between the donor and acceptor groups occurs through their binding π-conjugated bridge *(see Figure 2.1, part a)*.



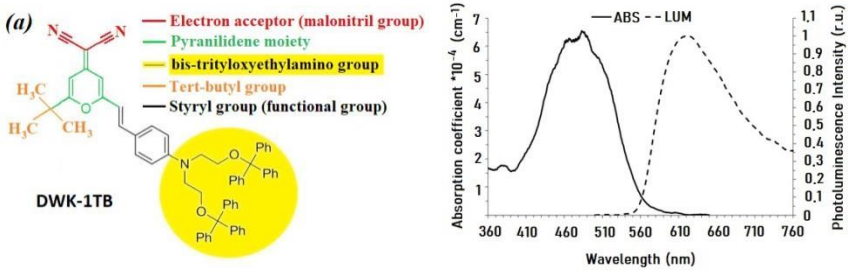
2.1. figure. *(a) DCM molecule and (b) absorption and emission spectra of DCM in methanol [29].*

In dichloromethane solution, the absorption maximum of DCM is about 470 nm. In contrast, its photoluminescence spectrum is strongly Stokes-shifted towards the red waves with a maximum at about 580-590 nm *(see Figure 2.1 part b)* [29]. The main factor that limits the use of DCM for the creation of an active medium of an organic solid laser is strong intermolecular interactions, which increase rapidly with dye concentration. Dense molecular packaging at high concentrations causes the occurrence of undesirable effects such as the interaction of excited states, formation of aggregates, etc., which, in turn, causes photoluminescence quenching [30, 31] making it impossible to induce amplified spontaneous emission (laser effect) in solid films formed only from DCM [28].

The strong intermolecular interaction and the resulting photoluminescence quenching can be reduced in several ways. One of them is to increase the spatial size of molecules during the synthesis process: by adding (to their chromophore part) bulky spatial groups; by substitution in the electron

donor and/or electron acceptor moiety as well as and/or addition of a functional group/moiety/chemical element (eg O, S, Cl, etc.). In the case of added passive spatial groups the absorption and emission spectral range of the molecule practically does not change (small changes in intensity shifted by a few nm)asthose do not participate in electron transfer processes. Their main function is to act as a "separator" between two adjacent emitter molecules preventing active interactions between their closely located chromophore moieties, thereby reducing their interactions, leading to an increase in PLQY and, in some cases, to a decrease in the amplified spontaneous emission threshold. Meanwhile, in the case of substitution of a donor or acceptor moiety, the substituents are no longer passive and actively participate in the electron transition processes, which leads to changes not only in the threshold energy of amplified spontaneous emission of the molecule but also in the range, form and intensity of its absorption and emission spectra.

One of the first compounds, whose strong intermolecular interactions in solid-state due to high concentration and their caused photoluminescence quenching were significantly reduced in such way was the famous red light laser dye DCM [32-34], at that time, it was widely used in liquid active media of dye lasers. For example, such compounds as 2-(2-(4-(*bis*(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile (DWK-1), 2-(2-(4-(*bis*(2-(trityloxy)ethyl)amino)styryl)-6-*tert*-butyl-4*H*-pyran-4-ylidene)malononitrile (DWK-1TB) and others were synthesized by modifying DCM: adding a *tert*-butyl group to the pyranylidene moiety and replacing dimethylaniline electron donor with trityloxyethylamino group.



2.2. figure. *(a) DWK-1TB molecule and it (b) absorption and emission spectra.*

The absorption spectrum of DWK-1TB (see Figure 2.2 part a) remained almost unchanged, while the emission spectrum shifted towards red waves, with a maximum at 623 nm (see Figure 2.2 part b), but E_{th} decreased to 155 μJ/cm^2 [33].

Leaving the pyranylidene fragment in the chromophore part of the molecule, butchanging the acceptor and donor fragments of the moleculethrough the synthesis processadded a variety of different spatial

groups and functional fragments, focusing on modifications that improved the optical and ASE properties of DCM and its derivatives, several types of molecules were designed and synthesized in RTU. The influence of the modified chemical structures on the morphology of solid films, glass transition temperatures, optical transitions of the electrons and improvements in optical and ASE properties, as well as the future application of the investigated compounds will be described in detail in the dissertation within the results and discussion section.

2.2. Host-guest systems formed by organic molecules and polymers and optical properties of those systems

The prospects for the use of light-emitting compounds in solid-state lasers and laser diodes are determined by their compliance with several requirements: the ability to form amorphous films from solution; high gain factors; low values of ASE excitation energy ($\leq$1 $\mu J/cm^2$). Achievement of such low energies in solid films is significantly hindered by the strong interaction of dye molecules and it caused various non-radiative transitions, that lead to quenching of potential, light-emitting states. It makes it impossible to achieve in the solid medium the same high light amplification parameters of the compound as within the liquid medium laser systems. One of the ways to lower the ASE excitation energy threshold of an emitter molecule or compound is through modifications to its chemical structure during the material synthesis, however, it is often not sufficient to achieve competitively low values which are required in commercial applications. In addition, there is always a sufficiently high probability of unforeseen side phenomena or /and effects (aggregation of a substance, isomerization, the presence of several conformations up to crystallization of the solid films) as a result of the modifications made in the synthesis process. Currently, one of the most efficient, inexpensive, and predictable ways to significantly reduce intermolecular interactions, contributing to the reduction of an ASE excitation energy threshold values, is possible in so-called guest-host systems. Those are obtained by mixing laser dyes into: (1) either an active, material that participates in energy transfer, such as Alq_3 [20]; (2) either in a passive, e.g., polymer matrix (PMMA [21], PVK [22], PSU, PS, etc.) with a high refractive index.

3. EXPERIMENTAL PART

3.1. Samples and the methods of their preparation

3.1.1. Sample preparation from solution by spin-coating method

All thin film samples were prepared from 0.25 – 0.3 mL solutions of investigated compounds dissolved in dichloromethane. Solutions were applied onto 2.5x2.5 cm^2 BK7 glass by the spin-coating method using „Laurell 650" device. The solution was deposited applied onto disc placed substrate and then rotated for 40 s, reaching 800 rpm. angular velocity and 800 rpm. angular acceleration. During rotation, the substrate is held at the disk by a vacuum pump, while the centrifugal force ensures an even distribution of the substance on the glass substrate. During rotation, most of the solvent evaporates and a uniform layer forms. To evaporate the remaining solvent and complete the formation of the solid film, the sample is transferred to a hot plate heated to 80°C for 10 minutes. Depending on the optical properties to be studied and the requirements of the measurement to be performed, three types of samples were prepared: (1) For absorbance measurements: 100-200 nm thin films, applied from a dichloromethane solution that contains 10 mg / mL of the compounds; (2) For photoluminescence, photoluminescence quantum yield and amplified spontaneous emission measurements: 300-400 nm films - from 35 mg/ml (compounds/dichloromethane) solution; (3) To determine the dependence of the laser dyes optical properties from its concentration in the guest-host system: 300 - 400 nm films were applied from 35 mg/ mL dichloromethane solutions that consists 1; 5; 10; 20; 30; 50; 70 weight percent (wt%) of laser dyes (guest) incorporated in the polymer matrix (host).

3.2. Equipment and methodologies for measuring

3.2.1. Investigation of the thickness and surface morphology of thin films

The thickness of the prepared thin films was determined with a Vecco "Dektak 150" profilometer. To apply the measurement, the layer was scratched off at several places on the surface of the sample. Determining the thickness of the film from the height difference obtained by recording the position of the profilometer needle sliding along the surface of the sample. The surface morphology of the samples was studied with a high-resolution optical microscope "Nikon Eclipse L150" by taking optical images of the surface of the prepared films at x20 magnification.

3.2.2. Measurement of the absorption spectra

The absorption spectra of the thin films were determined with a high-resolution Agilent spectrometer Cary 7000 Universal Measurement Spectrophotometer. Measurements were carried out by recording the spectra of

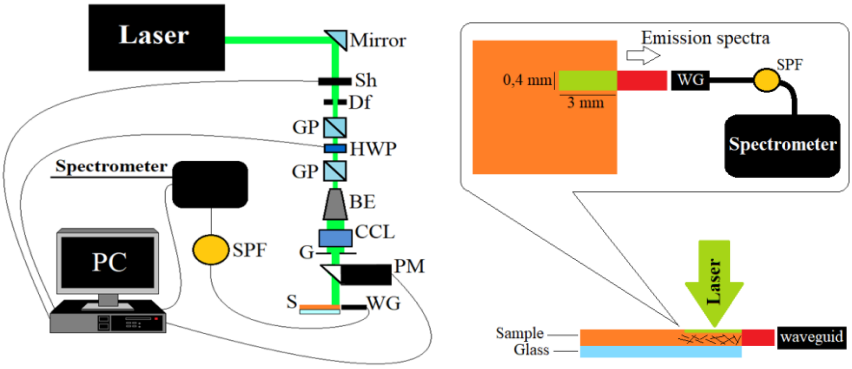
transmitted and reflected light of S and P polarized light falling on the surface of the sample at an angle of 45°, the spectrum of light absorbed by the film was determined by performing spectral data processing.

3.2.3. Measurement of photoluminescence and its properties

The photoluminescence spectra of thin films were determined with two different devices. For intensively absorbing compounds in the short-wave part of the spectrum, photoluminescence was excited by a continuous radiation laser diode at 405 nm and the photoluminescence spectrum emitted by the film was recorded with an Ocean Optics HR4000 spectrometer. For compounds that absorb intensively in the middle of the visible spectrum, photoluminescence excitation and recording were performed during the determination of the photoluminescence quantum yield by excitation with the wavelength corresponding to the absorption maximum of the compound. The photoluminescence spectrum and quantum yield of the sample films were determined with an industrially calibrated integrating sphere apparatus (Pico Master 1 fluorescence spectrometer (Photo Med GmbH)). The measurements of the photoluminescence quantum yield of the samples were performed with the equipment of the integrating sphere at Riga Technical University, the measurements were made by Dr.phys. Aivars Vembris. The calculation of the numerical value of the photoluminescence quantum yield obtained within the framework of the work was performed by computer software. Determining the quantum yield of photoluminescence from the fractional equation, at the excitation wavelength, dividing the integral intensity of light emitted from the substance by the integral intensity of light absorbed in the substance.

3.2.4. Experimental set-up for amplified spontaneous emission measuring

An improved and, with several new components, modified experimental scheme that was made in the laboratory earlier was used to capture the spectrum of amplified spontaneous emission and determination of the value of its excitation energy threshold *(see Figure 3.1, part a)*. The EKSPLA NT340/3UV series Q-tunable Nd:YAG nanosecond laser, with a second and third harmonic generator and an Optical Parametric Oscillator, OPO, which generates two lower frequencies from the frequency of the fundamental laser radiation, with the help of the second-order nonlinear optical interaction, was used as the excitation source. Laser pulse length 5 ns and repetition frequency 10 Hz. The excitation wavelength was set to the absorption maximum of each, definite sample.



(a) ***(b)***

3.1. Figure. ***(a)*** *Experimental set up for ASE measurements: Sh - shutter controlled by computer; Df - diaphragm, for obtaining a point excitation beam of uniform intensity; GP - Glan prism; HWP - half-wave plate, for controlling the intensity of the excitation beam with the help of a computer-controlled stepper motor; BE - beam expander; CCL - cylindrical collecting lens, which focuses the laser beam emitted by the slit on the sample in the form of a 0.4 mm wide rectangle; G – 3 mm gap, for obtaining the intensity distribution of the Gaussian profile of the laser beam falling on the sample; PM - power meter, for determining the falling power on the sample; S - sample, WG - a waveguide, for determining the emitted intensity of the sample; SPF - short wave filter (long pass filter), which cuts out the excitation laser signal from the intensity spectrum, which creates noise/interference;* ***(b)*** *Excitation and recording of amplified spontaneous emissions by irradiating a 3mmx0.4mm rectangular area.*

The threshold value of amplified spontaneous emission was determined by exciting a 3mmx0.4mm rectangular area on the sample surface *(see Figure 3.1, part b)*. Gradually rotating the half-wave plate, with a step of one degree, increasing the intensity of the light falling on the sample, after each change, the spectrum emitted by the sample was recorded in the spectrometer, with an integration time of 0.5-1 second. The intensity of the excited beam was increased until the peak of amplified spontaneous emission that appeared in the photoluminescence spectrum of the sample became sufficiently intense, strongly dominating the rest of the emission spectrum, and its rapid changes due to the increase in intensity no longer occurred (saturation occurred).

