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Luminescence Properties of PPV Derivatives Bearing Substituted Carbazole Pendants

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Summary: A series of PPV derivatives bearing substituted and unsubstituted carbazole and 2-ethylhexyloxy pendants were prepared and their photo- (PL) and electroluminescence (EL) properties were studied. Substituted carbazole structures were *N*-phenylcarbazole and 3,6-dimethoxycarbazole. The substituents on the carbazole pendants caused little change in UV-vis absorption, PL, and EL when compared with the polymer bearing the unsubstituted carbazole pendants. The presence of the benzene ring between the main chain and the carbazole pendant increased the threshold electric field in EL. We could obtain maximum brightness of ca. 17,000 – 30,000 cd/m^2 for the polymers carrying the unsubstituted and dimethoxy substituted carbazole pendants.

Keywords: conjugated polymers; luminescence

Introduction

In recent years, there have been published many reports concerning the photo- and electroluminescence properties of poly(*p*-phenylenevinylene) (PPV) derivatives[1-8] and other polyconjugated polymers.[9-12] The Cambridge group's[1] pioneering work on the light-emitting diodes (LED) fabricated with PPV generated a strong impetus to researches on organic polymer LED devices, some of which are expected to become commercialized in the near future. Previously, we reported the EL characteristics of LED devices prepared with PPV derivative bearing diphenyloxadiazole,[13,14] dialkylfluorene[15], and carbazole pendants[14,16] directly bonded to the PPV backbone. All of the PPV derivatives are green-light emitting polymers exhibiting excellent device performance. In particular, the PPV derivative (CzEh-PPV) having 2-ethylhexyloxy (Eh) and carbazole (Cz) pendants directly attached to the benzene rings in the backbone revealed a very high external quantum efficiency and a low threshold electric field. In addition, CzEh-PPV showed much more balanced mobility of the two carriers, i.e., positive hole and negative electron than PPV and MEh-PPV.[17,18] The low threshold electric field for this

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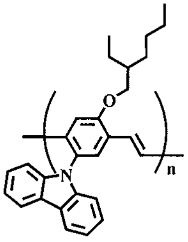
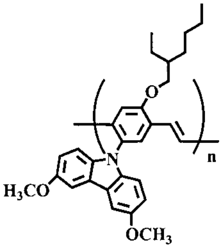
polymer could be ascribed to the formation of new intragap states when the polymer is contacted with the cathode metal such as calcium, which was supported by the near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. [17,18]

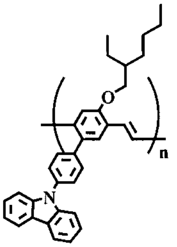
In this report we would like to compare the PL and EL properties of two new PPV derivatives bearing substituted carbazole pendants, MCzEh-PPV and PCzEh-PPV:



CzEh-PPV



MCzEh-PPV



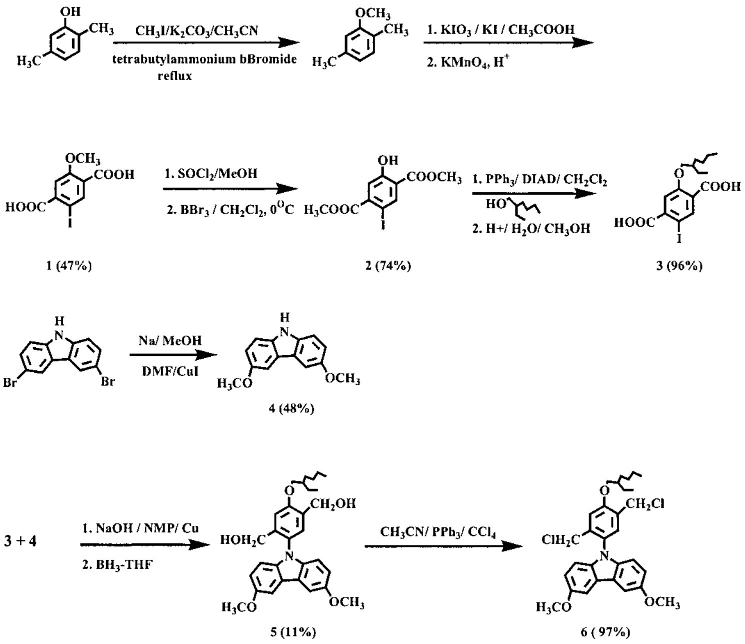
PCzEh-PPV

MCzEh-PPV carries two methoxy groups on the benzene rings in the carbazole moiety while in PCzEh-PPV exists an additional benzene ring bridge between the backbone and the carbazole moiety. These polymers were prepared by the Gilch polymerization[19] of the corresponding bis(chloromethyl) monomers.

