UNIVERSITY OF LATVIA

AIVARS VEMBRIS

OPTICAL AND OPTOELECTRICAL PROPERTIES OF PYRANYLIDEN FRAGMENT CONTAINING DYES

SUMMARY OF DOCTORAL THESIS

Submitted for the degree of Doctor of Physics
Subfield of Solid State Physics

Riga, 2012

University of Latvia
Faculty of Physics and Mathematics

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The doctoral thesis was carried out:

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The thesis will be defended at the public session of the specialized Doctoral Committee of physics, astronomy and mechanics, University of Latvia, at 15:00 on November 30, 2012 in the conference hall of the Institute of Solid State Physics at 8 Kengaraga street.

The thesis is available at the Library of the University of Latvia, Kalpaka blvd. 4.

This thesis is accepted for the commencement of the degree of Doctor of Physics on September 30, 20121 by the specialized Doctoral Committee of physics, astronomy and mechanics, University of Latvia.

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Abstract

This work is dedicated to original organic compounds containing pyranyliden fragment which are forming amorphous thin films from solutions due to attached trityloxyethyl groups.

The aim of the work is to investigate optical and electrical properties of these glassy forming organic compounds and to evaluate the possible use of them in light emitting diodes or organic solid state lasers.

In the work insignificant influence of trityloxyethyl groups on optical transitions in the molecules was confirmed. At the same time due to protection of active chromophore part from intermolecular interaction by these groups observation of photoluminescence takes place in the pure films of investigated compounds.. In case of two donor groups consisting molecules in pure films as well as in high concentration solutions second long wavelength band in photoluminescence spectra was observed. The origin of this band is well protected exited state from which low probable radiative transition takes place. Amplified spontaneous emission in the pure thin films was observed in the work. Till now it has not been obtained in thin films which consisted only from pyranyliden fragment containing molecules. More than one order of magnitude less threshold value of the amplified spontaneous emission was achieve in doped polymer films with investigated compound 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile in comparison to doped polymer with well known laser dye 4-(dicyanomethylene)-2-methyl- 6-(p-dimethylaminostyryl)-4H-pyran. It means that the investigated compound is more perspective as a laser material compared to previously studied. Electroluminescence measurements showed that the pure thin films of investigated compounds are not perspective in organic light emitting diodes due to low photoluminescence quantum yield and additional charge carrier trap levels.

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Introduction

Motivation of the work

Possible applications of organic compounds in field effect transistors, light emitting diodes, solar cells and lasers have been intensively investigated. Currently mobile phone and television sets with displays made from organic light emitting diodes, are available commercially [1–3]. There are first prototypes of solar cells from organic materials [4], [5]. Low cost, plasticity, high efficiency and variety of synthesised compounds are several of organic matter advantages. In previously mentioned devices thin films with the thickness from several nanometres till micrometers are typically used. Two approaches mostly have been employed for preparation of such thin films: a thermal evaporation in vacuum and a solution casting methods. Both of them possess some advantages and drawbacks. Special shape of layer could be obtained by the thermal evaporation in vacuum. Also hard dissolving compounds are easily processable by this method. Nevertheless there are several drawbacks of thermal evaporation: large consumption of matter, necessity for high thermal stability of compounds and expensive high vacuum processing systems. In the solution casting method such problems does not exist. It gives possibility to make thin films by simpler technology at lower temperature. Mostly in research laboratories two solution methods have been used: spin coating and blade casting. Both methods are simple and in case of large scale production could be replaced by roll to roll processing or inkjet printing. Both methods could be used to prepare patterned thin films. All those methods request highly soluble organic compounds which create glassy state films after deposition and solvent evaporation. Polymers fulfil these conditions; however the result of two sequential synthesis of the same polymer could yield different products. Average length of polymer chain and distribution of the length could be various as well as undesirable by-products. It could change physical properties and deposition conditions which are unacceptable for a large scale fabrication. More perspective is low weight organic compounds due to more repeatable synthesis. Unfortunately most of them cannot form amorphous state films from a solution. In recent years only few of such compounds were synthesised [6–9]. The investigation of properties and assessment for applications of such kind of materials has not been studied widely therefore investigations within this field are important for further progress in development of photonic devices.

The aim of the work

The aim of the work is to investigate optical and electrical properties of original glass forming organic compounds and to find the possible use of compounds in light emitting diodes and organic solid state lasers.

Following tasks were posed to achieve the aim:

- Investigate dependence of optical properties of original pyranyliden fragment containing organic compounds on there structure;
- Assessment of these compounds as an laser active media by studying amplified spontaneous emission properties of the compounds;
- Evaluation of these compounds for employment in organic light emitting diodes by studying electrical and electroluminescence properties of the compounds.

Author's contribution

By the author solely:

- was obtained optical images of thin films;
- was measured all absorption and luminescence spectra of thin films and part of solutions;
- was measured photoluminescence kinetics of the thin films and solutions;
- was done electroluminescence and spontaneous amplified emission measurements;
- built set-up for electroluminescence and amplified spontaneous emission measurements.

The author partially participates in fallowing experiments by proposing ideas and preparing samples:

- transient absorption investigation;
- photoluminescence quantum yield measurements;
- charge carrier trap state investigations.

The author gave suggestions about:

- necessary quantum chemical calculations.

Main part of results was defined by the author in discussion with colleges of Laboratory of Organic Materials and Lithuanian colleges. The results were presented in local and international conferences by the author.

Scientific novelty

Insignificant influence of glass forming trityloxyethyl groups on electron transitions in chromophore are proved for investigated molecules. Effect of molecule electron acceptor and donor group structure on absorption and photoluminescence spectra in solution is obtained. It is shown that in case of four trityloxyethyl groups electron donor as well as electron acceptor groups can be protected from environment influence.

For the first time in solutions and thin films second photoluminescence band of pyranyliden fragment containing molecules with two electron donor groups was observed. Origin of this additional photoluminescence long wavelength band is explained.

First time amplified spontaneous emission was observed in pure films of pyranyliden fragment containing compounds. More than one order of magnitude less threshold value of amplified spontaneous emission was achieve in doped polymer films with investigated compounds in comparison with well-known and widely used similar compounds.

Electroluminescent systems with pure film prepared from solution as luminescence layer were formed and investigated.

1. Physical background

1.1. Pyranyliden fragment containing molecules

One of well-known and widely applied pyranyliden fragment containing organic compound is -(dicyanomethylene)-2-methyl- 6-(p-dimethylaminostyryl)-4H-pyran (**DCM**) [10–14]. The molecule consists of electron acceptor and donor group which are connected by conjugated bridge. Malononitril group is electron acceptor and dimethylaniline is electron donating group (see Figure 1.1.).

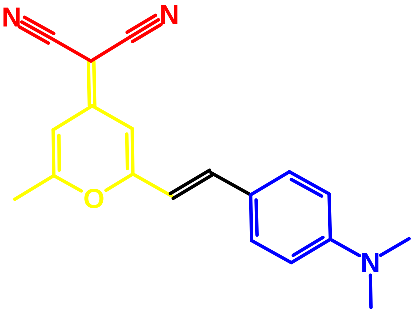

Figure 1.1. DCM molecule. Malononitril group is red, pyranyliden fragment is yellow and dimethylaniline is blue**.**

Absorption and photoluminescence maximum wavelength of this compound in dichloromethane is 470 nm and 580 nm, respectively (see Figure 1.3. a and b). Large photoluminescence quantum yield in a solution is one of main reason for intensive investigation of that molecule. It can reach 0.8 in dimethylsulfoxide [16]. This compound is used as electroluminescent and laser material. Only way to obtain thin films from this and other previous investigated and in this chapter mentioned compounds is thermal evaporation in vacuum. In pure evaporated **DCM** thin film photoluminescence can not be observed [14] due to large intermolecular interaction which quench luminescence [17], [18]. This problem has been overcome by preparing guest-

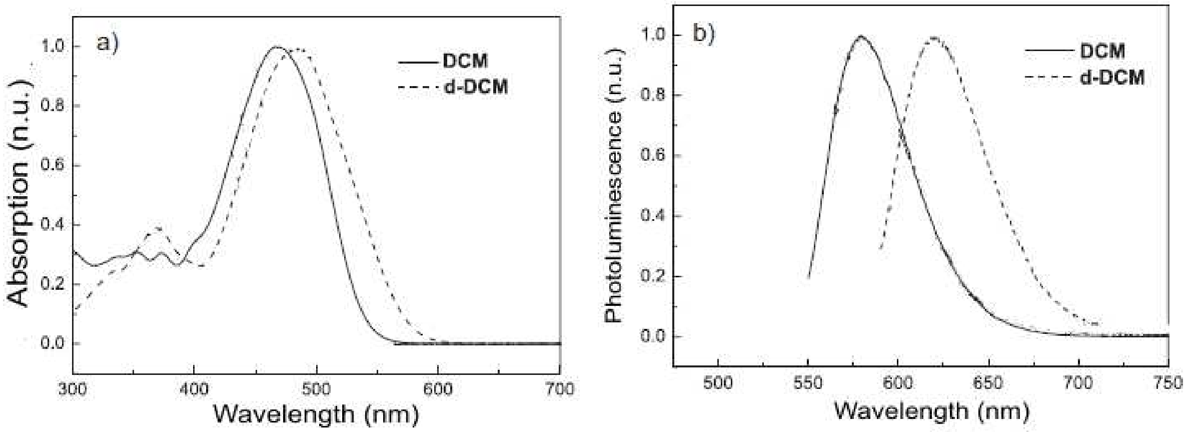

Figure 1.2. a) Absorption and b) photoluminescence spectra of **DCM** and **d-DCM** in dichloromethane. Graphs from the source [15] adapted to the work.

host system. Which mean mixing the molecules (guests) with other matter (host). Tris-(8-hydroxy quinoline) aluminium (**Alq$_3$**) was used as host in most of the cases due to the compatibility of the energy levels [19–21] (see Figure 1.3. a).

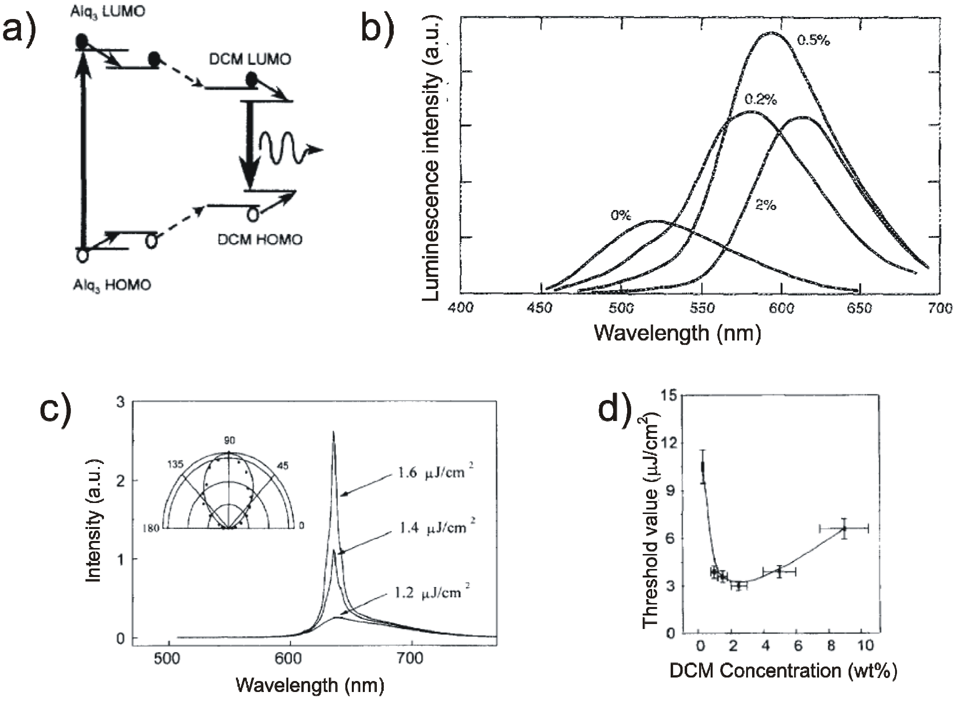

Figure 1.3. a) energy transfer from **Alq$_3$** to **DCM** molecule [22], b) photoluminescence spectra of different concentration **DCM** molecules in **Alq$_3$** matrix [14], c) amplified spontaneous emission of **DCM:Alq$_3$** system [22], d) threshold values of amplified spontaneous emission of **DCM:Alq$_3$** at various **DCM** molecule concentration [22].