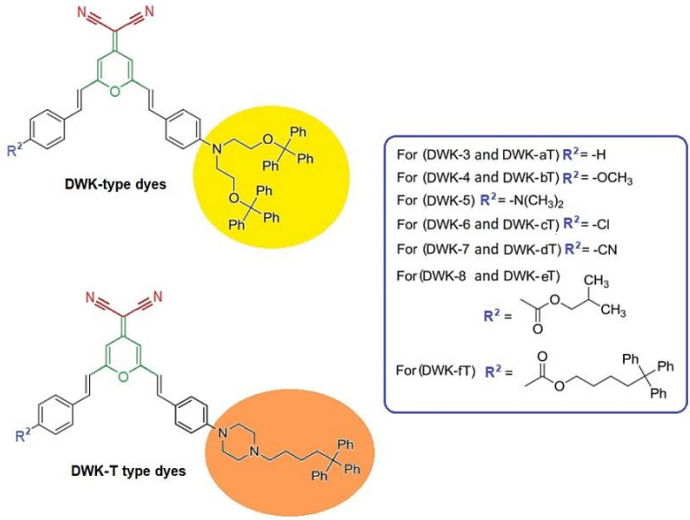
4. RESULTS AND DISCUSSIONS

4.1. Investigated derivatives and their molecular structures

In the frame of this workamorphous thin films obtained from the solution of glass-forming organic molecules were investigated: dyes containing a pyranylidene moiety (*bis*-styryl DWK [35] and *bis*-styryl DWK-T [34]) *(see Figure 4.1)*; 2-Cyanoacetic acid derivatives (symmetrical and asymmetric KTB-type laser dyes [32]) *(see Figure 4.2)*; 4*H*-pyran derivatives (asymmetric WK-1 and symmetric WK-2 laser dyes [36]) *(see Figure 4.3)* and 1*H*-pyridine derivatives (HAPPY dyes [36]) *(see Figure 4.4)*, synthesized by Dr. chem. Elmars Zarins in Riga Technical university, Faculty of Materials Science and Applied Chemistry. The main attention of the investigation conducted in this research was focused on the synthesized compound chemical structure modification dependence on their optical properties. One of the most notable advantages of all the investigated compounds is reduced interaction between molecules in their solid state as a result of the addition of large spatial groups, which not only makes it possible to form amorphous layers from solutions, but also significantly facilitates the preparation process thus reducing the consumption of substances and production costs. In terms of optical properties, this manifests itself in an increase in PLQY and a decrease in the ASE excitation threshold value, making these compounds more promising and competitive with the already well-known and commercialized laser dyes like DCM.

- ***Organic molecules with bis-styryl DWK and bis-styryl DWK-T containing pyranylidene fragments***

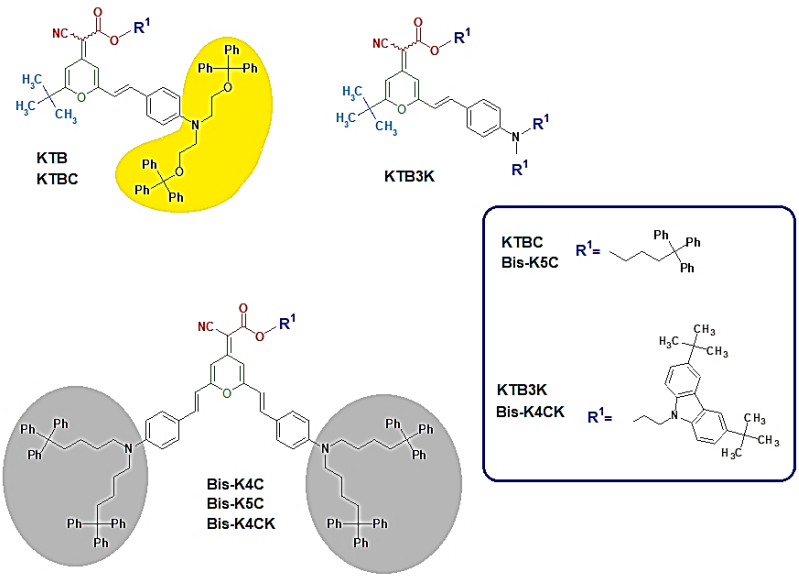
Bis-styryl DWK-type compounds *(see Figure 4.1)* are the result of modifications of symmetric DWK-2 molecule: synthetized by replacing N,N-dialkylamino and the spatial trityloxyethyl groups attached to one of it's styryl fragment with: hydrogen, chlorine and other functional groups. In the case of DWK-T-type compounds *(see Figure 4.1)*, both donor parts of the DWK-2 molecule were modified and the remaining 4-(N,N-dityriloxyethyl)amino group was replaced with one triphenylpiperazine spatial group [34, 35]. A common feature of bis-styryl DWK and DWK-T type molecules: those contain a pyranylidene moiety and the same electron acceptor =malononitrile group; DWK and DWK-T compounds also differ in the functional moieties added to the second styryl moiety *(see Figure 4.1)*.



4.1. figure. *Generalized structure of bis-styryl DWK type and bis-styryl DWK-T type organic molecules (bis-trityloxyethylamino group - highlighted in yellow;5,5,5-triphenylpentylpiperazine group - highlighted in orange).*

- ***2-Cyanoacetic acid derivatives***

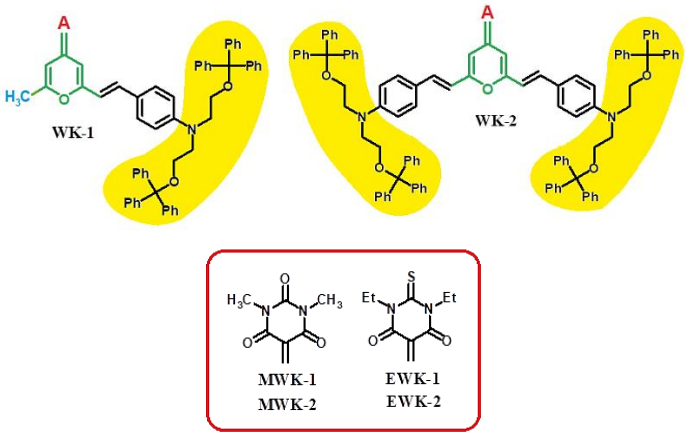
In the case of KTB-type compounds, a 2-cyanoacetic acid fragment is first incorporated into their electron acceptor part, to which spatial triphenyl or carbazole groups were later added, and the synthesis of the compounds is described in detail [32]. The distinguishing feature of connections is symmetry. In the case of symmetrical (bis-) compounds, through modifications, symmetrically in both electron-donating parts of WK-2-type compounds, spatial trityloxyethyl groups attached to nitrogen are replaced by spatial 5,5,5-triphenylpentyl group*(see Figure 4.2)*.



4.2. figure. *Generalized structure of 2-cyano-2-(4H-pyran-4-ylidene) acetate derivatives (red: 2-Cyanoacetate (electron acceptor); green: pyranylidene moiety; yellow: bis-trityloxyethylamino group; gray: triphenylpentylamino group; light blue: tert-butyl group).*

- ***4H-Pyran derivatives***

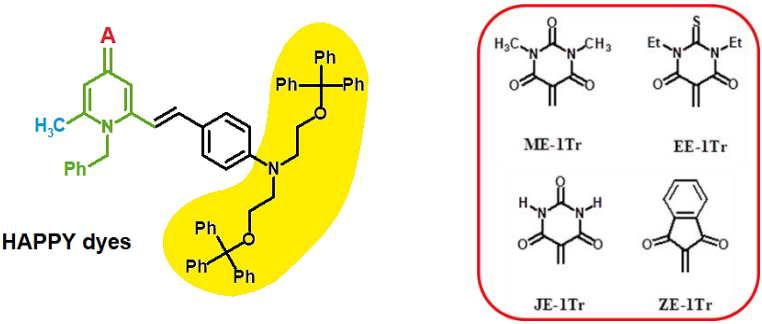
4*H*-Pyran derivatives are the result of modifications of asymmetric DWK-1 and symmetrical DWK-2, made in the malononitrile acceptor substitution, a detailed synthesis of compounds is described in [36]. Structurally, WK-1 and WK-2 have two distinctive features *(see Figure 4.3)*: *(1)* different electron acceptors: 1,3-dimethylpyrimidine-2,4,6-(*1H,3H,5H*)-trione (MWK-1 and MWK-2) and 1,3-diethyl-2-trioxididropyrimidine-4,6-(*1H,5H*)-dione (EWK-1 and EWK-2); and *(2)* symmetry, ie: asymmetric (*mono*-styryl) compounds with a single donor moiety to which a *bis*-trityloxyethylamino spatial group (WK-1: MWK-1 and EWK-1) and symmetric (*bis*-styryl) compounds - molecules with two identical donor styryl groups attached to the pyranylidene moiety with added *bis*-trityloxyethylamino spatial groups (WK-2: MWK-2 and EWK-2).



4.3. figure. *Generalized structure of 4H-pyran-4-ylidene derivatives (red: "A" different electron acceptor: 1,3-dimethylpyrimidine-2,4,6(1H,3H,5H) -trione (MWK) or 1,3- diethyl-2-trioxydydropyrimidine-4,6(1H,5H)-dione (EWK); green: pyranylidene moiety; yellow: bis-trityloxyethylamino group; light blue: methyl group).*

- ***1H-Pyridine derivatives (HAPPY dyes)***

HAPPY dyes radically differ from all earlier synthesized and studied laser dyes containing pyranylidene moieties. These asymmetric dye molecules are the result of WK-1- type derivative modifications, which appeared during the synthesis happened conversion of the 4*H*-pyran ring into the 1*H*-pyridine moiety *(see Figure 4.4)*.



4.4. figure. *Generalized structure of 1H-pyridine derivatives (red: "A" different electron acceptor: 1,3-dimethyl-pyrimidine-2,4,6(1H,3H,5H) -trione (ME-1Tr); 1.3 -diethyl-2-thioxidehydropyrimidine-4,6(1H,5H) -dione (EE-1Tr); pyrimidine-2,4,6(1H,3H,5H) -trione (JE-1Tr); 1H-indene- ,3 (2H) -dione (ZE-1Tr); light green: benzyl-pyridin-4(1H)-ylidene moiety; yellow: bis-trityloxyethylamino spatial groups; light blue: methyl group).*

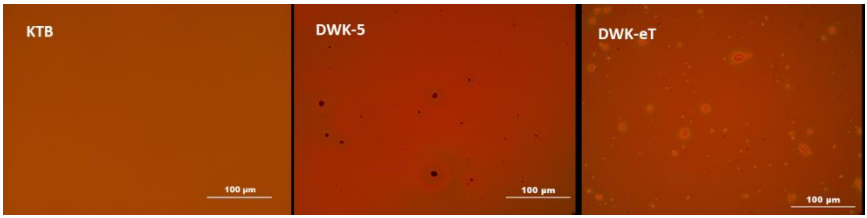
Their uniqueness is modified chromophoric part of the molecule, made by the addition of a benzyl group, i.e. replacement of the oxygen in the pyranylidene moiety with nitrogen to which a phenyl group has been added [36]. Structurally, the distinctive feature of the compounds is different electron acceptor groups: 1,3-dimethyl-pyrimidine-2,4,6-(1*H*, 3*H*, 5*H*)-trione (ME-1Tr); 1,3-diethyl-2-thioxidehydropyrimidine-4,6-(1*H*,5*H*)-dione (EE-1Tr); pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (JE-1Tr); 1H-indene-1,3 (2*H*)-dione (ZE-1Tr).

4.2. Dependence of thermoplastic properties on molecular structure

The addition of 9*H*-carbazole groups to the electron donor and electron acceptor moieties of the molecule was found to increase the thermal stability and glass transition temperature of the compound. For example, KTB3K, which has 9*H*-carbazole groups in both the electron donor and acceptor moieties, has the highest thermal stability and glass transition temperatures (T_d = 387°C, T_g = 137°C) compared to the other compounds. Thermal stability and glass transition temperatures were found to decrease with decreasing number of added 9*H*-carbazole groups. The glass transition temperatures of bis-styryl DWK type compounds are in the range of 71-119ºC, while the melting temperature is around 157-283ºC, but the decomposition temperature is in the range of 173-326ºC. The glass transition temperatures of 4*H*-pyran derivatives WK-1 are 77-101ºC and the decomposition temperature is 280-288ºC, while for WK-2, these values are slightly higher, respectively: 76-118ºC and 285-303ºC. The glass transition temperatures of 1*H*-pyridine derivatives or HAPPY dyes are 83-139ºC, but the thermal decomposition temperature is 260-296ºC.

4.3. Morphology of an amorphous thin film prepared from a solution

One of the main advantages of all studied compounds is under the influence of large spatial groups added to the molecule donor are practically eliminated aggregation and crystallization of compounds, improving their ability to form amorphous structures films *(see Fig. 4.5)*. Thanks to practically eliminated losses, i.e., light scattering, which occurred on the inclusions of the aggregates and crystallization centers in the film, their optical quality significantly improved, contributing to the increase of PLQY and decrease of the ASE excitation threshold value.



4.5. figure. *Optical images of surface morphology of investigated compounds thin films, captured at 200x magnification.*

The only group of pyranylidene compounds that form ideally smooth amorphous films are laser dyes of the KTB-type. However, in the case of some compounds, it has also failed to completely eliminate the structural deficiencies. In surface images, small bright spots indicate crystal formation (eg DWK-eT), but black dots indicate molecular agglomeration (e.g. DWK-5) *(see Figure 4.5)*. It was found that small formations with an insignificant fraction per cm^2 do not significantly affect the ASE properties of compounds. In the frame of the work has been determined regularity between the glass transition temperature of compounds and: *(1)* layer structure - the most homogeneous amorphous layers without the inclusion of crystals and aggregates are formed by compounds with the highest glass transition temperatures; *(2)* properties of ASE - compounds for which it was difficult or impossible to determine the glass transition temperature - ASE was not excitable even at extremely high excitation energies (> $2mJ/cm^2$), such as DWK-dT, DWK-eT and DWK-fT. As a result, it was concluded that the addition of the triphenylpiperazine spatial group (DWK-T compounds) negatively affects the optical quality of the formed film, making it difficult or impossible to excite ASE.

4.4. Dependence of the optical properties of the studied compounds on the molecular structure

It is known that the strong interaction between neighbour dye molecules in the solid state, in the film, is one of the main reasons for the quenching of photoluminescence and, consequently, the impossibility to excite ASE. These interactions can be reduced by modifying the molecules by adding to them spatial group (-s) during the synthesis. However, modifications may have shortcomings. Therefore, it is very important to study their influence on the electron-optical transitions occurring in the newly synthesized molecule.

