Macromol. Symp. **2004**, *212,* 281-286

Electroluminescence and Charge Photogeneration in Poly(9,9-dihexadecylfluorene-2,7-diyl) and Its Blends

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Summary: Photoluminescence, electroluminescence (EL), charge photogeneration and transport were studied in poly(9,9-dihexadecylfluorene-2,7-diyl) (PFC16), poly[(2,5-dihexadecyl-1,4-phenylene)(1,4-phenylene)] (PPPC16) and their blends. Blending of PFC16 with PPPC16 led to a significant improvement of the EL efficiency and stability compared with the devices fabricated from the neat polymers. Efficient blue and white light-emitting devices (LEDs) were fabricated using the blends. The increase in the EL efficiency was attributed to modification of the charge injection, transport and recombination properties in the blend.

Keywords: electroluminescence; LEDs; poly(1,4-phenylene)s; polyfluorenes; polymer blends

Introduction

Recently, an important issue under investigation has been the development of efficient and stable blue light-emitting materials. In this area, conjugated polymers with large bandgap such as poly(1,4-phenylene)s (PPP) and polyfluorenes (PF) are of particular interest due to their high photoluminescence (PL) efficiency in the blue spectral region.[1-7] The performance of polymer LEDs can be improved by optimizing the parameters of the active medium through polymer blending. We have shown that the aggregation of poly[2,5-bis(isopentyloxy)-1,4-phenylene] (SPPP) molecules could be avoided in blends composed of SPPP and poly[methyl(phenyl)silanediyl] (PMPSi).[6] Using polymers blends, the EL efficiency and time stability can be improved.[6,7]

In this paper we have shown that an increase in the EL efficiency and stability of blue emission in PF-based LEDs can be achieved using polymer blends composed of two electroluminescent polymers - poly(9,9-dihexadecylfluorene-2,7-diyl) (PFC16) and poly[(2,5-dihexadecyl-1,4-phenylene)(1,4-phenylene)] (PPPC16). We have shown that such blending can significantly improve the LED performance.

DOI: 10.1002/masy.200450831

Experimental

Chemical structures of the polymers under study are shown in Figure 1. PFC16 was synthesized by the Yamamoto coupling reaction [8] from 2,7-dibromo-9,9-dihexadecylfluorene using zinc, the nickel(II)/triphenylphosphine complex as a catalyst, and 2,2′-bipyridine as a coligand. SPPPC16 were prepared by the Suzuki coupling of bis(boronate) with the corresponding dibromo derivative in the presence of a palladium catalyst.[8]

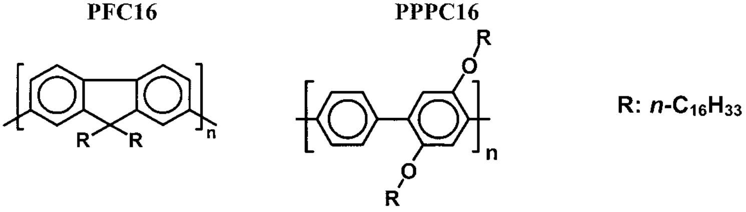

Figure 1. Chemical structures of the polymers under study.