DCM:Alq$_3$ thin film has been used as electroluminescence layer in light emitting diodes. Photoluminescence band moves from green spectral region to red by increasing **DCM** molecules concentration in **Alq$_3$** matrix (see Figure 1.3. b). The same relation has been observed in the electroluminescence spectra. It allows to obtain pure red colour at higher **DCM** concentration but unfortunately the intensity of emitted light start to decries which limits of preparation of high efficiency diodes [14].

The same **DCM:Alq$_3$** systems have been used as active medium for lasers. Authors observed arise of sharp peak on photoluminescence band by increasing pulse energy of the irradiating beam (see Figure 1.3. c). The smallest threshold value what they obtain was 3 μJ/cm^2 at 2 wt% of **DCM** molecules in **Alq$_3$** matrix (see Figure 1.3. d) [22].

Lot of works are devoted to improvement of **DCM** molecules by increasing photoluminescence quantum yield or tuning photoluminescence spectra in thin film. One of the possibilities is changing electron donating groups. Added additional same donor group is one of the simplest ways (**d-DCM**) (see. Figure 1.4.) [23]. The absorption and luminescence spectra of this compound are shifted to the red region compared to **DCM** (see Figure 1.2. a and b). Second most popular pyranyliden fragment containing molecule is 4-

(dicyanomethylene)-2-methyl-6- [2-(2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizin-9-yl)ethe- nyl]-4H-pyran (**DCM2**) (see Figure 1.4.). The purpose of synthesis of **DCM2** molecule was pure red colour (its photoluminescence maximum wavelength is 650 nm) and higher photoluminescence quantum yield compared to **d-DCM** [24]. With the similar aim was changed electron acceptor group. Barbiture acid and indandione group was chosen in some of the cases [25] [26].

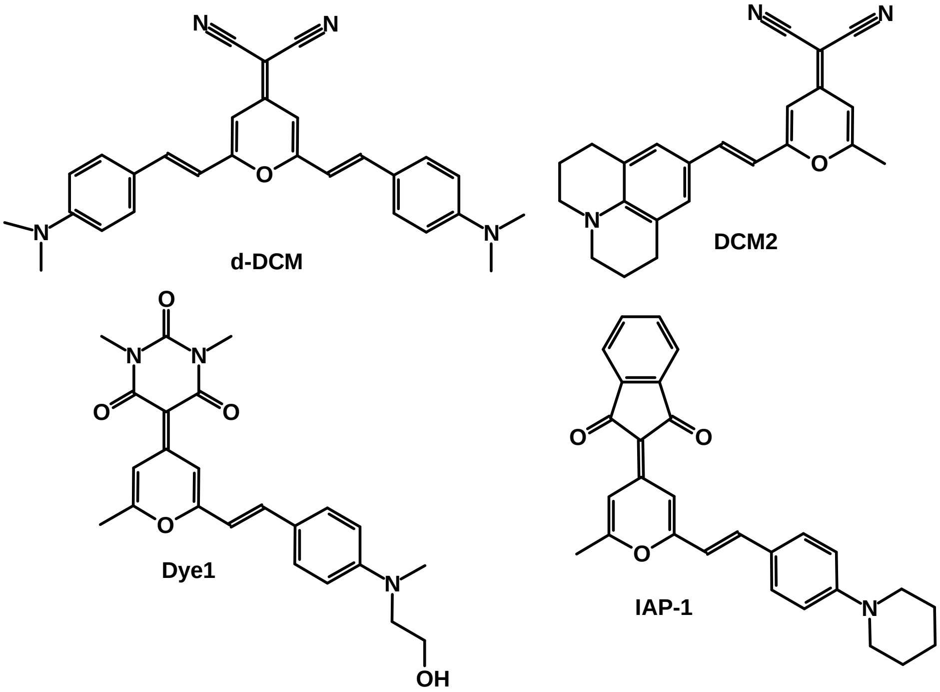

Figure 1.4. Chemical structures of pyranyliden fragment containing molecules [23–26]

Higher photoluminescence and electroluminescence quantum yield as well as pure red colour was main target for synthesis of new pyranyliden fragment containing molecules as it can be seen in this chapter. At the same time there are no works which would be dedicated to modification of such molecules with aim to obtain glassy structure from solution. Several advantages could possess if such compounds could be created. First of all casting methods can be applied, which are simpler than thermal evaporation in vacuum. Indirect advantage of such compounds are increased concentration Second: in the case of preparation of guests – hosts systems the concentration of chromophore in a matrix could be increase compared to other in this chapter discussed compounds due to less aggregation of molecules.

2. Experiments

2.1. Sample preparation

2.1.1. Samples for optical measurements

Solutions in quivets and thin films were prepared for optical measurements.

Dichloromethane was used for preparation of the solutions. In one case dimethylsulfoxide was used. Concentration of compounds in solvent was 10^{-5} mol/l. Prepared solutions was filled in fluorescent quartz quivets with 1 cm optical path length to perform measurements.

Pure thin films, with thickness from 300 nm to 400 nm, were prepared from dichloromethane solution on quartz glass by „Laureal" 650 series spin-coater. Host-guest systems with the concentrations 0.1, 1, 3, 5, 10 wt% of investigated molecules in polymer were obtained in the same way.

2.1.2. Samples for electrical measurements

Sandwich type samples were structured for electrical measurements. Organic layer between two electrodes was inserted. Glass covered with indium tin oxide (ITO glass) was used as a substrate. The solution with investigated molecules was deposited on the substrate by spin-coating method after which thin layer of aluminium was deposited by thermal evaporation in vacuum (EDWARD AUTO 360). Final configuration of the sample was ITO/organic compound (500 nm)/Al(100 nm)

2.1.3. Samples for electroluminescence measurements

ITO glass was used as a substrate for samples. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (**PEDOT:PSS**) and investigated matter was sequentially deposited on the substrate by spin-coating method. Thermal evaporation in vacuum was used to deposit lithium fluoride (LiF) and aluminium. Final configuration of the sample was ITO/**PEDOT:PSS**(40 nm)/organic compound (x nm)/LiF(1 nm)/Al(100 nm)

2.2. Experimental methods

2.2.1. Characterisation of thin film morphology

High resolution microscope "Nikon Eclipse L150" was used to obtain morphology of the prepared samples. Profilometer Vecco „Dektak 150" was used to measure the thickness of the samples.

2.2.2. *Equipments for measuring of photoluminescence characteristic*

Two type of equipment was used for measurements of photoluminescence spectra. Ocean Optics HR4000 spectrometer was used in first case. Continuum wave diode laser with wavelength 405 nm was as an excitation source.

Photoluminescence spectra and quantum yield was measured in second set of experiments. Experimental set-up consists of integrating sphere with attached Hamamatsu PMA-11 spectrometer. Light emitting diode was as excitation source. Monochromator was applied to get 517 nm wavelength light. Photoluminescence quantum efficiency was measured in Vilnius University under prof. Saulius Juršenas supervise.

„Edinburg Instruments Fluorescence Spectrometer F900” equipment was used for measurements of photoluminescence kinetics. Edinburgh EPL-375 pulse laser diode with wavelength 375 nm, repetition rate of 10MHz and pulse duration of 50 ps was as excitation source.

2.2.3. *Transient differential absorption measurements*

Light Conversion „Pump-probe spectrometer PPS-1” equipment was used for transient absorption measurements. Ti:Sapphire laser with wavelength 470 nm, repetition rate of 1 kHz and pulse duration of 130 fs was light source in this system. Transient absorption spectra in this work were obtained 5 ps after excitation. This experiment was done by Dr. Phys. Renata Karpic.

2.2.4. *Set-up for amplified spontaneous emission experiment*

Set-up for amplified spontaneous emission measurement was self made. Its experimental scheme is shown in Figure 2.1.

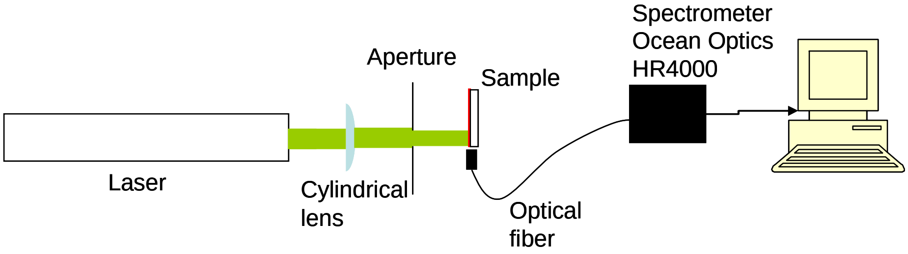

Figure 2.1. Experimental scheme of amplified spontaneous emission measurement

Ekspla SL 312 Nd:YAG pulse laser with wavelength 532 nm was used as excitation source. Pulse duration was 150 ps and repetition rate 10 Hz.Ocean Optics HR4000 spectrometer was used to register emitted light spectra. The emission spectra were obtained at different excitation intensities. The intensity was measured before each irradiation by thermal power sensor 3A and power meter Ophir „Laserstar”.

2.2.5. *Equipment for current-voltage characteristic and charge carrier trap state measurement*

Current-voltage characteristics was measured in the regime of space charge limited current (SCLC) and charge carrier trap states was obtained by the temperature modulated space charge limited current method (TM SCLC). All measurements (see Figure 2.2.) were performed in cryogenic system at pressure $9*10^{-9}$ Bar. The sample was heated and cooled in the range of 15 K from 235 K till 250 K to provide TM SCLC method.

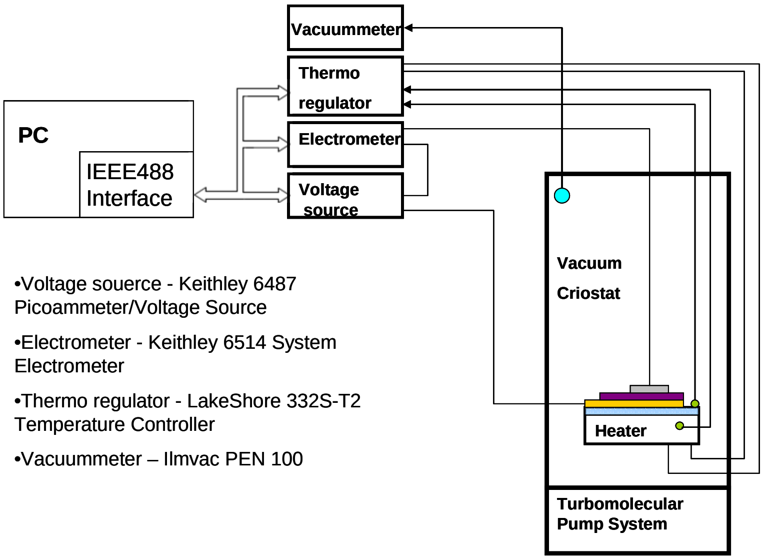

Figure 2.2. Experimental scheme of current voltage characteristic and activation energy measurement [27]

2.2.6. *Set-up for electroluminescence measurement*

Set-up for electroluminescence measurement was self made. Experimental scheme is shown in Figure 2.3. Electroluminescence measurements were performed in air.