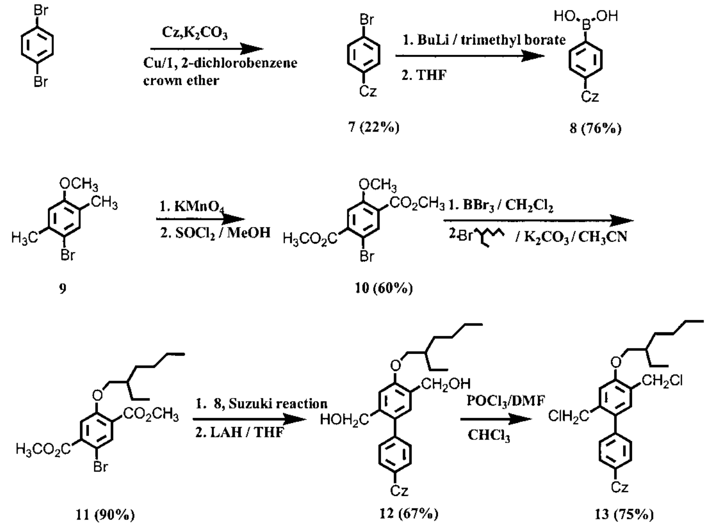
Results and Discussion

Synthesis of MCzEh-PPV and PCzEh-PPV

MCzEh-PPV and PCzEh-PPV were polymerized by the Gilch polymerization[19] of the two monomers, 1,4-bis(chloromethyl)-2-(3,6-dimethoxycarbazol-9-yl)-5-[(2-ethylhexyl)oxy]benzene (**6**) and 1,4-bis(chloromethyl)-2-(4-carbazol-9-ylphenyl)-5-[(2-ethylhexyl)oxy]benzene (**13**). Synthetic routes to the two monomers are shown in Schemes 1 and 2. The polymers were purified by Soxhlet extraction with methanol. Both polymers were readily soluble in common organic solvents such as tetrahydrofuran, chloroform, and 1,1,2,2-tetrachloroethane. The molecular weights of the two polymers measured by gel permeation chromatography (GPC) were $\overline{M}_n$ = 280,000 and 42,000, respectively. Their polydispersity indices were 3.0 and 2.1.



Scheme 1. Synthetic route to MCzEh-PPV monomer



Scheme 2. Synthetic route to PCzEh-PPV monomer

Uv-vis Absorption and PL Spectra, Electronic Energy Levels

Figure 1 compares the UV-vis absorption spectra of films of CzEh-PPV, MCzEh-PPV, and PCzEh-PPV. The absorption maxima (λ_{max}) responsible for the π - π* transitions of the backbone's π-electron systems are located at 461, 461, and 475 nm, respectively, for CzEh-PPV, MCzEh-PPV, and PCzEh-PPV. Insertion of the benzene ring between the main chain and the carbazole moiety causes a red shift, but attachment of methoxy substituents on the benzene rings of the carbazole moiety influenced little the λ_{max} position although absorption by the carbazole moiety is significantly red-shifted and appears at 313 and 373 nm from 295 and 341 nm. The electron-donor property of the methoxy group is well reflected by this red shift. In addition, the methoxy groups broadened the absorption peak for the π - π* transition.

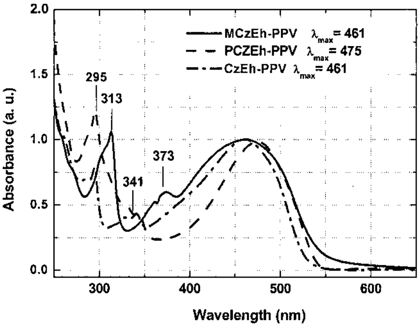


Figure 1. UV-vis absorption spectra of polymers.

The optical band gaps estimated from the absorption edges are 2.35 eV (528 nm), 2.28 eV (544 nm) and 2.30 eV (540 nm), respectively, for CzEh-PPV, MCzEh-PPV, and PCzEh-PPV. The presence of the methoxy and phenyl substituents slightly reduced the band gap energy.

The PL spectra of the polymers obtained for the excitation wavelength of 430 nm are given in Figure 2. All the three spectra reveal a similar feature that shows some vibronic details. The intensive major peak (at 530, 538 and 544 nm for CzEh-PPV, PCzEh-PPV and MCzEh-PPV, respectively) in the shorter wavelength region carries overlapped shoulder peaks on the longer wavelength side. Here again, we observe that the spectrum of MCzEh-PPV is broadest extending to 700 nm. All the three polymers emit green light, but MCzEh-PPV with an orange shade.

