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Glass-forming nonsymmetric DWK-dyes with 5,5,5-triphenylpentyl and piparazine moieties for light-amplification studies

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Abstract. A series of 2,6-bis-styryl-4*H*-pyran-4-ylidene fragment containing glass-forming organic compounds with bonded amorphous phase promoting bulky triphenyl moieties through piperazine structural fragment [2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4*H*-pyran-4ylidene)malononitrile derivatives (DWK)-T dyes] in a form of (5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-substituent attached to the 4*H*-pyran-4-yliden fragment in two-position have been synthesized and investigated as the potential light-amplification medium for organic solid-state lasers. DWK-T dye physical properties also depend on the structure of the other styryl-substituent attached to the 4*H*-pyran-4-ylidene backbone fragment in six-position. Thermal stability of synthesized dyes is above 312°C with the glass transitions from 97°C and up to 109°C. Obtained neat pure spin-cast films based on these compounds show photoluminescence with $\lambda_{\max}$ in range from 672 to 695 nm, ASE $\lambda_{\max}$ from 690 to 704 nm with ASE threshold values in range from 327 to 1091 $\mu\mathrm{J/cm}^2$, which are mostly influenced by the nature of the electron transition characteristics of various four substituents in a 6-styryl-fragment. The proposed synthetic approach could be useful for obtaining chemically stable and covalently bonded bulky triphenyl group containing glassy dyes, while the synthetic design allows to acquire different nonsymmetric 2,6-bis-styryl-4*H*-pyran-4-ylidene fragment-containing compounds for red and infrared light-emitting and light amplification applications. [DOI: 10.1117/1.JPE.8.046001]

Keywords: amplified spontaneous emission; laser dyes; 4*H*-pyran-4-ylidene; triphenyl moieties; piperazine moieties; molecular glasses.

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1 Introduction

Since Tang et al.[1] introduced the 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4*H*-pyran (DCM) laser dye, a great number of scientists around the world have been extensively studying the chemistry and physics of the mentioned dye. The number of citations (ISI Web of Science) of the first paper where DCM was reported[1] has reached over 2700. Various synthetic modifications of DCM-type derivatives have been obtained and investigated, mostly for potential applications in OLEDs, as dopants in the electroluminescence layer[2–4] and in DCM:Alq3 (tris(8-hydroxyquinolinato) aluminum) solid-state laser systems as the light-amplification or gain medium.[1,5–7] To maintain a high transparency and optical clarity of such systems, those are usually obtained by expensive and technologically complicated thermal evaporation in vacuum on the glass/indium tin oxide (ITO) substrates.[6–7]

Recently, we have demonstrated DCM-type dyes [= (2-(2-(4-(bis(2-(trityloxy)ethyl)amino) styryl)-6-methyl-4*H*-pyran-4ylidene)malononitrile derivatives (DWK)-type dyes] with additional incorporated bulky triphenyl moieties,[8–11] which provide the ability to form thin-solid films by non-expensive solution processing. Spin-coated neat films based on mono-styryl- and symmetric 2,6-bis-styryl-DWK-type dyes showed significantly increased photoluminescence quantum yields (PLQY) and notably lower amplified spontaneous emission (ASE) threshold energies in comparison

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with the conventional DCM dye.[8–11] However, the linking type of the bulky moieties via ether bonds is chemically unstable as de-trytilation may take place in slightly acidic conditions. It results in crystallization of the amorphous neat films, which leads to the decrease in the PLQY and increase in the ASE threshold values of the light-amplification medium. To prevent these drawbacks, a series of 2,6-*bis*-styryl-4*H*-pyran-4-ylidene fragment containing glass-forming organic compounds with the chemically stable bonding of bulky triphenyl moieties through piperazine structural fragment in a form of 2-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-substituent have been synthesized and investigated. As the other styryl-substituents attached to the 4*H*-pyran-4-ylidene backbone fragment in six-position contain a different substituent, the resulting bis-DWK-type dyes are no longer symmetrical. Such a synthetic approach has been briefly introduced in Refs. 12 and 13 using 3-cinnamoyl-substituted-4-hydroxy-6-methyl-2*H*-pyrane-2-ones[14] as the starting reactants; however, other nonsymmetric bis-DCM or bis-DWK-type dyes so far to the best of our knowledge have not been reported. The approach used for the synthesis of nonsymmetric bis-DWK-dyes also enables the physical property tuning possibility through the incorporation of various functional groups within the 6-styryl-fragment. Full preparation of dyes, obtained dye structural relation with their thermal, glass-forming, light-absorption, light-emitting, and ASE properties are discussed in this report.

2 Results and Discussion

2.1 *Synthesis of Dyes*

Glass-forming bis-DWK-type compounds have been obtained according to the scheme shown in Fig. 1. 2-Styryl-substituted-6-methyl-4*H*-pyran-4-ylidene derivatives 4a, 4b, 4c, and 4e were

