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Abstract. The organic light-emitting diode (OLED) has promising applications in flat-panel displays and novel light sources. Thus far, OLED structures have mostly been made by thermal evaporation in vacuum. An alternative approach is to use small molecules that form amorphous (glassy) structures from solutions. Such compounds can be used in ink-jet printing technologies and result in reduced OLED prices. 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), and its derivative 2-(2,6-bis(4-(bis(2-(trityloxy)ethyl) amino)styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK2), where the methyl group is replaced with a 4-substituted-styryl group. This change could improve the formation of glassy structures. The thickness of the electroluminescent layer in the device is optimized to the higher power efficiency and obtains: ITO/PEDOT:PSS (40 nm)/ZWK1 (95 nm)/LiF (1 nm)/Al (100 nm), and ITO/PEDOT:PSS (40 nm)/ZWK2 (85 nm)/LiF (1 nm)/Al (100 nm). The maximum of electroluminescence (EL) spectra for the device with the ZWK1 compound is 667 nm, which corresponds to the CIE coordinates $x = 0.65$ and $y = 0.34$. The power and luminance efficiency at a luminance of 100 cd/m² is 0.63 lm/W and 1.78 cd/A, respectively. Adding an additional 4-substituted-styryl group to the ZWK1 molecule shifts the maximum of EL spectra to the red region (705 nm) and decreases the efficiencies by one order. © 2011 Society of Photo-Optical Instrumentation Engineers. [DOI: [10.1117/1.3524819](https://doi.org/10.1117/1.3524819)]

Keywords: organic light-emitting diodes; red fluorescent materials; amorphous materials.

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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 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 (EL) 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 purity of obtained material. The previously mentioned 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 an 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) and its derivative 2-(2,6-bis(4-(bis(2-(trityloxy)ethyl) amino)styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione (ZWK2), capable of

forming a thin film from solution. The ZWK2 has an additional 4-substituted-styryl group attached instead of a methyl group. This change could improve the formation of glassy structures.

2 Experimental

2.1 Synthesis of Red Florescent Organic Compound

All the necessary reagents were purchased as commercial products from Acros (Thermo Fisher Scientific, Waltham, Massachusetts) and Aldrich (Saint Louis, Missouri). When required, solvents (pyridine and methylene chloride) were dried by refluxing with calcium hydride and distilled. The $^1\text{H-NMR}$ spectrum was obtained on a Varian (Agilent Technologies, Santa Clara, California) VRX-Unity NMR spectrometer (400 MHz).

The steps of ZWK1 and ZWK2 synthesis are shown in Fig. 1. The spectral data, characteristics, and detailed description of the synthesis are given only for the final product; however,