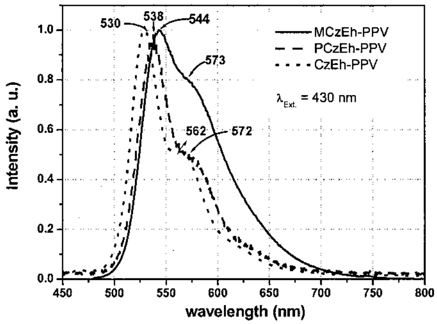


Figure 2. PL spectra of polymer thin films (thickness 80 nm).

We tried to obtain information on the electronic energy levels, i.e., HOMO and LUMO levels, of the polymers by cyclovoltammetry[20,21] and the results are summarized in Table 1. The optical bandgaps estimated from the absorption edges in the UV-vis spectra were utilized in the evaluation of the LUMO levels. We note that the HOMO and LUMO levels have not been altered much by either methoxy groups in MCzEh-PPV or the benzene ring in PCzEh-PPV when compared with HOMO and LUMO levels of CzEh-PPV, although the HOMO levels are elevated slightly more than LUMO levels.

Table 1. HOMO-LUMO values of polymers determined by CV.

	HOMO (eV)	LUMO (eV)
MczEh-PPV	5.40	3.14
PCzEh-PPV	5.44	3.15
CzEh-PPV	5.53	3.22

EL Spectra and Characteristics of LED Devices

We constructed LED devices having the configuration of ITO/ PEDOT:PSS (20 nm)/ polymer (80 nm)/ Li:Al. Poly[3,4-(ethylenedioxy)thiophene] (PEDOT) doped with poly(styrenesulfonic

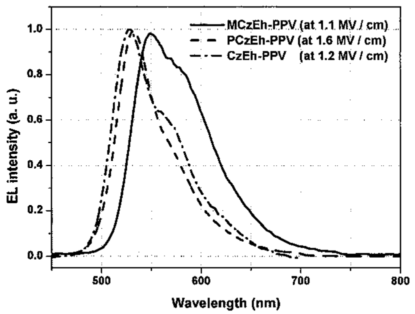


Figure 3. EL spectra of polymers (device structure: ITO/ PEDOT : PSS (20nm) / polymer (80 nm)/ Li:Al).

acid) (PSS) supplied by Bayer ($\sigma = 10$ Scm^{-1}) was spin-coated on the ITO-coated glass anode. Then the emitting polymer layer was spin-coated onto it using a solution (1 wt.%) in chlorobenzene. Finally, the cathode layer was vacuum-deposited using an alloy of aluminium and lithium (0.12 % Li). Figure 3 compares the EL spectra of the three devices obtained at the electric field indicated in the figure. The general profile of the EL spectra is very similar to those of the corresponding PL spectra shown in Figure 2.

Figure 4 compares the current density-electric field (Figure 4a) and electric field - emitted light intensity curves (Figure 4b) for the three devices. The threshold electric fields taken at the electric field for the current density of 0.1 mA/mm^2 are 0.82, 0.70, and 1.3 MV/cm, respectively, for CzEh-PPV, MCzEh-PPV, and PCzEh-PPV. The methoxy group reduced the threshold electric field whereas the phenylene group increased it. The maximum brightness observed was the highest (6,080 cd/m^2, at 1.4 MV/cm) for MCzEh-PPV and the lowest (280 cd/m^2 at 1.8 MV/cm) for PCzEh-PPV. The electric field – light output curve of Figure 4b tells us that PCzEh-PPV utilizes the injected carriers least efficiently among the three polymers.

Since the HOMO and LUMO levels of the present polymers are not much different from each other, it is conjectured that mobilities of carriers are least balanced in PCzEh-PPV resulting in poor device performance. Earlier, we[17,18] reported that CzEh-PPV exhibits a much greater balance in the mobility of carrier ($\mu_{h+} / \mu_{e-} \approx 5$) than PPV ($\mu_{h+} / \mu_{e-} \approx 200$) and MEh-PPV ($\mu_{h+} / \mu_{e-} \approx 100$).

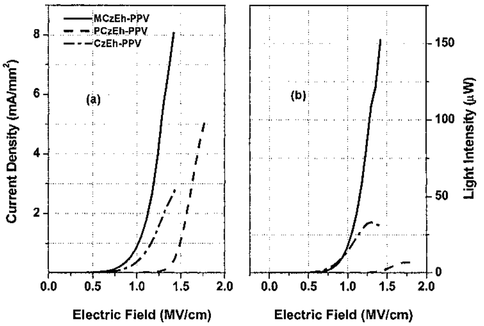


Figure 4. (a) Electric field vs. current density and (b) light intensity curves of polymers (device structure: ITO/ PEDOT:PSS (20 nm)/ polymer (80 nm)/ Li:Al).