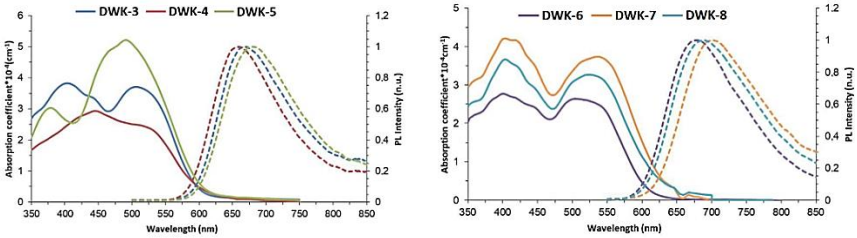
The modifications necessary for the improvement of the optical and ASE properties of the promising laser dyes for the applications of creating light active systems and organic solid state lasers were performed at the Faculty of Materials Science and Applied Chemistry of Riga Technical university. Where under Dr.chem. Elmars Zariņš leadership, in the successive synthesis processes, followed by, within the framework of the doctoral thesis, made investigations of the newly obtained compounds, as a result of which, optical and ASE

properties deteriorating groups, in further made modifications, were replaced by others - synthesizing new improved compounds.

It was found that the participation of the added groups in the electron optical transitions in the molecule, shown as: changes in the absorption and emission spectra (spectral shift, the appearance of additional absorption peak bands, spectral broadening, change in Stokes shift, ASE threshold, etc.); depends on the strength of those group electron donor or acceptor properties, their effect is also observed on the characteristic temperatures of the molecule: glass transition, melting and thermal decomposition.

4.4.1. Bis-styryl DWK type compounds

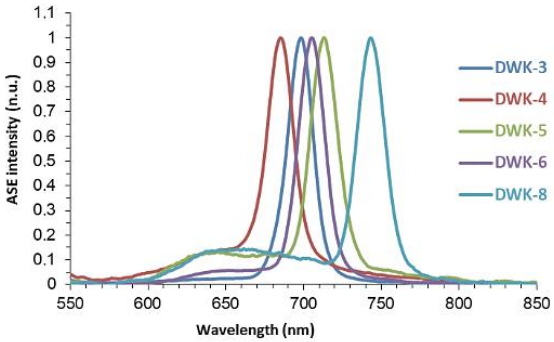
The optical and ASE properties of DWK compounds are mainly determined by electron transfer processes between the 2-(4-(bis(2-(trityloxy) ethyl)amino) styryl group of the electron donor part of the molecule and the malononitrile electron acceptor moiety. In the spectrum, to that corresponds to an intense, more than 200 nm wide, absorption in the range of 350 to 600 nm, and an equally wide, approximately 150 nm Stokes shifted photoluminescence. In turn, the blue shift between the maxima of DWK-type compounds is caused by additional electron transfer processes between the 2-(4-(bis(2-(trityloxy)ethyl)amino)styryl moiety and the substituent R^2 attached to the second styryl moiety of the molecule. However, since DWK compounds have several rotational conformations, it is not possible to unambiguously determine and define the regularities between the effects of electron transition processes in different compounds on their optical properties. Therefore, the absorption and photoluminescence spectra obtained are a mixture of all these conformations *(see Figure 4.6).*



4.6. figure. *Absorption (solid line) and photoluminescence (dashed line) spectra of amorphous thin films of bis-styryl DWK compounds.*

The appearance of two absorption peaks is associated with two different electron transfer processes: the shorter wavelength peak corresponds to the electron transfer processes between the 2-(4-(bis(2-(trityloxy)ethyl)amino)styryl moiety and the R^2 groups attached to the second styryl moiety of the molecule, in turn, shifted red from it, the second absorption maximum corresponds to the electron transitions between the 2-(4-

(bis(2(trityloxy)ethyl) amino)styryl group of the electron donor part of the molecule and the electron acceptor - malononitrile moiety. The stronger the electron acceptor properties of R^2 (e.g. cyano and isobutyloxycarbonyl), the more the photoluminescence spectrum of the compounds (DWK-7 and DWK-8, respectively) shifts red to a further range of IR waves. It was found that the addition of substituents with strong electron acceptor properties to the donor moiety of the styryl group, together with the styryl moiety containing it, becomes another acceptor moiety of this molecule, creating additional interactions between adjacent dye molecules, reducing PLQY and increasing ASE excitation energy threshold. For example, the addition of -CN groups (DWK-7) caused such an increase in intermolecular interactions that it made ASE excitation impossible even at extremely high excitation energies of 2 mJ/cm^2 [35]. Compared to previously studied asymmetric bis-styryl-DWK-T-type derivatives [34], for which ASE was not induced at all, and the precursor of bis-styryl-DWK derivatives: symmetric DWK-2, that contains two identical bis-trityloxyethylamino donor moieties [40, 41]; here, replacement of one of its bis-trityloxyethylamino group with $-COOCH_2–CH(CH_3)_2$ (DWK-8); -Cl (DWK-6) and -H (DWK-3) contributed to a decrease in the excitation threshold value of the compounds ASE by 160-12 $\mu J/cm^2$. In turn, replacement with $-OCH_3$ (DWK-4) and $-N(CH_3)_2$ (DWK-5) resulted in a 2-5-fold increase in the ASE excitation threshold. In contrast, the addition of a -CN (DWK-7) group to the styryl moiety converted it to another acceptor moiety of the molecule, creating a strong interaction of additional molecules in the solid layer, making ASE excitation impossible.



4.7. figure. *Amplified spontaneous emission spectra of neat bis-styryl DWK-type compounds ("n.u.-natural units").*

It has been experimentally shown that the properties of PLQY and ASE are closely related to the participation of R^2 substituents in the optical transitions in the molecule and are inversely proportional to the increase in their electron acceptor properties. The weaker the electron acceptor properties of the R^2 substituents attached to the styryl moiety, the lower the excitation threshold

values of the compound ASE. For example, the excitation energy of DWK-8, DWK-6 or DWK-4 that contains isobutylcarbonyl, chlorine or methoxy groups is more than 9-2.5 times lower than the excitation threshold value of DWK-5 ASE, which contains strong electron donor dimethylamino groups *(see Figure 4.7 and Table 4.1).* The excitation threshold values of the DWK-8 and DWK-6 ASE are up to 2 times lower than the DWK-2. In the case of DWK-5, the addition of a dimethylamino substituent to the styryl moiety of the electron donor moiety not only increased the strong molecular interaction in the solid layer but also caused aggregation of two adjacent molecules, confirming that the ASE properties of the compounds depend not only on the size of added spatial groups but also from the interactions caused by the added R^2 substituent groups on the parts of the molecule containing it and adjacent molecules [35].

4.1. table. *Absorption, photoluminescence, photoluminescence quantum yield (PLQY) and amplified spontaneous emission properties in thin films of neat bis-styryl DWK-type compounds [35].*

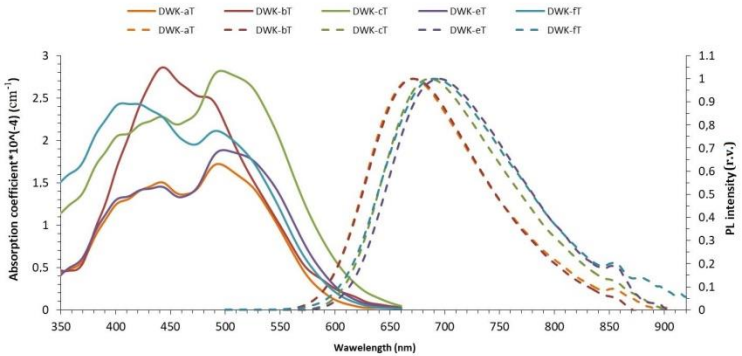
Compound	*DWK-3*	*DWK-4*	*DWK-5*	*DWK-6*	*DWK-7*	*DWK-8*
λ_{abs}, (nm)	508±2	502±2	492±2	505±2	535±2	530±2
λ_{PL}, (nm)	667±2	659±2	682±2	680±2	700±2	689±2
PLQY, (%)	3.1±1	3.1±1	3.0±1	4.2±1	2.0±1	2.3±1
λ_{ASE}, (nm)	699±2	684±2	713±2	703±2	-	743±2
FWHM, (nm)	14±2	17±2	18±2	17±2	-	18±2
E_{th}, (μJ/cm^2)	318±16	623±31	1589±79	199±10	-	170±8

λ_{abs} – wavelength of the absorption maximum; λ_{PL} – wavelength of the photoluminescence absorption maximum; PLQY – photoluminescence quantum yield; λ_{ASE} – wavelength of the peak of the amplified spontaneous emission peak; FWHM - half width of the peak of the amplified spontaneous emission peak at the maximum emission intensity; E_{th} – value of the excitation energy at which the amplified spontaneous emission occurs.

4.4.2. Bis-styryl DWK-T type compounds

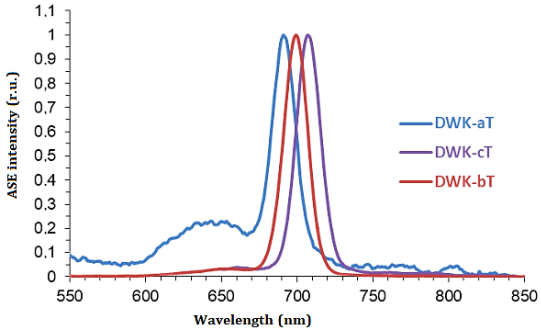
The optical and ASE properties of DWK-T compounds are mainly determined by electron transfer processes between the styryl group of the electron donor part of the molecule ((5,5,5-triphenylpentyl)piperazin-1-yl) and the electron acceptor - malononitrile moiety. Due to this transition, compared to DWK analogues, DWK-T absorption peaks are blue-shifted by 16-35 nm (DWK-bT~DWK-4 and DWK-eT~DWK-8, respectively) and are in the spectral range of 486 - 495 nm. In turn, the R^2 substituents added to the second styryl moiety, depending on their properties, affect these molecular transfer processes in two ways: either as electron donors when the molecule is excited, or as electron acceptors as they attract electrons at the time of the relaxation process. Similar to DWK compounds, there are two peaks in the DWK-T absorption spectra, where the intensity and location of the first peak depend to a large extent on the added R^2 substituent group and the way how dual nature of its properties affects the transfer processes. The decrease in the blue shift between peaks is due to the smaller spatial size of the 5,5,5-

triphenylpentyl)piperazin-1-yl) styryl group, which contributes to a decrease in the spatial size of the molecules and an increase in intermolecular interactions. In addition, the ((5,5,5-triphenylpentyl)-piperazin-1-yl)styryl group is not completely passive and affects the electron transfer processes in the molecule by interacting with parts of the molecule containing it as well as with adjacent molecules *(see Figure 4.8).*



4.8. figure. *Absorption (solid line) and photoluminescence (dashed line) spectra of amorphous thin films of bis-styryl DWK-T type compounds.*

For this reason, the expression of the dual nature of R^2, $-OCH_3$ and -Cl added in DWK-T molecules differs from that of DWK. The photoluminescence peaks of DWK-T are in the spectral range of 672-695 nm, which is redshifted by 9-13 nm (DWK-cT~DWK-6 and DWK-bT~DWK-4, respectively) compared to DWK analogues. Except for the isopropyloxycarbonyl group-containing DWK-eT, which is by 5 nm blue shifted from its analogue DWK-8. Similar to DWK compounds, the presence of substituents -CN (DWK-dT), $-COO-CH_2CH(CH_3)_2$) (DWK-eT) and $-COO-(CH_2)_4CPh_3$ (DWK-fT) causes a redshift of the absorption and photoluminescence spectra, here, from DWK-aT, $\leq$ 9 nm and $\leq$ 23 nm, respectively. In contrast, in the case of DWK-dT, an increase in the electron acceptor properties of the -CN group contributes to an extremely large increase in intermolecular interactions, leading to complete photoluminescence quenching. In contrast to DWK analogues, the ASE excitation threshold values of DWK-bT and DWK-cT, which contains $-OCH_3$ and -Cl, are 3 times lower than DWK-aT, 327 and 462 $\mu J/cm^2$ versus 1091 $\mu J/cm^2$, respectively.