Thin polymer films were prepared by spin-coating from toluene solutions. All films exhibited a good optical quality. Polymer LEDs with a hole-injecting indium-tin oxide (ITO) electrode and an electron-injecting aluminium (Al) electrode were fabricated. The ITO electrode was further optimized by coating with a thin layer of a conductive polymer, poly[3,4-(ethylenedioxy)thiophene]/poly(styrenesulfonate) (PEDT-PSS), to improve its hole-injecting properties. The 50-nm thick PEDT-PSS layers were also prepared by spin-coating. Two-layer ITO/PEDT-PSS/polymer/Al devices were studied. 60-80 nm thick Al electrodes were vacuum-evaporated on the top of polymer films. Typical active areas of the LEDs were 4 mm^2. Samples for charge transport and photogeneration measurements (film thicknesses from 700 to 1300 nm) were prepared by spin coating of the polymer solution in toluene onto stainless steel substrates. All polymer films were dried in vacuum (10^{-3} Pa) at 323 K for 6 h. Cyclic voltammetry was measured using a PA4 polarographic analyzer (Laboratory Instruments, CZ) and ionization potential was determined as described in Ref.[9], where more details are also given concerning the experimental setup. UV-vis spectra were measured on a Perkin-Elmer Lambda 20 spectrometer and EL and PL spectra using a home–made spectrofluorometer with single photon-counting detection (SPEX, RCA C31034 photomultiplier). LEDs were from a Keithley 237 source measuring unit, which served for simultaneous recording of the current passing through the sample. Current-voltage and EL intensity-voltage characteristics were recorded simultaneously using a Keithley 237 source measuring unit and a silicon photodiode with integrated amplifier (EG&G HUV-4000B) for detection of total light output. The measurements of the photogeneration efficiencies were carried out using the method of photoinduced surface potential discharge decay (xerographic).[10] Discharge experiments were performed with a home-built setup as described in Refs[9,11]. A polymer sample was charged to the initial surface potential with a corona and then discharged upon irradiation. The measurements were performed with irradiation incident on the positively charged surface. To ensure emission-limited conditions, the discharge was measured with photon fluxes as low as possible (10^{17}-10^{18} photon $m^{-2} s^{-1}$). Transport properties were studied by measurements of the dark surface potential decay.[12]

Results and Discussion

Typical absorption and PL of thin spin-coated films of PFC16 and PPPC16 on a fused silica substrate are shown in Figs 2a and 2b. Thin films of both PFC16 and PPPC16 exhibited efficient blue PL with the maxima at 425 nm and 415 nm, respectively. Also shown is the electroluminescence (EL) spectrum. In polyfluorene chains with long alkyls, the aggregate formation is not so pronounced as in polyfluorenes with shorter alkyls (octyl), where a red-shifted emission is observed already on freshly prepared films. But the EL efficiency and stability of the single-component PFC16 or PPPC16 devices is not high enough; a higher EL efficiency was detected in PPPC16 devices.

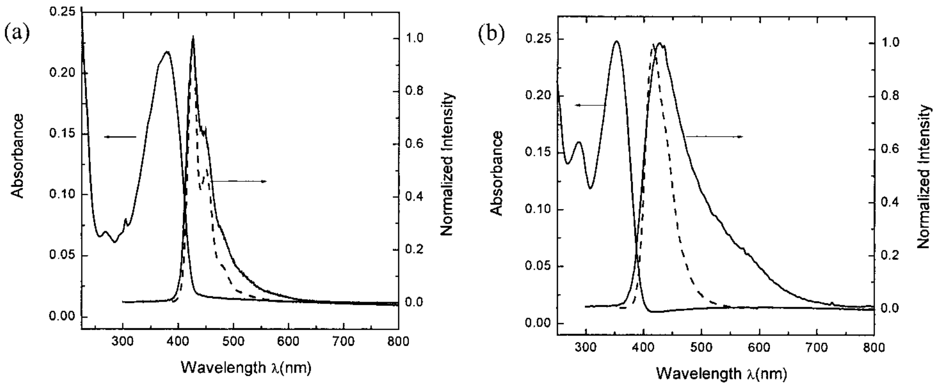

Figure 2. Absorption and photoluminescence (dashed line) spectra of thin polymer films and an electroluminescence (solid line) spectrum of ITO/PEDT:PSS/polymer/Al devices for polymers: (a) PFC16 and (b) PPPC16.

