Stimulated emission and optical properties of pyranyliden fragment containing compounds in PVK matrix

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ABSTRACT

Organic solid state lasers are thoughtfully investigated due to their potential applications in communication, sensors, biomedicine, etc. Low amplified spontaneous emission (ASE) excitation threshold value is essential for further use of the material in devices. Intramolecular interaction limits high molecule density load in the matrix. It is the case of the well-known red light emitting laser dye - 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran (**DCM**). The lowest ASE threshold value of the mentioned laser dye could be obtained within the concentration range between 2 and 4 wt%. At higher concentration threshold energy drastically increases. In this work optical and ASE properties of three original **DCM** derivatives in poly(N-vinylcarbazole) (**PVK**) at various concentrations will be discussed. One of the derivatives is modified **DCM** dye in which the methyl substituents in the electron donor part have been replaced with bulky trityloxyethyl groups (**DWK-1**). These sterically significant functional groups do not influence electron transitions in the dye but prevent aggregation of the molecules. The chemical structure of the second investigated compound is similar to **DWK-1** where the methyl group is replaced with the tert-butyl substituent (**DWK-1TB**). The third derivative (**DWK-2**) consists of two N,N-di(trityloxyethyl)amino electron donor groups. All results were compared with **DCM:PVK** system. Photoluminescence quantum yield (PLQY) is up to ten times larger for **DWK-1TB** with respect to **DCM** systems. Bulky trytiloxyethyl groups prevent aggregation of the molecules thus decreasing interaction between dyes and amount of non-radiative decays. The red shift of the photoluminescence and amplified spontaneous emission at higher concentrations were observed due to the solid state solvation effect. The increase of the investigated dye density in the matrix with a smaller reduction in PLQY resulted in low ASE threshold energy. The lowest threshold value was obtained around 21 $\mu J/cm^2$ (2.1 kW/cm^2) in **DWK-1TB:PVK** films.

Keywords: DCM, laser dye, glass forming low molecular weight compounds, amplified spontaneous emission, pyranyliden derivatives

1. INTRODUCTION

Organic solid-state lasers are currently a rapidly developing new optical technology field [1-3]. Optically pumped plastic lasers are opening new technological perspectives in communication [4], sensor [5-7], spectroscopy [8] and biochips [9, 10]. Easily processable functional materials, with high light amplification properties, are required for the development of such lasers. Low molecular weight compounds [11-15], polymers [11, 16-18] and dendrimers [19-21] are widely used as laser dyes and covers the entire visible spectrum. In spite of such a large selection of compounds, only several of them provide excitation threshold energy of amplified spontaneous emission (ASE) below few $\mu J/cm^2$. Mostly such low ASE threshold energy was obtained in doped systems where high refractive index polymer or small molecules are used as a matrix. The matrix provides separation of the laser dyes thus reducing molecule crystallisation and photoluminescence (PL) quenching. Typical concentration varies between 1 and 5 wt% [13, 22, 23]. It depends on the used laser dye and the matrix. At higher concentration PL quenching due to the intermolecular interaction take place [24, 25] which results in a significant increase of the ASE excitation threshold energy.

One of the lowest excitation threshold energy of amplified spontaneous emission was observed for widely used laser dye 4-(dicyanomethylene)-2-methyl- 6-(p-dimethylaminostyryl)-4H-pyran (**DCM**) in tris(8-hydroxyquinolinato)aluminium (**Alq₃**) matrix. Authors have reported as low as 3 $\mu J/cm^2$ in 2 wt% **DCM:Alq₃** system [23]. Such low energy was obtained due to the Foster energy transfer between **DCM** and **Alq₃** compounds which provide a higher density of excited **DCM** molecules at the same excitation energy. However, concentration quenching still limits its use in higher doping samples which would result in much lower ASE threshold energies.