4.9. figure. *ASE spectra of pure bis-styryl DWK-T compounds.*

As a result, here, the expression of the dual nature of -OCH_3 and -Cl can be explained by: *(1)* the unpaired electron shift (dissociation) of the -Cl and -OCH_3 substituent groups relative to the rest of the molecule during the excitation process of the compound; and/or *(2)* the effects of high electronegativity of chlorine and oxygen: they "pull" - shift electrons from the molecule. This, in turn, creates additional interactions between neighbouring molecules. The 6-styryl moiety of DWK-aT is also involved in these charge transfer processes, but to a much lesser extent. In the case of DWK-dT, DWK-eT and DWK-fT, in contrast to DWK-aT, DWK-bT and DWK-cT, the substituent R^2 attached to the styryl fragment have only electron withdrawing properties. This contributes to the appearance of additional interactions between neighbouring molecules, which eventually becomes the reason why these compounds ASE can't be excited even at extremely high (≥2 mJ/cm^2) excitation energies [34] *(see Figure 4.9 and Table 4.2).*

4.2. table. *Absorption, photoluminescence, PLQY and ASE properties of amorphous films of pure bis-styryl DWK-T compounds [34].*

Compound	***DWK-aT***	***DWK-bT***	***DWK-cT***	***DWK-dT***	***DWK-eT***	***DWK-fT***
λ_{abs}, (nm)	486±2	486±2	492±2	487±2	495±2	495±2
λ_{PL}, (nm)	672±2	672±2	689±2	-	695±2	691±2
PLQY, (%)	1.8±1	2.9±1	0.6±0.5	-	0.59±0,5	2 ±1
λ_{ASE}, (nm)	691±2	698±2	704±2	-	-	-
FWHM, (nm)	14±2	15±2	15±2	-	-	-
E_{th}, (μJ/cm^2)	1091±50	327±30	462±30	-	-	-

In contrast to the expected improvement in emission properties, replacement of the bis-trityloxyethylamino group with a 5,5,5-triphenylpentylpiperazine group for DWK-T compounds leads to a 0,07-6,5-fold decrease of their PLQY (DWK-4~DWK-bT and DWK-6~DWK-cT respectively) and 263-773 μJ/cm^2 increase of ASE excitation energy for DWK-cT ~ DWK-6 and DWK-aT~DWK-3, respectively. But, in the case of DWK-

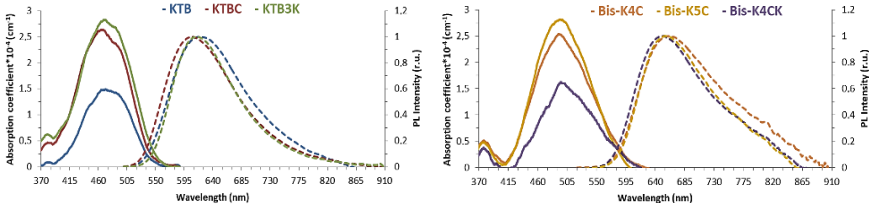
dT, DWK-eT, and DWK-fT, group interactions and much stronger R^2 electron acceptors: -CN (DWK-dT), -$COOCH_2CH(CH)_2$) (DWK-eT), and –COO-$(CH_2)_4CPh_3$ (DWK-fT); the expression of electron-binding properties became the reason for the impossibility of ASE excitation even at ≥2 mJ/cm^2 energies. Exception, DWK-bT~DWK-4, where the replacement of the spatial groups and its interaction with the methoxy substituent group contributed to a 2-fold decrease in ASE excitation energy. Comparing the effect of R^2 on the optical and ASE properties of DWK and DWK-T compounds, it was concluded that it is related and highly dependent on the number, size and participation of the spatial group added to the second styrene moiety of the donor moiety, as well as interactions with the molecule containing it parts and neighbour molecules. For example, in contrast to DWK-8, in the case of DWK-eT, under the influence of the -$COOCH_2$–$CH(CH_3)_2$ substituent group, the PLQY 3.5 fold decreases, but ASE excitation becomes impossible. One of the reasons is the spatially smaller size of the 5,5,5-triphenylpentylpiperazin-1-yl group, as a result of which the spatial size of the molecules decreases and thus the intermolecular interaction increases.

4.4.3. Mono-styryl and bis-styryl KTB type compounds: 2-Cyanoacetate derivatives

2-Cyanoacetate derivatives are unique, so far, they have not been synthesized for research, but used as a raw material in the synthesis of the electron acceptor part of various DCM type dye molecules. The investigated 2-cyanoacetate derivatives can be divided into: asymmetric *mono*-styryl KTB-type compounds (KTB, KTBC and KTB3K) and symmetrical *bis*-styryl KTB-type compounds (*Bis*-K4C, *Bis*-K5C and *Bis*-K4CK). Their optical properties are mainly determined by electron transfer processes between the 4-(N,N-dialkylamino)-styryl electron donor group/(-s) and the electron acceptor-2-cyanoacetate moiety. However, depending on the R^1 substituent attached to the electron acceptor moiety, the absorption and emission spectra of the respective compounds appear as small, blue or redshifts relative to KTB (or *Bis*-K4C) spectra.

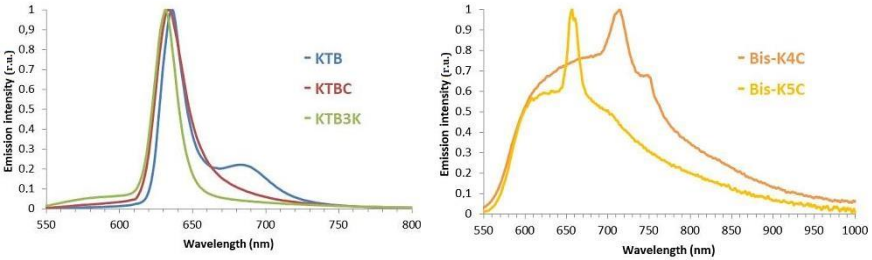
Based on the effect of 5,5,5-triphenylpentyl groups on electron transfer processes and molecular interactions identified in the study of DWK and DWK-T type compounds, in the case of KTB-type compounds, it was added to the electron acceptor fragment of the molecule 2-cyanoacetate (KTBC and *Bis*-K5C). Contrary to the expected improvements (PLQY and ASE), the modification contributed to a decrease in the electron acceptor properties, leading to a blue shift in the absorption spectrum and a decrease in Stokes shift (compared to KTB and *Bis*-K4C) *(see Table 4.3).* In the case of symmetric compounds containing two identical electron donor groups (*Bis*-K4C, *Bis*-K5C and *Bis*-K4CK), increased the conjugation length of the molecules, causing a redshift of the absorption and photoluminescence maxima from the spectra of asymmetric compounds containing the same acceptors, at 21-29 nm and 43-40

nm, respectively *(see Figure 4.10).* The increase in Stokes shift is due to the increasing time of the electron optical transitions in the molecule due to the increase in the conjugation length of the symmetric compounds, as evidenced by the shifts of the photoluminescence spectrum to the further IR range. In turn, a 2.5–4.5-fold decrease in PLQY and a 5–9-fold increase in ASE excitation energy is related to the "packing/compression" of spatially large molecules in the solid layer, contributing to an increase in their interactions.



4.10. figure. *Absorption (solid line) and photoluminescence (dashed line) spectra of amorphous thin films of 2-cyanoacetic acid derivatives.*

Even though the chromophore part of the molecule is not conjugated to the spatial 9*H*-carbazole moiety, its presence in the electron acceptor (*Bis*-K4CK) and the electron donor (KTB3K) promotes a redshift of the 3-5 nm absorption spectrum from other triphenyls (KTB, KTBC) and KTB-type molecules containing ethyl (*Bis*-K4C, *Bis*-K5C) groups. Evidence of the effect of the 9*H*-carbazole moiety on the electron optical transitions in the molecule, which increases with the number of moieties added, despite the lack of conjugation. Up to now, all the lowest ASE excitation energy values are shown by asymmetric, *mono*-styryl KTB, KTBC and KTB3K compounds, 24, 25 and 52 μJ/cm^2, respectively. Making them highly promising for use in a variety of light amplification applications and, in particular, for the creation of organic solid-state laser active media. In the case of *bis*-styryl KTB compounds, ASE was induced only in *Bis*-K4C and *Bis*-K5C samples, with excitation threshold values being orders of magnitude higher, 165 μJ/cm^2 and 223 μJ/cm^2, respectively.



4.11. figure. *ASE spectra of pure films of cyanoacetic acid derivative.*

Much higher ASE excitation energies of symmetric compounds are associated with a large area of overlapping absorption and photoluminescence spectral regions, resulting in an increase in the effect of the absorption coefficient, i.e. the reabsorption of the emitted light in the volume of the layer. Experimentally, this was observed as strong photosensitivity of *Bis*-K4C and *Bis*-K5C, manifested by fading of the less than 1 min prolonged laser-illuminated area. In contrast, even at $\geq$ 2 mJ/cm^2, non-excitable ASE in *Bis*-K4CK film was associated with the effect of 9*H*-carbazole groups on electron transitions and caused an increase in molecular spatial size, promoting molecular distortion in the solid film and increased interaction of neighbouring molecules. Another explanation for the higher ASE excitation energies of symmetric compounds is due to the fact that, compared to asymmetric compounds, the relaxation rates of their radiating excited states are slower, as proved in the journal Dyes and Pigments [32].

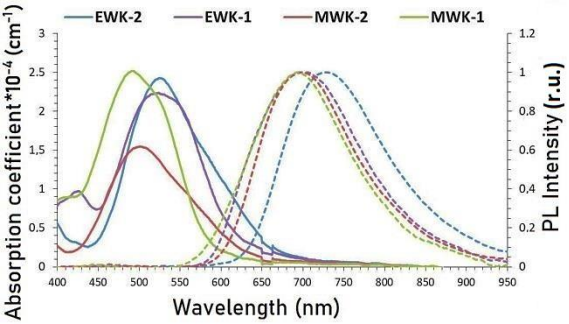
4.3. table. *Absorption, photoluminescence, PLQY and ASE properties of pure amorphous layers of 2-cyanoacetic acid derivatives[32].*

Compound	***KTB***	***KTBC***	***KTB3K***	***Bis-K4C***	***Bis-K5C***	***Bis-K4CK***
λ_{abs}, (nm)	471±2	465±2	470±2	492±2	494±2	495±2
λ_{PL}, (nm)	618±2	608±2	614±2	661±2	649±2	654±2
PLQY, (%)	23±1	16±1	16±1	5±1	7±1	7±1
λ_{ASE}, (nm)	633±2	629±2	626±2	714±2	659±2	-
FWHM, (nm)	15±2	15±2	19±2	20±2	12±2	-
E_{th}, (μJ/cm^2)	24±2	25±2	52±5	165±11	223±15	-

It is concluded that the addition of triphenyl and carbazole groups to the electron acceptor moiety of 2-cyanoacetate impairs the electron acceptor properties, as evidenced from in case of asymmetric compounds observed absorption (up to 6 nm) and photoluminescence (4-10 nm) maxima blue shift. In the case of all compounds observed due to the addition of groups caused a decrease in the Stokes shift, an increase in the overlap area of the absorption and photoluminescence spectral regions, and an increase in the ASE excitation energy. Compared to the previously studied asymmetric compounds containing *mono*-styryl-4*H*-pyran-4-ylidene moieties to which triphenyl groups (DWK-1TB) have been added [40], the KTB 24 μJ/cm^2 ASE excitation value is 8 times lower.

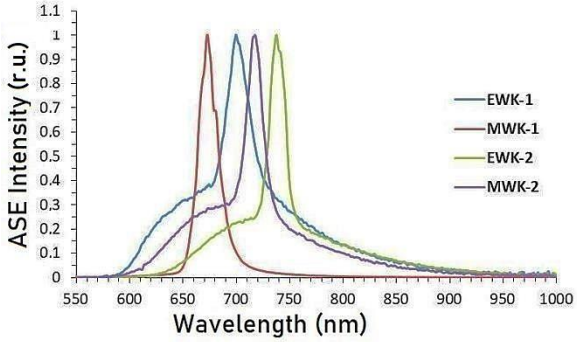
4.4.4. Mono-styryl WK-1 and bis-styryl WK-2 type compounds: 4H-pyran derivatives

Similar to its precursors WK-1 and WK-2 [33, 40], the thermal, optical and physical properties of MWK-1, EWK-1, MWK-2 and EWK-2 are mainly determined by a strong electron acceptor fragment *(see Figure 4.12 and 4.4. table).*



4.12. figure. *Absorption (solid line) and photoluminescence (dashed line) spectra of amorphous thin films of pure 4H-pyran derivatives.*

The blue shift of the absorption maxima (491 nm and 501 nm) of MWK-1 and MWK-2 from EWK-1 and EWK-2 (523 nm and 525 nm) *(see Figure 4.12)* indicates that 1,3-dimethyl pyrimidin-2,4,6(*1H,3H,5H*)-trione has much weaker electron acceptor properties than 1,3-diethyl-2-trioxydydropyrimidine-4,6(*1H,5H*)-dione. The minimal (2-10 nm) redshift of the absorption maxima of symmetric compounds from the spectra of asymmetric compounds indicates about the minimal effect of spatial bis-trityloxyethyl groups on the absorption properties. All WK-1 and WK-2 have a symmetry-independent 200-250 nm broad emission spectrum in the red part of the spectrum with peaks at 702, 701, 694 and 733 nm (MWK-1, EWK-1, MWK-2 and EWK-2). The decrease in WK-2 stoke shift and the blue shift of the emission peak from WK-1 *(see Table 4.4)* indicates about increasing intermolecular interaction between neighbour molecules in solid film, caused by the increase of the number of donor groups and doubling of the number of trityloxyethyl amino groups. This is evidenced by a 3-5-fold decrease in WK-2 PLQY values: MWK-1: 11.6% and MWK-2: 2.2%; EWK-1: 9.6% and EWK-2: 3.2%. The symmetry and doubling of the number of donor parts also negatively affect the ASE excitation of the compounds. Compared with MWK-1 and EWK-1 (respectively: 65 and 156 $\mu J/cm^2$), MWK-2 and EWK-2 ASE excitation threshold values increase 2.5-3.5 times (respectively: 201 and 347 $\mu J/cm^2$) *(see Figure 4.13 and Table 4.4)*.



