

Articles

Electroluminescence Properties of Systematically Derivatized Organic Chromophores Containing Electron Donor and Acceptor Groups

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We present electroluminescent (EL) properties of new blue–green organic dyes. The molecular structures of these dyes are based on 2,7-divinyl-9,9-bis(*tert*-butyl)fluorene, a π -electron bridge, end-capped with electron donor (D) and/or electron acceptor (A) group(s) to form D– π –A, D– π –D, and A– π –A structures. The donor group is a triphenylamine, and the acceptor group is a diphenyloxadiazaole. We studied EL properties of these dyes in a single-layer EL device having the following structure: ITO/PVK:DYE/Ca/Al. We found that both the wavelength of maximum emission and the threshold of EL depend on the structure and the concentration of the dye. Among the structure reported here, the D– π –A dye shows the highest EL performance, exhibiting a brightness of 498 cd/m² at an applied voltage of 25 V.

Introduction

Since the first demonstration of a green organic light-emitting diode (OLED) in 1987 by Tang and VanSlyke,¹ numerous organic molecules and polymers that exhibit electroluminescence (EL) in the blue, green, and red spectral regions have been found.^{2,3} Organic EL devices represent a low-cost route for large-area light-emitting display technology.⁴ For this reason there is a considerable interest in the study of EL organic dyes and polymers because of their structural flexibility, low cost of fabrication, and low operational voltages. A variety of organic materials including polymers,^{1–7} metal complexes,⁸ and dyes^{9,10} have demonstrated strong EL. The

efficiency of an OLED strongly depends on the choice of molecules and on the design of the device structure. Generally, multilayered devices exhibit a better performance than a single-layer device because the injection and recombination of holes and electrons in multilayered devices are better balanced.⁶ The efficiency of electron–hole recombination leading to the creation of singlet excitons is mainly influenced by the overlap of electron and hole densities that originate from carrier injection into the emitter layer.¹¹ To improve the efficiency of carrier injection, organic hole, and electron injection, layers with a low HOMO (highest occupied molecular orbital) or high LUMO (lowest unoccupied molecular orbital) level are chosen. In addition, the efficiency of an OLED can be further improved by introduction of a phosphorescent sensitizer to excite fluorescent dyes.¹²

In this work we have investigated EL properties of fluorescent organic dyes with systematically derivatized structures containing electron donor and acceptor groups.

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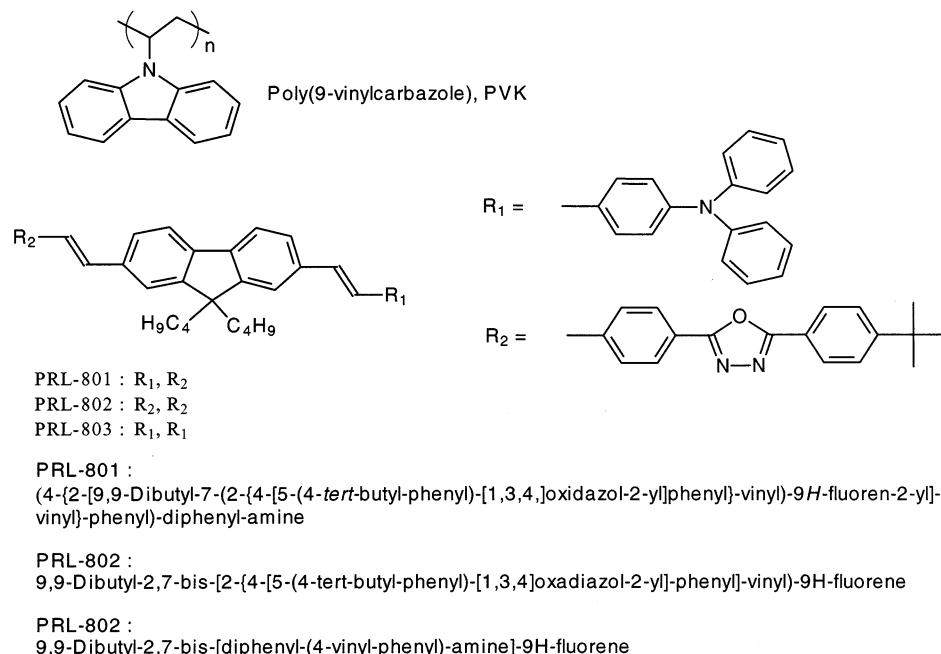


Figure 1. Molecular structures of PVK and the dyes.