Previously we have demonstrated original **DCM** derivatives with attached bulky trityloxyethyl groups [26, 27]. Such group incorporation contributes in the chromophore separation thus reducing intermolecular interaction. We were able to

observe photoluminescence even in the neat films which cannot be achieved in the pure evaporated **DCM** thin film [28]. An additional benefit of the bulky groups is replacement of thin film preparation method from expensive thermal evaporation in vacuum to cost-efficient wet casting method. Our synthesised **DCM** derivatives form amorphous thin films from solutions by spin coating method. ASE threshold energy below 100 μJ/cm^2 [26] was obtained in neat thin films. Nevertheless, it should be significantly lower in the host-guest systems.

In this work optical properties and stimulated emission of three original pyranyliden derivatives with the bulky trityloxyethyl groups in poly(N-vinylcarbazole) (**PVK)** matrix were investigated and compared with well-known laser dye **DCM** in **PVK** matrix. **PVK** is widely used matrix in organic light emitting diodes [29-31], and it has a high refracting index (1.696) to prepare efficient waveguide even on a glass substrate. **PVK** was also used as a matrix for **DCM** thin film lasers in a DFB configuration [32]. Guest – host systems with the investigated compounds in **PVK** at the concentration 1, 5, 10, 20, 35, 50, 75, 100 wt% were prepared and studied. Also **DCM:PVK** systems up to 15wt% were made for comparison. No influence on electron transitions due to attached trityloxyethyl group was observed. Optical images of the prepared samples were taken before further experiments. Dependence of photoluminescence quantum yield (PLQY), its spectra and ASE properties of all the investigated systems on concentration will be discussed.

2. MATERIALS AND METHODS

2.1 Investigated organic compounds

2-(2-(4-(Bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)malononitrile (**DWK-1**) molecule consists of **DCM** as a backbone with attached two bulky trityloxyethyl groups at the electron donor part (see Fig.1a). 2-(2-(4-(Bs(2-(trityloxy)ethyl)amino)styryl)-6-tert-butyl-4H-pyran-4-ylidene)malononitrile (**DWK-1TB**) is similar to **DWK-1** with incorporated tert-butyl group instead of a methyl group (see Fig.1b). It does not influence optical properties of the compound but increases synthesis yield from 12% in the **DWK-1** case to 75% for **DWK-1TB**. 2-(2,6-Bis(4-(bis(2-(trityloxy)ethyl)amino)styryl)-4H-pyran-4-ylidene)malononitrile (**DWK-2**) consists of two donor groups with attached two bulky trityloxyethyl groups at each electron donor part (see Fig.1c). Synthesis of the compounds is described elsewhere [33, 34].
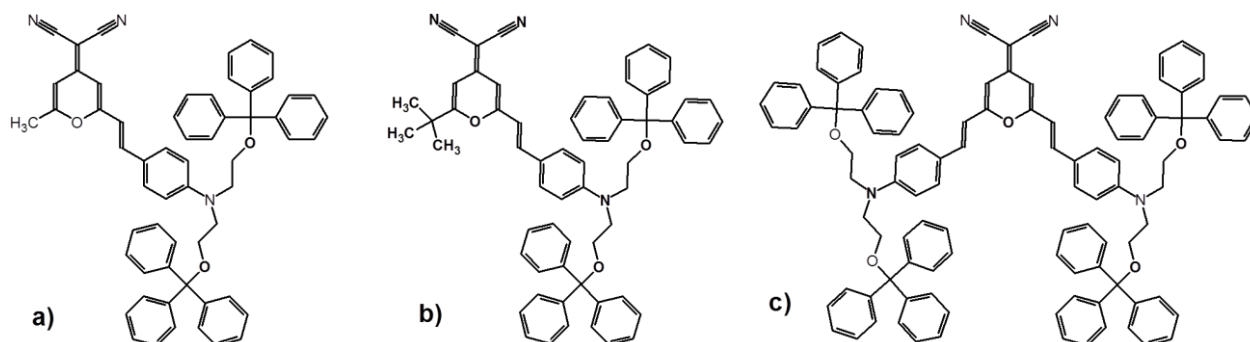

