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# NOVEL AMORPHOUS RED ELECTROLUMINESCENCE MATERIAL BASED ON PYRANYLIDENE INDENE-1,3-DIONE DERIVATIVE

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The organic light emitting diode (OLED) is a promising device for future technologies, like flat panel displays and novel light sources. So far the OLED structures have mostly been made by thermal evaporation in vacuum. An alternative approach is to use small molecules which form solid state with glassy structure from solutions. Such compounds can be used in the ink-jet printing technologies and result in reducing the OLED prices.

In this paper, we present an original red fluorescent organic compound 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK1), with the maximum of the photoluminescence spectrum for solid state at 657 nm. The structure of the electroluminescent device was ITO/PEDOT:PSS (40 nm)/ZWK1 (120 nm)/LiF (1 nm)/Al (100 nm). The electroluminescence spectra correspond to the CIE coordinates $x = 0.65$ and $y = 0.34$ with the maximum at 667 nm. The power and luminance efficiency at the luminance of 100 cd/m$^2$ is 0.43 lm/W and 1.97 cd/A, respectively.

**Key words:** *OLED, red fluorescent material, amorphous material.*

## 1. INTRODUCTION

Organic light emitting diodes (OLEDs) have attracted particular interest among scientists and engineers due to potential applications in flat panel displays and novel light sources [1–3]. The OLED systems are mostly made by thermal evaporation of small organic molecules in vacuum. To achieve higher efficiencies, such a system is formed by more than three layers [4–6]. In the last ten years polymer electroluminescence materials have become more promising because of the cheaper and simpler deposition technique, i.e., deposition of thin films from solutions [7, 8]. The drawback of polymers is repetition of the results of synthesis. The mentioned above small organic molecules, which can make a solid-state glassy structure prepared from solutions [9], could become the key for cheap deposition and easier synthesis.

In this work, we present the optical and electro-optical properties of original red emitting organic compound 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK1) capable of forming a thin film from solution.

## 2.1. Synthesis of red florescent organic compound

All the necessary reagents were purchased as commercial products from *ACROS* and *ALDRICH*. When required, solvents (pyridine and methylene chloride) were dried by refluxing with calcium hydride and distilled. The $^{1}$H-NMR spectrum was obtained on a Varian VRX-Unity NMR spectrometer (400 MHz).

The steps of ZWK1 synthesis are shown in Fig. 1. The spectral data, characteristics and detailed description of the synthesis are given only for the final product; however intermediate products have been characterized and confirmed by the $^{1}$H-NMR spectral data.

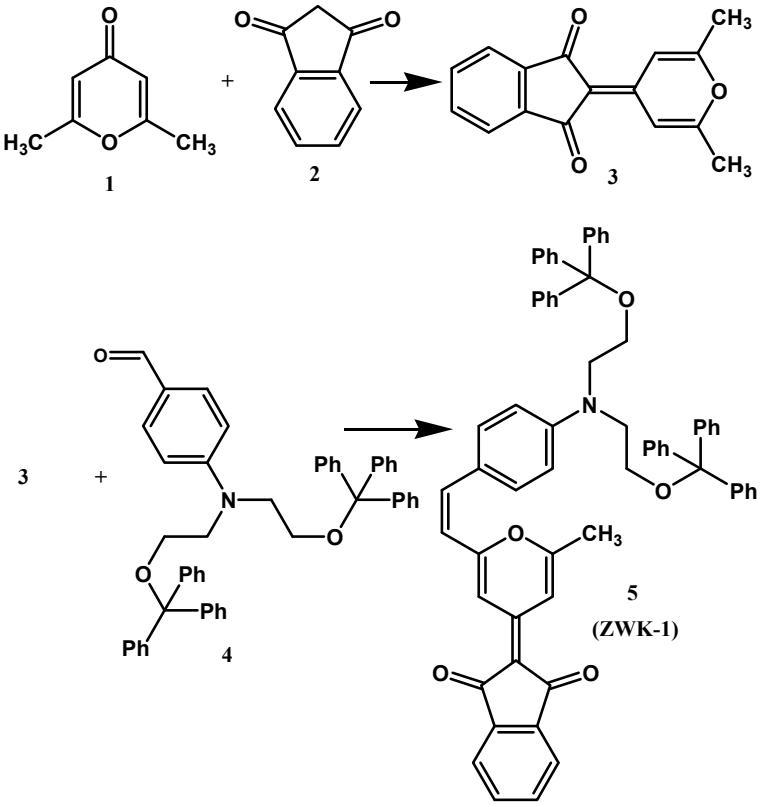



*Fig. 1.* Synthesis of ZWK1.