4.13. figure. *ASE spectra of undiluted 4H-pyran derivatives.*

4.4. table. *Absorption, photoluminescence, PLQY and ASE properties of pure 4H-pyran derivatives amorphous films [36].*

Compound	***MWK-1***	***MWK-2***	***EWK-1***	***EWK-2***
λ_{abs}, (nm)	491±2	501±2	523±2	525±2
λ_{PL}, (nm)	702±2	694±2	701±2	733±2
PLQY, (%)	11.6±1	2.2±1	9.6±2	3.2±1
λ_{ASE}, (nm)	674±2	714±2	701±2	743±2
FWHM, (nm)	20±2	16±2	21±2	16±2
E_{th}, ($\mu J/cm^2$)	65±6	200±20	156±15	347±35

Compared to precursors: MWK-1TB and EWK-1TB [33], in the case of MWK-1 and EWK- 1, the methyl group of the pyranylidene moiety has not been replaced by the *tert*-butyl group, which resulted in an improvement of the WK-1 properties: redshift of the absorption (5-8 nm) and photoluminescence (65-39 nm) maxima, an increase in the Stokes shift and, as a consequence, a decrease in the overlapping areas of absorption and emission spectra. The decrease in WK-1 intermolecular interactions is evidenced by a 3.7-6-fold higher PLQY, a 2.5-3-fold lower ASE excitation energy, and a redshift of ASE peak for 18 nm. The rapid improvement in the properties of WK-1 can be explained by the variation of the conformations of the positions of attachment to the pyranylidene moiety inherent in the synthesis process of the *tert*-butyl group of WK-1TB and, despite the absence of conjugation, the pronounced expression of electron acceptor properties. Unlike the *tert*-butyl group, the methyl group has only one conformation and does not have the nature of a sterile interaction, therefore, its participation in electron transfer processes is insignificant. Summarizing the results and experimental observations, it is concluded that the excitation energies of symmetric WK-2, lower PLQY, and higher ASE is mainly related to the enhancement of the emission caused by the possible aggregation of molecules of non-symmetrical compounds in a solid layer, which was facilitated by closer intermolecular distances. As evidenced by the redshift of the photoluminescence spectrum from the photoluminescence

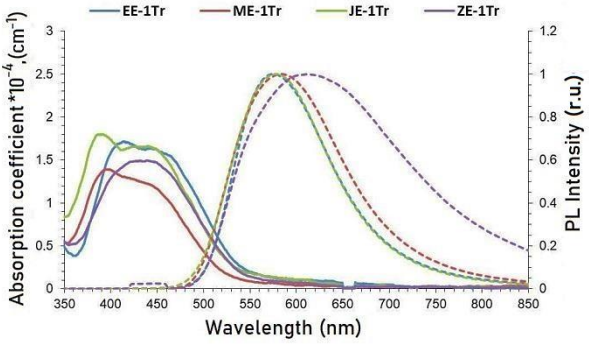
spectrum of *mono*-styryl and the rapid non-radiative relaxation [40, 42]. The occurrence of such a specific intermolecular interaction in a solid film leads to the fact that another, previously forbidden, additional radiation transition becomes permitted. Therefore, even a small fraction of emission enhancement per unit area of the solid film due to possible aggregation of compound molecules can significantly affect the photoluminescence spectrum and PLQY of the compound [40]. On the other hand, the existence of several allowed transitions promotes the redistribution of excitation energy between two possible emission states, causing symmetric *bis*-styryl compounds to have much higher (up to non-excitable) ASE excitation energies than asymmetric, *mono*-styryl compounds.

4.4.5. HAPPY dyes: non-symmetric mono-styryl 1H-pyridine derivatives

1*H*-Pyridine derivatives are asymmetric laser dye molecules obtained by synthesis by the conversion of the 4*H*-pyran ring contained in WK-1 to a 1*H*-pyridine moiety by reaction with benzylamine. From the above-mentioned pyranylidene derivatives, HAPPY dyes are distinguished by the chromophore part of the molecule modified with a benzyl group, created by the reaction described in references [36] and [41], where instead of oxygen places nitrogen with attached benzyl group. Consistent with the expected improvements in optical and ASE properties, the addition of bulky *bis*-trityloxyethiamine spatial groups to the styryl moiety of the donor moiety contributed to an increase in intermolecular distance, followed by the decrease of the number of molecules in s-trans conformation and decrease of aggregation inducing molecular interactions – i.e. decreasing unpredictability effects on optical and ASE properties of compounds. The only difference between HAPPY dyes, which also basically determines their optical and physical properties - different electron acceptors Compared to 4*H*-pyran derivatives (WK-1) containing the same acceptor fragments (WK-1) [36, 40], here, conversion to the 1*H*-pyridine moiety contributed to a narrowing of the HAPPY dyes absorption spectrum by 100 nm and, a 54-130 nm, blue shift. Similar to WK-1 and WK-1TB [33], also for 1*H*-pyridine derivatives, the increase in the electron acceptor properties of the acceptor moiety contributes to the redshift of the absorption peak, from weakest to strongest, respectively:

- ❖ pyrimidine-2,4,6(*1H,3H,5H*)-trione: JE-1Tr (386 nm);
- ❖ 1,3-dimethylpyrimidine-2,4,6(*1H,3H,5H*)-trione: ME-1Tr (395 nm);
- ❖ 1,3-diethyl-2-thioxidehydropyrimidine-4,6(1*H*,5*H*)-dione: EE-1Tr (413nm);
- ❖ 1*H*-indene-1,3(2*H*)-dione: ZE-1Tr (431 nm).

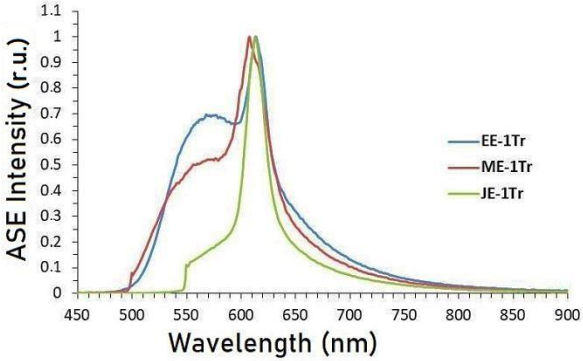
Due to the modification of the chromophore of the molecule, the photoluminescence spectrum of 1*H*-pyridine derivatives shifts blue from the spectra of the corresponding WK-1.



4.14. figure. *Absorption (solid line) and photoluminescence (dashed line) spectra of amorphous thin films of pure HAPPY dyes.*

Nevertheless, compared to WK-1 [36], the increase in Stokes shift and smaller absorption and photoluminescence overlaps areas, which according to the theory should promote lower re-absorption of emitted light and increase the photoluminescence quantum yield, contrary to the expected JE-1Tr and ZE-1Tr PLQY 2–4.5 fold decreases by 5.9% and 2.8%, respectively. In contrast, ME-1Tr, for which, compared to MWK-1, the Stokes shift by 22 nm decreases and the area of absorption and photoluminescence overlap increases, PLQY ~ 1/3 increases (15.1%). In the case of EE-1Tr alone, a reduction in PLQY to 2.8% does not contradict with the theoretic claimant about the effect of a Stokes shift decrease and overlapped areas increase *(see Table 4.5).*

ASE was induced in only 3 of the 4 HAPPY dyes *(see Figure 4.15).*



4.15. figure. *ASE spectra of amorphous thin films of pure HAPPY dyes.*

Compared to WK-1, HAPPY dyes ASE peaks are blue shifted to the middle of the red spectrum: 615 nm (ME-1Tr), 614 nm (EE-1Tr), and 603 nm (JE-1Tr). However, in contrast to WK-1, they are shifted red from the photoluminescence peaks: by 90 nm (ME-1Tr), 43 nm (EE-1Tr) and 27 nm

(JE-1Tr). Conversion of WK-1 4*H*-pyran derivatives to 1*H*-pyridine compounds contributed up to 3-fold reduction in ASE excitation energy threshold values: EE-1Tr=46 μJ /cm^2, ME-1Tr=65 μJ/cm^2 and JE-1Tr=76.5 μJ/cm^2 *(see Table 4.10)*.

4.5. table. *Absorption, photoluminescence, PLQY and ASE properties of amorphous films of pure HAPPY dyes [36].*

Compounds	***ZE-1Tr***	***JE-1Tr***	***ME-1Tr***	***EE-1Tr***
λ_{abs}, (nm)	431±2	386±2	395±2	413±2
λ_{PL}, (nm)	612±2	576±2	584±2	571±2
PLQY, (%)	2.8±1	5.9±1	15.1±1	5.1±1
λ_{ASE}, (nm)	603±2	603±2	615±2	614±2
FWHM, (nm)	-	19±2	23±2	12±2
E_{th}, (μJ/cm^2)	-	77±7	65±6	46±4

The impossibility of ASE excitation in the ZE-1Tr layer even at excitation energies of ≥2 mJ/cm^2 may be related to, determined in the nuclear magnetic resonance spectrum of its synthesis intermediate ZE-1 [36], probability of the existence of the s-trans conformation inducing intermolecular aggregation and predominance of s-trans over s-cis.

Based on the results and observations, it is concluded that: The molecules ME-1Tr and EE-1Tr containing 1,3-dimethyl-pyrimidine-2,4,6(*1H,3H,5H*)-trione and 1,3-diethyl-2-thioxidehydropyrimidine-4,6 (*1H,5H*)-dione acceptors are promising for further applications in the creation of organic solid state laser active media. It is concluded that, contrary to theoretical statements about the reduction of absorption and photoluminescence overlap areas: lower re-absorption of emitted light in the volume of the substance, expected increase in PLQY and decrease in ASE excitation energy; Deterioration of the properties of HAPPY dyes is mainly caused by the incomplete elimination of molecular aggregation-inducing s-trans conformation predominance in the substance. In contrast to 4*H*-pyran derivatives, where the addition of bulky *bis*-trityloxyethylamino spatial groups minimized or eliminated the predominance of aggregation-inducing s-trans conformations, in the case of 1*H*-pyridine compounds, it did not eliminate this problem.

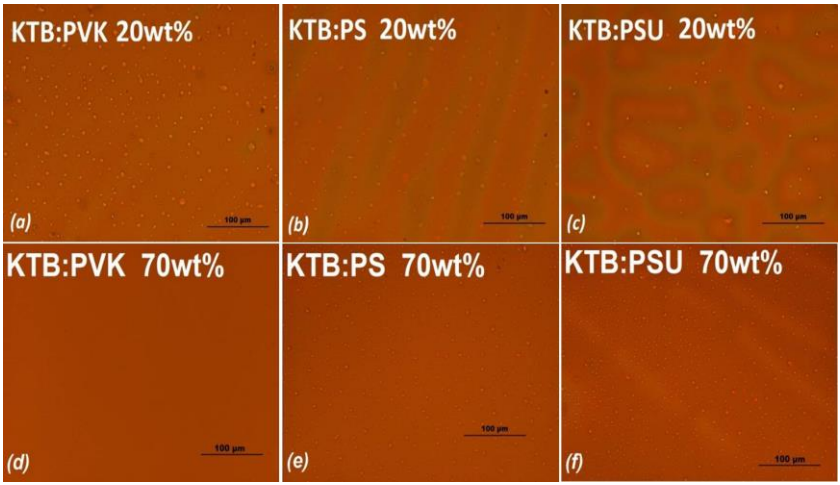
4.5. Optical property of amorphous thin films of guest-host systems

At high concentrations of dye molecules in the solid film, due to their close proximity, strong interactions may promote aggregation of the substance, and the formation of crystals or insoluble "islands" which, when excited, may act as scattering centres, causing the appearance of additional luminescent bands and, ultimately, reduce PLQY and increase ASE excitation energy. To improve the optical quality and the above properties from the solution applied layers and to reduce the strong interactions due to the close proximity of dye

molecules; for the purpose of organic solid state laser light amplifying active media creation the most promising laser dyes (KTB; ME-1Tr and EE-1Tr) at 10, 20, 30, 50 and 70wt% dye concentrations, were mixed into the polymer polyvinyl carbazole (PVK, in the case of KTB also in polysulfone, PSU, and polystyrene, PS) matrix in that way creating corresponding guest-host systems.

4.5.1. Influence of laser dye concentration on amorphous thin film morphology

To satisfy conditions of the good planar waveguide optical quality and ensure efficient light guiding in it is provided by the refractive index of the active medium (core) of the waveguide (for the input light) which is higher than the refractive index of the surrounding medium (shell). Larger differences in refractive indexes correspond to larger refractive angles of the guided light at their boundary, resulting in reduced losses due to light passing through the core-cladding boundary. Equally important is the amorphous nature of the active environment of the waveguide. To improve the emission properties of the laser dye KTB, at concentrations of 1, 5, 10, 20, 30, 50 and 70wt% were mixed into PVK, PSU and PS polymer matrices, obtaining 3x7 guest-host systems. The choice of matrix polymers was made based on: their suitability for efficient light guiding in the planar waveguide structure (high n_{PVK}=1.69, n_{PSU}=1.63 and n_{PS}=1.59); their good mixing with organics and solubility in it dissolving, non-polar solvents. BK7 glass was used as a base (n=1.52). To determine the dependence of the optical quality (surface morphology) of the prepared guest-host system films on: *(1)* polymer and *(2)* dye concentration in the polymer matrix, surface optical images were taken from the samples. For the sake of clarity, in the following section, only the most characteristic and most detailed examples of systems (KTB:polymer) are shown and characterized *(see Figure 4.16).*



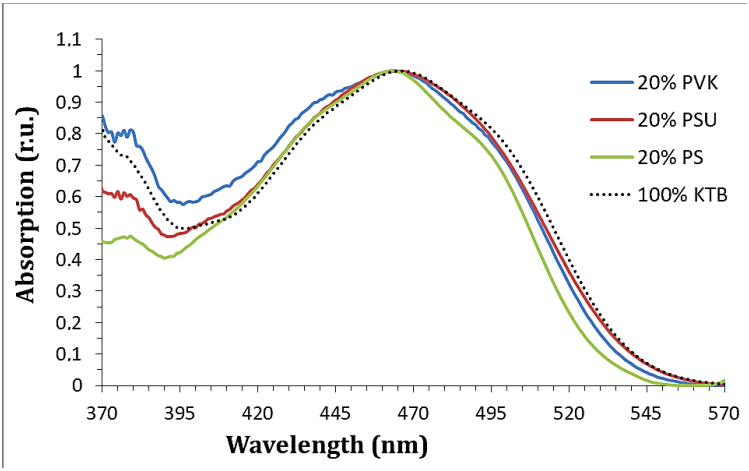
4.16. figure. *From the solution applied, KTB: polymer guest-host system, film surface optical images at 20wt% and 70wt% KTB concentrations in PVK, PSU and PS matrix. Optical images were obtained at x200 magnification*.