Figure 1. Chemical structure of a) **DWK-1**, b) **DWK-1TB** and c) **DWK-2.**

2.2 Sample preparation for optical characterization

All of the investigated compounds were dissolved in dichloromethane. The necessary amount of prepared solution was added to **PVK** (Sigma-Aldrich No. 368350, average M$_n$ 25 000-50 000) to obtain a guest-host system with **DCM** concentration of 1, 2.5, 5, 7.5, 12.5 and 15 wt% and with **DCM** derivatives concentration of 1, 5, 10, 20, 35, 50, 75 and 100 wt%. Organic compound mass to the solvent volume ratio was kept constant (30 mg/ml) for all the prepared solutions. Such approach provided similar film thickness for all the samples. Before the deposition of the thin organic layer, the glass substrate was cleaned in dichloromethane. The solutions were spin-coated on the substrates for 40 s at 1000 rpm and acceleration of 1000 rpm/s. All the film thickness was about 300 nm which satisfied optical waveguide conditions.

2.3 Measurement systems

Optical images of the samples were obtained by high-resolution optical microscope Nikon ECLIPSE L150. The sample thickness and surface was measured by Surface Profile Measuring System Veeco „Dektak 150".

Spectrophotometer Ocean Optics HR 4000 was used for recording of absorption spectra of the investigated samples. PLQY were measured by the calibrated system Fluorescence spectrometer Pico Master 1 (Photo Med GmbH). It consists of xenon lamp – monochromator – integrated sphere – monochromator – detector. Spectral resolution in all the measurements was set to 2 nm. The excitation wavelength was chosen at the absorption maximum for each compound. Firstly excitation and emission spectrum were obtained when only glass slide was in the sphere. Afterwards, excitation

and emission spectrum were recorded when the thin film was in the sphere. All four spectra were used for PLQY calculation.

ASE measurements were performed by the variable stripe length technique [35]. Setup for ASE measurement is self-made, and its scheme is shown in Fig. 2. Ekspla 310 series pulse laser with wavelength 532 nm was used as the excitation source. Pulse duration was 10 ns and repetition rate 10 Hz. The pulse energy was tuned by Glan prism/half wave plate/Glan prism system. Beam expander was used to expanding beam 5 times to 25 mm. The beam was focused by a cylindrical lens to 0.4 mm wide stripe on the sample surface. The slit was used to cut-off edges of the beam to get 4 mm long equal intensity line on the sample. Beam splitter diverts 10% of laser light to a power meter (calibrated silicon diode). The emitted light was collected from the edge of the sample by optical fibre, which was connected to the calibrated Ocean Optics spectrometer HR 4000. Half wave plate and sample position were adjusted by a step motor. The experiment was controlled, and data was recorded by Personal Computer.
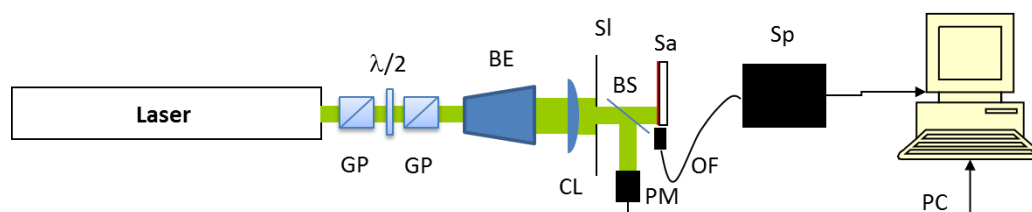

Figure 2. Experimental scheme of the amplified spontaneous emission measurement. GP – Glan prism, λ/2 – half wave plate, BE – beam expander, CL – cylindrical lens, Sl – slit, BS – beam splitter, PM – power meter, Sa – sample, OF – optical fibre and Sp – spectrometer Ocean Optics HR400, PC – Personal Computer.

3. RESULTS AND DISCUSSION

3.1 Optical images

Some structure can be observed for the samples of the concentration below 20wt% (see Fig.3). In the high-resolution images, it appears as islands with different colours. All the images were taken in reflecting mode, and this structure is light interference due to different optical length in the sample. Two reasons could be count: different thickness of the layer or some other inhomogeneities in the film. Surface profile measurements showed surface roughness from 35 nm for any 1wt% samples to 3 nm for any 100wt% samples which point to the thickness changes in the sample as a reason of such islands. **PVK** is the most likely cause of thickness changes because roughness decreases at lower **PVK** concentrations in the sample. Nevertheless, these defects didn't influence further experiments.