Probably, the presence of the benzene ring between the backbone and the carbazole moiety in PCzEh-PPV deprives the carbazole structure from its ability to stabilize the positive carrier which would bring about the improvement in the balance of carriers mobilities as in CzEh-PPV. Our recent optically detected magnetic resonance (ODMR) study[22] clearly demonstrates that the carbazole unit directly attached to the PPV backbone is involved in the stabilization of positive polarons formed along the backbone.

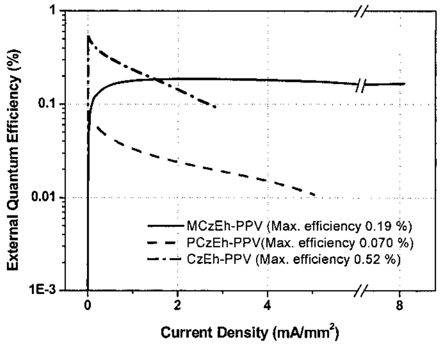


Figure 5. Comparison of external quantum efficiency of polymers (device structure: ITO/ PEDOT:PSS (20 nm)/ polymer (80 nm)/ Li:Al).

The device constructed with MCzEh-PPV not only showed the highest maximum brightness, but also excellent device stability as shown in Figure 5. This figure compares the external quantum efficiency of the three devices. Although the initial quantum efficiency is the greatest for CzEh-PPV, at current density higher than 2 mA/mm^2 it becomes greater for MCzEh-PPV than for CzEh-PPV. Moreover, the device efficiency of MCzEh-PPV remained practically constant at about 0.2 % until it failed. On the other hand, the device efficiency of the other two polymer devices decreased rapidly as the current density is increased. The device stability observed for MCzEh-PPV is rather remarkable, although its electronic structure is not much different from the other two.

Highly Luminescent Devices

After observing that MCzEh-PPV performs the best among the present polymers, we decided to construct another LED device of ITO/ PEDOT:PSS(20nm)/ polymer (80 nm)/ Ca/ Al and to study its performance. Earlier, we[16] learned that the ITO/ PEDOT:PSS (20nm)/ polymer (80 nm)/ Ca/ Al device produced higher brightness than the ITO/ PEDOT:PSS (20nm)/ polymer (80 nm)/ Li:Al device, especially when we used PPV derivatives for the fabrication of the devices. In order to protect the calcium cathode, aluminium was vacuum-deposited on the cathode.

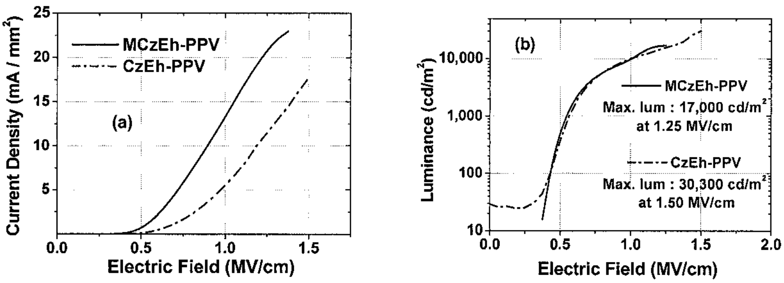


Figure 6. Comparison of (a) electric field vs. current density and (b) electric field vs. luminance properties of MCz-PPV and CzEH-PPV (device structure: ITO/ PEDOT:PSS (20 nm)/ polymer (80 nm)/ Ca/ Al).

Figure 6a and 6b compare characteristics of the devices fabricated with MCzEh-PPV and CzEh-PPV. We can see that the two devices exhibit very similar electrical properties. The threshold electric fields are 0.40 and 0.50 MV/cm for 0.1 mA/mm^2, respectively, for MCzEh-PPV and CzEh-PPV. The dependence of luminescence on the applied electric field (Figure 6b) of the two devices is very much the same up to 1.25 MV/cm, where the device of MCzEh-PPV failed after reaching the maximum brightness of 17,000 cd/m^2 at the applied electric field of 1.25 MV/cm. The CzEh-PPV device's maximum brightness was 30,300 cd/m^2 at the applied field of 1.50 MV/cm. The two devices exhibited the brightness of 200 cd/m^2 commonly at the applied field of 0.46 MV/cm. The major difference between the two devices, however, can be noted in their luminance efficiency as shown in Figure 7. The luminance efficiency in lm/W of the device of MCzEh-PPV decreases from 0.65 lm/W to 0.26 lm/W, as the applied field was increased to 1.25 MV/cm. This decrease in efficiency is much less than the decrease observed for the CzEh-PPV device, which revealed the initial luminance efficiency higher than 3 lm/W, decreasing rapidly to and stabilized at 0.45 lm/W. The device efficiency at 200 cd/m^2 was 0.60 lm/W for MCzEh-PPV and 2.95 lm/W for CzEh-PPV.