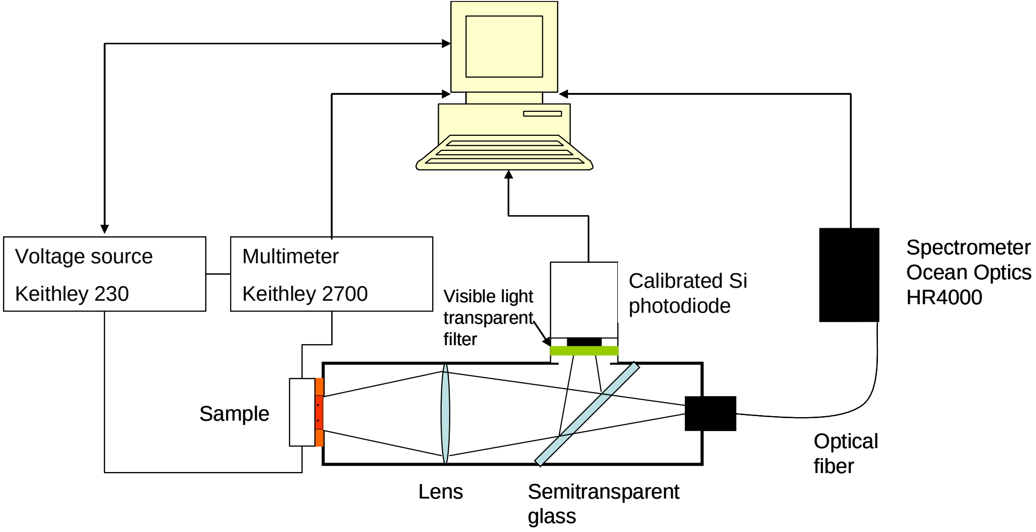

Figure 2.3. Experimental scheme of electroluminescence measurement

3. Results and discussion

3.1. Effect of molecule structure on optical properties

3.1.1. Structure of original pyranyliden fragment containing molecules

Six pyranyliden derivatives, which form amorphous state, were synthesized in Faculty of Materials Science and Applied Chemistry of Riga Technical University under prof. Valdis Kokars supervises. These molecules can be divided in three sets by electron acceptor groups (see Figure 3.1). In each group are molecules with one or two electron donor groups. 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile (**DWK-1**) is modified **DCM** molecule (see 1.1. chapter), where butyl group is replaced with two bulky trityloxyethyl groups (see Figure 3.2.).

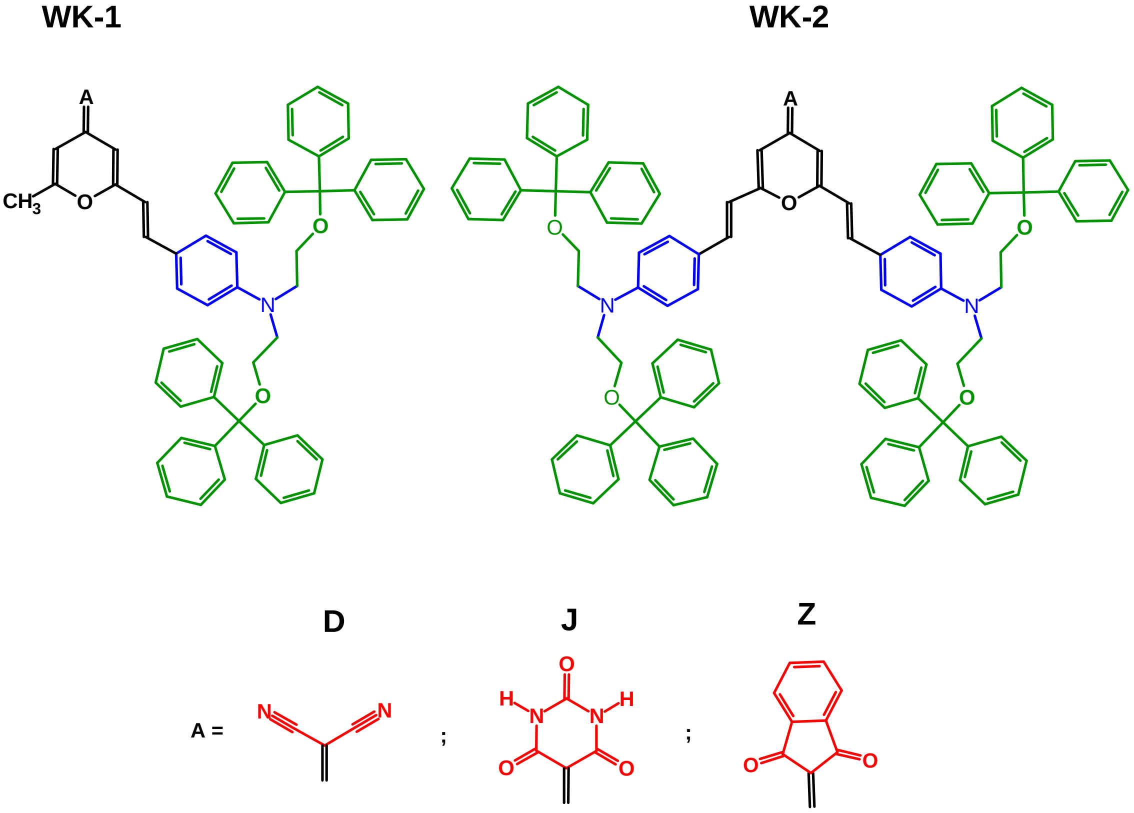

Figure 3.1. Investigated compounds which form amorphous structure. Nicknames of the compounds are made from letters of chosen electron acceptor group. Black – pyranyliden fragment, Red – electron acceptor group, blue – electron donor group and green – bulky trytiloxyethyl group. Full names of the compounds are in text**.**

Incorporation of such bulky groups allows molecules to form amorphous thin films from solutions. All investigated molecules have this trityloxyethyl groups. Second molecule with malononitrile as electron acceptor group is 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile (**DWK-2**).

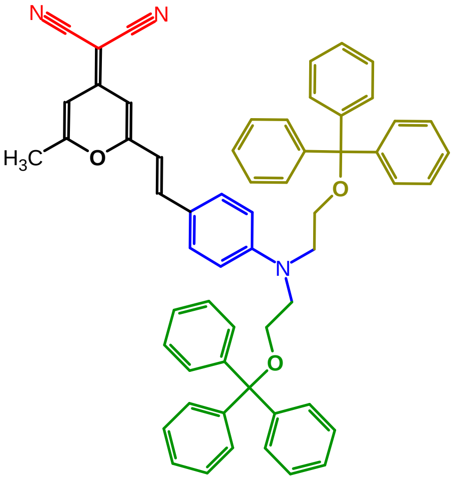

Figure 3.2. Molecule **DWK-1.** Red – electron acceptor group, Blue – electron donor group, green – bulky trityloxyethyl group

Barbitur acid is electron acceptor group for molecules 5-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**JWK-1**) and 5-(2,6-bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)pyrimidine-2,4,6(1H,3H,5H)-trione (**JWK-2**) but indandione group for molecules 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (**ZWK-1**) and 2-(2,6-bis(4-(bis(2-(trityloxy)ethyl) amino)styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (**ZWK-2**). Chemical structures of the investigated compounds are shown in Figure 3.1**.** and there synthesis are described elsewhere [28].

Glass transition temperature of these compounds is higher than 100ºC, melting temperature above 140ºC and decomposition temperature above 260ºC [28].

Small aggregates were observed in few of films prepared from investigated compounds but there influence on optical quality of the films was insignificant.

3.1.2. Influence of trityloxyethyl group on optical transitions in molecule

Amorphous thin films could be form due to covalently linked bulky trityloxyethyl group to the chromophore. It is important to check the influence of these groups on optical transitions in the molecule. In the case of proven such group insignificant influence on optical properties, one could use that chemical modification route to obtain amorphous thin films based on other chromophores. . For comparison two compounds **DCM** and **DWK-1** were chosen. They contain the same chromophore. Trityloxyethyl group which is a part of **DWK-1** molecule is only difference between them. Absorption spectra in dichloromethane solution shows insignificant (8 nm) red shift of **DWK-1** compound with respect to **DCM** (see Figure 3.3.).

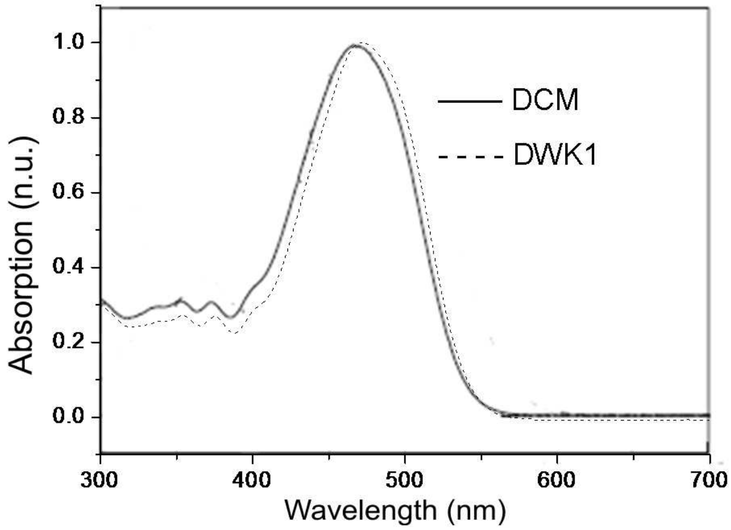

Figure 3.3. Absorption spectra of the compounds **DCM** [15]and **DWK-1** in dichloromethane solution

Shift of absorption spectra could be conformed by quantum chemical calculations. Them were done by Gaussian 09W software package by DFT method with hybrid B3LYP & 6-31G (p,d) functional. Optimisation of

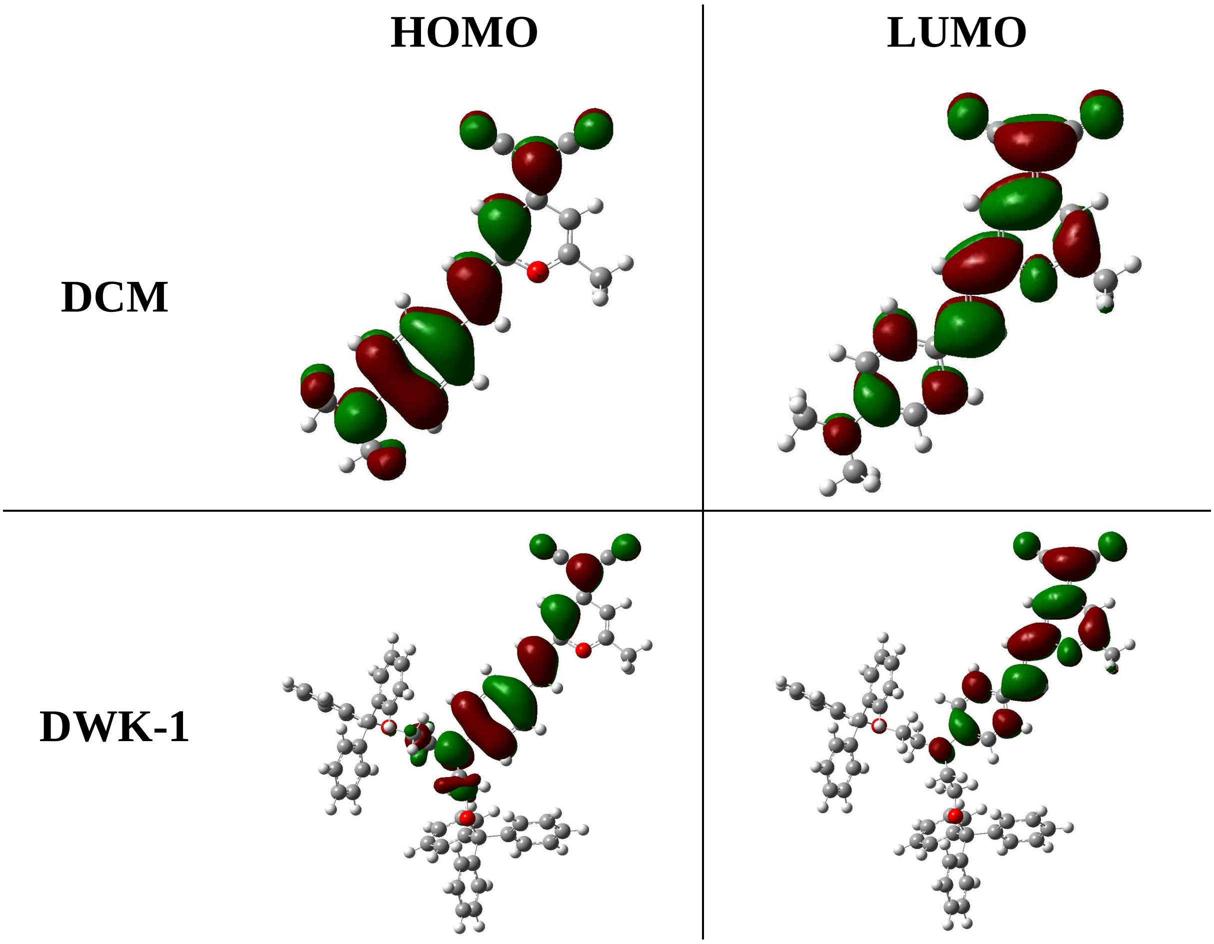

Figure 3.4. Highest occupied and lowest unoccupied molecular orbitals of **DCM** un **DWK-1**.

geometry was done before modelling of the electronic properties of the molecule by TD DFT method.