The main structural component of the dye is 2,7-divinyl-9,9-bis(*tert*-butyl)fluorene that forms a π -electron bridge. The two substituents are an electron donor triphenylamine group (D) and an electron acceptor diphenyloxadiazole group (A). The following dyes were synthesized: D- π -A, A- π -A, and D- π -D, hereafter called dyes PRL-801, PRL-802, and PRL-803, respectively. In addition to the electron-donating properties, the substituent D also has good hole-transporting properties while the substituent A possesses electron-transporting properties.

The D- π -A, or "push-pull" type molecules, have been used as effective emitters in OLED structures for quite a while. The original red-emitting dye, 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran (DCM) introduced by Tang et al.,¹³ has the structure of this type as well as its dual-condensed derivatives that were recently studied by Jung et al.¹⁴

Several papers^{15,16} review EL properties of organic materials and discuss in detail OLEDs containing different organic molecules. Recently, a substituted polyfluorene symmetrically capped with bis(4-methylphenyl)phenylamine was used as an effective blue emitter in OLED structures.¹⁷

Here, we present experimental results that suggest that a judicious choice of D and A substituents leads to optimization of chromophore structures that are better suited as emitters in OLED applications. In a single-layer OLED structure, wherein the emitting dye, dispersed in a poly(9-vinylcarbazole) (PVK) matrix, is sandwiched between ITO and Ca/Al, the asymmetrically substituted D- π -A (PRL-801) structure exhibits the best EL properties among the studied dyes.

Experimental Section

The three chromophores PRL-801, PRL-802, and PRL-803 were synthesized as follows. The preparation of compounds PRL-803 and PRL-802 is accomplished by the cross-coupling between the central π -bridge (2,7-dibromo-9,9-dibutylfluorene) moiety, the functionalized electron-donating part (*N,N*-diphenyl-4-vinylaniline), and the electron-withdrawing part (2-[4-[(*tert*-butyl)phenyl]-5-(4-vinylphenyl)]-1,3,4-oxadiazole), through a standard palladium-catalyzed Heck coupling reaction with a good yield (~70%).^{18,19} The key intermediate for the central π -bridge, 2,7-dibromo-9,9-dibutylfluorene, is prepared by alkylation at the 9,9 position of commercially available 2,7-dibromofluorene.²⁰ The electron-donor part, *N,N*-diphenyl-4-vinylaniline, is synthesized via a Wittig vinylation method²¹ by using 4-(diphenylamino)benzaldehyde²² and methylphosphonium iodide salt as the starting materials. The preparation of the electron-acceptor part is accomplished according to the established procedure.²² Compared to the above-mentioned two chromophores, the synthesis of compound PRL-801 is somewhat more laborious because of its more complex structure. This asymmetrically substituted structure is synthesized by performing the Wittig reaction, first on one end between the fluorene unit, [(7-bromo-9,9-dibutyl-9H-fluoren-2-yl)methyl]-(triphenyl)phosphonium bromide,²³ and the electron-donor moiety, 4-(diphenylamino)benzaldehyde. This step is followed by a standard Heck coupling reaction on the other end between the previously obtained donor-fluorene adduct and 2-[4-[(*tert*-butyl)phenyl]-5-(4-vinylphenyl)]-1,3,4-oxadiazole. The chemical structures of all three dye molecules are confirmed by both ¹H NMR and high-resolution mass spectroscopy. Fluorescence quantum yield determinations are generally made relative to an optically dilute standard fluorophore solution with well-known quantum yield. In the current work, the fluorescence