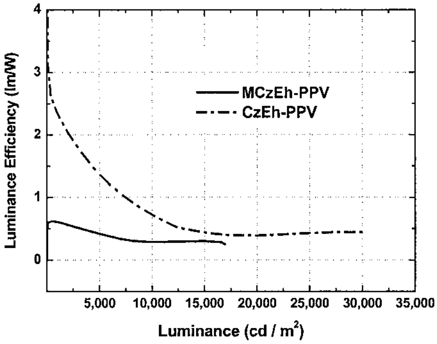


Figure 7. Comparison of luminance efficiency of MCz-PPV and CzEH-PPV (device structure: ITO/ PEDOT:PSS (20 nm)/ polymer (80 nm)/ Ca/ Al).

This observation again proves that MCzEh-PPV shows much more consistent device performance than CzEh-PPV. The scientific reason for this is not yet clear. One major difference between the polymers is in their average molecular weights: the MCzEh-PPV sample utilized in this study is of a very high molecular weight, $\overline{M_n}$ = 280,000 and $\overline{M_w}$ = 850,000, whereas $\overline{M_n}$ and $\overline{M_w}$ values of the CzEh-PPV sample are much lower (49,800 and 72,000, respectively). It is well known that, in general, low-molecular-weight polymers exhibit poorer thermal stability and experience easier molecular migration. These two factors are expected to lower the LED device performance as Joule heat is evolved when the device is in operation. Therefore, the particular stability of the MCzEh-PPV device is ascribed to its very high molecular weight.

Conclusion

We have prepared two new PPV derivatives, MCzEh-PPV and PCzEh-PPV, bearing substituted carbazole moieties as pendants and their EL properties were compared with CzEh-PPV. Among the three polymers, MCzEh-PPV imparted to the LED device the highest stability most probably owing to its high molecular weight. CzEh-PPV and MCzEh-PPV performed significantly better than PCzEh-PPV in LEDs. The maximum brightness of LED devices fabricated with MCzEh-PPV and CzEh-PPV easily reached 17,000 – 30,000 cd/m^2 when device configuration was ITO/ PEDOT:PSS/ polymer/ Ca/ Al. All the three polymers emit green light.

Experimental

Synthesis of polymers: Synthetic details will be published elsewhere.[23]

Device fabrication and characterization: The patterned ITO-coated glass slides were cleaned by successive sonication in acetone, propan-2-ol and distilled water each for 13 min, and finally cleaned by UV - ozone for 13 min. The conducting polymer solution of poly(3,4-ethylenedioxy-2,5-thiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) (Bayer) was spin-coated (Laurell, U.S.A) at 3300 rpm for 1 min and dried at 150 °C for 30 min. The electric conductivity of this film measured by the four-line probe method was 10 Scm^{-1}. The solution (1wt %) of polymer in purified 1,1,2,2-tetrachloroethane was spin-coated at 1000 rpm for 1 min and the film was subjected to thermal treatment at 150 °C for 1 h under vacuum. The Ca cathode 2000 Å thick was vacuum-deposited from the tungsten boat at a deposition rate of 2 Å/s under the pressure of 3.0 x 10^{-7} torr. An Al capping layer was then evaporated to protect the Ca cathode at a deposition rate of 4 Å/s under the same pressure. The active area of the EL devices was 4 mm^2. Photoluminescence (PL) and electroluminescence (EL) spectra were recorded on a PC1 photon counting spectrofluorometer (ISS Inc., USA). Current-voltage (*I-V*) characteristics and the intensities of EL emission were simultaneously measured with a Keithley 238 SMU electrometer and a BM7 luminance meter (Topcon Technologies, Inc., USA). Device fabrication and all the measurements were performed in a dry argon filled glove box without exposing to air.

Cyclovoltammetry:[20,21] The polymer thin films were spin-coated on the ITO-coated glasses. Chlorobenzene was used as the solvent. The electrolyte solution employed was 0.1 M tetrabutylammonium perchlorate in dimethylformamide. The Ag/AgCl and Pt wire (600 μm in diameter) electrodes were utilized as reference and counter-electrodes, respectively.

Acknowledgment

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