### *2.1.1. Synthesis of 2-(2,6-dimethyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione*

A mixture of 2,6-dimethylpyran-4-one (**1)** (7.56 g, 61.0 mmol), indan-1,3-dione (**2**) (8.91 g, 61.0 mmol) and acetic anhydride (20.0 ml) were refluxed for 4 hours. After cooling the solution, the obtained pale yellow solid was filtered and washed with 50 ml cold methanol. Yield: 10.88 g (70.7%) of brownish yellow solid with m.p. 250 $^{o}$C [10]. The obtained compound (**3**) could be recrystallized from huge amount of methanol, but it is pure enough to use in further reactions without recrystallization.

*2.1.2. Synthesis of 2-(2-(4-(bis(2-(trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK1)*

A solution of 2-(2,6-dimethyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (**3**) (0.30 g, 12.0 mmol) and 4-(bis(2-(trityloxy)ethyl)amino)benzaldehyde (**4**) (0.82 g, 12.0 mmol) in 10 ml dry pyridine was refluxed for 8 hours. A red fluorescent color was observed during the reaction. The reaction was controlled with TLC (dichloromethane, silicagel) by the quantity of compound **3** in solution of reaction. The solution was cooled to room temperature and poured in 20 ml isopropylalcohol after compound **3** was fully reacted. As a result, the dark red product was obtained. The compound ZWK1 was purified using the liquid column chromatography over silica gel and dichloromethane (DCM) as eluent. $^{1}$H-NMR (200 MHz; $CDCl_3$) δ, m.d.: 2.39 (3H; s), 3.25 (4H; t), 3.55 (4H; t), 6.47 (2H; d, $^{3}J$ = 9.3 Hz), 6.54 (1H; d, $^{3}J$ = 16.3), 7.15–7.40 (32 H; m), 7.54 (2H, m), 7.69 (2H, m), 8.19 (1H; d), 8.35 (1H; d).

**2.2. Sample preparation**

The ITO glass (*Präzisions Glas & Optik GmbH*) with a sheet resistivity of 40 Ω/cm$^2$ was used as a substrate. A 12 mm wide ITO strip line was made by wet etching at the middle of the substrate. Before the deposition of layers the substrates were ultrasonically cleaned in acetone, water with 3 vol% of Hellmanex II detergent and isopropylalcohol, each for 15 min, and finally blown dry with nitrogen. Immediately after the cleaning, polyethylenedioxythiophenne:polystyrenesulfonate (PEDOT:PSS) (from H.C. Starck) was spin-coated on the ITO glass and dried at 160 ºC for 30 min. The obtained PEDOT:PSS layer was 60 nm thick. ZWK1 was dissolved in dichloromethane and the solution was processed in a centrifuge to separate unsolved crystallites. The solution was spin-coated on the PEDOT:PSS layer at 6000 rpm and dried at 80 ºC for 15 min. LiF (1 nm) and Al (100 nm) layers were deposited by thermal evaporation at a pressure of $7 \cdot 10^{-6}$ mBar in an EDWRD 306 vacuum coating unit. The thickness of LiF and Al layers was determined by a quartz crystal thickness monitor. The active emitting area was 16 mm$^2$, which is defined by the overlapping area of the cathode and the anode. The finale structure of the device was ITO/PEDOT:PSS (40 nm)/ZWK1 (120 nm)/LiF (1 nm)/Al (100 nm). For the electroluminescence (EL) measurements the device was not encapsulated.

For the photoluminescence measurements the ZWK1 solution was spin-coated on a quartz glass under the same conditions as for the EL device.

**2.3. Measurement systems**

Absorption spectra of ZWK1 in the solution and in the solid state were measured by an Ocean Optics HR4000 spectrometer.