From the obtained optical images and profilometer measurements, it was determined that surface roughness and structural defects decrease with increasing dye concentration (> 20wt%) until practically disappear at higher concentrations in samples *(see case d-f in Figure 4.16).* The most pronounced structural defects were observed in samples with 1-20 wt% concentrations *(see case a-c in figure 4.16),* where high surface roughness and the distribution of structural defects can be explained by the high proportion of polymer in the system. As a result, the structure of the formed film is mainly determined by the spatial orientation of the chains formed by the polymer and their "mixing" with the laser dye. In the case of *figures 4.16 a-c cases*, at low concentrations of dye molecules in optical images, the colourful "structures" on the surface are the interference of light on the sample surface relief with different optical lengths, which appeared as a result of the complex nature of the formation of several possible orientations of polymer molecular chains during the formation of solid film. As a result of careful study of the structure and properties of polymers, it is assumed that the small transparent dots similar to frozen bubbles shown in *figures 4.16 (a-c)* are agglomerates of KTB molecules, the number and distribution of which per mm^2 are related to the polymer structure. In turn, the reason for their formation may be related to the formation of a non-eutectic system under the influence of higher polymer (PVK and PSU) glass transition temperatures, where, at the used drying temperatures, in films corresponding to low dye concentration are forms vitreous areas of KTB. In contrast, their disappearance, at higher KTB concentrations in the samples: with equalization of the glass transition temperature of the system. The best surface quality of

KTB:PVK samples can be explained by the high polarity and density of polyvinylcarbazole, of which: first one, promotes good dissolution of KTB, and the second one, formation of an equally smooth solid film surface. On the other hand, KTB:PS surface roughness and poorer optical quality - with lower polystyrene polarity and density, as a result of which KTB "dissolves" (solvates) much worse.

4.5.2. KTB:polymer guest-host systems

All guest-host systems have the same, approximately 170 nm, wide, to the 100% KTB sample characteristic shape and intensity spectrum of absorption bands in the 370 - 540 nm range. A clearly expressed 20 nm wide absorption band corresponding to spatial trityloxyethyl groups and, subsequently, a less intense ~15 nm wide absorption band characteristic of the *–CN* group [32, 43]. For a 100wt% KTB, 471 nm, 460-480 nm and 480-495 nm, respectively *(see Figure 4.17)*.

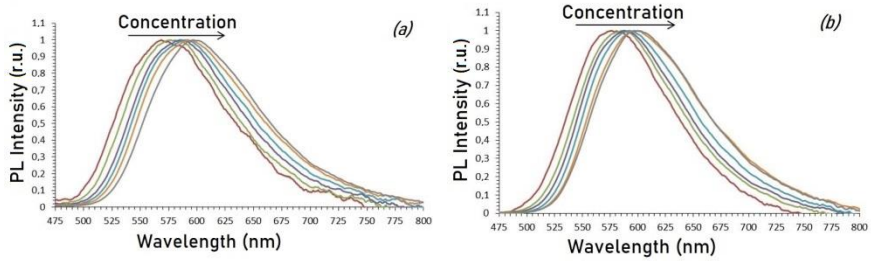


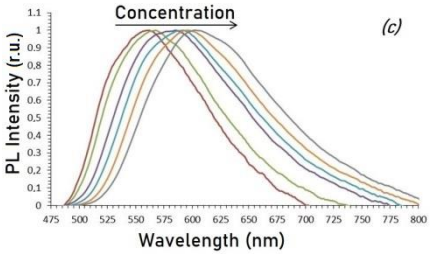
4.17. figure. *Standardized absorption spectra of 20 wt% KTB:polymer systems. The designations of the systems are given in the figure*.

The absorption spectral range and the position of the maxima are practically independent of changes in the dye concentration in the system. In turn, the intensity of the absorption bands is directly proportional to the increase in KTB concentration in the system. The incorporation of KTB into a PVK, PSU or PS matrix results in a change in different "solid solution", systems, dielectric constant and refractive index, contributing to a different 8-11 nm blue shift of the absorption maxima from the 100wt% KTB films absorption maximum *(see Figure 4.17)*. The different nature of the shift is due to: *(1)* different solvations of KTB in the polymers. Respectively, under the influence of the polymer ("solid solvent"), the dielectric constant of the guest-

host system ("solid solution") changes, promoting the re-orientation (rearrangement) of "solvent" (host) and "dissolved" molecules (guests) in solid solvate complexes. This changes the stabilization of the ground state and the first excited state of the dye molecules, which in turn strongly influences the intermolecular transitions and interactions. Contributing to the shift of the absorption spectrum, here, positive solvatochromic (ε ↑; polarity ↑; redshift) and changes in the intensity of the bands corresponding to the transitions [44]. *(2)* A more common reason for the different intensities of the absorption bands of the systems (more pronounced in KTB: PS systems): is different molecular weights of polymers, i. different density (proportion) of polymers per film area in guest-host systems with an equal mass fraction (concentration) of KTB molecules; polymer composition; spatial distribution and polarity, which influence the solvation of KTB molecules in the system and the process of merging (formation) of long polymer chains [45]. The absorption spectrum of KTB: PVK and KTB: PSU systems is comparable to 100wt% KTB, whereas in the case of KTB: PS, a slight increase in intensity is observed in the 420-450 nm absorption band. Unlike PS, PVK and PSU are strongly polar, in consequence of that, in the KTB: PS solid solvate system occurs re-stabilization of the KTB molecule in the ground state and first excited state, i.e.: re-orientation of KTB, by facing the polymer the electron donor part. Thus, by promoting the greater involvement of the electron donor part of KTB in the electron transfer processes taking place in the molecule, which corresponds to an increase in the intensity of the 420-450 nm band in the absorption spectrum. Quantum chemical calculations were performed to confirm or deny made claim. From which it appears that: the increase in absorption intensity at 420–450 nm can be explained by the $\pi \rightarrow \pi^* / n \rightarrow \pi^*$ energy transition (maximum at about 448 nm), which is almost completely limited in the vinylaniline moiety. The transition has a pronounced quinoid-like character, where the electron donor is an N atom and a (formal) vinyl group, but the acceptor is two ring-centered bonds parallel to the main conjugation direction.

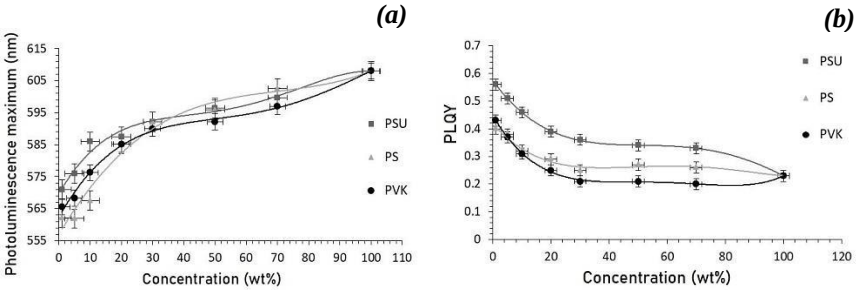
It was found that: The shape of the photoluminescence spectra of KTB: polymer systems are independent of the choice of polymer (PVK, PSU and PS) and the dye concentration in the system *(see Figure 4.18)*.





4.18. figure. *Photoluminescence spectra of KTB:polymer films depending on KTB concentration (5-70wt%) in: a) PVK; b) PSU and c) PS matrix.*

The photoluminescence spectra of all systems are for a 95 - 140 nm (1-70wt% KTB) Stokes shifted. The photoluminescence spectrum has an uncharacteristic, typical in solution systems, shift - solvatochromic effect: shift of the photoluminescence spectrum of the emitter mixed in the solution due to changes in solvent polarity (dielectric constant). In the case of solids, the guest-host system can be approximated as a "solid solution" where the KTB is "dissolved" in the polymer matrix. In which, as in solutions, the dielectric permittivity of the system changes following with the changes in its components, contributing to the spectral shift. In the case of solid systems, this is called the solid solvation effect. In all KTB: polymer systems, the increase in KTB concentration corresponds to the nature of positive solvatochromic: in the redshift of the peak of the photoluminescence spectrum, as a result of the increasing dielectric constant of the system *(see Figure 4.19, part a).*

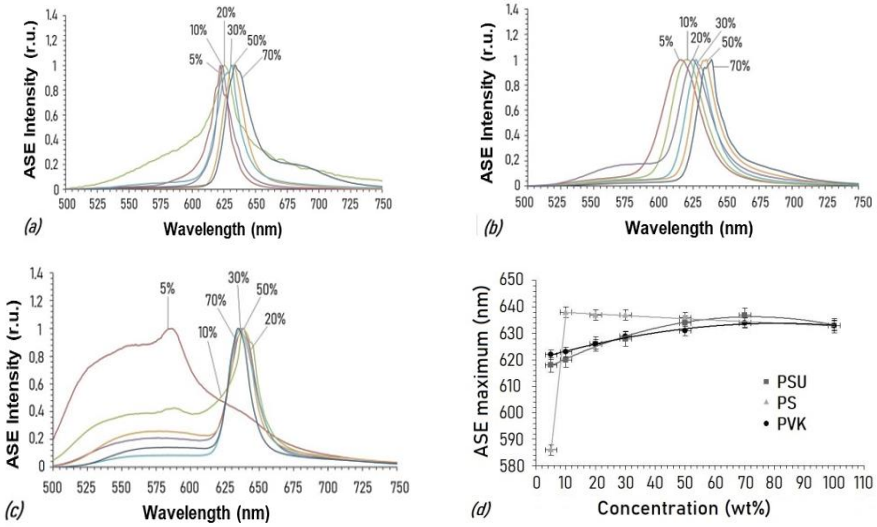


4.19. figure. *Dependence of the KTB: polymer systems: (a) photoluminescence maxima and (b) PLQY on KTB concentration in PVK, PS and PSU matrix.*

In turn, photoluminescence quantum yield decreases with the increasing concentration of laser dye in the system *(see Figure 4.19, part b).* Which were contributed by the increase of the concentration of KTB molecules in the system, followed by a decrease in intermolecular distance and an increase in interactions. The highest PLQY values were achieved in the KTB: PSU system, with a maximum of 56% at 1 wt% KTB. In KTB:PS and KTB:PVK systems to

1wt% KTB concentration corresponds to much lower values, 40% and 43%, respectively. Reasons for drastically different PLQY values: *(1)* Different lengths and structures of PSU, PVK and PS polymer chains (spatial orientation). High PLQY values in KTB:PSU systems can then be explained by the peculiarities of the formation of PSU molecular chains, which ensure sufficiently good separation of KTB molecules by attenuating the intermolecular interactions leading to photoluminescence quenching. As a result, even at 70wt% KTB concentration in the system, obtaining 33% PLQY, which is 1/3 times higher than the pure KTB 23% PLQY value; *(2)* Different dielectric permittivity of (solid solvate) systems and the resulting different reorientation of KTB molecules, that in turn leads to changes in electron donor and acceptor parts involvement in energy transfer processes. Then, the reason for the high PLQY values can be explained by the higher polarity (dielectric permittivity) of the KTB:PSU system, as a result of that, the combination and length of the chains of PSU molecules are much greater than in other systems; *(3)* Passivity of the PSU - its involvement in charge transfer processes is so small that, to some extent, into it mixed KTB molecules can be considered as isolated, assuming that most of their intermolecular interactions, which causes non-emission transition are prevented as they are "suppressed" by the properties of the PSU matrix.

In all film samples of the guest-host system at 5-70 wt% KTB concentration was possible to excite amplified spontaneous emission *(see Figure 4.20).*



4.20. figure. *The ASE spectrum of the systems for different KTB concentrations in the (a) PVK; (b) PSU; (c) PS matrix and (d) Dependence of ASE maximum from*

KTB concentration.

The ASE peak of all systems is shifted in red from the photoluminescence peak corresponding to this KTB concentration *(see Tables 4.6-4.8).* The redshift of the ASE from the photoluminescence peak is in line with the theoretical statement that this can be explained by the fact that the cross-sectional area of the stimulated emission must be larger at the right from the photoluminescence maximum [46]. Depending on the concentration of KTB in the polymer matrix, the shift varies unstructured: in KTB: PVK system from 54-37 nm (5-70 wt%); in KTB: PSU system from 42-34 nm (5-10 wt%); in KTB: PS system from 24-70 nm (5-10 wt%) or 70-31 nm (10-70 wt%). The exact location of the formation of the ASE peak can be determined according to 4.1. equation [46]:

$$\sigma_{em}(\lambda) \sim F(\lambda) \cdot \lambda^4 \qquad (4.1)$$

where $\sigma_{em}(\lambda)$ - cross section of the stimulated emission, $F(\lambda)$ - fluorescence quantum distribution function, λ - wavelength of light.