Insignificant dye aggregation takes place in the sample above 10wt% and 50wt% for **DCM** and its derivatives, respectively. Observation of **DCM** derivatives aggregation at a higher concentration than **DCM** conform efficiency of bulky groups.
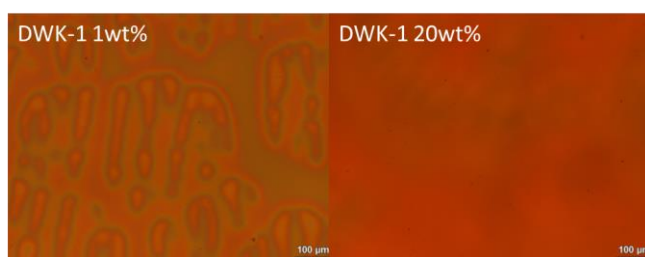

Figure 3. High-resolution images of the **DWK-1** samples. Compound concentration in the matrix is given on each image.

3.2 Optical properties

Normalised absorption spectra of the samples containing 5wt% investigated compounds in **PVK** matrix are shown in Fig. 4. The absorption spectrum of **DCM** is broader with the same maximum position compared to **DWK-1** and **DWK-1TB** compounds. Broader spectra could be explained by intermolecular excitonic interaction which should be larger for **DCM** molecules compared to the **DCM** derivatives. **DWK-1** and **DWK-1TB** compounds have the same absorption spectra. Some mismatch between them is related to the experimental error. It means that there is the negligible influence of the bulky trityloxyethyl and tert-butyl group on the electron transitions in the molecule. The absorption spectrum of **DWK-2** is red shifted with respect to other compounds due to the longer conjugation length in the molecule [33]. No concentration influence on the absorption spectra was observed for all the compounds.
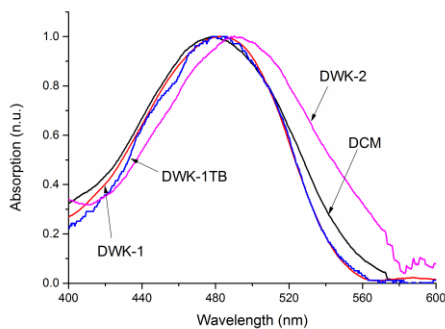
Figure 4. Absorption spectra of 5 wt% investigated compounds in **PVK** matrix.

Photoluminescence quantum yield decreases at higher concentration (see Fig.5). It is the result of stronger intermolecular interaction between the molecules due to the shorter distance between them. **DWK-1** and **DWK-1TB** have 2-fold higher PLQY compared to **DCM** and **DWK-2** molecules at low (<5wt%) concentrations. This difference increases more than ten times at higher concentration. As it was expected PLQY rapidly decreases in the case of **DCM** molecule and only a few percent are left at 15wt% **DCM:PVK** sample thus verifying large molecule interaction. Similar PLQY values with less pronounced decrease compared to **DCM:PVK** system is for **DWK-2:PVK**. V. A. Pomogaev et al. has experimentally shown and theoretically explained that symmetrical **DCM** derivatives express less PLQY in solution compared to nonsymmetrical ones [36]. Authors explain it with the appearance of the second singlet level with lower oscillation strength near the S_1. Most of the emission comes from S_2 accordingly it dramatically influences PLQY. **DWK-1TB** molecule shows the highest PLQY at all concentrations, but **DWK-1** has only a few percent less. The only reason of higher PLQY between **DCM** and **DWK-1** or **DWK-1TB** is attached bulky group which reduces interaction between molecules thus decrease photoluminescence quenching. Even at pure (100wt%) **DWK-1TB** thin films the PLQY is still 10%. By looking at these results, we could expect that we should be able to achieve lower ASE excitation threshold value at higher **DWK-1** and **DWK-1TB** load in the matrix compared to **DCM**.
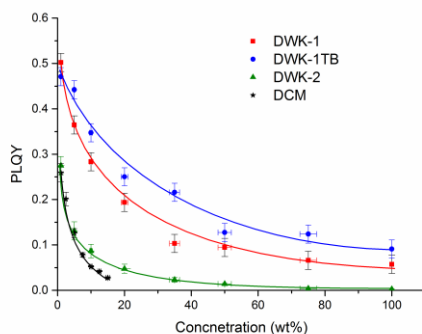