Light absorption is attributed to the electron transition from highest occupied (HOMO) to lowest unoccupied (LUMO) molecular orbital. Quantum chemical calculations of **DCM** and **DWK-1** show equal HOMO and LUMO between molecules as it can be seen in Figure 3.4. There is no trityloxyethyl group influence on molecular orbital. Equal molecular orbitals also means that transition energy between the orbitals should be equal due to the same chromophore part in both molecules.

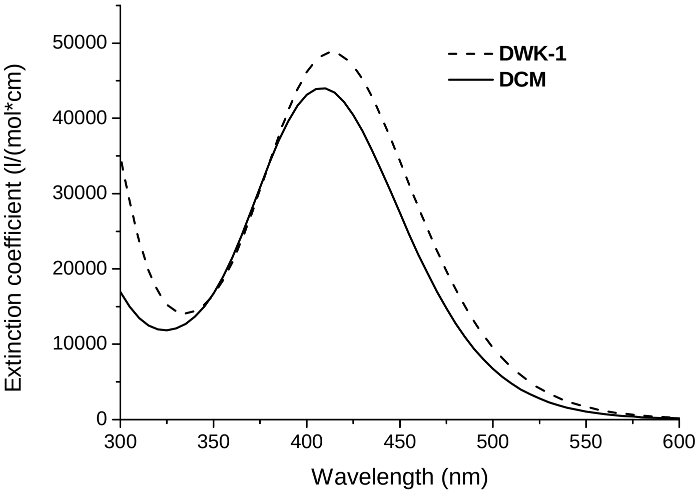

Figure 3.5. Calculated absorption spectra of **DWK-1** un **DCM** compound in vacuum.

Calculations of transition energies (the same as absorption band) was performed and 5 nm red shifted of **DWK-1** compound in vacuum in comparison to **DCM** (see Figure 3.5.) was obtained. An experiment and quantum chemical calculation confirms that trityloxyethyl groups have negligible influence on optical transitions in molecule.

3.1.3. Absorption and photoluminescence properties of solutions and amorphous thin films

Absorption and photoluminescence spectra of the investigated compounds in dichloromethane solution are shown in Figure 3.6. Absorption band of all compounds in the solution and thin films are located in spectral region between 400 nm and 650 nm. Moreover it consisted from several overlapping bands which could be clearly distinguished only in few cases. Origin of these bands could be different configuration of the molecules. For simplicity, only the most expressed absorption maximum will be taken for comparison. The maximum of absorption spectra of **ZWK-1** and **JWK-1** has 40 nm red shifts compared to compound **DWK-1**. Absorption spectra of compounds with two electron donor groups have red shift with respect to compounds with one electron donor group. Absorption maximum of **DWK-2**

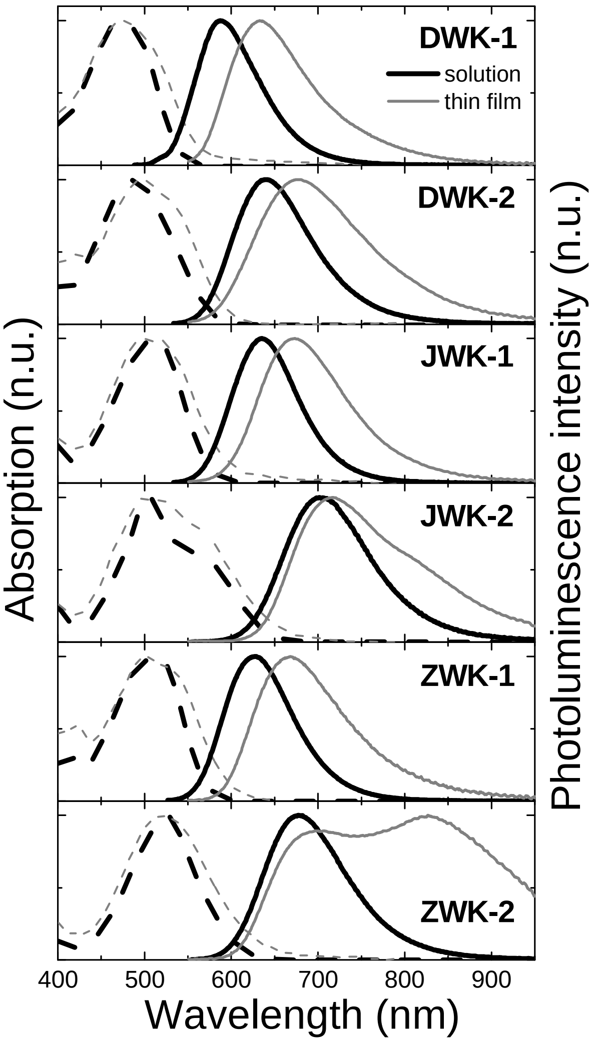

Figure 3.6. Absorption (dashed line) and photoluminescence spectra (solid line) of solution (black) and thin films (grey)

and **ZWK-2** is shifted to larger wavelength compared to **DWK-1** and **ZWK-2** by 17 nm and 11 nm, respectively.

Similar red shift was observed by compared **DCM** (one electron donor group) and **d-DCM** molecules (two electron donor groups) [23]. It was explained by different conjugation length. Additional explanation could be stronger donor group. Electron donating properties is enhanced by simultaneously working of both donor groups. The shape of the absorption spectrum of **JWK-2** is different from the absorption spectrum of **JWK-1**. Oscillator strength of the absorption band at about 502 nm became more intense.

Photoluminescence spectra have 115 nm large Stokes shift in the solution of the compound **DWK-1**. Photoluminescence band of **JWK-1** and **ZWK-1** in the solution is similar to **DWK-1** photoluminescence band with Stokes shift of 124 nm and 113 nm, respectively. Stokes shift of the compounds with two donating groups in the solution could reach 150 nm.

The absorption spectra of the thin solid films are practically unchanged with respect to the solutions spectra. The red shift of the absorption spectra maximum corresponds sequentially to **ZWK-1**, **JWK-1** and **DWK-1**, as a stronger acceptor group induces a larger red shift. For the molecules **ZWK** and **DWK** with two donor groups the absorption spectra shifts by 21 nm and 22 nm, respectively. The changes of maxima positions of the absorption spectra for **JWK** molecules is hard to estimate due to noticeable second maximum of molecule with two electron donor groups which is hard to distinguish in molecules with one donor group.

The photoluminescence spectra of all films are red-shifted in comparison with those of the solution. For molecules with one donor group, the shape of the photoluminescence spectra of the thin films is very similar to that in the solution. Meanwhile the derivatives with two donor groups exhibit an additional band at longer wavelengths. It barely observable in the case of **DWK-2** and **JWK-2** molecules where its maximum intensity respect to main photoluminescence maximum intensity is only 0.1 and 0.5, respectively. For **ZWK-2** compound it became dominant with rate 1.1 from main photoluminescence maximum intensity.

The second maximum of **ZWK-2** is not observable in dimethyl sulfoxide (dielectric constant is ten times larger than for chloroform) which shows that it does not depend on dielectric properties of surrounding media. Also it should not be due to formation of dimmers because the small maximum intensity of second band is observable in 1 and 3 wt% **ZWK-2** molecule in polymer. Some intermolecular interaction which is not associated with aggregates could be only explanation.

In high concentration solution stronger intermolecular interaction takes place and second band should appear. It was obtained in dichloromethan solutions with **ZWK-2** molecules at the concentration of $2.2*10^{-2}$ mol/l (see Figure 3.7. inset) which is three orders of magnitude higher than in previously investigated solutions. The long wavelength maximum relative intensity reduces by decreasing concentration three times and becomes barely observable in solutions with 9 times less **ZWK-2** molecule concentration in the solution. Nevertheless it can be found not only in these concentration solutions but also in much smaller concentration solutions by deconvolution the photoluminescence spectra in two Gaussian bands. Relative photoluminescence integral intensity of each spectral band for all three concentration solutions was obtained from the bands covered areas. Short wavelength luminescence is dominating at smaller concentration solutions and this is a reason of barely observable long wavelength luminescence. Both luminescence intensities decrease by increasing concentration due to stronger intermolecular interaction. Short wavelength photoluminescence intensity decreases faster than long wavelength photoluminescence (see Figure 3.7.). That’s why long wavelength luminescence became possible to see at higher concentration solutions.

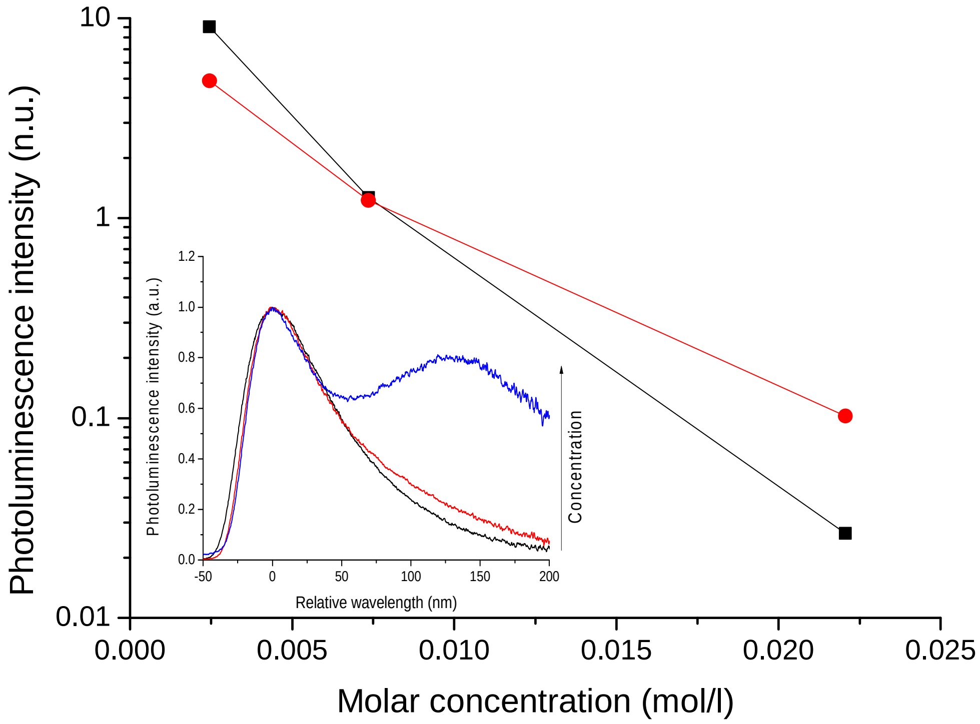

Figure 3.7. Dependence of relative short (black) un long (red) wavelength photoluminescence intensity on **ZWK-2** molecule concentration in dichloromethane solution (inset - photoluminescence spectra of various concentration **ZWK-2** molecules in dichloromethane solution)

The origin of two luminescence bands could be two exited state levels where transition from one is more probable than from the second. We think that trityloxyethyl groups can protect both exited states but better protection is for exited state which gives long wavelength luminescence (see Figure 3.8.).

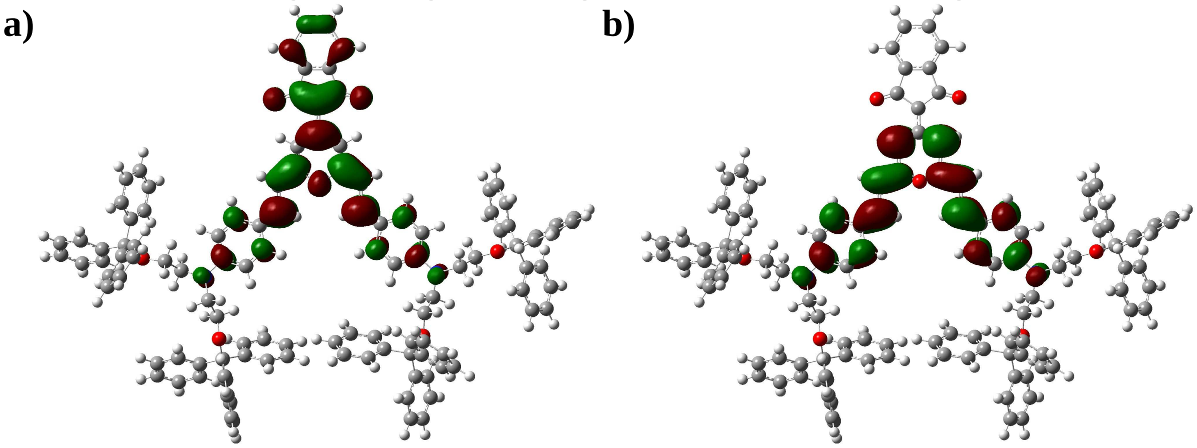

Figure 3.8. Molecular orbitals corresponding to a) less protected and b) more protected exited states of **ZWK-2** compound.