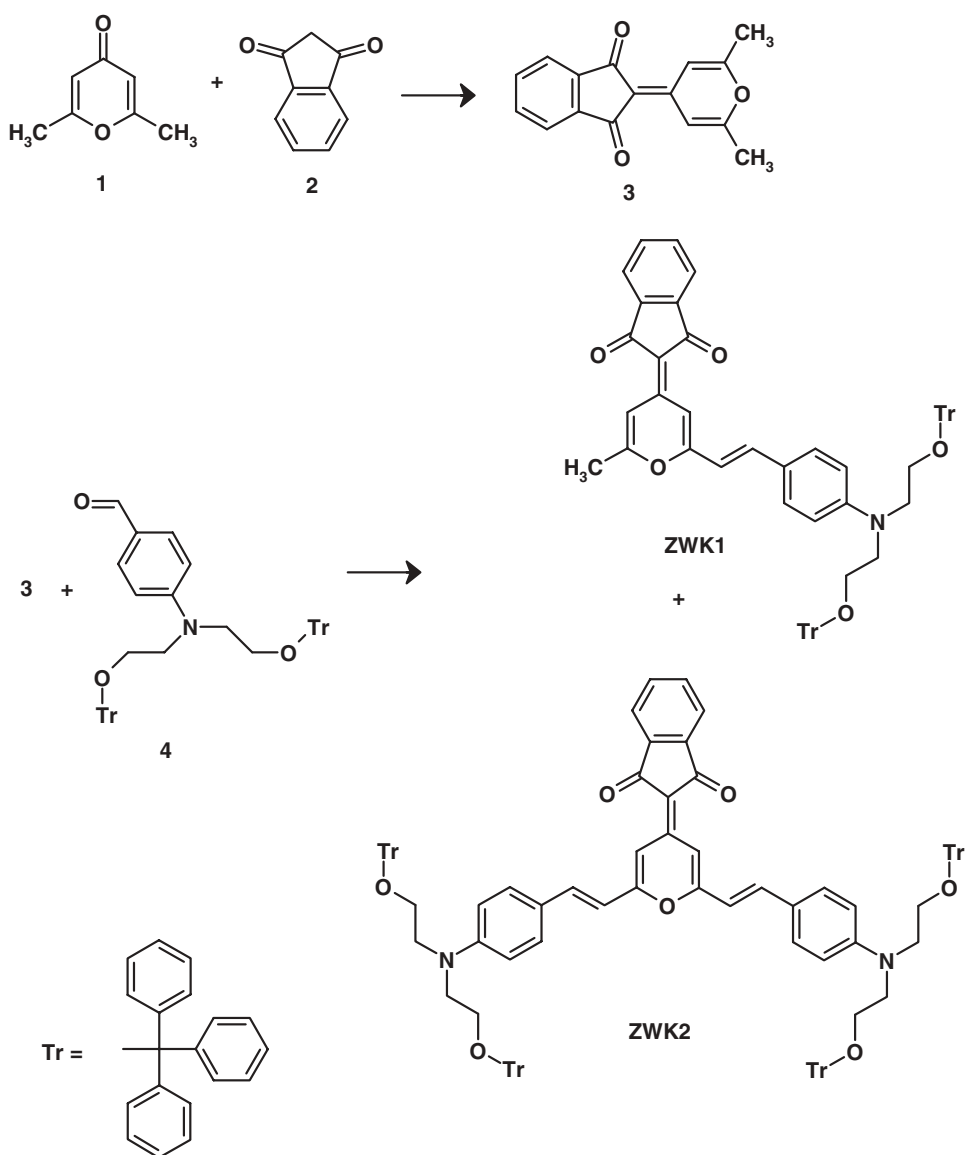


Fig. 1 Synthesis of ZWK1 and ZWK2.

intermediate products have been characterized and confirmed by the $^1\text{H-NMR}$ spectral data.

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 h. After cooling the solution, the obtained pale yellow solid was filtered and washed with 50 ml cold methanol. Yield was 10.88 g (70.7%) of brownish yellow solid with m.p. 250°C .¹⁰ The obtained compound (**3**) could be recrystallized from a 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) and 2-(2,6-bis(4-(bis(2-(trityloxy)ethyl) amino)styryl)-4H-pyran-4-ylidene)-1H-indene-1,3(2H)-dione

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 h. A red fluorescent color was observed during the reaction. The reaction was controlled with TLC (dichloromethane, silicagel) by the quantity of compound **3** in a solution of reaction. The solution was cooled to room temperature and poured into 20-ml isopropylalcohol after compound **3** was fully reacted. As a result, a dark red product was obtained that is a mixture of compounds ZWK1 and ZWK2. These compounds were obtained separately by using liquid column chromatography over silica gel and dichloromethane (DCM) as an eluent.

ZWK1: $^1\text{H-NMR}$ (200 MHz; CDCl_3) δ , m.d.: 2.39 (3 H; s), 3.25 (4 H; t, $^3\text{J} = 5.5$ Hz), 3.55 (4 H; t, $^3\text{J} = 5.5$ Hz), 6.47 (2 H; d, $^3\text{J} = 9.3$ Hz), 6.54 (1 H; d, $^3\text{J} = 16.3$ Hz), 7.15–7.40 (32 H; m), 7.54 (2 H, m), 7.69 (2 H, m), 8.19 (1 H; d, $^4\text{J} = 1.6$ Hz), 8.35 (1 H; d, $^4\text{J} = 1.6$ Hz).

Elemental analysis: calcd. for ZWK-1 ($\text{C}_{65}\text{H}_{53}\text{NO}_5$): C, 84.12; H, 5.76; N, 1.51, found C, 83.96; H, 5.74; N, 1.39.

ZWK2: $^1\text{H-NMR}$ (200 MHz; CDCl_3) δ , m.d.: 3.28 (8 H; t, $^3\text{J} = 4.7$ Hz), 3.59 (8 H; t, $^3\text{J} = 4.7$ Hz), 6.47 (4 H; d, $^3\text{J} = 9.3$ Hz), 6.63 (1 H; d, $^3\text{J} = 15.6$ Hz), 7.10–7.40 (64 H; m), 7.53 (2 H, m), 7.69 (2 H, m), 8.36 (2 H; s).