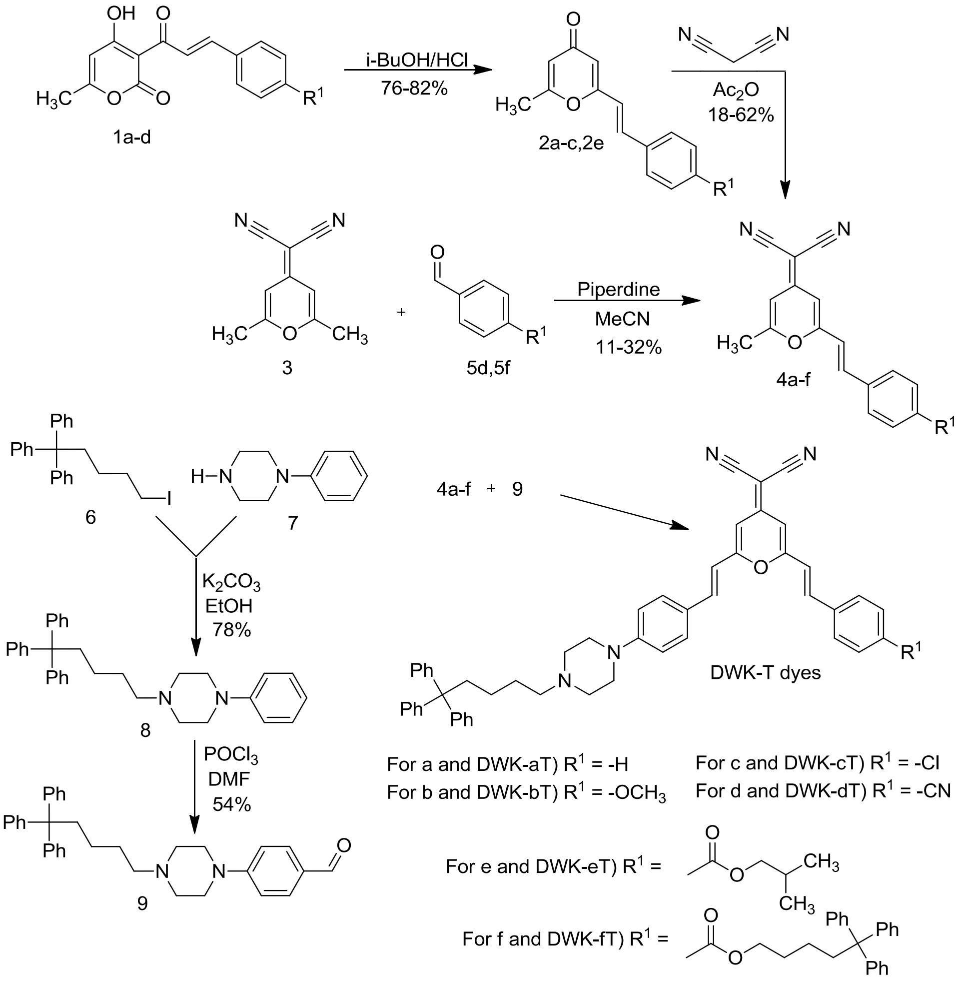

Fig. 1 Synthesis of nonsymmetric bis-styryl-DWK-type glassy dyes.

Table 1 Yields and thermal properties of glass-forming DWK-T compounds.

Structure	R^1	Yield, (%)	T_g, (°C) first heating	T_g, (°C) second heating	m.p., (°C)	T_d, (°C)
DWK-aT	-H	93	107	n/o	162	333
DWK-bT	$-OCH_3$	73	102	101	164	333
DWK-cT	-Cl	36	110	109	164	312
DWK-dT	-CN	11	n/o	n/o	155	318
DWK-eT	$-COO-CH_2CH(CH_3)_2$	56	n/o	97	n/a	n/a
DWK-fT	$-COO-(CH_2)_4CPh_3$	36	n/o	n/o	n/a	n/a

Note: Substituent R^1 is incorporated in four-position within the 6-styryl-fragment; T_g, glass transition temperature; m.p., melting point; T_d, thermal decomposition temperature at the level of 5% weight loss; n/o, not observed; and n/a, not applicable.

obtained in "Fries rearrangement" of 3-cinnamoyl-substituted-4-hydroxy-6-methyl-2*H*-pyran-2-ones 1a–d[14] and subsequent "Knoevenagel" condensation reactions[8,10] with malononitrile of the afforded 2-styryl-substituted-6-methyl-4*H*-pyran-4-ones 2a, 2b, 2c, and 2e. It is worth to mention that "Fries rearrangement" of 4-(3-(4-hydroxy-6-methyl-2-oxo-2*H*-pyran-3-yl)-3-oxoprop-1-enyl)benzonitrile (1d) resulted in additional hydrolysis of cyano-group with further esterification in acidic conditions affording isobutyl 4-(2-(6-methyl-4-oxo-4*H*-pyran-2-yl)vinyl) benzoate (2e). Therefore, a different synthetic approach was applied to obtain 2-styryl-substituted-6-methyl-4*H*-pyran-4-ylidene derivatives 4d and 4f, respectively. These key compounds were obtained from 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile (3)[8] in "Knoevenagel" condensation reactions[8,10] with benzaldehydes 5d and 5f. 4-(4-(5,5,5-Triphenylpentyl)piperazin-1-yl)benzaldehyde (8) required for the formation of final products was synthesized from and (5-iodopentane-1,1,1-triyl)tribenzene (6)[15] and 1-phenylpiperazine (7) followed by the "Vilsmeier–Haack" formilation[8,15] of the intermediate 8. DWK-T dyes were successfully synthesized from 4*H*-pyran-4*H*-ylidene derivatives 4a–f in reaction with 4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)benzaldehyde (9) and investigated further.