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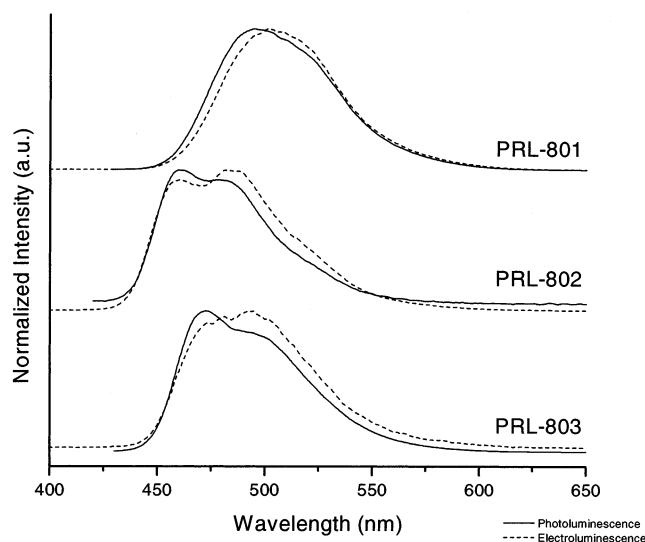


Figure 2. PL and EL spectra of the single-layer OLED structure containing the same concentration (16.66 wt %) of the respective dye.

quantum yields were determined by using the standard procedure described in the literature.^{21,24}

Figure 1 shows molecular structures of the materials used in this study. The triphenylamine substituent (R_1 in Figure 1) has properties of a hole-transporting media, while the oxadiazole substituent (R_2 in Figure 1) can act as an electron-transporting medium. Furthermore, the fluorene molecule, which constitutes the central part of the π -electron bridge, is known as a highly fluorescent dye and, when substituted with alkyl chains at the ninth position, exhibits increased solubility and/or miscibility.

To fabricate EL devices, a secondary standard grade PVK from Aldrich was employed as a host polymer. PVK is well-known as a hole-transporting and electron-blocking medium. Thin films of PVK doped with dye were prepared by spin coating from a PVK:DYE chloroform solution containing different dye concentrations. Indium–tin oxide (ITO) coated glass substrates with a sheet resistance of 20 Ω /square were etched to form 2 mm wide strips and were used as the device's anode. The thickness of the PVK:DYE film was about 140 nm. A single-layer type of EL device consisting of ITO/PVK:DYE/Ca/Al was constructed. Calcium and aluminum were thermally deposited in a Denton high-vacuum chamber at 6×10^{-6} Torr pressure. The optimal electrode thickness for calcium was experimentally determined to be 100 nm. The aluminum thickness was observed to have very little or no effect on the device efficiency because it served mainly as a protective layer. The luminescent areas of these devices were fairly large: 7.9 mm² for the small cell and 18 mm² for the large cell. The turn on voltage varied with the dye type and concentration. Both photoluminescence (PL) and EL spectra were measured at room temperature and under atmospheric pressure. The samples were not hermetically sealed from the atmosphere. EL was measured in a continuous dc mode. The I–V characteristics of the device were recorded using a Keithley 208 high-current source instrument. The absolute luminescence intensity was measured with a Minolta LS-110 luminance meter.

Results and Discussion

Figure 2 shows the PL and EL spectra of the single-layer OLED structure containing the same concentrations of PRL-801, PRL-802, and PRL-803 dyes. It is observed that the central wavelength of the emission peak depends on the dye's structure. Clearly, the PRL-