3.1.4. *Photoluminescence quantum yield*

The results on photoluminescence quantum yield of all compounds in solution and thin films are summarised in Table 3-1.

Table 3-1. Photoluminescence quantum yield of investigated compounds in solution and thin films.

	Solution	**Thin film**
DWK-1	**0.32**	**0.026**
DWK-2	**0.43**	**0.009**
JWK-1	**0.47**	**0.011**
JWK-2	**0.32**	**0.007**
ZWK-1	**0.54**	**0.01**
ZWK-2	**0.4**	**0.003**

DWK, **JWK** and **ZWK** compounds in the solution exhibit values between 0.3 and 0.55. These values are similar to the results of **DCM** dye in chloroform 0.35 [29]. The **ZWK-1** compound has the highest photoluminescence quantum yield. As the acceptor group becomes weaker, the value of photoluminescence quantum yield decreases, the lowest one being for **DWK-1** molecules. The compounds with two donor groups show smaller values of quantum yield in comparison with the molecules containing one donor group. The only exception is the **DWK** molecule where **DWK-1** has a smaller photoluminescence quantum yield than **DWK-2**. For comparison, **d-DCM** molecules have been reported to have at least five times lower photoluminescence quantum yield compared to **DCM** [23]. The explanation may lie in the bulky trityloxyethyl groups. All investigated molecules consist from stilben like part where both trans and cis isomers could be in the same time in solution. In the case of **DWK-2** molecules the volume of the malononitril group is small so that in the case of cis isomer it can be surrounded by phenyl rings, which tend to decrease the electron acceptor group interaction with the solution, thus increasing the quantum yield.

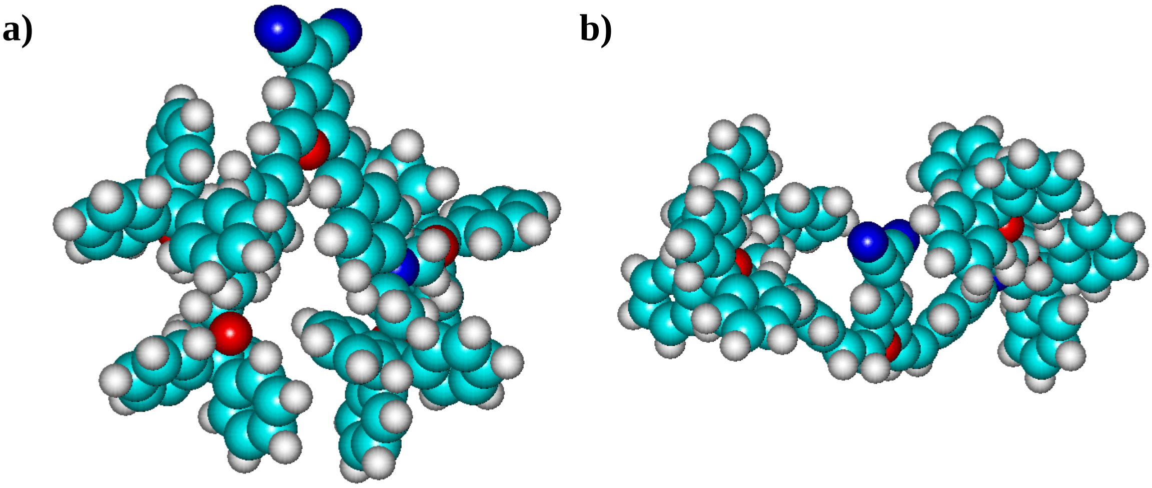

Figure 3.9. a) unprotected and b) protected electron acceptor group of DWK-2 molecule.

The fluorescence efficiency is more than one order less in the thin solid films than in solution. This decrease is due to the smaller intermolecular distance between molecules in the thin solid films which gives rise of interaction of exited state and provoke larger number of nonradiative relaxation thus smaller photoluminescence quantum yield.

3.1.5. Photoluminescence kinetics

Luminescence kinetics was measured at wavelength, which correspond to the peak of the photoluminescence bands. Shorter wavelength photoluminescence band maximum was chosen for the samples with two luminescence bands. It was done due to the photoluminescence registration limits at longer wavelength. Photoluminescence of all investigated molecules in the solutions decays exponentially with decay times ranging from 1.4 to 2.8 ns. Photoluminescence of the pure films decays much faster and the photoluminescence kinetics is clearly non-exponential. The non-exponential decay supports the relaxation mechanism based on the fluorescence quenching which is more pronounced in solid state due to smaller intermolecular distance. In our case approximation by the bi-exponential decay function was used. Exited state lifetimes of all compounds in solution and thin film are shown in Table 3-2.

Table 3-2. Exited state lifetimes of all compounds in solution and thin films. τ_s – exited state lifetime in the solution, τ_r, τ_{nr} – radiative and nonradiative exited state lifetime in the solution, τ_{k1}, τ_{k2} – exited state lifetime in the thin films

	Solution			**Thin films**	
	τ_s	τ_{nr}	τ_r	τ_{k1}	τ_{k2}
DWK-1	**1,4**	**2,1**	**4,4**	**1,4**	**0,3**
DWK-2	**2,1**	**3,1**	**4,9**	**1,1**	**0,3**
JWK-1	**2,3**	**4,3**	**4,8**	**1,5**	**0,5**
JWK-2	**2,3**	**3,4**	**7,2**	**0,9**	**0,3**
ZWK-1	**2,1**	**4,6**	**3,9**	**1,3**	**0,4**
ZWK-2	**2,8**	**4,6**	**7,0**	**0,8**	**0,2**

Radiative exited state lifetime in the solutions is two times larger for **JWK-2** and **ZWK-2** molecules compared to **JWK-1** and **ZWK-1**. One of explanation could be symmetric form of molecule which provides longer living and better protected from quenching exited state compared to asymmetric molecules.

The radiative decay time of molecules in the pure films was not possible to obtain due to the non-exponential relaxation nevertheless comparison of both fast and slow luminescence intensity decay times is done. The difference between time constants is not as expressed as it was in solutions however smaller time constant is for molecules with two electron donor group which is contrary to observations in the solutions. The compounds with two electron donor group exhibit small photoluminescence quantum yield in the thin films which mean that most of electron transitions is nonradiative. Such transitions are fast and this is a reason of small time constant.

The radiative decay rate which is inverse of exited state lifetime is an important parameter to determinate applicability of molecules for the light amplification since it is directly related to the stimulated emission cross section [30]:

$$\sigma_{em}(\lambda) = \frac{F(\lambda)\lambda^4}{8\pi n^2 c} k_r \text{,} \qquad \mathbf{3\text{-}1}$$

where $F(\lambda)$ is the fluorescence quantum distribution function, λ is the light wavelength, n is the refractive index of the surrounding media, c is the speed of light, κ_r is the radiative decay rate. Unfortunately we do not know radiative decay rates in the solid thin films but analyses of these rates in the solutions show that **DWK-1**, **DWK-2**, **JWK-1** and **ZWK-1** compounds could be perspective as media for laser applications. Thus, slower radiative decay rates of **JWK-2** and **ZWK-2** molecules allow us to predict that these compounds are less suitable for the light amplification.

3.2. Properties of amplified spontaneous emission

3.2.1. Transient differential absorption

Transient differential absorption investigations had been performed in order to get more information about possible stimulated emission properties of the studied materials. The differential absorption spectra at 5 ps delay time of all investigated compounds in dichloromethane solutions and of the pure films are shown in Figure 3.10.

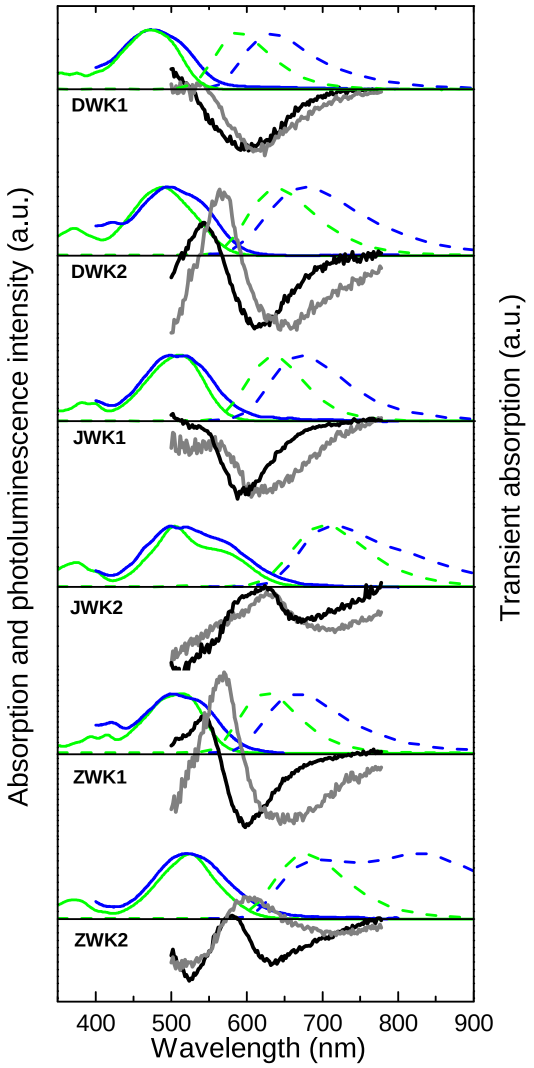

Figure 3.10. Transient differential absorption spectra of investigated compounds in solution (black) and thin film (grey). Absorption (solid line) and photoluminescence (dashed line) spectra of compounds in solution (green) and thin films (blue) are added for easier analysis.

The differential absorption spectra reveal three main components: absorption bleaching, stimulated emission and excited state absorption. Generally the differential absorption spectrum may be described as:

$$\Delta A(\lambda) = n*[(-\sigma(\lambda) - \sigma_{em}(\lambda) + \sigma*(\lambda)], \tag{3-2}$$

where n^* is the density of excited molecules, σ_0, σ_{em} and σ^* are cross sections of the ground state absorption, stimulated emission and excited state absorption. As it can be seen in formula 3-2 ground state absorption and stimulated emission decrease difference absorption spectra and only exited state absorption increase it.

The minimum of differential absorption of all compounds in solution and thin films is observable in the spectral region where photoluminescence is. The only reason of negative values could be due to stimulated emission because there is no ground state absorption in this region. It means that the amplification efficiency is directly proportional to the intensity of the negative transient absorption.

Less negative transient absorption is for compounds **JWK-2** and **ZWK-2** in the pure thin films. It is in good agreement with previously observed small radiative decay rate (see. 3.1.5. chapter). Consequently we could say that these two compounds are probably less suitable for light amplification.

Generally the stimulated emission spectrum is related to the fluorescence spectrum through stimulated emission cross section as $\sigma_{em}(\lambda) \sim F(\lambda)\lambda^4$, which shows that the stimulated emission band shall be slightly red-shifted relative to the photoluminescence band. This relation is approximately valid only for the **DWK-1** in the solution. Other compounds as well as all compounds in the solid films have stimulated emission bands blue-shifted relative to the corresponding photoluminescence bands. A dynamic long wavelength shift of the fluorescence band, which calls spectral diffusion, is the most straightforward reason for the disagreement; the fluorescence spectrum experiences a shift to the long wavelength side in time. Therefore, the time-integrated spectrum is shifted to the long wavelength side in comparison with the spectrum revealed by the stimulated emission at 5 ps delay.

3.2.2. Amplified spontaneous emission in pure thin films

In order to demonstrate the light amplification perspectives we prepared samples of all compounds on a quartz substrate for amplified spontaneous emission measurements. Only for four compounds, **DWK-1**, **DWK-2**, **JWK-1** and **ZWK-1,** the amplified spontaneous emission has been observed. For other two samples, **JWK-2** and **ZWK-2**, we were unable to observe any amplified spontaneous emission signal even at high irradiation pulse energy (>1000 μJ/cm^2). It is in agreement with the above expressed predictions.