Using blends made of PFC16 and PPPC16, more efficient blue LEDs with the EL maximum at about 425 nm have been fabricated. An example of the PL and EL spectra for a blend LED is shown in Fig. 3a. The PL emission spectra of neat polymers and their blends indicated that PL emission from PFC16 dominates in blends. The EL onset and driving voltages of neat PFC16 and blend devices were nearly the same, even lower values were observed in the blend devices. Performance of the devices is shown Fig. 3b. Blending led to a significant improvement of the EL efficiency and stability compared with the devices made of neat EL polymers. In the blend LEDs, the EL efficiency and EL spectra depended on the contents of the components (see Fig. 3). The EL efficiency in the blends was up to one order of magnitude higher than that in PFC16 LEDs. The EL results can be mainly explained by modification of charge injection, transport and recombination in the polymer blend layer.

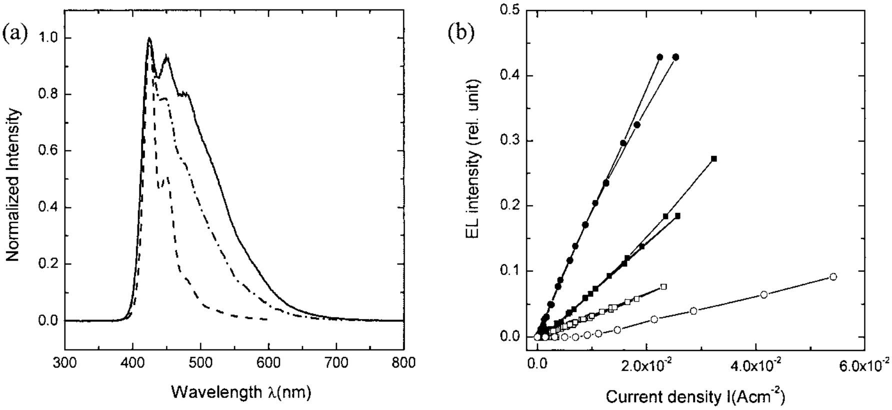

Figure 3. (a) PL spectrum (dashed line) of a thin film of a polymer blend and EL spectrum (solid line) of the ITO/PEDT:PSS/polymer blend/Al device for polymer blends composed of PFC16 and PPPC16 (7:3 - solid line, 1:1 – dash-and-dot line). (b) Spectrally integrated EL intensity as a function of the current density of the LEDs: ITO/PEDT:PSS/PFC16/Al (open circles), ITO/PEDT:PSS/PPPC16/Al (open squares), ITO/PEDT:PSS/PFC16+PPPC16 (1:1)/Al (solid squares) and ITO/PEDT:PSS/PFC16+PPPC16(7:3)/Al (solid circles).

From cyclovoltammetric measurements the value of ionization potential (I_P) of PFC16 and PPPC16 close to 5.8 eV and 5.5 eV were determined, respectively. The I_P value determined for PPPC16 is lower than that for PFC16, so the PPPC16 molecules can facilitate hole injection into PFC16. Transport properties of thin films were studied from the dark decays of the surface potential. Typical dark decay curves are shown in Fig. 4a. The decay curves were analyzed by a model of trap-controlled hopping.[12] The effective hole mobility and other model parameters such as the capture and release rates of charge carriers in a deep trap were determined by curve fitting. The fastest dark decay (curve 1 in Fig. 4a) was observed in PFC16, which corresponded to the highest effective mobility, i.e. the mobility of charge carriers controlled by energetically shallow traps in thermal equilibrium with the transport states. It is significantly higher than that in PPPC16 (curve 2). Depending on the contents of the components in the blend, the effective mobility could be modified (see curve 3 and 4). Due to the lower ionization potential, the PPPC16 molecules act as traps for holes in blend layers, which results in the charge transport modification, i.e. in a lower effective mobility.