Figure 5. Dependence of photoluminescence quantum yield on the laser dye concentration in **PVK** matrix.
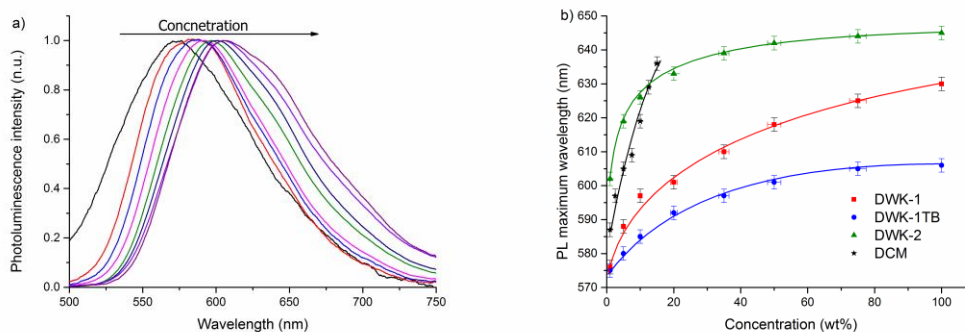

Figure 6. a) Photoluminescence spectra at different **DWK-1TB** concentrations in the **PVK** matrix. b) Photoluminescence maximum position at various concentrations.

The red shift of the PL spectra was observed at higher dye concentration in **PVK** matrix (see Fig.6) for all the investigated compounds. As an example in Fig.6a are shown **DWK-1TB:PVK** photoluminescence spectra at different concentrations. Such PL spectral shift in a solid state is not ordinary. Typically position of photoluminescence spectra for particular compound could be tuned in solutions by using different polarities (dielectric constant) solvents, which is known as a solvatochromic effect. Guest-host systems where molecules are dissolved in a matrix could be considered as solid solutions, and solvatochromic effect may take place. It is so called solid state solvation effect (SSSE). Such shifts were observed in different guest-host systems with pyranyliden derivatives [37, 38]. It is related to dielectric constant changes due to the increase of the investigated compounds in the polymer. The most pronounced shift is for **DCM** compound which has 49 nm red-shifts within 14 wt%. Next larger shift is for **DWK-1** with 54 nm photoluminescence maximum difference between 1 and 100 wt% samples. Further, follow **DWK-2** (43 nm) and **DWK-1TB** (31 nm). Red shift in similar dyes depends on a load of molecules. **DCM** is at least twice lower molecular weight than **DWK-1** or **DWK-1TB** which mean that at the same weight concentration there will be twice more molecules which result in the higher PL shift.

3.3 Amplified spontaneous emission

Similar but less pronounced red shift of emission maximum was observed in the ASE spectra (see Fig. 7). The position of the amplified spontaneous emission peak to the photoluminescence peak can be determined according to the relation [39]:

$$\sigma_{em}(\lambda) \propto F(\lambda) * \lambda^4 \quad , \tag{1}$$

where $\sigma_{em}(\lambda)$ is the stimulated emission cross section, $F(\lambda)$ is the fluorescence quantum distribution function, λ is the light wavelength. Expression (1) shows that red shift of amplified spontaneous emission should be even larger than that of the photoluminescence. The disagreement could be explained by light absorption. Expression (1) gives information only about stimulated emission cross section but not about light amplification. ASE emission appears in the region where the amplification coefficient is larger than 0. The amplification coefficient is described as:

$$P(\lambda) = ((\sigma_{em}(\lambda) - \sigma^*(\lambda))n^* - \sigma(\lambda)(N - n^*)) \quad , \tag{2}$$