The highest yields and thermal stabilities among the obtained DWK-T dyes (see Table 1) were observed for compounds with 6-styryl-(DWK-aT) and 6-(4-methoxy-)styryl-(DWK-bT) fragments. Dyes with 6-(4-chloro-)styryl- (DWK-cT) and 6-(4-cyano-)styryl-(DWK-dT) showed notably lower yields of synthesis due to the electron withdrawing nature of –Cl and –CN groups. Dyes DWK-eT and DWK-fT contain significantly weaker electron withdrawing carboxyl-alkyl groups in comparison with strong electron withdrawing cyano-group (DWK-dT) and therefore were obtained in satisfactory yields. The increased yield of synthesis for DWK-eT over DWK-fT is explained by the smaller sterical dimensions of isobutyl group in comparison with 5,5,5-triphenylpentyl group.

2.2 *Thermal and Glass-Forming Properties*

Introducing substituents in four-position (R^1) with electron withdrawing properties (DWK-cT, DWK-dT, and DWK-eT) reduced thermal stabilities by 15 to 20 °C (see Table 1) but increased glass transition (T_g up to 109°C for DWK-cT) in comparison to glasses with neutral (DWK-aT) or weak electron donating groups (DWK-bT). The stabilities of the amorphous state in DWK-dT and DWK-fT were insufficient to detect their glass transitions. Dye DWK-aT showed best film quality (see Fig. 2) followed by dyes (DWK-bT, DWK-cT, and DWK-dT) with sterically small substitutent at four-position (R^1). Even though DWK-dT contains a strong electron withdrawing moiety (R^1 = -CN) within the 6-styryl-fragment, fewer crystallites were observed in its neat film in comparison with DWK-bT and DWK-cT. One of the explanations would be the dual nature of -Cl and $-OCH_3$ groups within the dyes DWK-bT and DWK-cT. Both groups contain unpaired electrons that could be dislocated (or "given") to the rest of the molecule upon excitation. From the other hand, due to the electronegativity of chlorine and oxygen, the electrons are "pulled"

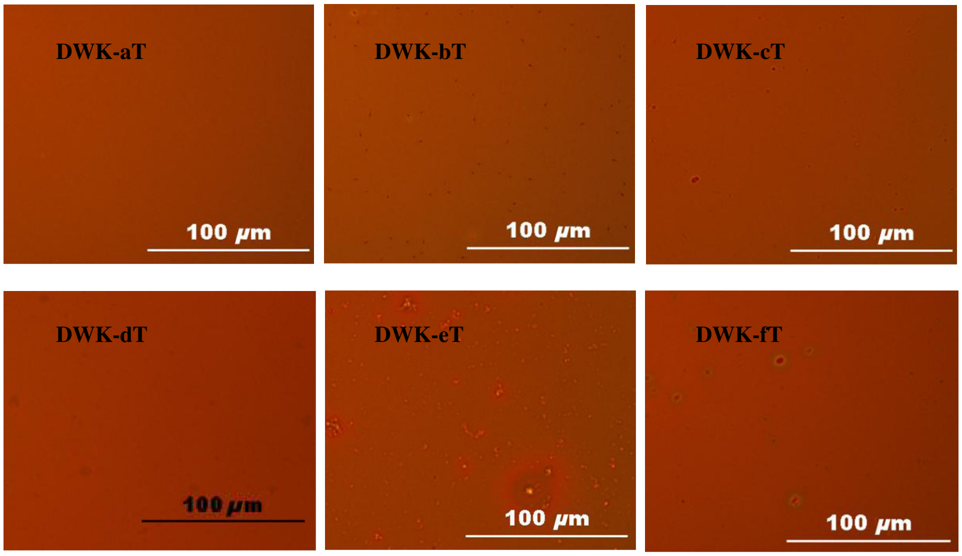

Fig. 2 Optical microscope images (magnification ×1000) of the pure films of the investigated DWK-T dyes. Dots on the neat film surface represent compound crystalline state, while the rest smooth area shows an amorphous solid state.

from the molecule. Such electron transition effects may facilitate additional interaction between the corresponding dye molecules in their solid state, which would result in crystallization. Although one amorphous structure promoting 2-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-fragment is covalently incorporated within the dye chemical structure, the large sterical dimensions of the substituent at four-position (R^1) in 6-styryl-group for DWK-eT and DWK-fT lead to a decreased optical quality of their spin-cast films.

The incorporation of sterically large substituent with an average electron withdrawing properties (-COO-) at four-position (DWK-eT and DWK-fT) most likely makes the 6-styryl- fragment to become the additional electron acceptor part of the chromophore instead of an amorphous phase-promoting moiety. That also makes the dimensions of a single 5,5,5-triphenylpentyl bulky group insufficient to ensure the complete amorphous structure in the solid state of the corresponding DWK-T dye molecules. Therefore, a small substituent would be the best choice in the design of dyes with similar chemical structures.

Table 2 Optical and ASE characteristics of synthesized DWK-T dyes in pure thin films.

Structure	R^1	λ_{abs}, nm	λ_{PL}, nm	PLQY, %	λ_{ASE}, nm	E_{th}, $\mu J/cm^2$
DWK-aT	-H	486 ± 2	672 ± 3	1.84 ± 0.15	691 ± 2	1091 ± 50
DWK-bT	$-OCH_3$	486 ± 2	672 ± 3	2.86 ± 0.15	698 ± 2	327 ± 30
DWK-cT	-Cl	492 ± 2	689 ± 3	0.62 ± 0.15	704 ± 2	462 ± 30
DWK-dT	-CN	487 ± 2	*n/o*	*n/a*	*n/a*	*n/a*
DWK-eT	$-COO-CH_2CH(CH_3)_2$	495 ± 2	695 ± 3	0.59 ± 0.15	*n/o*	*n/a*
DWK-fT	$-COO-(CH_2)_4CPh_3$	495 ± 2	691 ± 3	1.97 ± 0.15	n/o	n/a

Note: Substituent R^1 is incorporated in four-position within the 6-styryl-fragment; λ_{abs}—wavelength of the most red-shifted absorption maximum, responsible for intermolecular charge transfer upon excitation; λ_{PL}—wavelength of photoluminescence maximum; PLQY—photoluminescence quantum yield; λ_{ASE}—wavelength of amplified spontaneous emission maximum; E_{th}—irradiation threshold energy density at which amplified spontaneous emission appears; n/o, not observed; n/a, not applicable.