In KTB: PVK and KTB:PSU systems, the increase of KTB concentration from 5-70wt% corresponds redshift of the ASE peak and, respectively, in 12 nm and 19 nm spectral range, tuneable ASE peak *(see Figure 4.20, part d).* The ASE shift is related to the area of overlap between the absorption and photoluminescence spectral bands, which is determined by the relationship between the optical gain and the optical loss factor. According to which amplified spontaneous emission can only occur in the photoluminescence spectral region where the optical gain is greater than the optical loss factor [47] - where the difference between the stimulated emission and the absorption overlap area is greater than zero because there is also an amplification factor greater than zero. The amplification factor of the relevant environment can be determined by 4.2. equation:

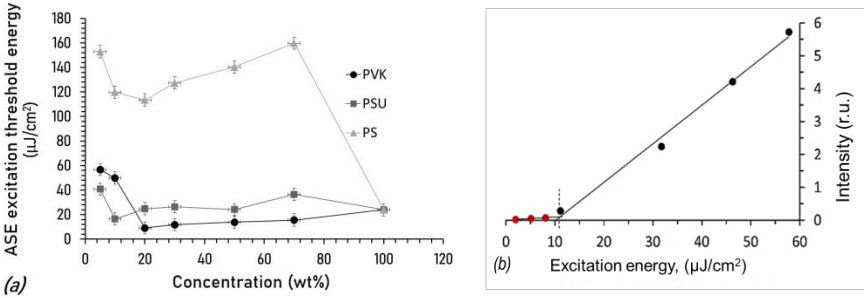
$$P(\lambda) = \left(\left(\sigma_{em}(\lambda) - \sigma^*(\lambda) \right) n^* - \sigma(\lambda) \cdot (N - n^*) \right) \qquad (4.2)$$

where n - density of the excited molecules, N - total density of the molecules, $\sigma(\lambda)$, $\sigma_{em}(\lambda)$ un $\sigma^*(\lambda)$ - cross-sections of the ground state, stimulated emission and excited state absorption, respectively.*

The absorption and photoluminescence spectra of all guest-host systems overlap on the left side of the photoluminescence band. It follows that the difference between the stimulated emission and the absorption overlap area will be greater than zero on the right side of the photoluminescence band. However, it is also necessary to take into account, with the increase of the laser dye concentration, the increasing absorption effect or reabsorption of the emitted light in the volume of the substance and the approach of the dielectric

permittivity of the guest-host system to the value of pure KTB dielectric permittivity. It follows that the redshift of ASE is caused not only by the effect of absorption but also by the solvation effect of solids, which becomes predominant at high dye concentrations. As a result, changes in KTB concentration from 5 to 100 wt% in KTB: PVK, KTB: PSU and KTB: PS in the guest-host systems correspond to the 11 nm, 15 nm and 52 nm tuneable ASE spectra *(see Tables 4.6-4.8).*

In KTB:PVK and KTB:PSU systems, the redshift of the ASE peaks corresponding to the increase in KTB concentration is of the nature of positive solvatochromic *(see cases a and b in Figure 4.20)*. In contrast, in the KTB:PS system, the shift is of two types. As a result of 5-10wt% KTB concentration changesthe switching between two ASE peaks *(see cases c and d in Figure 4.20)* from 586 nm (at 5wt % KTB) to 638 nm (at ≥10wt% KTB) is observed. The reason for the switching is, due to the higher dye concentration, opening of the more energy-efficient, additional transition, as a result of which, in case of 5wt% and ≥10wt%, electron transitions occur from different excited emission states. In turn, in the 5-10 wt% range, both transitions are allowed, as a result of which two ASE peaks appear simultaneously, of which at 5wt% KTB dominates the peak in the nearest wavelength range - 586 nm, but in the case of 10wt% - further in the red wavelength range - 638 nm, moreover, here, the peak intensity at least 2.5 times exceeds the intensity of the first peak. At higher (> 10wt%) KTB concentrations, only the further ASE peak is observed. In the PS matrix, the blue shift of the ASE peak corresponding to the increase of KTB concentration from 10-100 wt% has the character of negative solvatochromic *(see case c-d in Figure 4.20 and Table 4.8)*. Only in the PS matrix observed switching can be explained by the specific interactions between KTB molecules caused by the properties of the polymer, as a result of which, at concentrations of ≥10wt%, another transition becomes allowed and energetically more advantageous. However, this has not been proven. On the other hand, one of the experimentally proven explanations is related to the fact that the laser dye (KTB) used was obtained as a mixture of diastereoisomers [32], the formation ratio of which is 1:1. The claim is confirmed by NMR analysis of the compound, the results of which have been published in the journal „Dyes and Pigments" [32].



4.21. figure. *(a) ASE excitation threshold energy for different KTB concentrations and (b) determination of excitation energy for a sample with 30wt% KTB in the PVK matrix.*

In all systems, the excitation energy of ASE decreases with increasing KTB concentration. In the PVK and PS matrix, changes in KTB concentration from 5→20 wt%, with a minimum at 20wt%, correspond to energy reductions from 57 to 9 μJ / cm^2 and from 153 to 114 μJ/cm^2 *(see Figure 4.21 and Figures 4.6 and 4.8. tables)*, but the following increase of energy up to 16 μJ/cm^2 and to 160 μJ/cm^2, corresponding to increase of concentration, respectively. In KTB:PSU system, the excitation energy of the ASE decreases from 41 to 16 μJ/cm^2 (from 5→10wt%), reaching a minimum at 10wt%, after which increases to 37 μJ/cm^2 with increasing KTB concentration *(see Figure 4.21 and Figure 4.12. table)*. In KTB: PVK and KTB:PSU systems, 5-70wt% KTB samples were achieved, ASE excitation energy threshold values are lower than 60 μJ/cm^2. In turn, in KTB: PS systems, they significantly exceeded 100 μJ/cm^2, which may be due to: *(1)* redistribution of excitation energy between the energy levels of several permitted co-existing transitions, from which the less energy-efficient later discharges through non-radiative transitions; or *(2)* the reorientation of KTB molecules under the influence of PS properties and related intermolecular interactions.

It has been determined that in all KTB: polymer guest-host systems, to the changes of KTB concentration from 5-70wt% correspond in 11 nm (KTB:PVK), 15 nm (KTB:PSU) and 52 nm (KTB:PS) spectral range tuneable ASE emission spectra. It was found that all the lowest KTB ASE excitation energy values are achieved in the PVK matrix, in the range of 20-70wt% KTB concentrations, with a minimum of 9 μJ/cm^2 at 20wt% KTB. As a result, KTB:PVK guest-host systems have high prospects for the use in organic solid state lasers to create an active medium. Compared to the previously studied guest-host systems containing pyranylidene derivatives, where the lowest ASE excitation energy value of 21 μJ/cm^2 was reached in the DWK-1TB:PVK system [22], the 9 μJ/cm^2 value corresponding to the 20wt% KTB sample in the KTB system is two times lower.

4.6. table. *Optical properties of the from solution made films of KTB:PVK guest-host systems at different KTB concentrations in PVK matrix.*

Conc. wt%	λ_{ABS}, nm	λ_{PL}, nm	$FWHM_{PL}$, nm	PQLY, %	λ_{ASE}, nm	$FWHM_{ASE}$, nm	E_{th}, $\mu J/cm^2$
1	461±2	566±2	108±1	43±2	-	-	-
5	461±2	568±2	112±2	37±2	622±2	17±2	57±6
10	461±2	576±2	112±2	32±2	623±2	14±2	50±5
20	461±2	585±2	101±2	25±2	626±2	22±2	9±1
30	461±2	590±2	116±2	21±2	629±2	21±2	12±1
50	461±2	592±2	119±2	21±2	631±2	22±2	14±1
70	461±2	597±2	114±2	20±2	634±2	21±2	16 ±2

4.7. table. *Optical properties of the from solution made films of KTB:PSU guest-host systems at different KTB concentrations in PSU matrix.*

Conc., wt%	λ_{ABS}, nm	λ_{PL}, nm	$FWHM_{PL}$, nm	PQLY, %	λ_{ASE}, nm	$FWHM_{ASE}$, nm	E_{th}, $\mu J/cm^2$
1	463±2	571±2	100±1	56±2	-	-	-
5	463±2	576±2	102±2	51±2	618±2	33±2	41±4
10	463±2	586±2	107±2	46±2	620±2	29±2	16±2
20	463±2	588±2	108±2	39±2	626±2	24±2	25±2
30	463±2	592±2	105±2	36±2	628±2	23±2	26±3
50	463±2	596±2	114±2	34±2	634±2	19±2	24±2
70	463±2	600±2	115±2	33±2	637±2	19±2	37±4

4.8. table. *Optical properties of the from solution made films of KTB:PS guest-host systems at different KTB concentrations in PS matrix.*

Conc., wt%	λ_{ABS}, nm	λ_{PL}, nm	$FWHM_{PL}$, nm	PQLY, %	λ_{ASE}, nm	$FWHM_{ASE}$, nm	E_{th}, $\mu J/cm^2$
1	460±2	562±2	101±1	40±2	-	-	-
5	460±2	562±2	105±2	38±2	586±2	14±2	153±15
10	460±2	568±2	111±2	32±2	638±2	17±2	120±12
20	460±2	585±2	129±2	29±2	637±2	19±2	114±11
30	460±2	592±2	122±2	25±2	637±2	21±2	127±13
50	460±2	596±2	128±2	27±2	636±2	19±2	140±14
70	460±2	603±2	133±2	26±2	634±2	17±2	160±16

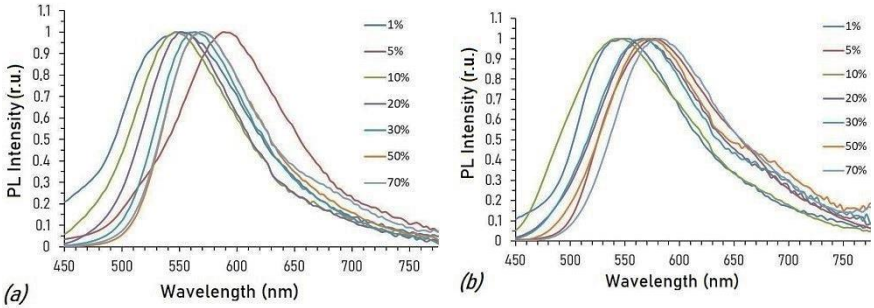
(*KTB: λ_{abs} – 471 nm, λ_{PL} – 608 nm PLQY – 23%, λ_{ASE} – 633 nm, $FWHM_{PL}$ – 170 nm, $FWHM_{ASE}$ – 15 nm, Eth – 24 $\mu J/cm^2$* [46]*).*

The study concludes that in order to achieve a low ASE excitation energy value, the matrix polymer must have high dielectric constant, high refractive index, passivity and "insensitivity" to the high intensity and wavelength of the source used for laser dye excitation.

4.5.3. ME-1Tr:PVK and EE-1Tr:PVK guest-host systems

Based on the research results of KTB: polymer systems, the most promising HAPPY dyes emitters, EE-1Tr and ME-1Tr, were also mixed into

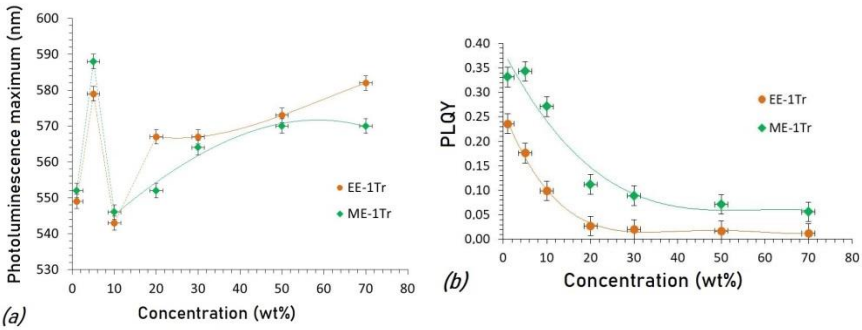
the polyvinylcarbazole matrix to improve the optical and ASE properties. It was determined that the incorporation of EE-1Tr and ME-1Tr into the polymer does not change their absorption spectrum, within the error limits of the spectrometer it corresponds to the absorption spectrum of pure compounds. In guest-host system, in the concentration range from 1 to 70 wt%, can be obtained: *(1)* in the 42 nm wide spectral range tuneable photoluminescence spectrum of ME-1Tr and *(2)* in the 39 nm spectral range tuneable photoluminescence spectrum of EE-1Tr *(see figure.4.22 - 4.23.)*. In the case of both compounds, in the concentration range between 5-10wt%, the emission peak of the photoluminescence switch from the farthest to the nearest *(see figure 4.22)*. Thus, dividing the photoluminescence spectrum of in PVK mixed dyes into two areas of positive solvatochromic: 1-5wt% and 10-70wt%, which depend on the concentration.



4.22. figure. *Photoluminescence spectra of (a) ME-1Tr:PVK and (b) EE-1Tr:PVK systems film samples.*

Switching of the photoluminescence spectrum can be related to the HAPPY dyes inherent property of coexistence of s-trans and s-cis molecular conformations, i.e. high probability of predominant s-trans conformation in the sample, solid layer, and as a consequence of which - caused aggregation of adjacent molecules [36] and its effect on the emission property of the compound *(see section 4.4.5)*. Due to the structure of s-trans and s-cis, the orientation of the molecules in this conformation in polyvinylcarbazole, in a solid solvate solution, will be different - the stabilization of the molecules in the ground state and the excited state will be different, or it will depend on the concentration and will change with it. Based on the fact that the appearance of emission bands corresponds to the case of molecular aggregation in the red spectrum range, in some cases the redshift of the whole emission spectrum, it is assumed that the aggregation of molecules in the s-trans conformation is associated with concentration-dependent, different solvation (re-orientation) in the PVK matrix. As a result, the Stokes shift value of in PVK mixed dyes varies depending on the concentration: ME-1Tr from 151-193 nm (10-5wt%), but EE-1Tr from 130-169 nm (10-70wt%), which only at 5wt% ME-Tr concentration

and > 30wt% EE-Tr exceeds the Stokes shift value of 100wt% ME-1Tr (189 nm) and EE-1Tr (158 nm) *(see Tables 4.9-10).*

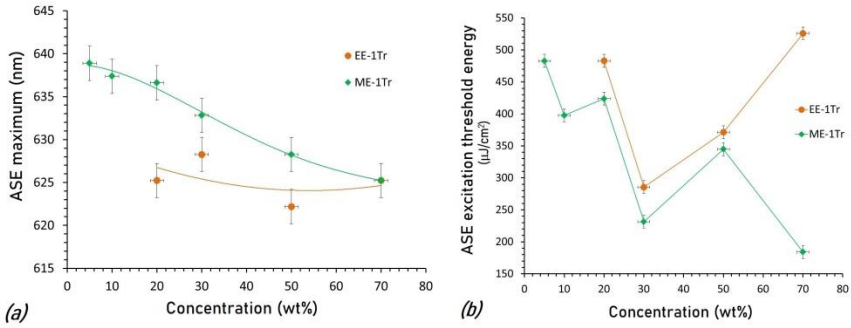


4.23. figure. *ME-1Tr: PVK and EE-1Tr: PVK systems: (a) photoluminescence maxima and (b) PLQY dependence of laser dye concentration in PVK matrix. The designations of the systems are given in the figures.*

In similar to the previously studied guest-host systems with PVK host matrix, also in the case of ME-1Tr and EE-1Tr film PLQY is inversely proportional to the increase of dye concentration in the polymer *(see Figure 4.23 part b and Tables 4.9-4.10).* But, in contrast to the KTB:polymer systems, the PLQY of the ME-1Tr: PVK and EE-1Tr: PVK systems only at ≤10wt% dye concentrations exceeded the PLQY of the 100wt% compounds PLQY, which is contrary to theoretical assumptions. One of the possible reasons for the decrease in ME-Tr and EE-1Tr PLQY in the guest-host system (≥10wt% of samples) may be related to the possible concentration-dependent aggregation of the molecules in s-trans conformation, mentioned-above. Thus, it is concluded that the decrease in PLQY in the guest-host system is caused by the coexistence of molecules in the s-cis and s-trans conformations and their concentration-dependent interactions. However, this has not been proven.