Elemental analysis: calcd. For ZWK-2 ($\text{C}_{114}\text{H}_{94}\text{N}_2\text{O}_7$): C, 85.36; H, 5.91; N, 1.75, found C, 85.18; H, 5.89; N, 1.64

2.2 Sample Preparation

ITO glass (Präzisions Glas and Optik GmbH, Iserlohn, Germany) with a sheet resistivity of $40 \Omega/\text{cm}^2$ was used as a substrate. A 12-mm-wide ITO strip line was made by wet etching in 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 (Hellma Analytics, Müllheim, Germany), and isopropylalcohol, each for 15 min, and finally blown dry with nitrogen. Immediately after the cleaning, polyethylenedioxythiophene:polystyrenesulfonate (PEDOT:PSS) (H.C. Starck, Goslar, Germany) was spin-coated onto the ITO glass and dried at 160°C for 30 min. The obtained PEDOT:PSS layer was 40 nm thick. Without the PEDOT:PSS layer, the efficiency of the system was at least one order less. ZWK1 or ZWK2 was dissolved in dichloromethane, and the solution was processed in a centrifuge to separate unsolved

aggregates. The solution was spin-coated on the PEDOT:PSS layer at 6000 rpm and dried at 80°C for 15 min. LiF (1 nm) and Al (100 nm) layers were deposited by thermal evaporation at a pressure of 7×10^{-6} mBar in an Edward's 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 mm², which is defined by the overlapping area of the cathode and anode. The final structure of the device was ITO/PEDOT:PSS (40 nm)/ZWK1(xnm)/LiF(1 nm)/Al(100 nm), and ITO/PEDOT:PSS (40 nm)/ZWK2(xnm)/LiF(1 nm)/Al(100 nm). The thickness of the EL layer was varied from 40 to 150 nm to optimize sample geometry and obtain higher efficiency. For the EL measurements, the device was not encapsulated. For the photoluminescence (PL) measurements, the ZWK1 and ZWK2 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 and ZWK2 in the solution and in the solid state were measured by an Ocean Optics (Dunedin, Florida) HR4000 spectrometer. PL was excited by a wavelength-tunable pulsed solid state laser (pulse duration 30 ps) from Ekspla (Vilnius, Lithuania) (PG401/SH pumped by the third harmonics of a Nd:YAG laser). The luminescence light was dispersed in a spectrum by a spectrograph/monochromator from Bruker Optics (Billerica, Massachusetts) (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 (Cleveland, Ohio) 617 unit. The electroluminescence spectrum and intensity were measured by the Ocean

