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Characteristics of Electroluminescent Polythiophene Derivatives Containing Electron Transporting Moiety

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Spin-coated polymer LEDs were characterized by UV-Vis and fluorescence spectroscopies. Electrochemical properties of poly 3(2-(5-chlorobenzotriazolo) ethyl)thiophene LEDs as the emitting materials was studied by cyclic voltammetry. In cyclic voltammogram, PCBET shows reversible peaks at $E^0_{\text{red}} = -2.1$ V and $E^0_{\text{ox}} = +0.91$ V. Quantum efficiency of PCBET was much enhanced by introducing a benzotriazole moiety on the side chain.

Keywords: polythiophene; electroluminescence; bandgap; quantum efficiency

INTRODUCTION

Electroluminescence from conjugated polymers was first reported using poly(phenylene vinylene) (PPV) as the single semiconductor layer between metallic electrodes¹. Poly(3-alkyl)thiophenes and their derivatives have good electronic and mechanical properties and has been used in polymer LEDs.² Electron-transporting (ET) materials are placed between the cathode and polymer LEDs for improving quantum efficiency by facilitating electron injection from the cathode.³ However, ET layer has the disadvantages of crystallization and phase separation between cathode and polymer.⁴ To solve this drawback, we have synthesized poly 3(2-(5-chlorobenzotriazolo)ethyl)thiophene (PCBET), by directly introducing an electron-

withdrawing moiety on the side chain which can accept electron efficiently.⁴ Also copolymer $P(OT_{0.9}\text{-co-CBET}_{0.1})$ was synthesized. In this paper, we describes the electroluminescence properties and the enhancement of quantum efficiency (Q.E) of PCBET and $P(OT_{0.9}\text{-co-CBET}_{0.1})$ compared with poly(3-octyl)thiophene (POT).

EXPERIMENTAL

Samples of PCBET were prepared by chemical polymerization using $FeCl_3$. Figure 1 shows the structure of PCBET and $P(OT_{0.9}\text{-co-CBET}_{0.1})$. Thin film (about 800 Å) of polymers were fabricated by spin-coating at 1000 rpm at 30 sec from a chloroform solution with a concentration of 20 mg/ml.

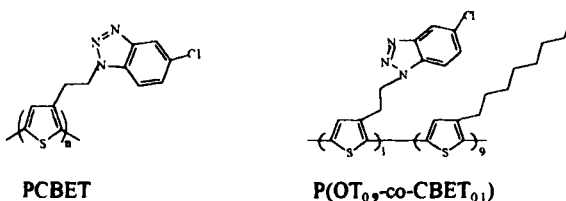


FIGURE 1 Structure of PCBET and $P(OT_{0.9}\text{-co-CBET}_{0.1})$

ITO-glass was used as anode and Al (about 1200 Å) as a cathode which was vacuum deposited at pressure below 10^{-6} torr. UV spectra of polymer films were recorded with a HP 8452 A spectrometer. Luminescence properties of polymer films characterized by ISS PC 1 spectrofluorometer. Q.E of devices were obtained by Keithley 236 Source/ Measure Unit. Electrochemistry was carried out BAS 100 W potentiostat/galvanostat. The cell was consisted with three electrodes in N_2 atmosphere. A Pt electrode was used as the working electrode with corresponding platinum wire as counter electrode. Potentials were measured against Ag/Ag^+ electrode which was consisted a silver wire in a solution of 0.01 M $AgNO_3$ / 0.05 M Bu_4NClO_4 / ACN ; ca. + 0.34 V vs SCE and scan rate was 100 mV/sec.

RESULTS AND DISCUSSION

The absorption and emission spectra of polymer films are shown in Figure 2, 3 and 4. In the absorption spectra of PCBET, the polymer has strong absorption bands at around 2.68 eV and 4.30 eV, which are attributed to the $\pi - \pi^*$ transitions of the conjugated segments and substituted benzotriazole derivatives, respectively. PL spectra of PCBET and $P(OT_{0.9}\text{-co-CBET}_{0.1})$ are significantly blue-shifted due to the bulky benzotriazole substituent which compared with that of POT. Photoluminescence spectra show features similar to those of the broad absorption spectra. EL maximum peaks of polymers which contains larger fractions of benzotriazole substituent were also blue-shifted. From PL and EL spectra it is believed that the enhancement of emission intensity in PCBET compared to the emission intensities of POT and $P(OT_{0.9}\text{-co-CBET}_{0.1})$ is from benzotriazole moiety in the thiophene structure. Redox properties of polymers were characterized by CV. Figure 5 shows the redox properties of PCBET. In CV spectra, PCBET reversible peaks show $E^{\circ}_{\text{red}} = -2.1$ eV and $E^{\circ}_{\text{ox}} = +0.91$ eV. Usually, polythiophenes are not easily n-doped⁵. A reduction peak was observed by the presence of electron-withdrawing moiety in PCBET which effects the stabilization the negative charge carries. Q.E of PCBET is tabulated with spectral properties in Table I. Therefore Q.E of PCBET was enhanced from that of POT and PHT. Orange light emission lights at 12 V in the forward bias.

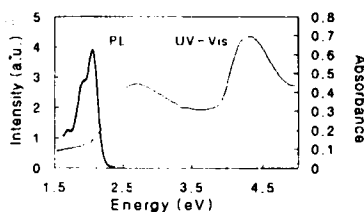


FIGURE 2 UV-Vis and PL spectra of PCBET film.

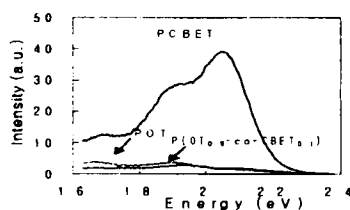


FIGURE 3 PL spectra of PCBET, POT and $P(OT_{0.9}\text{-co-CBET}_{0.1})$

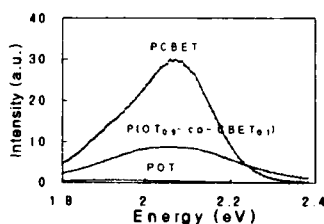


FIGURE 4 EL spectra of ITO/
Polymer/Al LEDs.

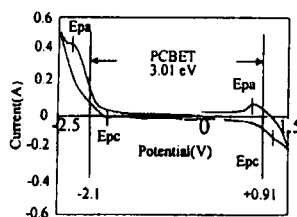


FIGURE 5 Cyclic voltammogram
of PCBT.

TABLE I Spectral properties of polythiophene derivatives

	UV(eV)	PL (eV)	EL(eV)	Bandgap (eV)	Q.E.(%)
PCBT	2.68	2.05	2.06	3.01	0.01
POT	2.55	1.91(1.67)	1.94	2.96	0.001
POT _{0.9} -co-CBT _{0.1})	2.51	1.94	2.05	2.97	0.005
PHT	-	-	-	-	0.008 ^[6]

CONCLUSION

PCBT containing an electron-withdrawing moiety shows higher quantum efficiency compared to simple poly(alkyl)thiophenes. PL and EL emission peaks were appeared at around 2.05 eV. Orange emission lighted at 12 V in the forward bias. In cyclic voltammogram, PCBT shows reversible peaks with bandgap of 3.01 eV.

Acknowledgements

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