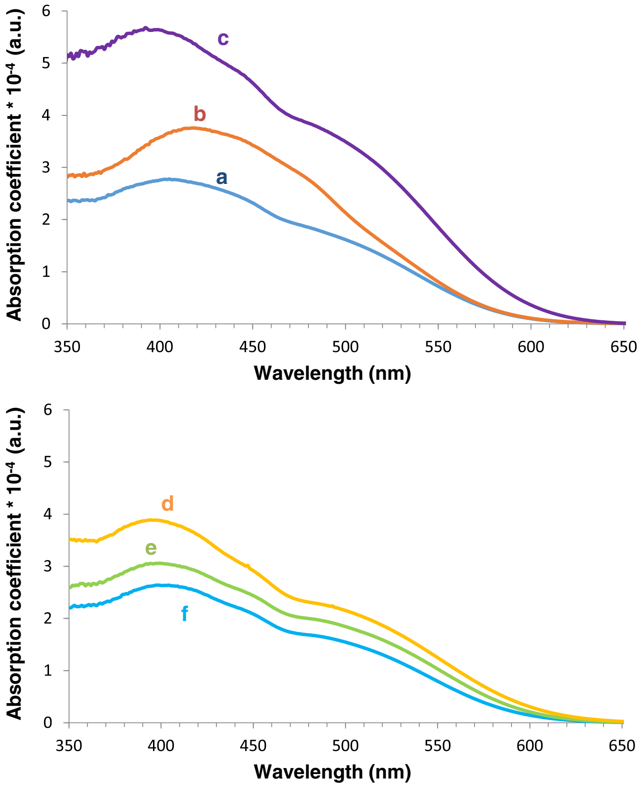

Fig. 3 Absorption spectra of compounds in pure spin-cast films. (a) DWK-aT, (b) DWK-bT, (c) DWK-cT, (d) DWK-dT, (e) DWK-eT, and (f) DWK-fT.

2.3 *Optical and Amplified Spontaneous Emission Properties*

Light absorption, photoluminescence, and ASE characteristics in pure solution-processed DWK-T dye films are shown in Table 2 and (Figs. 3 and 4)[13] Fig. 5. All dyes were excited at their absorption maxima for PL and ASE properties determination.

Introducing substituents (R^1) with stronger electron withdrawing properties at the four-position in 6-styryl-fragment in DWK-dT, DWK-eT, and DWK-fT dyes lead to a small bathochromic shift of PL; however, it had less influence on absorption.

The most red-shifted maximum (see Fig. 3) varying from 485 to 495 nm corresponds to the electron transitions from 2-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl) an electron donating part of the molecule to the malononitrile electron acceptor groups in a similar way as described in the previously investigated mono-styryl-4*H*-pyran-4-ylidene fragment containing glassy compounds.[8–10]

The strong electron withdrawing properties of -CN group within R^1 in DWK-dT was most likely the reason why no PL was observed from its neat film. Authors believe that such a functional group causes strong intramolecular interaction and photoluminescence quenching processes take place. Under certain conditions, some -CN group containing organic molecules can be found, which emit light in solid and aggregated forms Ref. 14. Such a physical phenomenon is known as aggregation-induced emission (AIE), which is contrary to quenching. Even though some triphenyl groups are incorporated within the DWK-T dyes, DCM- and DWK-type compounds are typical quenching type molecules.[8–9,11] A well-written distinction between quenching type and AIE-type compounds can be found elsewhere.[15]

Dyes DWK-bT and DWK-cT showed up to three times lower ASE excitation threshold values (327 to 462 μJ/cm^2 due to the already mentioned dual nature of -Cl and -OCH$_3$ groups in comparison with 6-styryl fragment containing dye DWK-aT (1091 μJ/cm^2). As the main charge transfer process occurs from the ((5,5,5-triphenylpentyl)piperazin-1-yl)styryl- electron donor part to the malononitrile electron acceptor fragment, additional functional groups within the other styryl-fragment can contribute to this process either by providing an electron upon