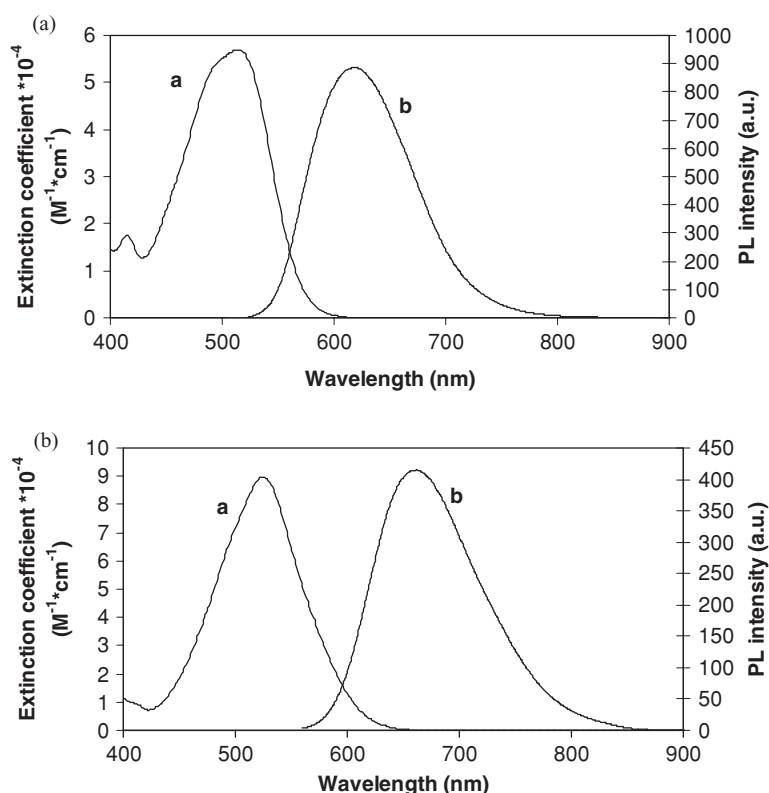


Fig. 2 Absorption (curve *a*) and PL (curve *b*) spectra in dichloromethane solution. (a) ZWK1 ($l = 0.2$ cm and $c = 6 \times 10^{-5}$ mol/l), and (b) ZWK2 ($l = 0.5$ cm and $c = 1.12 \times 10^{-5}$ mol/l).

Optics HR4000 spectrometer and a calibrated silicon photodiode, respectively. The correct luminance (L) was calculated assuming a Lambertian spatial emission. All measurements were carried out in an ambient atmosphere at room temperature. The element analyses of compounds ZWK1 and ZWK2 were obtained with a Costech Instruments (Valencia, California) ECS 4010 CHNS-O elemental combustion system.

3 Results and Discussion

The absorption spectra of ZWK1 and ZWK2 in dichloromethane are shown in Fig. 2 (curves a). The ZWK1 absorption band consists of two overlapping bands. As can be seen from the ZWK1 molecule structure shown in Fig. 1, it consists of a stilbenelike 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.¹¹ Both conformations could be present in a solid film and cause similar doubling of the absorption band [see Fig. 3(a) curve a]. In the case of ZWK2 molecules, there is only one absorption band, which means that an additional 4-substituted-styryl group instead of a methyl group limits the creation of other conformations.

PL spectra were measured in dichloromethane. The excitation wavelength was 524 nm which corresponds to the absorption maximum of the compounds. The maximum of the PL spectrum for ZWK1 is 620 nm and ZWK2 is 660 nm. Adding an additional 4-substituted-styryl group shifted the PL spectrum to the red region.

Also, the maximum of the PL spectrum is redshifted in a more polar solvent, such as chloroform, for both compounds. For example, for ZWK1 in chloroform (1.02D, $\epsilon = 4.81$) the

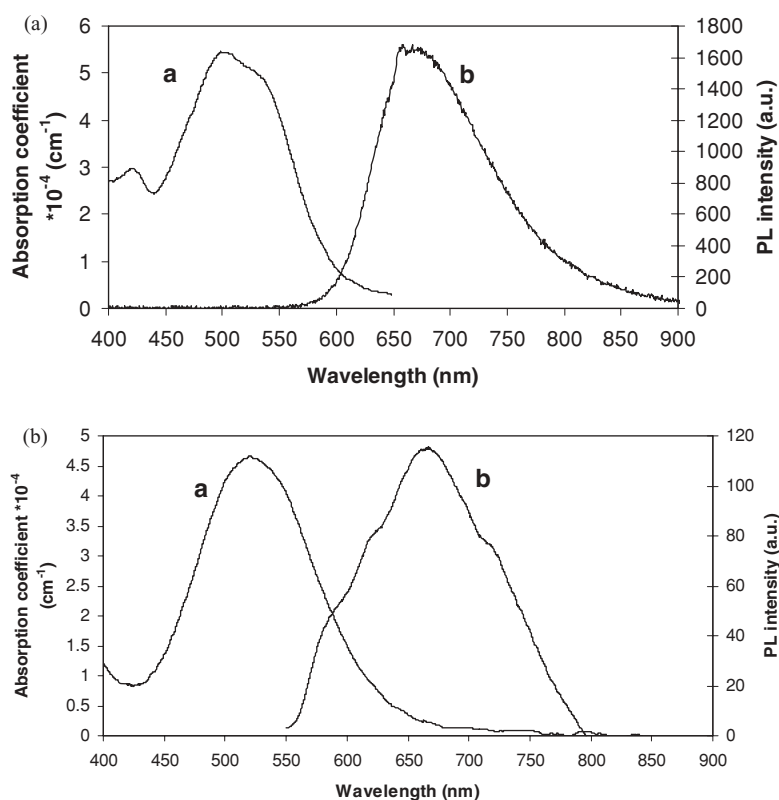


Fig. 3 Absorption a and PL b spectra of (a) ZWK1 and (b) ZWK2 in 55-nm thin solid films.

