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Luminescence Properties of Poly(*p*-phenylenevinylene) Derivatives Carrying Directly Attached Hole-Transporting Carbazole and Electron-Transporting Phenyloxadiazole Pendants

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SUMMARY: New poly(p-phenylenevinylene) (PPV) derivatives (**polymer 1** and **2**) that carry hole-transporting carbazole and electron-transporting phenyloxadiazole pendants were synthesized and their photo- and electroluminescence properties were studied. **Polymer 1** is poly[2-(N-carbazolyl)-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] that has both carbazole and 2-ethylhexyl pendant groups. And **polymer 2** is poly[2-{4-[5-(4-*t*-butylphenyl)-1,3,4-oxadiazolyl]phenyl}-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], which bears the 2-(4-t-butylphenyl)-5-phenyl-1,3,4-oxadiazole pendants. The optical properties of the polymer films were studied by UV-vis absorption, photoluminescence (PL) and electroluminescence (EL) spectroscopy. EL devices with the configuration of ITO/poly(3,4-ethylenedioxy-2,5-thienylene) (PEDOT) polymer/Ca/Al were constructed and the device performances were compared. **Polymer 1** emits bright yellowish green light (λ_{max}= 530 nm), whereas **polymer 2** emits yellowish orange (λ_{max}= 540 nm) light. The device fabricated using **polymer 1** showed a low turn-on electric field of 0.31 MV/cm and the maximum luminance of 30,390 cd/m^2 at 1.50 MV/cm. **Polymer 2** exhibited a little poorer device performance (turn-on electric field: 0.94 MV/cm; maximum luminance: 5,720 cd/m^2 at 2.74 MV/cm). Maximum photometric efficiencies of the devices were 4.4 and 1.3 cd/A, respectively.

Introduction

Electroluminescence properties of and light-emitting diode (LED) devices based on poly(p-phenylenevinylene) (PPV)[1)] and its derivatives,[2)] and other polyconjugated polymers[3)] are attracting a considerable amount of attention due to their possible application in displays. In fact, polymer LED (PLED) devices are expected to be commercialized soon in the world market. The devices are usually consisted of the indium-tin oxide (ITO) coated glass anode, a thin light-emitting polymer layer, and vacuum deposited metal cathode. In order to facilitate

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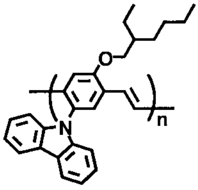
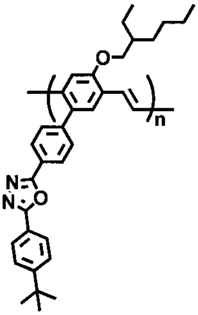
hole and/or electron injection from the electrode(s), multilayer devices using an additional conducting polymer layer such as poly(3,4-ethylenedioxy-2,5-thienylene) (PEDOT) doped with poly(styrene sulfonate) and a layer of tris(8-quinolinolato)aluminum (Alq_3). In LED devices electrons and holes are separately injected from the anode and cathode, respectively, under a bias electric field into the light-emitting layer, where the injected carriers form excitons. The excitons can decay away via various routes, one of them is radiative decay. Therefore, achievement of balance in injection and mobility of negative and positive carriers is considered to be prerequisite for an improved device performance.

Since it is well known that the poly(vinylcarbazole) (PVCz)[4] and 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD)[5] are hole-transporting (HT) and electron-transporting (ET) materials, respectively, we have synthesized the following two polymers. **Polymer 1** has the HT carbazole pendants, whereas **polymer 2** carries the ET phenyloxadiazole pendants. Both polymers bear an additional pendant, the 2-ethylhexyloxy group.



Polymer 1



Polymer 2

In this report, we would like to discuss the electronic structures, and PL behavior and EL properties of the two polymers. We constructed devices having the ITO/PEDOT/polymer/Ca/Al geometry and their performance was studied. Earlier, we reported PL and EL properties of the polymers bearing either the carbazole substituents or the 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (BPD) pendants without the 2-ethylhexyl substituents.[6]

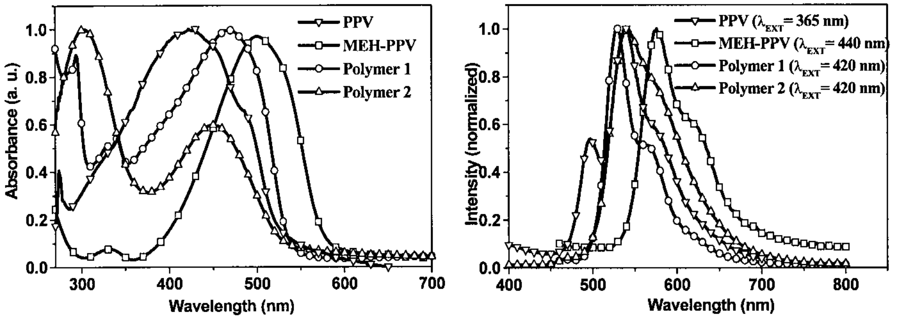
Experimental Part

Synthetic methods of the two polymers will be published elsewhere. Both polymers were prepared by polymerizing bis(1,4-bromomethylbenzene) derivatives in THF in the presence of potassium *t*-butoxide.7) **Polymer 1** was found to have a molecular weight of $\overline{Mw}$ = 72,000 by GPC against polystyrene standard. It's polydispersity index (PDI) was 1.40. **Polymer 2** had a molecular weight of $\overline{Mw}$ = 16,500 with PDI of 1.32.