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, respectively.
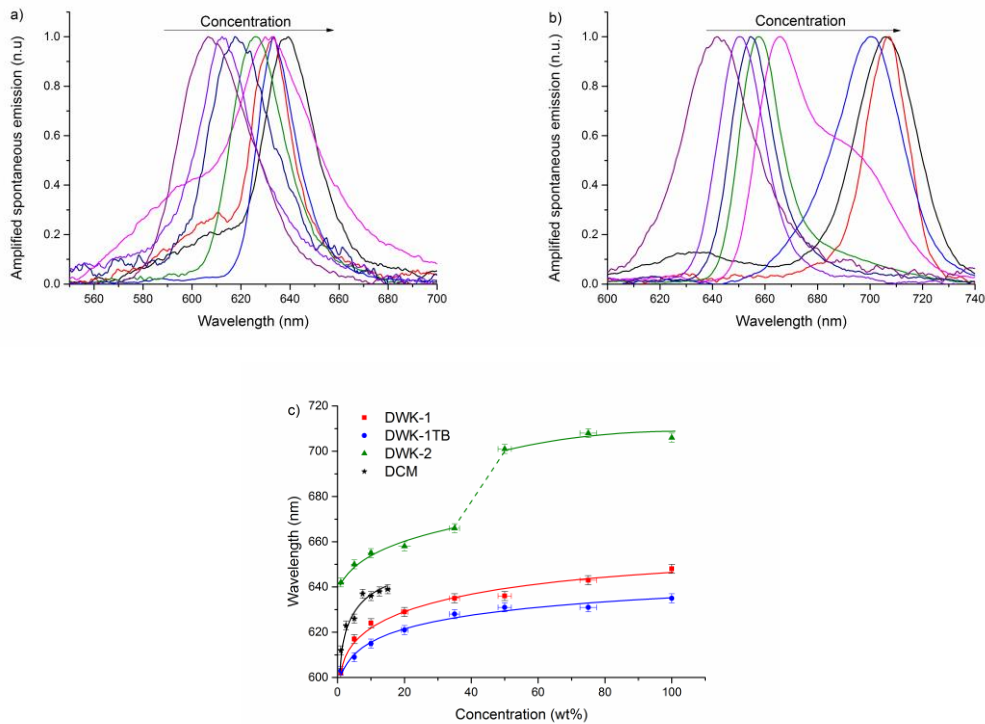

Figure 7. Amplified spontaneous emission spectra at different dye concentrations in the matrix for a) **DWK-1TB**, b) **DWK-2**. c) Dependence of ASE maximum wavelength on dye concentration.

As it can be seen from equation (2) absorption could impact light amplification coefficient. The absorption spectrum is not changing on the dye concentration in **PVK**. At small concentrations, PL band has larger overlap with absorption band. Therefore, ASE maximum is red shifted by cause of both absorption and SSSE but at higher concentration red-shift is only due to SSSE. ASE peak could be tuned by 46nm, 32nm and 27 nm for **DWK-1**, **DWK-1TB** and **DCM** compounds (see Fig 7c), respectively.