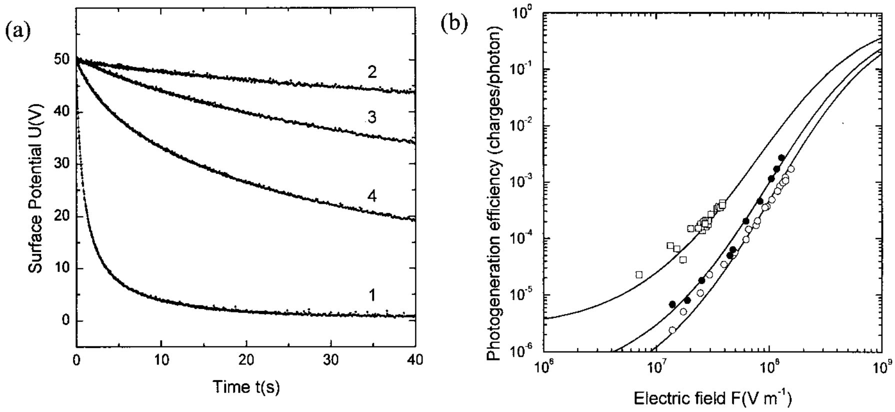

Figure 4. (a) Dark decay curves measured on thin films of (1) PFC16, (2) PPPC16, (3) PFC16+PPPC16(1:1) and (4) PFC16+PPPC16(7:3). (b) The electric field dependences of the photogeneration efficiency in PFC16 (open squares), PPPC16 (open circles), and PFC16+PPPC16(7:3) (solid circles). Solid lines were calculated using the Onsager theory with the Gaussian distribution of electron-hole pair radii with the parameters given in Table 1.

Charge photogeneration was studied to get information about charge dissociation and/or recombination in the electric field. The charge photogeneration efficiency, η_{ph}, was measured as a function of the electric field. η_{ph} in PFC16 was more than one order of magnitude higher than that in PPPC16 and the blends. The results fitted by the Onsager theory of geminate recombination [13] with the Gaussian distribution function of electron-hole (e-h) pair radii $g(r) = (\pi^{-3/2}\alpha^{-3})\exp(-r^2/\alpha^2)$,[14,11] which gave the best description of the experimental data, are shown in Fig. 4b. The full lines represent the best theoretical fits to our experimental data with parameters given in Table 1. From the distribution parameters, the most effective separation distances of e-h pairs r_{le} and r_{he} at low and high electric fields, respectively, were determined. Compared with PFC16 in the blend, shortening of the separation distances without a change of the primary quantum yield $\eta_{0\alpha}$ was observed. This indicates a decrease in the geminate recombination quenching at the electric field, which is favorable for EL. On the other hand, compared with PPPC16, the separation distances have not changed or only slightly increased in the blend, which indicates a similar charge dissociation or recombination in PPPC16 and the blends.

In conclusion, the EL efficiency and time stability of polymer LEDs were improved using polymer blends made of PFC16 and PPPC16 compared with the single-component LEDs made of the EL polymers. The EL results can be explained mainly by modification of charge injection, transport and recombination, which was demonstrated by the charge transport and photogeneration measurements.

Table 1. The parameters α and $\eta_{0\alpha}$ obtained from fitting of the experimental dependences η_{ph} vs. F (see Fig. 4) using the Onsager model with the Gaussian distribution of e-h pair radii. The most effective separation distances of e-h pairs, r_{le} and r_{he}, at low and high electric fields, respectively.

Polymer	α **(nm)**	$\eta_{0\alpha}$	r_{le}	r_{he}
PPPC16	0.60	1.0	1.20	0.60
PFC16	0.80	1.0	1.60	0.80
PFC16+ PPPC16(7:3)	0.65	1.0	1.30	0.65
PFC16+PPPC16(1:1) (3:7)	0.60	1.0	1.20	0.60

We would like to acknowledge support of the Grant Agency of the Czech Republic (grants No. 102/98/0696 and No. 203/01/0512) and of the Grant Agency of Academy of Sciences of the Czech Republic (grant No. AVOZ 4050913).

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