The peak positions of amplified spontaneous emission are shifted to a longer wavelength side as compared with the photoluminescence band maxima (see Figure 3.11.). The shift values are 14, 18, 10 and 31 nm for **DWK-1**, **DWK-2**, **JWK-1** and **ZWK-1,** respectively.

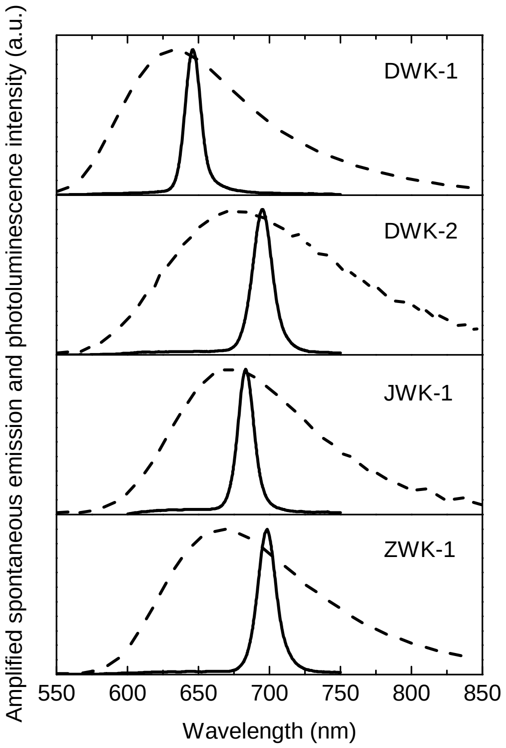

Figure 3.11. Photoluminescence an amplified spontaneous emission spectra of compounds in the pure thin films.

The position of amplified spontaneous emission peak to the photoluminescence peak is according to relation $\sigma_{em}(\lambda) \sim F(\lambda)\lambda^4$. Its confirm hypothesis about spectral diffusion as main reason of blue shift in transient absorption measurement. Spectral diffusion is not enough 5 ps after excitation but is fully proceed after 150 ps what was duration of excitation of amplified spontaneous emission.

The amplified spontaneous emission develops in the spectral position where the light amplification coefficient has the maximal value. The amplification coefficient may be described as:

$$P(\lambda) = ((\sigma_{em}(\lambda) - \sigma^*(\lambda))n^* - \sigma(\lambda)(N - n^*), \qquad 3\text{-}3$$

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

However, even weak ground state absorption may significantly influence the amplification coefficient. This is because large part of excited molecules gives nonradiative decay to ground state which could absorb sample emitted light. Therefore, even a weak tail of the absorption band may strongly reduce the amplification coefficient or make it negative. Thus, the absorption band tails are evidently also responsible for the shifts of the amplified spontaneous emission spectra to the long wavelength side in comparison with the maxima of the fluorescence bands.

Variations of the peak intensity and a full width at half maximum of the amplified spontaneous emission spectra by changing the pump beam energy are shown in Figure 3.12. From the obtained data amplified spontaneous emission threshold values were estimated to be 90±10, 330±20, 95±10, 225±20 μJ/cm^2 for **DWK-1**, **DWK-2**, **JWK-1**, and **ZWK-1**, respectively. These numbers are relatively large in comparison with threshold values of several micro joules per square centimetre reported for some other materials [31], [32]. However, direct comparison is difficult because amplified spontaneous emission threshold, in addition to material properties, depends also on the sample and excitation geometries, film thickness and optical quality as well as on excitation pulse durations. Nevertheless it is the first time of observation of amplified spontaneous emission in pure thin films consisting from pyranyliden derivatives.

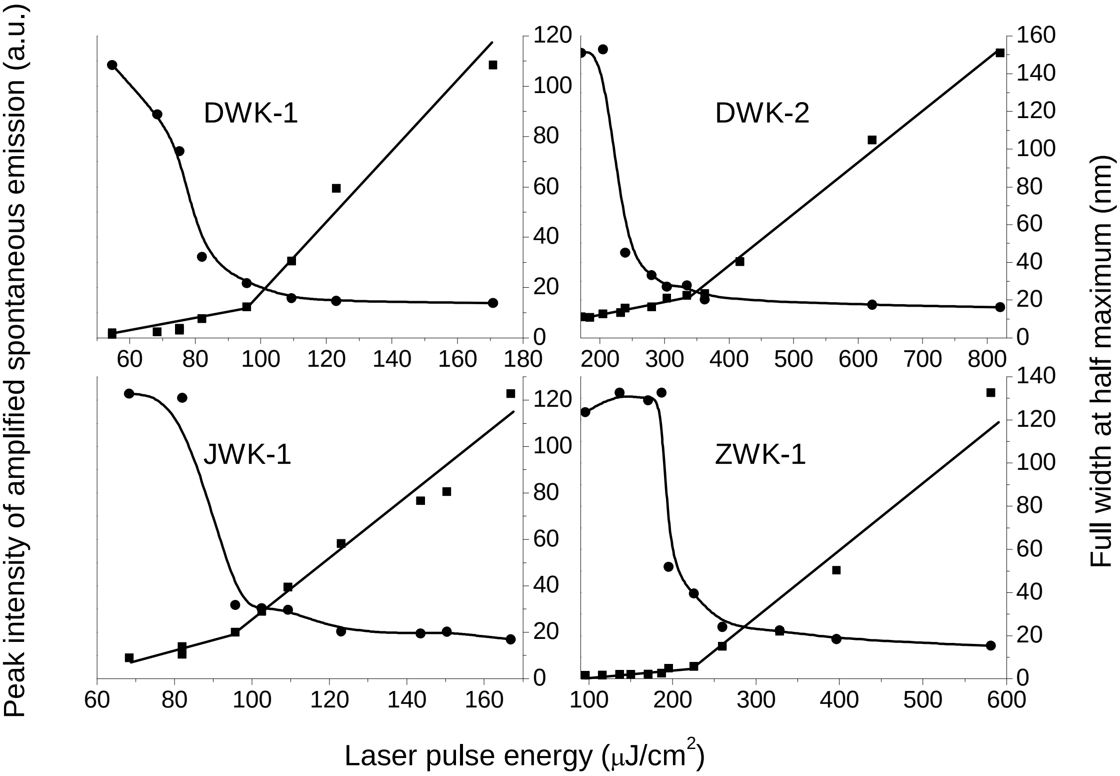

Figure 3.12. Dependence of emission maximum intensity and full width at half maximum of the spectra on excited laser beam pulse energy in thin films.

3.2.3. *Amplified spontaneous emission of polymer matrix doped with DWK-1 and DWK-2 compounds and its relation to system optical properties*

In literature the best results of amplified spontaneous emission were obtained in host – guest systems where active molecules are doped in matrix. It helps to decrease chromophore intermolecular interaction thus decreasing threshold values of amplified spontaneous emission [31], [33–36]. In most cases the optimal concentration was 2wt%.

DWK-1 and **DWK-2** molecules were doped in poly(methyl methacrylate) (**PMMA**) at the concentration 0.1, 1, 3, 5, 10 wt%. The same concentration samples were prepared with **DCM** molecules for comparison.

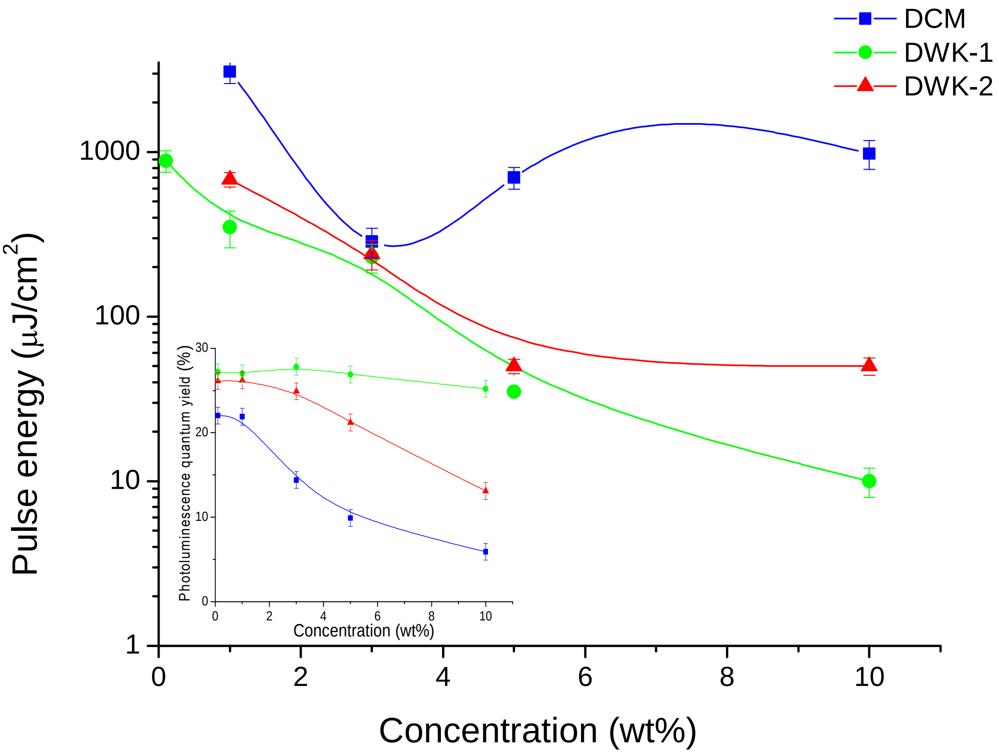

Figure 3.13. Dependence of the threshold values of amplified spontaneous emission on active molecule concentration in **PMMA** matrix (inset - photoluminescence quantum yield of the same systems).

Photoluminescence quantum yield for all systems are shown in inset of Figure 3.13. **PMMA** films doped with **DWK-1** and **DWK-2** molecules at low concentration (<1 wt%) exhibited somewhat lower photoluminescence quantum values as compared to those obtained in the solution. This discrepancy of the photoluminescence quantum values in the solution and the polymer film at low doping level may be attributed to the sensitivity of the molecules to the polarity of the surrounding media. At high concentrations the **DWK-1** molecule showed negligible photoluminescence quenching dependence on concentration. On the other hand the molecule with two donor groups exhibited more pronounced quenching. Photoluminescence efficiency of the polymer film doped with 10 wt% of **DWK-2** molecules decreased 2-time compared to the film with 10 wt% **DWK-1** molecules. This decrease should be do to second photoluminescence band in **DWK-2:PMMA** system as it was in previously investigated **ZWK-2:PMMA** system The laser dye **DCM** dispersed in the polymer matrix at high concentration showed remarkable fluorescence quenching. For example, at a 10 wt% concentration, **DCM** molecules, up to a 4-time decrease of photoluminescence quantum yield is observed in comparison with the same concentration of **DWK-1** molecules. Thus incorporation of bulky trityloxyethyl groups prevents the formation of aggregates of the dye molecules and remarkably reduces photoluminescence quenching dependence on concentration.

Threshold value of amplified spontaneous emission was obtained for the samples to estimate concentration dependence on emission properties (see Figure 3.13.). Amplified spontaneous emission was not possible to observe in polymer system with 0.1 wt% **DWK-2** and **DCM** molecules. At the beginning threshold value decrease by increasing molecule concentration in polymer (see Figure 3.13.). Threshold value starts to increase above concentration of 5wt% for **DCM** compound. Similar concentration was obtain in other works where active matrix was used [22]. The best result of threshold value (10 µJ/cm2) was reached for 10 wt% **DWK-1:PMMA** matrix. Its at least one order of magnitude less compared to the best system of **DCM:PMMA**. It means that **DWK-1** molecule is perspective for laser media.

During the investigation of amplified spontaneous emission was found that emission maximum has red shift by increasing active molecule concentration in polymer (see Figure 3.14.). Similar red shift was observed also in photoluminescence spectra.