The conducting polymer solution of PEDOT doped with polystyrene sulfonate (Bayer, σ = 10 Scm^{-1}) was spin coated onto a patterned ITO-coated glass slides pre-cleaned as described in literature.8) Solutions (1 wt %) of the polymers in 1,1,2,2-tetrachloroethane was spin coated and the films were subjected to thermal treatment at 150°C for 3 hours. The Ca cathode 2000 Å thick was vacuum deposited at 3.0 x 10^{-7} Torr. An aluminum (Al) capping layer was then deposited to protect the Ca cathode. The UV-vis, PL and EL spectra were recorded as described in our earlier reports.6) The UPS9) and NEXAFS10) spectra were obtained in the manner as found in literature.

Results and Discussion

Fig. 1 compares the (a) UV-vis and (b) PL spectra of **polymer 1 and 2** with that of PPV and MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene]). **Polymer 1** shows an absorption from the carbazole moiety with λ_{max} at 340 nm, whereas **polymer 2** absorbs strongly centered around λ_{max}= 302 nm arising from the oxadiazole (BPD) pendant. And the absorption by **polymer 1** at 350-540 nm (λ_{max}= 461 nm) and that by **polymer 2** at 370-530 nm (λ_{max}= 450 nm) are originated from the π-π^* transitions of their main chain.



(a) (b)

Figure 1. Comparison of (a) UV/vis absorption and (b) photoluminescence (PL) spectra of PPV, MEH-PPV, **polymer 1** and **2**. The values in parentheses are the corresponding excitation wavelengths.

The absorption edges are 526 and 540 nm, respectively for **polymer 1** and **2**, which correspond to the optical bandgaps of 2.4 and 2.3 eV. In comparison, PPV absorbs at λ_{max}=

430 nm with the bandgap energy of 2.4 eV. Therefore, absorptions by **polymer 1** and **2** are slightly red-shifted when compared with PPV. The well-known polymer, MEH-PPV, absorbs at 350-570 nm with λ_{max}= 503 nm.

According to the PL spectra shown in Fig. 1(b), **polymer 1** emits light over 490-650 nm (yellowish green; maximum emission at 490 nm), whereas **polymer 2** emits over the wavelength range of 500-670 nm (yellowish orange; maximum emission at 541 nm). Emitted lights by the both polymers are slightly red-shifted as compared with PPV, a green light emitter.

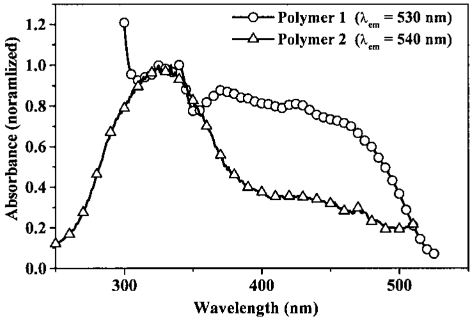


Figure 2. Comparison of excitation spectra of MEH-PPV, **polymer 1** and **2**. The values in parentheses are the emission wavelengths.

Fig. 2 shows excitation spectra of **polymer 1** and **2**. One notes that they are not exactly same as the corresponding absorption spectra as shown in Fig. 1(a). It is clear that absorption either by the carbazole (λ_{max}= 345 nm) or by the oxadiazole pendants (λ_{max}= 300 nm) makes a strong contribution to the emission by the backbone. This must be due to a facile excited state energy transfer from pendants to backbone. That is why we do not observe the occurrence of separate emissions by the pendants. In addition, we observed that the PL spectra of **polymer 1** and **2** are invariant to the excitation wavelength indicating that the emissive state is the same even with high-energy excitation.

Fig. 3 compares the EL characteristics of ITO/PEDOT (20-25 nm)/polymer (75-80 nm)/Ca/Al devices fabricated using **polymer 1** and **2**. For the sake of comparison, data for MEH-PPV also are included in Fig. 3. According to the data shown in Fig. 3, the turn-on electric field (the value at 0.1 mA/mm^2) increases in the order of MEH-PPV (0.37 MV/cm) < **polymer 1** (0.50 MV/cm) < **polymer 2** (1.20 MV/cm). And the maximum brightness obtainable was 30,390 (1.5 MV/cm), 20,540 (1.4 MV/cm), and 5,720 (2.7 MV/cm), respectively for **polymer 1**, MEH-PPV, and **polymer 2**.