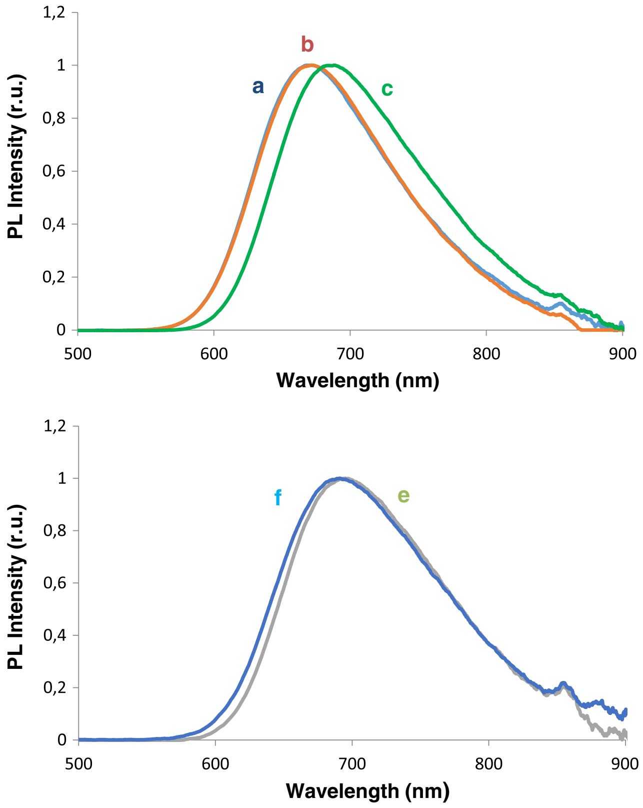

Fig. 4 Photoluminescence spectra of compounds in pure spin-cast films. (a) DWK-aT, (b) DWK-bT, (c) DWK-cT, (e) DWK-eT, and (f) DWK-fT.

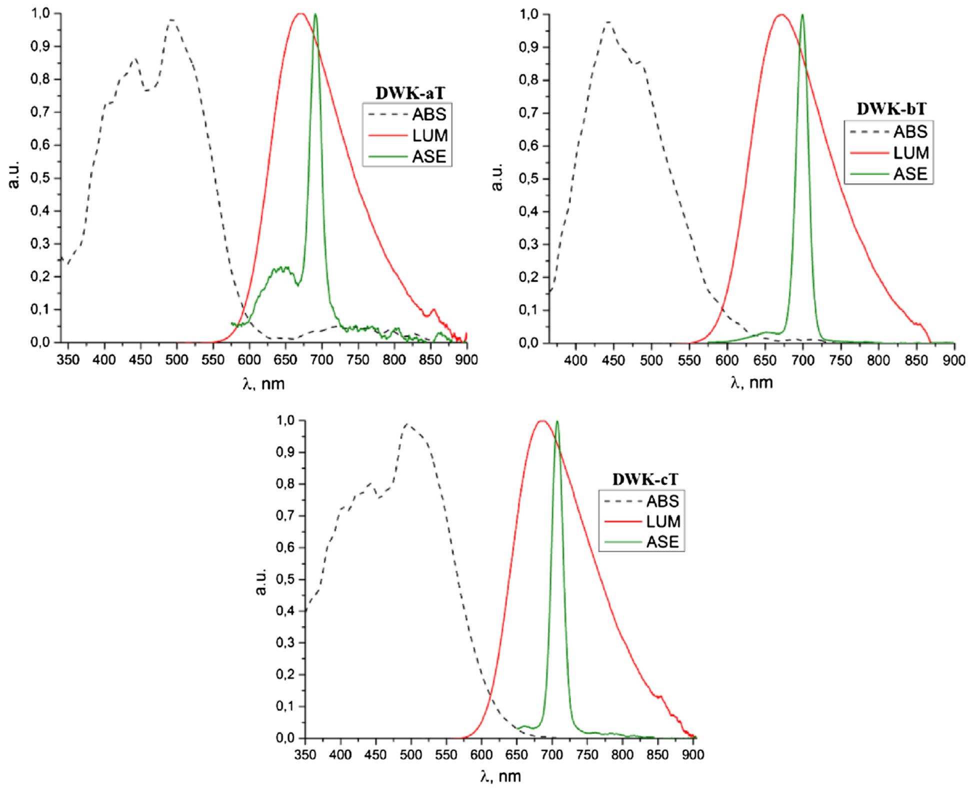

Fig. 5 Optical phenomena of several DWK-T dyes in neat films. ABS—absorption, LUM—photoluminescence, and ASE—amplified spontaneous emission.

excitation or accept an electron upon relaxation. It resulted in enhancing the ASE processes within dye DWK-bT and DWK-cT molecules. 6-Styryl-fragment within DWK-aT can also contribute to these electron transitions to some extent, so ASE is still observed with higher laser irradiation energy. From these three dyes, the highest PLQY values were observed for DWK-bT and DWK-aT. Dyes DWK-dT, DWK-eT, and DWK-fT contain substituents (R^1) with electron withdrawing properties only, which is the main reason why no ASE was observed. There is no direct relation between PLQY and ASE excitation threshold energy. We have to take in mind that ASE will appear when optical gain will be bigger than optical loses. Optical loses are related to self-absorption and the quality of the waveguide, like refraction index difference between thin film and substrate, scattering centers in the thin film, and roughness of the surface. Additionally light absorption also will influence the ASE excitation threshold value. Deeper investigation should be done to clarify the most probably reason of differences in ASE excitation threshold values or ASE absence. Most of the previously mentioned optical loses could be reduced by doping DWK-T dyes in a polymer matrix similarly as reported for DWK-type compounds obtained previously.[8–9,11]

3 Conclusions

Six 2-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-6-(4-substituted)-styryl-4*H*-pyran-4-ylidene fragment containing glass-forming DWK-T dyes have been synthesized. Introduction of sterically large substituents with electron withdrawing properties at four-position in 6-styryl-fragment was insufficient to prevent PL quenching caused by the close interaction of molecules in the solid state. This resulted in no ASE effect to be observable, notably decreased the quantum yield of spin-coated thin films, decreased thermal stability, but slightly increased the glass transition, and red-shifted the photoluminescence maximum of the corresponding final products. Incorporation of sterically small -Cl and -OCH_3 groups with dual nature of their electron transition characteristics slightly decreased thermal stability and glass-forming ability, practically had no effect on light absorption, PL, and glass transition. However, such modification notably improved ASE properties of the respective dyes by lowering the ASE irradiation threshold energy density up to three times in comparison to dye DWK-aT with no additional substituents in a 6-styryl fragment. The proposed synthetic approach could be useful for obtaining stable covalently bonded bulky triphenyl group containing glassy compounds, although the presence of more amorphous phase promoting moieties would be required to improve the glass-forming and thermal properties. At the same time, DWK-T dyes with a sterically small four-substituent in a 6-styryl fragment and the possible dual nature of their electron transitions show potential as materials for red/infrared light-emitting and light amplification studies.