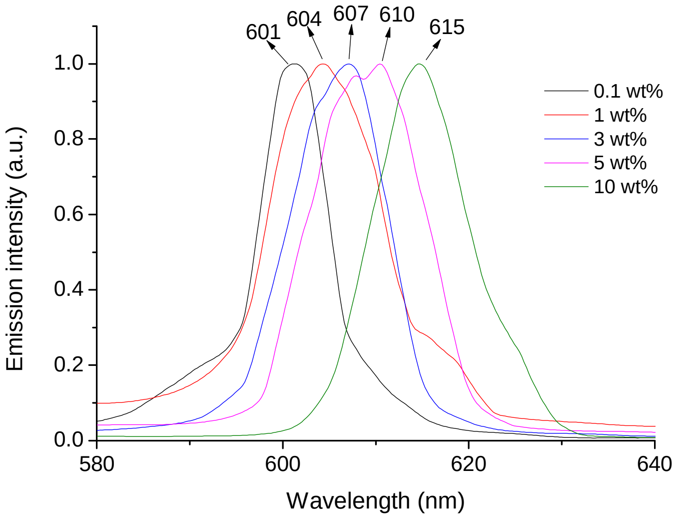

Figure 3.14. Dependence of amplified spontaneous emission spectra on DWK-1 molecule concentration in PMMA matrix

Red shift was observed for all compounds which were doped in polymer matrix (see Figure 3.15. a,b,c). Similar photoluminescence shift was observed for **DCM** molecules in various dielectric constant solvents [16], [23]. It is explained by solvatochromic effect. Usually this effect is observable in solutions. At the same time it also could be applied to host – guest system where molecules are dissolved in solid solution. In our case we prepare two component systems where it is possible to change dielectric constant of all system by increasing the amount of one component. Reorientation of dipoles is less probable in solid state that’s why only electron polarizability part of dielectric constant should be take in to account to explain solvatochromic effect in solid films. This part can be obtained from dielectric constants at light frequencies. Quantum chemical calculation shows that nonresonance dielectric constant for **DWK-1** compound is 2.76, **DWK-2** is 2.75 and **DCM** is 3.07.

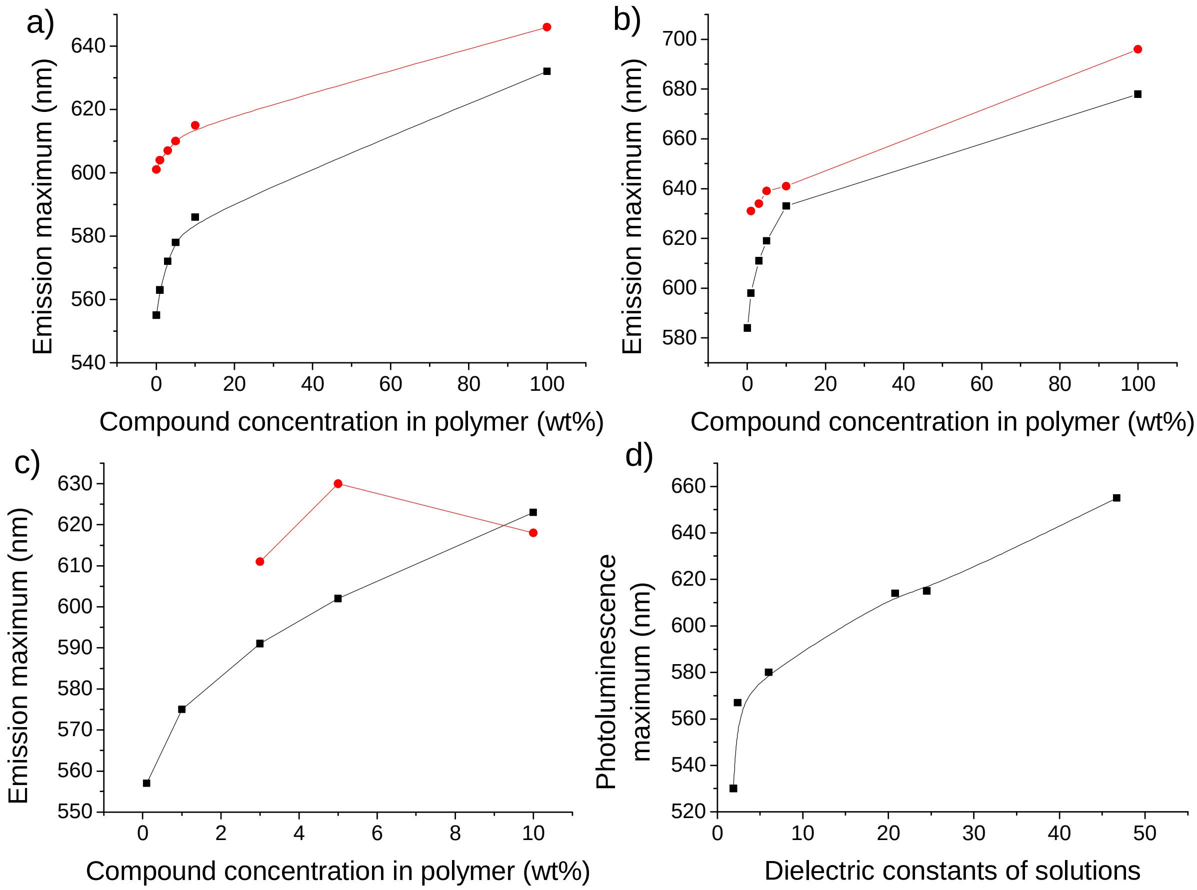

Figure 3.15. Dependence of amplified spontaneous emission (red) and photoluminescence (black) maximum wavelength on molecules a) **DWK-1**, b) **DWK-2**, c) **DCM** concentration in polymer matrix. c) Photoluminescence maximum wavelength of **DCM** compound in various dielectric constant solvents [16], [23]. Lines is guideline for eyes

These values are larger compared to experimentally measured optical dielectric constant of 2.22 for **PMMA** [37]. It means that dielectric constant of the system was increased by increasing the amount of the active molecules [38]. This is in good agreement with our observed red shift of emission spectra. First time such effect noticed Bulovic et al. in the electroluminescence spectra of various concentration **DCM2** molecules in **Alq$_3$** matrix [39]. Later they observed red shift of photoluminescence spectra in the system **DCM2:** N,N′-Bis(3-methylphenyl)-N,N′-diphenylbenzidine (**TPD**) [40].

3.3. Electroluminescence and electrical properties of ZWK-1 and ZWK-2 compounds

Despite low photoluminescence quantum yields electroluminescence system was made in this work. Compounds with indandione group as electron acceptor group (**ZWK-1** and **ZWK-2**) was chosen for electroluminescence measurement. Such choice was made by to reasons. First – photoluminescence spectra is in red spectral region which gives pure red colour. Second – indandione derivatives are one of the most investigated compounds in the laboratory.

3.3.1. Electroluminescence properties

Samples with the structure ITO/**PEDOT:PSS**(40nm)/**ZWK1**(x nm) or **ZWK2**(x nm)/LiF(1nm)/Al(100nm) was made for electroluminescence measurements. **PEDOT:PSS** and LiF layers was used to improve charge carrier injection in the sample. The best result was obtained with the active layer thickness of 95 nm for **ZWK-1** and 85 nm for **ZWK-2**. Electroluminescence spectra of prepared samples are shown in Figure 3.16. a and b.

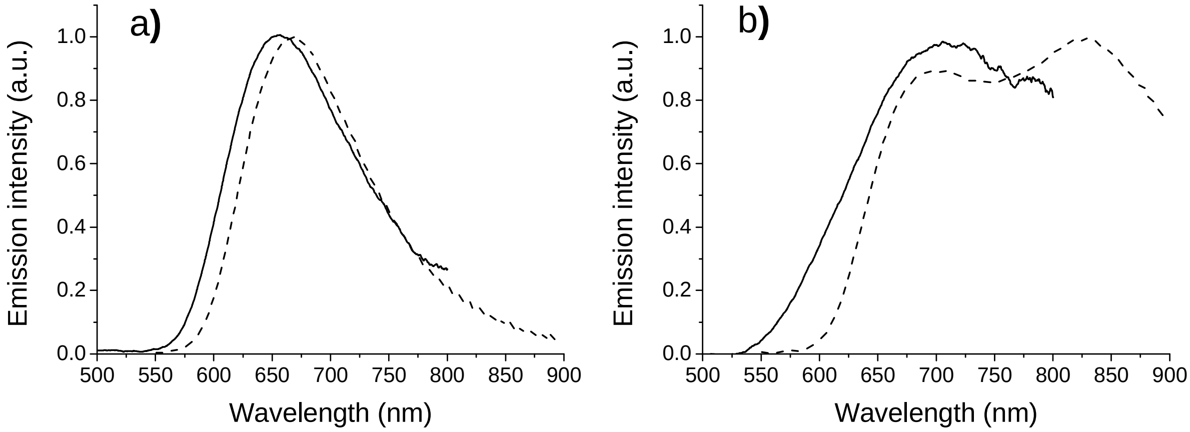

Figure 3.16. Electroluminescence (solid line) and photoluminescence (dashed line) spectra of the compounds a) ZWK-1 and b) ZWK-2.

The measured current-voltage curves are almost the same when positive voltage was applied to the bottom ITO electrode or top Al electrode. It shows that in both cases equal number of charges carriers was injected. Electroluminescence was not observed in reverse direction, when electrons were injected from ITO and holes from aluminium. It means that in reverse direction only one type of charges were injected. Electroluminescence was achieved in forward direction what is proof that both types of charges were injected. Unfortunately symmetrical current-voltage characteristics indicate poor injected charge balance in forward direction. In such case the efficiency of organic light emitting diode will be reduced. One type of charge carrier injection (when square law of current dependence on voltage starts) starts at voltage of 5 V and 7 V for **ZWK1** and **ZWK2**, respectively.

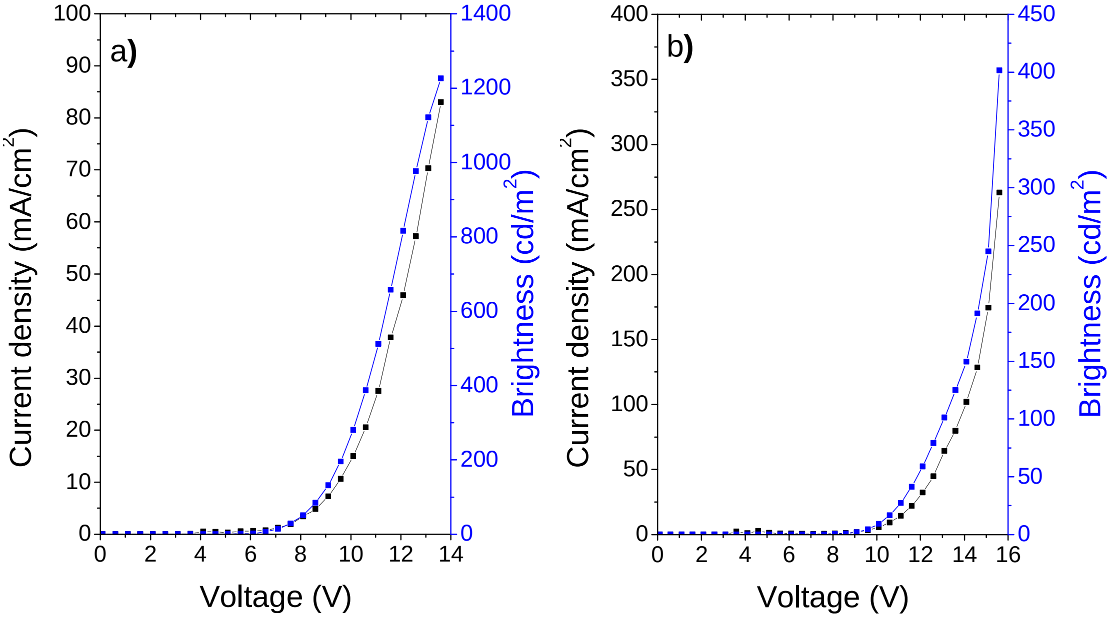

Figure 3.17. Current – voltage (black) and electroluminescence brightness – voltage (blue) of prepared samples with compound a) ZWK-1 and b) ZWK-2.

The turn on voltage of the device was 5.6 V and 8.6 V (when the luminance is ~ 1 cd/m^2) for **ZWK-1** and **ZWK-2**, respectively. The brightness increases with the forward voltage and reach 1200 cd/m^2 and 400 cd/m^2 in the case of **ZWK-1** and **ZWK-2**, respectively (see Figure 3.17.).