In ME-1Tr:PVK system, ASE could be excited in 5-70wt% concentration sample films. The ASE peaks are 51-55 nm redshifted from the corresponding photoluminescence maximum. In ME-Tr systems, in the concentration range of 5-70wt%, the ongoing blue shift of ASE emission peaks from 639 nm (5wt%) to 625 nm (70wt%) has a negative solvatochromic nature *(see Figure 4.24 a).* As a result, to the 5-70 wt% ME-1Tr concentration changes in the system corresponds in 14 nm range tuneable ASE emission spectrum *(see Figure 4.24, part a and Table 4.9).* In contrast, in the EE-1Tr:PVK system, ASE was excitable only in ≥20wt% concentration samples. In the whole concentration range, ASE peaks are 61-43 nm (30-70wt%) redshifted from the corresponding photoluminescence maximums. The dependence of the ASE on the concentration is unstructured. Approximately, to EE-1Tr concentration changes from 20 to 70wt% correspond to 6 nm spectral range,

from 622 to 628 nm, tuneable ASE emission spectrum *(see Figure 4.24 part a and Table 4.10).*



4.24. figure. *ME-1Tr:PVK and EE-1Tr:PVK systems (a) ASE peak and (b) excitation threshold energy at different laser dye concentrations in the PVK matrix. The designations of the systems are given in the diagram.*

In both systems, the ASE peaks are shifted red from the ASE peaks of the 100% wt compounds, but the concentration dependence of the ASE threshold is not clearly defined *(see Figure 4.24 part b).* In turn, in guest-host systems determined values of ASE excitation energy threshold: 483–184 μJ/cm^2 ME-1Tr and 526–286 μJ/cm^2 EE-1Tr, ~7.43–2.83 and 11.5–6.2 times exceeds in the 100wt% compounds films obtained values, respectively: 65 μJ/cm^2 and 45 μJ/cm^2 *(see Figure 4.24 part b and 4.9-4.10 tables).* The concentration dependence of the ASE properties of in PVK matrix mixed ME-1Tr and EE-1Tr dyes strongly differ from ASE properties of pyranilidene moieties containing laser dyes mixed in the PVK [22] and other polymers [21] matrix. The sharp difference in emission properties can be explained both: by the different conformational effects inherent to the compounds and by the effect observed for 100wt% HAPPY dyes: aggregation-induced emission enhancement (AIEE) [36].

4.9. table. *Optical properties of ME-1Tr:PVK guest-host systems amorphous films at different concentrations of ME-1Tr in PVK matrix. ME-1Tr: λ_{abs} – 395 nm, λ_{PL} – 584 nm PLQY – 15,1 %, λ_{ASE} – 615 nm, Eth – 65μJ/cm^2* [36])

Conc., wt%	λ_{ABS}, nm	λ_{PL}, nm	PQLY, %	λ_{ASE}, nm	E_{th}, μJ/cm^2
1	395±2	552±2	33.1±2	-	-
5	395±2	588±2	34.3±2	639±2	483±48
10	395±2	546±2	27.1±2	637±2	398±40
20	395±2	552±2	11.2±2	637±2	424±42
30	395±2	564±2	8.9±2	633±2	232±23
50	395±2	570±2	7.1±2	628±2	345±34
70	395±2	570±2	5.6±2	625±2	184±18

4.10. table. *Optical properties of EE-1Tr:PVK guest-host systems amorphous films at different concentrations of EE-1Tr in PVK matrix. (EE-1Tr: λ_{abs} – 413 nm, λ_{PL} – 571nm PLQY – 5,1 %, λ_{ASE} – 614 nm, Eth – 46μJ/cm^2* [36]*)*

Conc., wt%	λ_{ABS}, nm	λ_{PL}, nm	PQLY, %	λ_{ASE}, nm	E_{th}, μJ/cm^2
1	413±2	549±2	23.6±2	-	-
5	413±2	579±2	17.6±2	-	-
10	413±2	543±2	9.9±2	-	-
20	413±2	567±2	2.7±2	625±2	483±48
30	413±2	567±2	22.0±2	628±2	286±28
50	413±2	573±2	1.7±2	622±2	371±37
70	413±2	582±2	1.2±2	625±2	526±52

5. CONCLUSIONS AND THESIS

5.1. Conclusions

- The addition of strong electron acceptors to the chromophore promotes the redshift of the absorption and emission spectra (or specific bands) of the compound.
- The formation of intensive, absorption maximum encompassing, plateau or two separated, differently intensive, maximums in the spectra of *bis*-styryl compounds, is associated with two different electron transfer processes. In the case of the plateau, transitions occur between close levels, resulting in the convergence of several absorption peaks in a wide band with flat variable intensity. In turn, the two separated maxima correspond to the transitions between the acceptor of the molecule and the two styryl fragments of the donor moiety. For a molecule with two donor groups, there are two possible light-emitting electron transitions, the probability of which depends on the properties of the added spatial groups or fragments.
- The addition of substituents with strong electron acceptor properties to the 6-styryl moiety converts it to another electron acceptor moiety of the molecule. Moreover, it creates additional interactions between neighbouring molecules, promoting a decrease in PLQY and an increase in ASE excitation energy (> 2 mJ/cm^2). The increase in the acceptor properties of the added groups results in an increase in: (1) the intensity of the corresponding absorption maxima; (2) in the case of bis-styryl compounds, the blue shift of the first absorption peak from the second peak; (3) redshift of the photoluminescence spectrum to a further red/IR wave range, such as cyano- (DWK-7) and isobutyloxycarbonyl- (DWK-8).
- DWK and DWK-T type compounds. It has been found that: the replacement of the bis-trityloxyethyl spatial groups added to the styryl moiety with the 5,5,5-triphenylpentylpiperazin-1-yl group causes: a blue shift of the absorption bands, a redshift of the luminescence bands, reduces PLQY and extremely increases the ASE excitation energy. Indicating about due to decrease in the number and spatial size of newly added 5,5,5-triphenylpentylpiperazin-1-yl groups, caused the decrease in intermolecular distance, that in turn contributed to a sharp increase in intermolecular interactions.
- The incorporation of a 2-cyanoacetate moiety as the electron acceptor of the *mono*-styryl pyranylidene moiety-containing compounds significantly reduces intermolecular interactions, resulting in improvement of solution made films amorphous structure and optical quality, thusly contributing to an increase in PLQY and a significant decrease in ASE excitation energies. As a result, the 2-cyanoacetate derivatives KTB and KTBC have the highest 23% and 16% PLQY and the lowest 24 $\mu J/cm^2$ and 25 $\mu J/cm^2$ ASE excitation energy values.

- The presence of spatial 9*H*-carbazole fragments in the electron acceptor (*Bis*-K4CK) and the electron donor (KTB3K), despite the lack of conjugation, strongly influences the electron transitions in the molecule. An increase in the number of added 9*H*-carbazole groups contributes to an increase in thermal stability and glass transition temperatures.
- The co-existence of the s-trans conformation of the 1*H*-pyridine compound molecules in together with s-cis, in solid film, promotes molecular aggregation and, thus, an increase in ASE excitation energy. The unpredictability of conformational relationships and in the case of s-trans predominance molecular aggregation-induced emission enhancement (AIEE) make it impossible to improve the properties of ME-1Tr and EE-1Tr ASE in a guest-host system with a passive polymer matrix. Thus, reduces their prospects for use in applications for the formation of active media for organic solid-state lasers.
- Asymmetric, *mono*-styryl compounds containing the 4*H*-pyran-4-ylidene fragment with a single electron donor group exhibit up to 5-fold higher PLQY and orders of magnitude lower ASE excitation energies compared to symmetric, *bis*-styryl compounds containing the 4*H*-pyran-4-ylidene fragment with two donor groups. The reason for this is the possible aggregation-induced enhancement of the emission in a solid layer, due to the decrease of the intermolecular distance between the molecules of the unsymmetrical compounds. The occurrence of this specific interaction between molecules can contribute to the "opening" of another previously forbidden transition, which is evidenced by the appearance of another emission peak (ASE peak) in the distant IS spectrum region.
- The co-existence of several permitted transitions promotes the redistribution of excitation energy between two possible emission states, thus, causing an increase in ASE excitation energy (up to >>2 mJ/cm^2).
- The energy values of PLQY and ASE excitation energies obtained in the film of the pure compounds can be several times improved in guest-host system. The incorporation of dye molecules into a passive polymer matrix contributes to their distancing, and reduces intermolecular interactions, resulting in a decrease in photoluminescence quenching in systems with low molecular concentrations, thus increasing PLQY and decreasing ASE excitation energy values.
- Changes in the concentration of the laser dye in the guest-host system contribute to the change in the dielectric constant of the environment, causing the solid state solvation effect (SSSE). Making it possible to shift the photoluminescence and enhanced spontaneous emission spectra of a laser dye over a range of several nanometers depending on changes in its concentration in the polymer matrix. Due to the increase in concentration, the increasing dielectric permittivity of the system environment causes two types of emission spectrum shift: positive or red (KTB:PVK and KTB:PSU) and

negative or blue (KTB:PS and ME-1Tr:PVK). The nature of the shift depends on the dielectric constant of the "solid solution", the refractive index and the properties of the polymer matrix, which determine the nature of molecular interactions, orientation to polymer and other dye molecules - stabilization of the excited and ground state and the resulting electron transfer. As a result, a previously prohibited transition between two different emission levels may become permitted and switching between two ASE emission peaks may occur. Changes of KTB concentration from 1-100wt% in the matrix of PVK, PSU and PS correspond to in the 11, 15 and 52 nm spectral range tuneable ASE spectrum, but changes in ME-1Tr and EE-1Tr concentrations in PVK correspond to in the 14 and 6 nm spectral range tuneable ASE spectrum.

- At 10wt% KTB in the PS matrix, occurring switching between two ASE peaks, from the nearest (586 nm) to the farthest (638 nm), may be related to: *(1)* the specific intermolecular interactions between KTB molecules caused by properties of PS and/or *(2)* KTB inherent diastereoisomerization.
- The greatest reduction in pure KTB ASE excitation energy can be achieved in KTB:PVK guest-host systems, reaching a minimum of 9 $\mu J/cm^2$, at 20wt% KTB in the PVK matrix. As a result, KTB:PVK systems have high prospects to be used in the creation of an active media for organic solid state lasers.
- Quantum chemical calculations and absorption spectra show that: differences in KTB absorption and emission properties, nature of solvatochromic shift and ASE properties in PS, PSU and PVK matrices are related to the significantly different involvement and influence of different parts/groups of KTB molecule in energy transfer processes in different polymer matrixes.

5.2. Thesis

- Comparing the measured physical characteristics of all investigated compounds containing pyranylidene fragments, it was found that the PLQY and ASE E_{th} values depend most on the symmetry of the compounds: The highest photoluminescence quantum yield (PLQY) and the lowest amplified spontaneous emission (ASE) excitation energy threshold (E_{th}) values have all for more unsymmetrical compounds, i.e. *mono*-styryl derivatives (e.g. 2-cyanoacetic acid derivatives: KTB and KTBC). On the other hand, the higher PLQY of the unsymmetrical *bis*-styryl-4*H*-pyran-4-ylidene compounds compared to the PLQY of the symmetric bis-styryl-4*H*-pyran-4-ylidene compounds indicates of the existence of a physical effect of the possible enhancement of the aggregation induced emission (English: Aggregation Induced Emission Enhancement [AIEE]) in solid films of unsymmetrical bis-styryl-4*H*-pyran-4-ylidene compounds.
- The incorporation of a 2-cyanoacetate moiety in the electron acceptor part of *mono*-styryl compounds (which contains a pyranylidene moiety) significantly reduces intermolecular interactions, resulting in the highest PLQY and lowest

ASE excitation energy values of KTB and KTBC compound films: 23%, 16%, and 24, 25 μJ/cm^2, respectively.

- An increase in distance between dye molecules is achieved by mixing them in passive polymer matrix, thus, reducing their intermolecular interactions, as a result of which the PLQY and ASE excitation energy values obtained in the pure films can be several times improved in the guest-host system thus prepared. The lowest amplified spontaneous emission excitation energy values of 9 μJ/cm^2 were obtained for ethyl 2-(2-(4-(*bis*(2-(trityloxy)ethyl)amino)styryl)-6-(*tert*-butyl)-4*H*-pyran-4-ylidene-2-cyanoacetate:polyvinylcarbazole (KTB:PVK) in the guest-host system, at 20wt% KTB concentration in the polyvinylcarbazole matrix. As a result, KTB:PVK guest-host systems are considered to be the most promising for use in organic solid-state laser as an active media because the red light ASE excitation energies found in the literature so far are a few μJ/cm^2

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