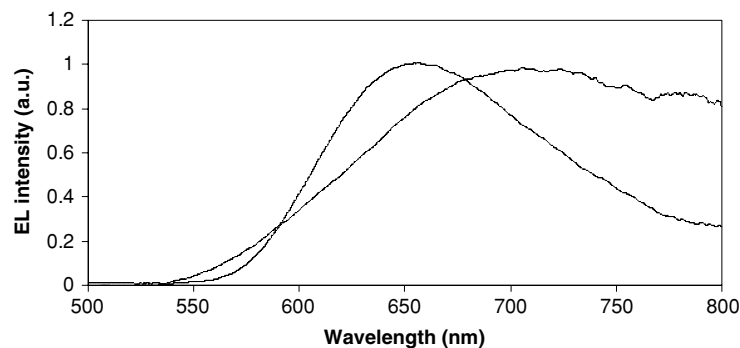


Fig. 4 Electroluminescence spectrum of the ITO/PEDOT:PSS(40nm)/ZWK1(95nm)/LiF(1nm)/Al(100nm) (solid line) and ITO/PEDOT:PSS(40nm)/ZWK2(85nm)/LiF(1nm)/Al(100nm) (dashed line) system. The applied voltage is 14V at positive ITO electrode.

maximum of the PL spectrum is 601 nm, and in dichloromethane (1.54D, $\epsilon = 9.1$) – 620 nm. It could be due to higher interaction energy between the organic compound and solvent molecules (well known as the solvation effect).

The PL spectra of the ZWK1 and ZWK2 films were excited at 500 and 525 nm, respectively, which is close to the maximum absorption of the samples [see Figs. 3(a) and 3(b), curves *a*]. The maximum of the PL spectrum was observed at 657 and 668 nm for ZWK1 and ZWK2, respectively. The lifetime of the luminescence in both cases was <50 ps. The intensity of the PL of ZWK2 was much weaker than the ZWK1 PL intensity.

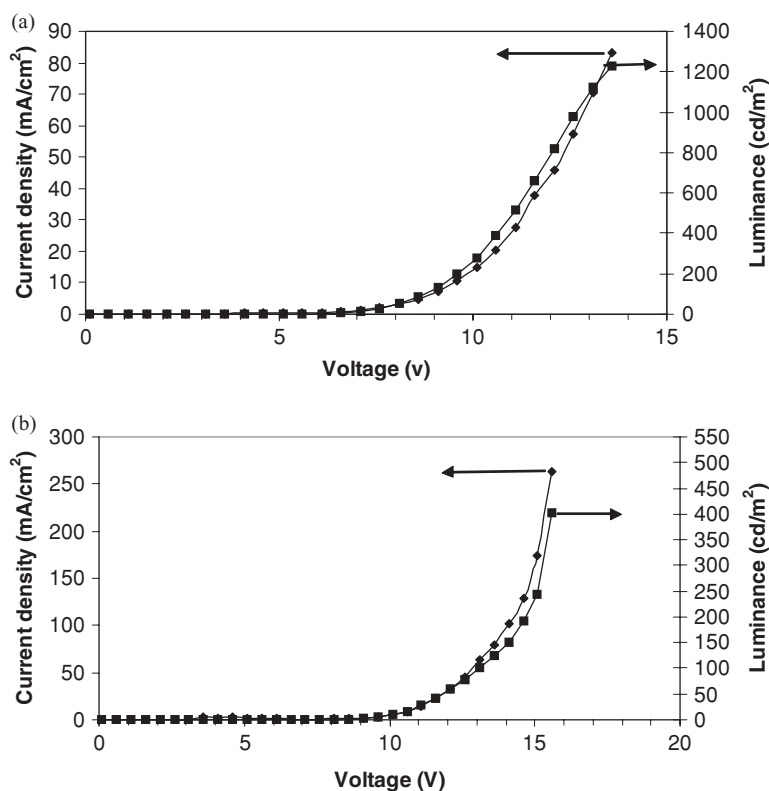


Fig. 5 J – L – U characteristics of the OLED device with a positive ITO electrode: (a) ZWK1 and (b) ZWK2.