Current and power efficiency are shown in Figure 3.18. Both efficiencies at the beginning increase with current density due to improved balance of injected charge carriers. One type of charge carriers are injected at low voltage and only at higher voltage second type of charge carriers star to inject in the sample and then electroluminescence appears. Power and current density start to decrease by further increased current density. The reason could

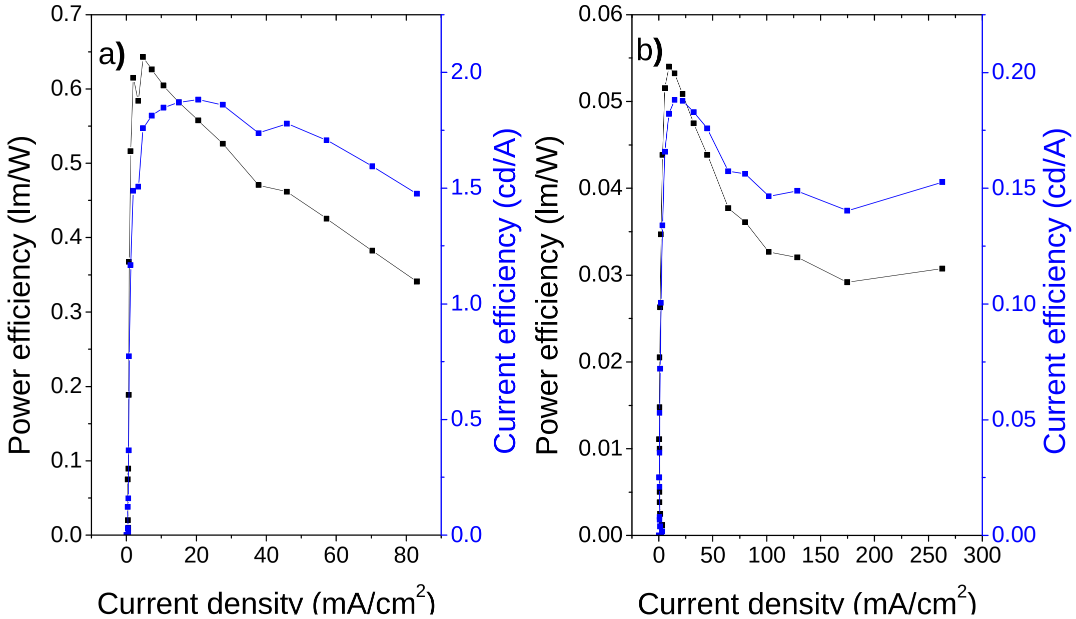

Figure 3.18. Power (black) and current (blue) efficiency of the samples with compounds a) ZWK-1 un b) ZWK-2.

be different charge carrier mobility which reduces charge balance and efficiency.

Compound **ZWK-1** is at least 10 times more efficient than **ZWK-2**. It can not be explained only by the 3 times difference of photoluminescence quantum yield of the thin films. Electrical properties, like, charge carrier local trap state, also could give some influence.

3.3.2. Charge carrier trap states in thin films

Electrical properties of thin solid films were measured in space charge limited current (SCLC) regime. The thickness of the sample was 500 nm to realise this regime. Current-voltage characteristics were measured at both polarities: positive voltage was applied to ITO and aluminium electrode. The characteristics are shown in Figure 3.19. Each current-voltage characteristics, except **ZWK-1** at positive aluminium electrode, could be divided in three parts: omic, square and higher order. There is no third part for **ZWK-1** at positive aluminium electrode. Third part in SCLC regime attributed to trap filled current but in some cases it could be due to bipolar injection of the charges. Determination of alignment of Fermi level of metals respect to ionization energy of organic molecule and electron affinity energy is important to make correct conclusions.

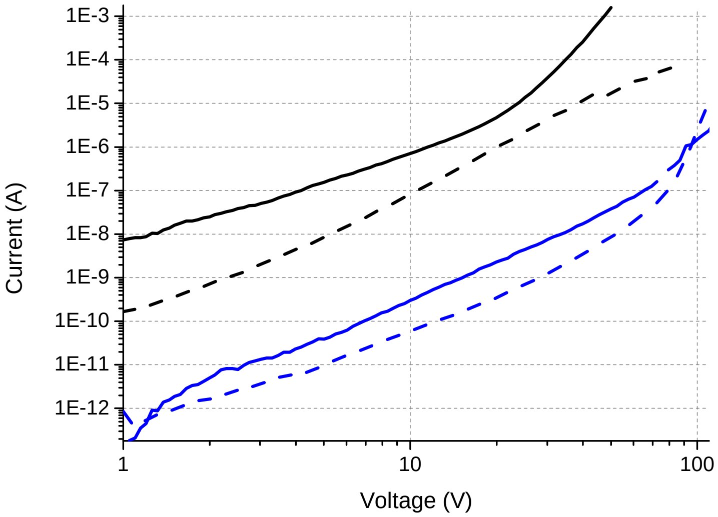

Figure 3.19. Current – voltage characteristics of thin films of **ZWK-1** (black) un **ZWK-2** (blue). Positive voltage is applied to ITO (solid line) and aluminium (solid line) electrode.

Higher current was observed at applied positive voltage to ITO than aluminium electrode. It is easy to understand if we look on work function alignment respect to organic molecule energy levels. Unfortunately we do not have information about ionisation potential of **ZWK** molecule, but we can use the experimental value 5.4 eV of **DCM** molecule which should be close to **ZWK** value. Work function of ITO is 4.7 eV which is close to ionisation energy of **DCM** molecule [41]. Band gape, which vas obtained from absorption spectra, of compound **ZWK** is around 2 eV thus electron affinity is around 3.4 eV. We got that work function of aluminium is somewhere in the middle of band gap of **ZWK** compound (see Figure 3.20.). It means that aluminium electrode can inject electrons and holes but ITO electrode only holes.

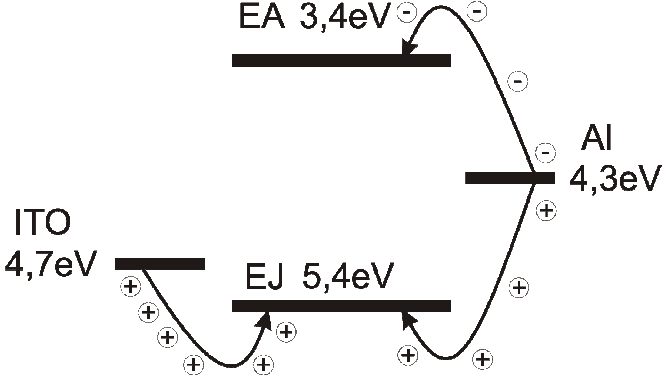

Figure 3.20. Energy level diagram of charge carrier injection from ITO and aluminium electrode. EA – electron affinity and EJ – molecule ionisation energy.

Further analysis can be done only for positive aluminium electrode due to the monopolar injection. Temperature modulated space charge limited current method was used to obtain charge carrier local trap states. The method is based on analysis of dependence of charge carrier activation energy on applied voltage (see Figure 3.21.).

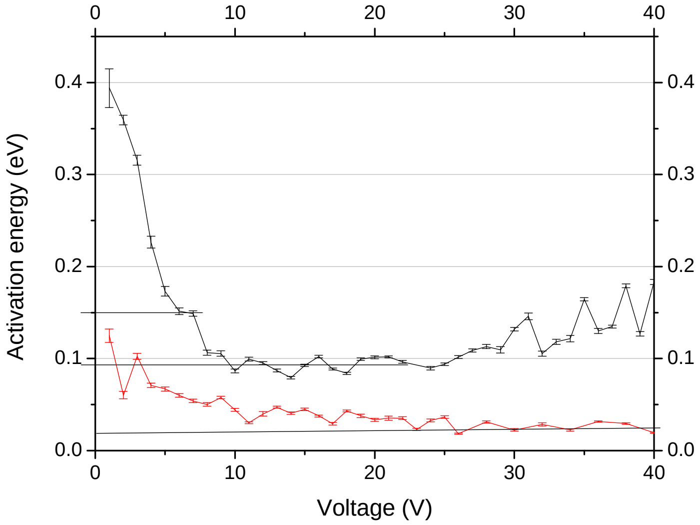

Figure 3.21. Dependence of activation energy on applied voltage on ZWK-1 (red) and ZWK-2 (black) thin films. Positive voltage applied to aluminium electrode.

Activation energy rapidly decreases by increasing applied voltage on the thin film with **ZWK-1** molecules till it reach 0.025 ± 0.001 eV. This value is similar to kT value 0,026 eV at room temperature that shows the level is due to the activation of charges in conducting energy level.

Activation energy decrease more slowly by increasing voltage for **ZWK-2** compound compared to **ZWK-1** and it does not decreasing more than 0.10 ± 0.01 eV. Broader energy distribution of conductivity level is the reason of slower decrease of activation energy. It could be due to more conformations of molecules in the case of **ZWK-2** compared to compound **ZWK-1**.

Additional hole trap state level was observed at energy 0.15 ± 0.01 eV when positive voltage was applied on aluminium electrode.

Electrical properties is worse for thin films consisting **ZWK-2** molecules respect to films with **ZWK-1** molecules due to broader energy distribution of conductivity levels and additional charge carrier trap state which also reduce electroluminescence efficiency.

Conclusions

Trityloxyethyl groups have negligible influence on optical transition in molecule. Two radiative transitions are characteristic of molecules with two electron donor groups, where less probable transition is more protected by bulky trityloxyethyl groups from environment influence.

Reduced average intermolecular distance, thus larger (more probable) interaction of excited states in pure solid films, is the reason of photoluminescence quantum yield reduction by one order of magnetude in comparison to the solutions of molecules.

Photoluminescence quantum yield is practically unaffected by increasing **DWK-1** molecule concentration in polymer matrix. Mean while it rapidly decreases by increasing **DCM** molecule concentration in the same polymer. Trityloxyethyl group reduces intermolecular interaction. Consequently it is possible to increase active molecule concentration in matrix while optical properties, like, photoluminescence quantum yield stay the same.

Photoluminescence kinetics and differential transient absorption measurements show possible application as active laser media four of six investigated compounds. This prediction was confirmed by the amplified spontaneous emission measurements of the pure thin films. Till now there were no observations of amplified spontaneous emission in pure films which consist only from pyranyliden derivatives. Further reduction of threshold value of amplified spontaneous emission was achieved by preparing host-guest systems. Moreover, we are able to reduce for more than one order of magnitude threshold value in the system **DWK-1:PMMA** compared to the system **DCM:PMMA**. It means that **DWK-1** compound is perspective for practical use in light amplification systems. Photoluminescence and amplified spontaneous emission spectra exhibit red shift with increasing active molecule concentration in polymer. It is explained by positive solvatochromic effect when dielectric constant in system is increasing with the active molecule concentration.

Electroluminescence efficiency is higher for the systems with **ZWK-1** compound compared to systems with **ZWK-2** compound due to higher photoluminescence quantum yield and better electrical properties. Energy distribution of conductivity levels is wider for **ZWK-2** molecules compared to **ZWK-1**. It could be due to more conformations of **ZWK-2** molecules. Holes trap states was observed in the thin films of **ZWK-2** compound. Application of the pure thin films of these compounds in organic light emitting diode is limited due to low electroluminescence efficiency. More perspective could be use of such compounds in matrix.

Thesis

- Attachment of trytiloxyethyl groups shows no significant influence on optical transitions in chromophore molecules. These groups could provide capability of different molecules to form amorphous state for solutions meanwhile not changing optical properties of molecule.
- Bulky trytiloxyethil groups protecting chromophore from interaction with surrounding molecules. It can be observable in three ways. High photoluminescence quantum yield. Photoluminescence in the pure thin solid films. Additional relative high intensity photoluminescence band are observable for molecules with two donor group in high concentration solutions and thin films. The reason is two radiative transitions where less probable transition is more protected by bulky trityloxyethyl groups and is origin of second band.
- The compounds **DWK-1** is most promising candidate from investigated compounds for application as laser dye. Performance of **DWK-1** is expected to be even better then widely used laser dye **DCM**. Threshold value of amplified spontaneous emission in the host-guest system is at least one order of magnitude less in case of **DWK-1** molecules in comparison with similar system based on **DCM** molecules.
- Small photoluminescence quantum yield of the pure films is the reason of low electroluminescence efficiency of **ZWK-1** compound. Additional decrease of the efficiency of **ZWK-2** compound is due to charge trap levels in the film.

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