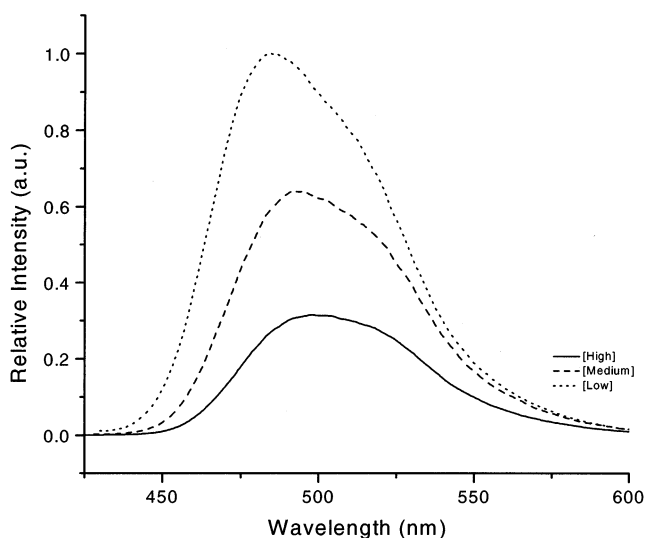


Figure 3. Relative PL spectra of a single-layer OLED structure containing PRL-801 dye at different concentrations (28.5 wt %, high; 16.66 wt %, medium; 4.76 wt %, low).

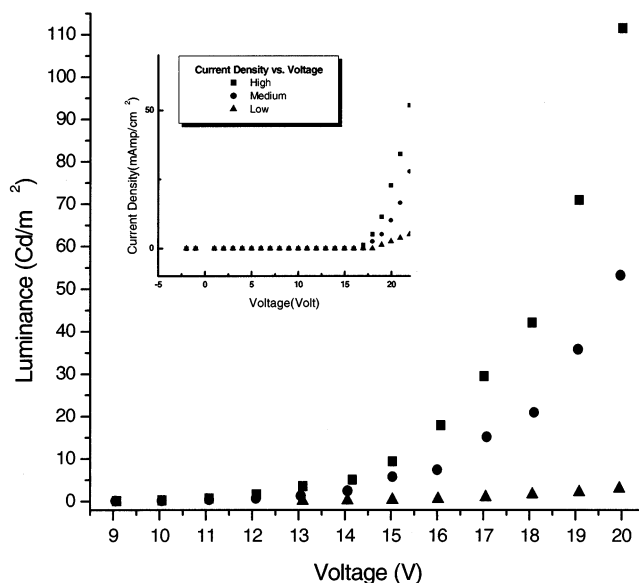


Figure 4. I–V and EL–V characteristics of the single-layer OLED structure with the PRL-801 emitter at different concentrations (28.5 wt %, high; 16.66 wt %, medium; 4.76 wt %, low).

801 dye having a D– π –A structure exhibits the longest wavelength at the maximum emission band among the three dyes studied here because its molecular structure permits increased charge-transfer character in the excited state. The PL spectra of a single-layer OLED structure containing different concentrations of the PRL-801 dye are shown in Figure 3. As expected, the PL maximum shifts toward longer wavelength and decreases in intensity with increased dye concentration because the probability of the excimeric states formation at higher concentrations is greater.²⁵

Figure 4 shows the I–V and EL–V characteristics of the single-layer OLED structure containing different concentrations of the PRL-801 dye. The measured EL intensities at 19 V bias for 28.5, 16.66, and 4.76 wt %

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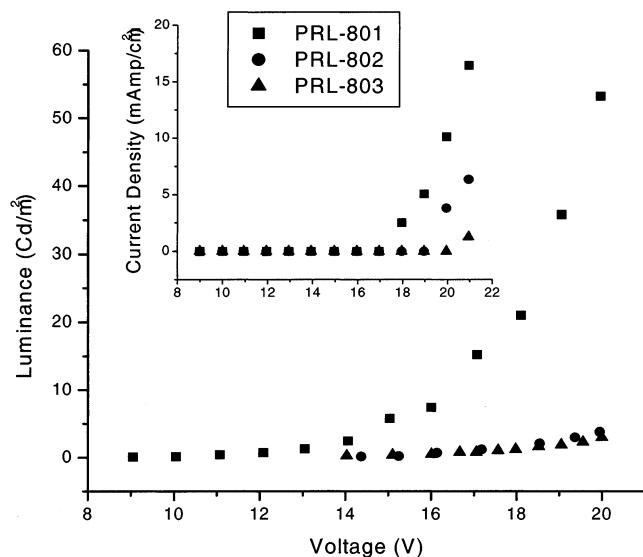