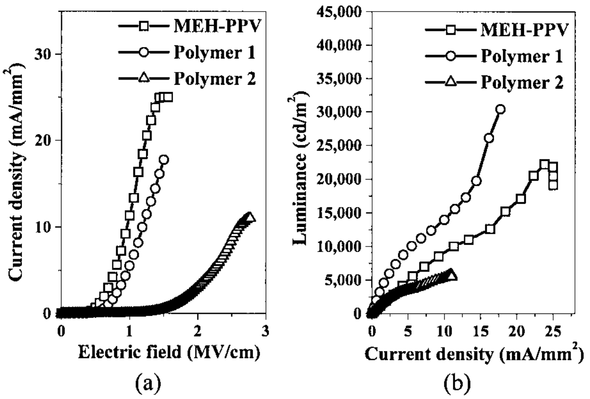
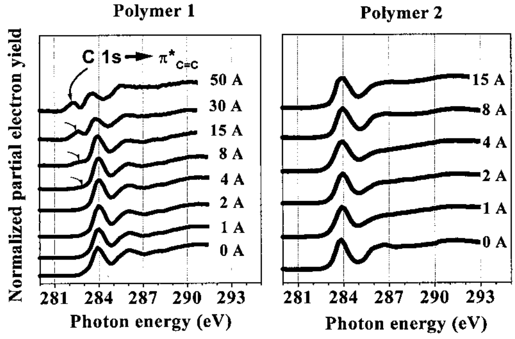


Figure 3. Comparison of (a) electric field - current density and (b) current density - luminance curves of MEH-PPV, **polymer 1** and **2**.

These observations are rather surprising especially for the lower turn-on electric field and better EL performance of **polymer 1** when compared with **polymer 2**. Since the BPD pendant should have a higher electron affinity than the carbazole pendant, one may expect that **polymer 2** would reveal a more facile electron acceptance from the cathode than **polymer 1**. In fact, the LUMO levels of the polymers determined by the UPS7) and from the optical bandgaps, 3.2 eV for **polymer 1** and 4.0 eV for **polymer 2**, suggest again that electron-injection should be easier for **polymer 2** than for **polymer 1**. Their HOMO levels were 5.6 and 6.3 eV, respectively.

We, however, observed very interesting contrasting NEXAFS (near-edge X-ray absorption fine structure) spectroscopic behavior for the two polymers. Fig. 4 compares the NEXAFS spectra of the polymers obtained as we deposit Ca metal on the polymer films. In the case of **polymer 1**, a new peak starts to appear in the low photon energy side for $C_{1s} \rightarrow \pi^*_{C=C}$ transition even when the thickness of the Ca deposition was only 4 Å thick. Appearance of this new peak can be ascribed to the formation of new intragap states by the electrons donated from calcium to the polymer. 10) The main peak at 284 eV slowly moved to 283.5 eV as the calcium electrode was deposited. The difference between the original peak and the new peak at the deposited electrode thickness of 50 Å is 1.3 eV. In contrast, **polymer 2** did not display appearance of any new peak in the NEXAFS spectra. This difference can be explained by the conjecture that, in the case of **polymer 1**, the donated electrons from calcium to the polymer tend to remain in the π-system of the main chain due to the electron-donating character of the two pendants, carbazole and 2-ethylhexyloxy substituents. This assumption is also in line with the relatively low turn-on electric field for **polymer 1**. The same situation can not occur in **polymer 2** where the oxadiazole pendants with strong electron affinity are expected to capture the electrons donated from the electrode material draining out them from the backbone π-system.



(a) (b)

Figure 4. Evolution of C 1s NEXAFS spectra of (a) **polymer 1** and (b) **2** during the Ca deposition onto the polymer films.

Lastly, it should be pointed out that the presence of different pendants onto the PPV backbone should change the carriers mobility and, thus, balance thereof. This will greatly influence the device performance. According to our preliminary experimental results, the carbazole and BPD pendants greatly improve the balance in the carriers mobility.[11a,b)] Especially, the ratio of hole and electron mobility determined by the time-of-flight method, μ_h/μ_e, was only 5.3 for **polymer 1**. The same value for PPV was 230. Detailed results will be published elsewhere in future.[11c)]

Conclusion

Luminescence properties of two new PPV derivatives bearing either electron-donating carbazole pendants or electron-attracting phenyloxadiazole pendants reveal several interesting scientific facts. Electronic interactions between the π-system of the polymer backbone and pendants are rather limited in the ground state according to their UV-vis absorption characteristics. The interactions, however, appear to be pronounced in the excited states reflected by the PL and excitation spectra of the two polymers. The LUMO and HOMO levels and, thus, bandgap energies are influenced significantly by the pendants. When compared with spectral characteristics of MEH-PPV, the two pendants seem to exert a steric hindrance to the coplanarity of the backbone resulting in a blue shift in their absorption of UV-vis light.

In other words, they seem to partially destroy the coplanarity of the backbone π-system resulting in a reduction of the conjugation length. As far as the maximum brightness attainable is concerned, **Polymer 1** was found to perform best in EL among the three polymers described in this article, most probably due to the easy electron injection from the cathode and balanced carriers mobility.

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