Photoluminescence (PL) was excited by a wavelength-tunable pulsed solid state laser (pulse duration 30 ps) from Ekspla (PG401/SH pumped by the 3$^{rd}$ harmonics of a Nd:YAG laser). The luminescence light was dispersed in spectrum by a spectrograph/monochromator from BRUKER Optics (250 is/sm) and detected by a streak camera from HAMAMATSU (C4334-01). The overall temporal resolution of the system was not worse than 50 ps.

The current density–voltage (*J–U*) characteristics were measured by a Keithley 617 unit. The electroluminescence spectrum and intensity were measured

by the Ocean Optics HR4000 spectrometer and calibrated silicon photodiode, respectively. The correct luminance was calculated assuming a Lambertian spatial emission. All measurements were carried out in ambient atmosphere at room temperature.

## 3. RESULTS AND DISCUSSION

The absorption spectrum of ZWK1 in dichloromethane and ZWK1 thin film are shown in Fig. 2 (curve *a*) and Fig. 3 (curve *a*), respectively. The absorption band in both cases consists of two overlapping bands. The quantum-chemical calculation (Gaussian G09W program, method "ZINDO" and solvation model "IEFPCM") predicts a single absorption band for ZWK1 in the green region. At such molecular concentration ($c = 6 \cdot 10^{-5}$ mol/l) the presence of at least two absorption bands due to aggregation (dimmerization) in the solution is hardly probable. As can be seen from the ZWK1 molecule structure shown in Fig. 1 it consists of a stilbene-like part for which two isomers (*cis*- and *trans*-) are well known. Most likely, the ZWK1 molecule also has two different conformations, and therefore two slightly different wavelength bands. Both conformations could be present in a solid film and cause similar doubling of the absorption band.

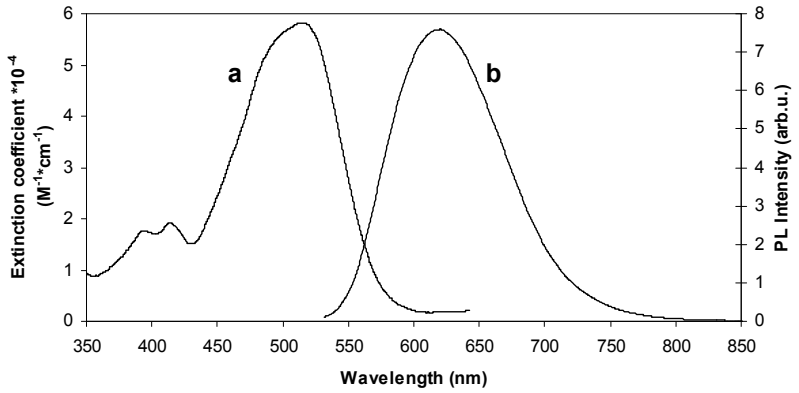



*Fig. 2*. Absorption (*a*) and PL (*b*) spectrum of ZWK1 in dichloromethane solution ($l = 0.2$ cm and $c = 6 \cdot 10^{-5}$ mol/l).

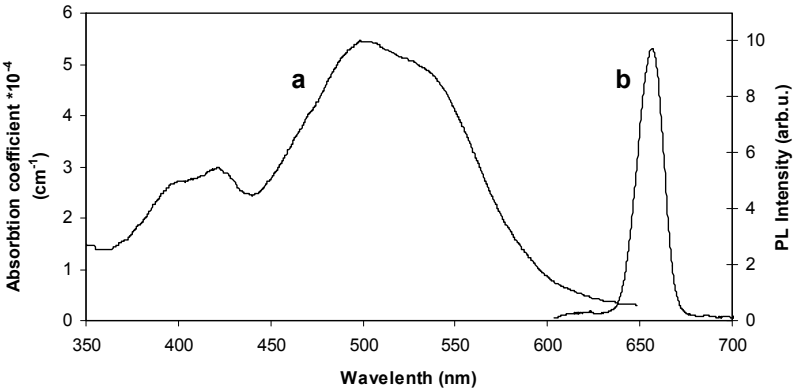



*Fig. 3*. Absorption (*a*) and PL (*b*) spectrums of ZWK1 in 55 nm thin solid films.