Switch between two ASE maximum wavelengths was observed for the **DWK-2** compound. At low concentrations (<20wt%) and high (>50wt%) concentrations, only one maximum was observed. Two ASE maximums appear at 35wt% concentration (see Fig.7b) where ASE maximum switch from smaller to a higher wavelength. Such ASE or PL switching has not been observed till now in pyranyliden derivatives. It could be attributed to specific interactions between the molecules which open additional transition which was forbidden at a lower concentration. There could be mentioned several possible explanations: excimer formation, intramolecular charge transfer or intramolecular twisting phenomena. The deeper systematic investigation should be performed to explain the origin of the second band.
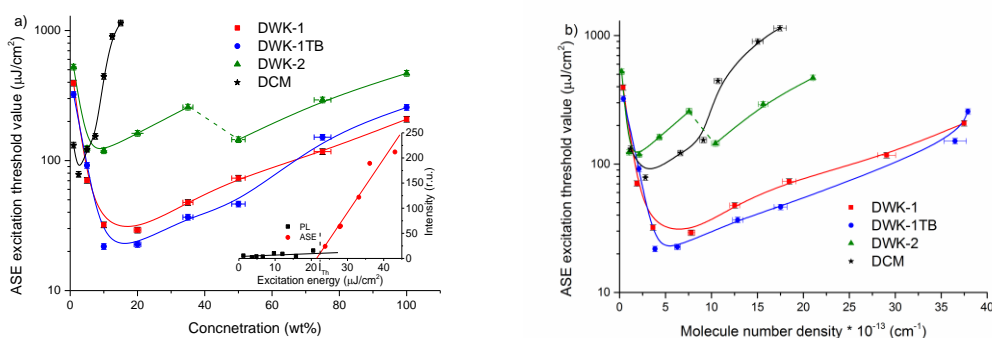

Figure 8. Amplified spontaneous emission excitation threshold energy for different dye a) concentration and b) molecule load in **PVK** matrix. Inset: determination of the ASE threshold energy.

ASE excitation threshold value was determined from the dependence of the light emission intensity of the excitation energy. Photoluminescence was detected at low excitation energy. Steep emission intensity increase was observed at ASE appearance. Both PL and ASE dependence could be described by the linear function. Determined excitation energy at the cross point of the lines is the ASE threshold value (see inset of Fig. 8a).

At low concentrations, ASE excitation threshold energy decreases by increasing molecule concentration in the polymer (see Fig. 8a). Threshold value sharply increases above a concentration of 2.5wt% for **DCM** compound. Similar concentration dependence characteristics were obtained in other work [40]. Threshold energy in the **DCM** derivatives systems increases from around 10 to 20 wt%. ASE excitation threshold energy below 100 $\mu J/cm^2$ ($10kW/cm^2$) could be obtained between 5 and 50 wt% of **DWK-1** and **DWK-1TB** systems. It provides emission spectra tuning within 25 nm by changing dye concentration. The lowest excitation energy (21 $\mu J/cm^2$, 2.1 kW/cm^2) was obtained for 20wt% **DWK-1TB:PVK** system. It is 4 times lower compared to the best system of **DCM:PVK** (80 $\mu J/cm^2$, 8 kW/cm^2).

The difference in molecular weight between the investigated compound is two to three times. Therefore molecule number density in the sample should be used instead of concentration (see Fig. 8b). Molecule number density in the samples was calculated by taking into account only the **PVK** density (1.2 g/cm^3). Now it can be seen that threshold energy is similar for all compounds below molecule density $2*10^{13}$ cm^{-2}. It was expected because the intermolecular interaction is still very low. Further increase of molecule density makes it worse for **DCM:PVK** system but not to **DWK-1** and **DWK-1TB** in **PVK** matrix.

Attached trityloxyethyl decrease intramolecular interaction between molecules thus it is possible to load higher density dye in the polymer matrix that reduces ASE excitation threshold energy. It means that **DWK-1** and **DWK-1TB** molecules in a polymer matrix could be perspective for laser media.

4. CONCLUSIONS

Bulky trityloxyethyl groups attached to the electron donor part of the **DCM** molecule prevents its aggregation in the polymer matrix which results in a slower decrease of photoluminescence quantum yield on the concentration. Photoluminescence and amplified spontaneous emission spectra of the investigated compounds in matrix exhibit solid state solvation effect which could be used for emission spectra tuning by changing laser dye concentration in the system. In the best case, such tuning could be done within 25 nm at the same time holding reasonable threshold energies. Amplified spontaneous emission switch between two maximums was observed for 35wt% **DWK-2:PVK** system. The

most probable reason could be intermolecular interaction which appears only at high concentration samples. Both **DWK-1** and **DWK-1TB** are perspective compounds for light amplification due to lower ASE threshold energy compared to well-known laser dye **DCM**. But if the yield of synthesis is taken into account than **DWK-1TB** is more perspective as it can be obtained with 6-fold higher yield.

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