Figure 5. I-V and EL-V characteristics of the single-layer OLED structure containing PRL-801, PRL-802, or PRL-803 dye at a constant concentration of 16.66 wt %.

dye concentrations are 71.00, 35.85, and 2.16 cd/m^2 , respectively. It is interesting to notice that, while there is more than a 30 times increase in the EL intensity when comparing EL intensities for the case of 28.5 wt % PRL-801 dye concentration versus that of 4.76 wt % dye concentration, at the same time there is more than a 3 times decrease in the respective PL intensities because of the concentration quenching effects. There is also a noticeable reduction in the turn-on voltage with increasing concentration of the dye: 13 V for low and 9 V for high PRL-801 dye concentration.

Figure 5 shows the I-V and EL-V characteristics of a single-layer OLED structure containing the same concentration (16.66 wt %) of PRL-801, PRL-802, and PRL-803 dyes. The turn-on voltages are 9, 14, and 14.05 V for PRL-801, PRL-802, and PRL-803 dyes, respectively. The EL intensities for PRL-801, PRL-802, and PRL-803 at 19 V bias are 35.85, 2.94, and 1.87 cd/m^2 , respectively. These results clearly show that our D- π -A dye structure (PRL-801) is most effective in EL processes among the three dyes studied here.

Figure 6 shows the relative PL intensity of a single-layer OLED structure containing the same concentration (16.66 wt %) of PRL-801, PRL-802, and PRL-803 dyes. The measured PL quantum yields for the above dyes in the tetrahydrofuran solution are 0.52 for PRL-802, 0.48 for PRL-803, and 0.35 for PRL-801. However, we observe that the measured EL intensity at 19 V bias for the PRL-801 dye containing device is more than 20 times higher than that of the PRL-802 and PRL-803 dye containing device, which one would not expect based solely on the consideration of their PL quantum yield. Therefore, the experimental data show that the strength of the dye's EL cannot be correlated to its PL efficiency. Similar observations that the EL efficiency depends more on the dye concentration than on its PL efficiency in OLED devices have already been reported.²⁶

The EL emission light from the PRL-801 containing device was clearly visible under room light. As the voltage is increased, both the injection current and the

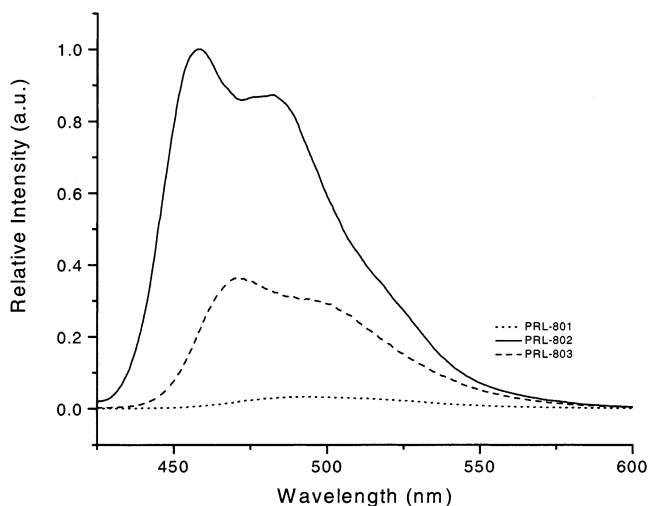


Figure 6. Relative PL intensity of a single-layer OLED structure containing the same concentration (16.66 wt %) of PRL-801, PRL-802, and PRL-803 dyes.