Photoluminescence (PL) spectrums were measured for two ZWK1 solutions: in dichloromethane and chloroform. The excitation wavelength was 515 nm for dichloromethane and 519 nm for chloroform solution, which corresponds to the absorption maximum of respective solutions. In chloroform with the dipole moment 1.02D ($\varepsilon = 4.81$) the maximum of PL spectrum is 601 nm, and in dichloromethane (1.54D, $\varepsilon = 9.1$) – 620 nm. The maximum of PL spectrum is red shifted in more polar solvents. It could be due to higher interaction energy between organic compound and solvent molecules (well known as the solvation effect). At the same time the PL spectrum of the ZWK1 film was excited at 500 nm, which is close to the maximum absorption of the sample (see Fig. 3, curve *a*). The maximum of the PL spectrum was observed at 657 nm. The lifetime of the luminescence was less than 50 ps.

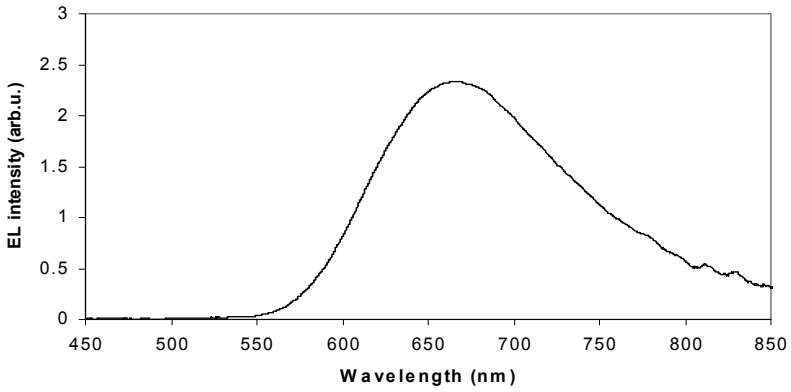



*Fig. 4*. Electroluminescence spectrum
of the ITO/PEDOT:PSS (40 nm)/ZWK1 (120 nm)/LiF (1 nm)/Al (100 nm) system.
The applied voltage is 15V at positive ITO electrode.

The EL spectrum of the device is estimated in CIE coordinates: $x = 0.65$ and $y = 0.34$. The spectral maximum was at 667 nm (see Fig. 4), which is slightly shifted to the red region as compared with the PL spectrum of ZWK1 thin film (see Fig. 3, curve *b*). This could be explained by the interaction of molecules and charges injected into the device. At the same time, the EL spectrum is four times broader as compared with the PL spectrum of the thin film. So far, the reason for such a large difference is not clear.

For the OLED device the characteristic current density–voltage and luminance–voltage dependences (*J–L–U*) were measured (see Fig. 5). The measured *J–U* curves were almost the same when positive voltage was applied to the bottom ITO electrode or top Al electrode. Up to voltages $U = 2$ V a linear dependence of the current density on the applied voltage was observed. At higher voltages the dependence of current density can be described in compliance with Schottky's effect [11]. In this case, when holes are injected from the positive ITO electrode and electrons are injected from the negative Al electrode, the electroluminescence process is observed (see Fig. 5). On the contrary, when the negative voltage is applied to the ITO electrode no electroluminescence process occurs.

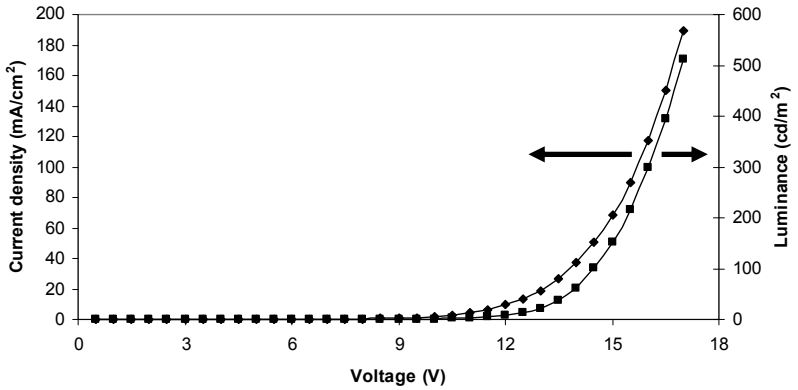



*Fig. 5*. *J-L-U* characteristics of the OLED device with a positive ITO electrode.