4 Materials and Methods

4.1 *Synthesis and Characterization of Compounds*

General method (I)[16] of synthesis of compounds 2a-c,e. About 117.00 mmol of the respective 3-cinnamoyl-substituted-4-hydroxy-6-methyl-2*H*-pyrane-2-one (one from 1a–d) was suspended in a mixture of 200 mL of either n-butyl alcohol or 2-methylpropan-1-ol and 120-mL concentrated (12M) hydrochloric acid. The obtained mixture was refluxed for 6 hours until the formation of gas had somewhat suspended. The majority of the solvents were removed by distillation under the reduced pressure leaving about 20 mL of reaction mixture. Afterward, the crude liquid was put in a fridge (in around 0°C to +5°C) to cool down for 30 min. The afforded precipitates were filtered and dried. Obtained products could be purified by several recrystallizations from various alcohols; however, in our research the obtained intermediates were used in the next reaction step without additional purification.

2-Methyl-6-styryl-4*H*-pyran-4-one (2a). Yield: 82.1%; m.p. 170°C.

2-(4-Methoxystyryl)-6-methyl-4*H*-pyran-4-one (2b) Yield: 75.6%; m.p. 175°C.

2-(4-Chlorostyryl)-6-methyl-4*H*-pyran-4-one (2c). Yield: 82.2%; m.p. 154°C.

4-(2-(6-Methyl-4-oxo-4*H*-pyran-2-yl)vinyl)benzonitrile (2d). Unfortunately, the 2.08 g of the obtained yellow solid mostly contained a different compound—isobutyl 4-(2-(6-methyl-4-oxo-4*H*-pyran-2-yl)vinyl)benzoate (2e). It was used in further reactions as obtained.

General Method (II)[10] of synthesis of compounds 4a–c,e. A solution of the respective 2-styryl-substituted-6-methyl-4*H*-pyran-4-one (one from 2a–c,e) (10.0 mmoL) and malononitrile (10.0 mmoL) in acetic anhydride (5.0 mL) was stirred for 8 h at 110°C to 120°C, then left overnight to cool to the room temperature. Afforded precipitates were filtered, washed with cold methyl alcohol (20 mL), dried and in most cases used in the next step of synthesis without any further purification.

2-(2-Methyl-6-styryl-4*H*-pyran-4-ylidene)malononitrile (4a). Yield: 33.2%; m.p. 207-208 °C; ^{1}H-NMR (400 MHz; $CDCl_3$) δ, ppm.: 2.35 (3H, s), 6.49 (1H, s), 6.63 (1H, s), 6.67 (1H, s), 7.35 (4H, m), 7.47 (2H, dd, $^3J = 7.5$ Hz, $^4J = 1.9$ Hz).

2-(2-(4-Methoxystyryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile (4b). Yield: 62.0%; m.p. 262°C; ^{1}H-NMR (400 MHz; $CDCl_3$) δ, ppm.: 2.33 (3H, s), 3.80 (3H, s), 6.46–6.60 (3H, m), 6.88 (2H, d, $^3J = 8.6$ Hz), 7.34 (1H, d, $^3J = 16.0$ Hz), 7.43 (2H, d, $^3J = 8.6$ Hz).

2-(2-(4-Chlorostyryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile (4c). Yield: 43.5%; m.p. 264°C; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 2.35 (3H, s), 6.49 (1H, s), 6.62 (1H + 1H, d, $^3J = 15.8$ Hz), 7.39–7.43 (5H, m).

Isobutyl 4-(2-(4-(dicyanomethylene)-6-methyl-4*H*-pyran-2-yl)vinyl)benzoate (4e). Yield: 17.6%; m.p. 200°C; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 0.98 (6H, d, $^3J = 6.7$ Hz), 2.05 (1H, m), 2.36 (3H, m), 6.51 (1H, s), 6.72 (2H, m), 7.40 (1H, d, $^3J = 16.1$ Hz), 7.54 (2H, d, $^3J = 8.4$ Hz), 8.03 (2H, d, $^3J = 8.3$ Hz).

General method (III)[8] of synthesis of compounds 4d and 4f. To a solution of 2-(2,6-dimethyl-4*H*-pyran-4-ylidene)malononitrile (3) (10.0 mmoL) and the respective benzaldehyde (5d or 5f) (5.0 mmoL) in acetonitrile (30.0 mL) five drops of piperidine were added. The reaction mixture was stirred under reflux for 8 h and then left overnight to reach room temperature. Afforded precipitate was filtered off and the filtrate was evaporated under reduced pressure to dryness. The crude product was then further purified by flash chromatography (silicagel, dichloromethane).

2-(2-(4-Cyanostyryl)-6-methyl-4*H*-pyran-4-ylidene)malononitrile (4d). Yield: 11.1%; m.p. 275°C; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 2.36 (3H, s), 6.51 (1H, s), 6,72 (2H, m), 7.35 (1H, d, $^3J = 16.1$ Hz), 7.56 (2H, d, $^3J = 8.3$ Hz), 7.65 (2H, d, $^3J = 8.3$ Hz).