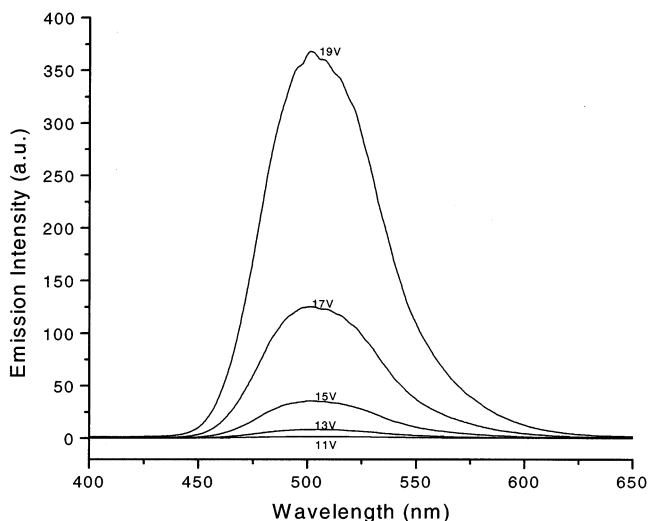


Figure 7. EL of the single-layer structure containing PRL-801 dye (28.5 wt %) at various operating voltages.

luminescence intensity increase in an exponential manner. Figure 7 shows the EL spectra at different applied bias voltages at room temperature for the device with the PRL-801 emitter at a concentration of 16.66 wt %. As the bias voltage increases, the brightness also increases and reaches a value of 498 cd/m^2 at an applied voltage of 25 V for this structure. However, above 25 V the diode experienced catastrophic failure. We are currently in the process of optimizing the OLED structure in order to increase its lifetime and stability.

The EL spectrum of the individual dye is very similar to its PL spectrum, which indicates that the light emission occurs directly from the dye and not from the PVK host. The PRL-801 dye doped PVK is the most efficient EL system among the three dyes studied in this work. This is clearly illustrated when comparing the I-V and EL-V curves shown in Figure 5. All emitters, PRL-801, PRL-802, and PRL-803, show the same trend: an exponential increase of the current density and the EL with increased voltage. However, the PRL-801 emitter exhibits the highest values for the same voltage. This behavior could be expected because the EL is determined by both the charge injection efficiency and the

PL quantum efficiency. The PRL-801 dye containing device shows the highest charge injection efficiency and at the same time shows efficient PL as compared to the other dyes (see Figure 6). On the other hand, devices with PRL-802 and PRL-803 dyes show very similar EL efficiencies even though the respective carrier injection efficiencies (I-V curve) exhibit relatively large differences. This result is somewhat surprising. We can speculate that most of the injected charges do not get trapped within the emitter to produce radiative recombination.

The results shown here suggest that the PRL-801 emitter offers an optimized structure for both the charge injection and the luminescence, resulting in a more effective EL. In most organic LEDs reported so far, the EL originated from singlet excited states of the fluorescent dyes or polymers used as the emitting materials. Ionization potentials, I_p , and electron affinities, E_a , are not yet available for our dye. However, we believe that the holes injected from ITO to PVK can be transferred to the PRL-801 dye because its I_p is close to that of PVK. Electrons cannot be injected from Ca to PVK because the work function energy of Ca is much greater than the E_a of PVK but, we think, can be injected/trapped into the oxadiazole part of the molecule having good electron-transporting properties. Assuming validity of these processes, the better EL performance of the PRL-801 dye containing device may be derived from a better balance in the number of injected holes and electrons

compared to the other dyes because the emitting dye contains both the hole- and electron-transporting groups.

Conclusions

Our results show that the new electroactive molecule having both electron- and hole-transporting groups in their structure produces efficient EL emission in a single-layer device. We think that the effectiveness of the dye's EL performance can be further improved through careful molecular engineering of the dye structure. It can be done by varying the electron-donating or -accepting strength of the charge-transporting end groups, by introducing additional groups in the central part of the molecular structure to vary the charge distribution, and/or by varying the effective conjugation length of the molecule.

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