In order to characterize our device, the luminance ($L$) was measured, and the power and luminance efficiencies were calculated according to [12]. The turn on voltage of the device was 10 V (when the luminance is ~ 1 cd/m$^2$). The luminance increases with the forward voltage, and at $U$ = 17 V it reaches $L$ = 510 cd/m$^2$. The power and luminance efficiencies at the luminance 100 cd/m$^2$ are 0.43 lm/W and 1.97 cd/A, respectively. As is seen in Fig. 6, the maximum efficiencies of our device are 0.50 lm/W and 2.70 cd/A. These values are saturated at higher current densities. It should be noted that the measured EL parameters are for non-optimized samples; after optimization they may be improved.

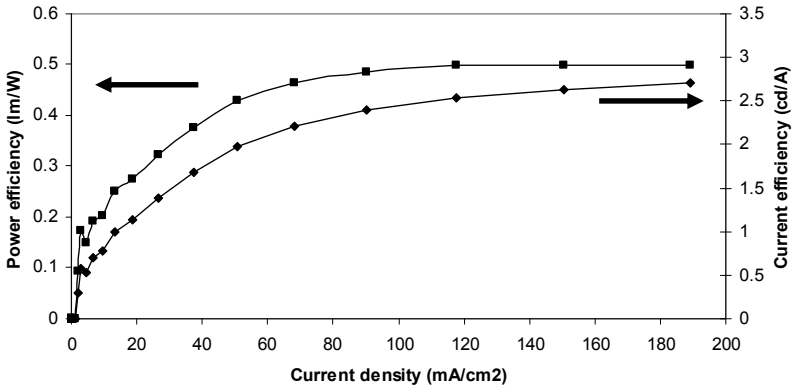



*Fig. 6*. Dependence of the power and luminance efficiencies on the current density of the device.

## 4. CONCLUSION

The original organic compound 2-(2-(4-(bis(2 (trityloxy)ethyl)amino)styryl)-6-methyl-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione is suitable as an electroluminescent material. The maximum of electroluminescence spectrum is at 667 nm (in the red spectral region). The obtained non-optimized EL system gives the maximum values of 0.50 lm/W for power efficiency and of 2.70 cd/A for luminance efficiency.

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## JAUNS AMORFS SARKANĀS ELEKTROLUMINISCENCES MATERIĀLS VEIDOTS UZ PIRANILIDEN INDĀN-1,3-DIONA ATVASINĀJUMA BĀZES

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K o p s a v i l k u m s

Organiskās gaismas emitējošās diodes (OGED) ir perspektīvas nākotnes apgaismes iekārtās un plānos ekrānos. Vairums OGED struktūru veido no plānām kārtiņām, izmantojot sublimēšanas metodi vakuumā. Alternatīva pieeja ir izmantot vielas, kuru šķīdumus uznesot uz pamatnes, veidojas kārtiņa ar stiklveida struktūru. Sagaidāms, ka tas palētinātu OGED ražošanu.

Šajā darbā ir apskatīts oriģināls fluorescējošs organisks savienojums 4-(indān-1,3-dionil)-6-metil-2-(4-(N,N-di-tritil-oksi-etil)-amino)stiril-4H-pirāns (ZWK1). Fotoluminiscenci kārtiņai novēro spektra sarkanajā rajonā ar maksimumu pie 657 nm.

Elektroluminiscences mērījumiem ir izveidota daudzslāņu struktūra ITO/PEDOT:PSS (40 nm)/ZWK1 (120 nm)/LiF (1 nm)/Al (100 nm). Parādīts, ka elektroluminiscences spektra maksimums ir pie 655 nm. Jaudas un strāvas efektivitātes ir novērtētas pie spožuma 100 $cd/m^2$ un ir atbilstoši 0.52 lm/W un 2.35 cd/A.