5,5,5-Triphenylpentyl 4-(2-(4-(dicyanomethylene)-6-methyl-4*H*-pyran-2-yl)vinyl)benzoate (4f). Yield: 32%; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.30 (2H, m), 1.82 (2H, m), 2.45 (3H; s), 2.67 (2H, m), 4.30 (2H, t, $^3J = 6.5$ Hz), 6.59 (1H, d, $^4J = 1.0$ Hz), 6.78 (1H, d, $^4J = 1.0$ Hz, 6.83 (1H, d, $^3J = 16.1$ Hz), 7.10–7.35 (15H, m), 7.49 (1H, d, $^3J = 16.1$ Hz), 7.60 (2H, d, $^3J = 8.4$ Hz), 8.00 (2H, d, $^3J = 8.3$ Hz.

1-Phenyl-4-(5,5,5-triphenylpentyl)piperazine (8). To a solution of 5,5,5-triphenylpentan-1-iodide (6),[17] (5.00 g, 11.74 mmoL) in warm ethanol (10 mL) 1-phenyl-piperazine (7) (1.35 mL, 9.05 mmoL) was added, followed by potassium carbonate (1.62 g, 11.74 mmoL). The reaction mixture was refluxed for 48 h, then cooled down to room temperature. The solvent was removed under reduced pressure and the remaining residue was diluted with 50-mL distilled water and extracted four times with dichloromethane (25 mL each time). The combined organic phases were dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure. The obtained crude product was purified by flash chromatography (dichloromethane/ethyl acetate (v3/v1), silicagel) yielding 4.03 g (77.5%) of 1-phenyl-4-(5,5,5-triphenylpentyl)piperazine (8) as an oily yellow liquid. ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.16 (2H, m), 1.60 (2H, m), 2.36 (2H, m), 2.63 (6H, m), 3.23 (2H, m), 6.80 (1H, t, $^3J = 7.3$ Hz), 6.97 (2H, d, $^3J = 8.1$ Hz), 7.25 (17H, m).

4-(4-(5,5,5-Triphenylpentyl)piperazin-1-yl)benzaldehyde (9). DMF (1.51 mL, 20.83 mmoL) was cooled to 0°C…5°C and $POCl_3$ (1.94 mL, 20.83 mmoL) was slowly added. The obtained solution was stirred at the 0°C…5°C temperature for 1 h. 1-Phenyl-4-(5,5,5-triphenylpentyl) piperazine (8) (4.75 g, 10.40 mmoL) was added to the reaction mixture and it was heated at 70°C for 5 h, then poured onto crushed ice (~100 g). The formed suspension was neutralized with sodium acetate trihydrate (11.34 g, 83.32 mmoL) until pH 7 and the product was extracted four times with ethyl acetate (30 mL each time). Afterward the combined extract was dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and the obtained product was purified by flash chromatography (dichloromethane/ethyl acetate (v5/v1), silicagel) yielding 2.70 g (53.6%) of 4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)benzaldehyde (9) as a white solid substance. ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.19 (2H, m), 1.60 (2H, m), 2.36 (2H, m), 2.57 (4H, m), 2.65 (2H, m), 3.42 (4H, m), 6.93 (2H, d, $^3J = 8.9$ Hz), 7.25 (15H, m), 7.78 (2H, d, $^3J = 8.8$ Hz), 9.81 (1H, s).

General method (IV) of synthesis of DWK-T derivatives.[8,10] To a solution of the corresponding 2-styryl-substituted-6-methyl-4*H*-pyran-4-ylidene derivative (one from 4a–f) (1.00 mmoL) and 4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)benzaldehyde (9) (1.00 mmoL) in dry pyridine (5 mL), three drops of piperidine were added. The reaction mixture was stirred for 8 h at 90°C to 100°C, then left overnight to cool down to room temperature. The dark-red slurry was poured into 100-mL ethanol and the formed precipitates were filtered, washed with 10-mL cold methanol, dried, and then purified using flash chromatography (silicagel, V(ethyl acetate)/V(dichloromethane = from 1/4 to 1/10).

2-(2-Styryl-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-4-ylidene)malononitrile (DWK-aT with R^1 = -H). Yield: 97%; m.p. 162°C; ^{1}H-NMR (300 MHz; DMSO-d_6) δ, ppm.: 1.06 (2H, m), 1.49 (2H, m), 2.26 (2H, m), 2.50 (6H, m), 3.27 (4H, m), 6.50 (1H, s), 6.55 (1H, s), 6.58 (1H, d, $^4J = 1.6$ Hz), 6.62 (1H, m), 6.86 (2H, d, $^3J = 8.6$ Hz), 7.10–7.30 (16H, m), 7.35–7.46 (6H, m), 7.52 (2H, m).

2-(2-(4-Methoxystyryl)-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-4-ylidene)malononitrile (DWK-bT with $R^1 = -OCH_3$). Yield: 73%; m.p. 164°C; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.13 (2H, m), 1.57 (2H, m), 2.34 (2H, m), 2.58 (6H, m), 3.33 (4H, m), 3.85 (3H, s), 6.51–6.60 (4H, m), 6.87–6.97 (4H, m), 7.10–7.35 (15H, m), 7.38–7.54 (4H, m).