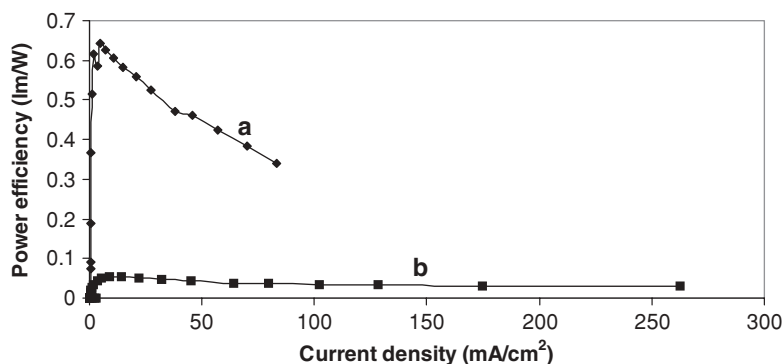


Fig. 6 Power efficiencies of the optimized device, where *a* represents ZWK1 and *b* represents ZWK2 compounds.

The thickness of the EL layer was varied to obtain higher efficiency. In our system, the higher efficiency showed the OLED devices with thicknesses of 95 nm for ZWK1 and 85 nm for ZWK2. The EL spectrum of the device is estimated in CIE coordinates: $x = 0.65$ and $y = 0.34$ for ZWK1, and $x = 0.64$ and $y = 0.36$ for ZWK2. The spectral maximum was at 667 and 705 nm (see Fig. 4), which is slightly shifted to the red region compared to the PL spectrum of ZWK1 and ZWK2 thin films [see Figs. 3(a) and 3(b), curves *b*]. This could be explained by the interaction of molecules and charges injected into the device. 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 $U = 5$ V, a dependence of current density can be described in compliance with Schottky's effect.¹² At higher voltages, the charge injection was observed. The elimination of the Schottky barrier at the interface could reduce the injection voltage. 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.

In order to characterize our device, the luminance (L) was measured and the power and luminance efficiencies were calculated according to Ref. 13. The turn-on voltage of the device was 5.6 and 8.6 V (when the luminance is ~ 1 cd/m²) for ZWK1 and ZWK2, respectively. The luminance increases with the forward voltage in both cases. The OLED device with ZWK1 molecules reaches $L = 1200$ cd/m² at $U = 14$ V [see Fig. 5(a)]. The power and luminance efficiencies at luminance 100 cd/m² are 0.63 lm/W and 1.78 cd/A, respectively. As is seen by

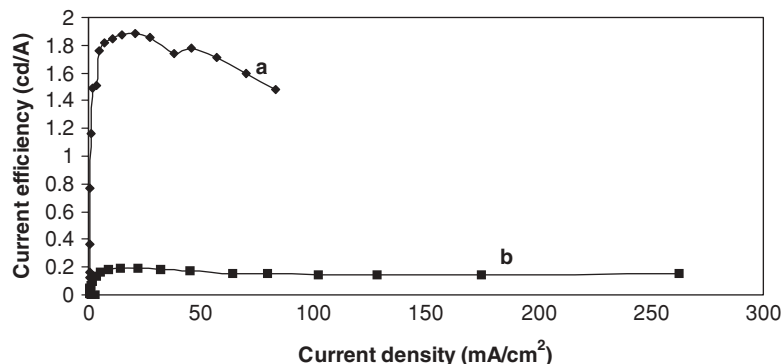


Fig. 7 Current efficiencies of the optimized device where *a* represents ZWK1 and *b* represents ZWK2 compounds.

line *a* of Figs. 6 and 7, the maximum efficiencies of the device are 0.65 lm/W and 1.9 cd/A, respectively.

In the case of a device with ZWK2, compound luminance reaches 400 cd/m² at $U = 15.5$ V. The power and luminance efficiencies at luminance 100 cd/m² are one order less than for devices with ZWK1. They are 0.04 lm/W and 0.16 cd/A, respectively. As is seen by line *b* of Figs. 6 and 7, the maximum efficiencies of the device are 0.054 lm/W and 0.19 cd/A, respectively. The reason for such a small efficiency of ZWK2 is due to the EL spectrum. At least half of the intensity is emitted at wavelengths of > 700 nm, where the photopic response is close to zero.

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 shown as an electroluminescent material. The maximum of the electroluminescence spectrum is at 667 nm (in the red spectral region). The obtained optimized EL system gives maximum values of 0.65 lm/W for power efficiency and 1.9 cd/A for current efficiency. Adding an additional 4-substituted-styryl group in ZWK1 instead of a methyl group could improve the formation of the amorphous structure, but it shifts the maximum of the EL spectrum to the red region (705 nm) and decreases the efficiencies by approximately one order.

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