2-(2-(4-Chlorostyryl)-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-4-ylidene)malononitrile (DWK-cT with R^1 = -Cl). Yield: 36%; m.p. 164°C; ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.13 (2H, m), 1.56(2H, m), 2.32 (2H, m), 2.54 (6H, m), 3.32 (4H, m), 6.52–6.68 (4H, m), 6.90 (2H, d, $^3J = 8.3$ Hz, 7.10–7.35 (15H, m), 7.38–7.52 (8H, m).

2-(2-(4-Cyanostyryl)-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-4-ylidene)malononitrile (DWK-dT with R^1 = -CN). Yield: 11%; m.p. 155°C; IR (paraffinic oil) υ, cm^{-1}: 2918, 2848, 2812, 2764, 2226, 2205, 1959, 1638, 1609, 1597, 1546, 1492, 1302, 1247, 1203, 1176, 1104. ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 1.06 (2H, m), 1.51 (2H, m), 2.27 (2H, m), 2.46–2.58 (6H, m), 3.28 (4H, s), 6.53 (1H, d, $^3J = 15.9$ Hz), 6.59 (2H, d, $^4J = 2.0$ Hz), 6.67 (1H, d, $^4J = 2.0$ Hz), 6.79 (1H, d, $^3J = 16.1$ Hz), 6.85 (2H, d, $^3J = 8.8$ Hz), 7.10–7.30 (15H, m), 7.36–7.46 (4H, m), 7.61 (2H, d, $^3J = 8.4$ Hz), 7.68 (2H, d, $^3J = 8.4$ Hz).

Isobutyl 4-(2-(4-(dicyanomethylene)-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-2-yl)vinyl)benzoate (DWK-eT with $R^1 = -COOCH_2CH(CH_3)_2$). Yield: 56%; IR (paraffinic oil) υ, cm^{-1}: 2943, 2205, 1716, 1639, 1594, 1492, 1176. ^{1}H-NMR (300 MHz; $CDCl_3$) δ, ppm.: 0.99 (6H, d, $^3J = 6.5$ Hz), 1.09 (2H, m), 1.51 (2H, m), 2.05 (1H, m), 2.27 (2H, m), 2.50 (6H, m), 3.28 (4H, m), 4.08 (2H, d, $^3J = 6.4$ Hz), 6.50–6.66 (3H, m), 6.74–6.88 (3H, m), 7.10–7.35 (15H, m), 7.38–7.50 (4H, m), 7.58 (2H, d, $^3J = 7.8$ Hz, 8.05 (2H, d, $^3J = 7.7$ Hz).

5,5,5-Triphenylpentyl 4-(2-(4-(dicyanomethylene)-6-(4-(4-(5,5,5-triphenylpentyl)piperazin-1-yl)styryl)-4*H*-pyran-2-yl)vinyl)benzoate (DWK-fT with $R^1 = -COO(CH_2)_4CPh_3$). Yield: 36%; IR (paraffinic oil) υ, cm^{-1}: 2944, 2209, 1706, 1645, 1493, 1177. ^{1}H-NMR (300MHz; $CDCl_3$) δ, ppm.: 1.08 (2H, m), 1.19 (2H, m), 1.53 (2H, m), 1.75 (2H, m), 2.27 (2H, m), 2.48–2.58 (8H, m), 3.28 (4H, m), 4.22 (2H, m), 6.50–6.68 (3H, m), 6.76–6.88 (3H, m), 7.10–7.35 (30H, m), 7.39–7.51 (4H, m), 7.55 (2H, d, $^3J = 7.7$ Hz), 7.94 (2H, d, $^3J = 7.9$ Hz).

4.2 *Sample Preparation and Measurement Systems*

Thermogravimetric analysis (TGA) measurements were made using "Simultaneous Thermal Analyzer STA 6000". Thermal decomposition temperatures (T_d) of compounds were determined in the temperature range from +30°C to +510°C at a heating rate of 10°C/min at the level of 5% weight loss. Differential scanning calorimetry (DSC) measurements were carried out using "Mettler Toledo DSC 1/200W" equipment under a nitrogen atmosphere. Three thermo cycles were performed for the determination of glass transition temperature (T_g). The first scan was conducted within the temperature range from +25°C to +250°C at a heating rate of 10°C/min. After the first heating, scan samples of the compounds were cooled to 25°C at a rate of 50°C/min and heated for a second time from +25°C to +250°C at a rate of 10°C/min. Whenever possible, the T_g values were obtained from the first and second heating scans.

The thin films on a glass substrate were prepared for the absorption, photoluminescence (PL), and ASE measurements. Prior to the deposition of the thin organic layers, the substrates were cleaned in dichloromethane. Dye solutions of chloroform with 30 mg/mL concentration were spin-cast on glass substrates for 40 s at a spin speed of 800 rpm and acceleration of 800 rpm/s and then dried at 85°C for 10 min. Thicknesses of the produced films were measured by surface profiler "Dektat 150" and were about 300 nm. Absorption spectra of the thin films were measured by an "Ocean Optics HR4000 spectrometer." Photoluminescence spectra and quantum yield (PLQY) were measured by the calibrated system Fluorescence spectrometer "Pico Master 1 (Photo Med GmbH)". It consists of a xenon lamp—monochromator—integrated sphere—monochromator—detector. Spectral resolution was set to 2 nm. The excitation wavelength was chosen at the absorption maximum for each compound. First, excitation and emission spectrum were obtained when only glass slide was in the sphere. After which excitation and emission spectrum were recorded when the thin film was in the sphere. All four spectra were used for PLQY calculation. Setup for ASE measurement is described elsewhere.[11]

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