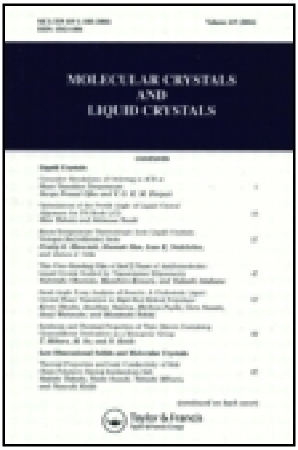

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Synthesis and Characterization of Polythiophene Derivatives Containing Electron Transporting and Hole Transporting Moieties

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Novel luminescent copolymers, poly(3-(2-benzotriazoloethyl)thiophene-co-octylcarbazolylene) ($[(BET)_m\text{-}OcCz_2]_n$) that contain both electron transporting benzotriazole and hole transporting octylcarbazole moiety were synthesized by oxidation of ferric chloride with changing the composition ratio of BET and OcCz. The absorption peak of UV-VIS was blue-shifted from $\lambda_{max} = 440$ nm in poly(3-(2-benzotriazoloethyl)thiophene) (PBET) to $\lambda_{max} = 412$ nm in $[(BET)_4\text{-}OcCz_2]_n$. The photoluminescence (PL) and electroluminescence (EL) intensities of the polymers were decreased with presence of carbazole moieties in the copolymer.

Keywords polythiophene; carbazole; LEDs.

INTRODUCTION

Since EL based on poly(p-phenylene vinylene) (PPV) was discovered by Burroughes et al. [1], a variety of conjugated polymers have been focused on their applications as active materials in light-emitting diodes (LED). EL of conjugated polymers is generated by the recombination of electrons and holes injected through electrodes and then the formation of excited carriers that can decay radiately. To improve the efficiency of LEDs, a multilayer system used to be generally applied. The multilayer system consists of an electron transporting layer to improve electron injection and a hole transporting layer to balance injected carriers. But, a multilayer system has a disadvantage such as phase separation and crystallization. Another efforts were performed on the incorporation of electron and hole transporting moieties with luminescence polymers that have merits of multilayer systems without surface problems between a light-emitting layer and electrodes. Especially, polythiophene in conjugated polymers have drawn much attention as a light emitting source to radiate red light with potential applications. The electronic and optical properties of polythiophenes could be controlled by introduction of other functional groups. In this work, copolymers of octylcarbazole and thiophene derivatives ($[(BET)_m\text{-}OcCz_2]_n$) were synthesized by introducing octylcarbazole (OcCz) to enhance both the solubility and the balance of holes and electrons and by introducing benzotrizole units as electron transporting material to accept electrons efficiently. The PL and EL characteristics of PBET and copolymers were investigated by UV-VIS, PL/EL emission spectroscopy.

EXPERIMENTAL

3-(2-Benzotriazoloethyl)thiophene (BET) was synthesized from a solution of 10 g (52.4 mmol) of 3-(2-bromoethyl) thiophene, 9.0 g (60 mmol) of benzotriazole, and 11.4 g (104.7 mmol) of potassium carbonate in 150 ml of acetone [2]. N-Octylcarbazole was prepared from mixture of 10g (59.8mmol) of carbazole and 2.39 g (59.8 mmol) of sodium hydride in 100ml of THF, and 10.39 g (53.8 mmol) of bromooctane [3]. PBET and $[(BET)_m\text{-}OcCz_2]_n$ were polymerized by oxidation of ferric chloride as catalyst with changing the composition ratio of BET and OcCz, the polymers were extracted with methanol and acetone. The composition of polymers was confirmed with ^{1}H NMR. Table 1 showed the composition ratio of the copolymers.

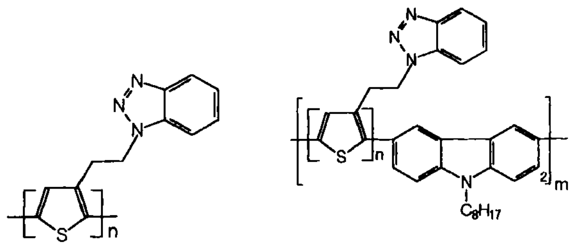
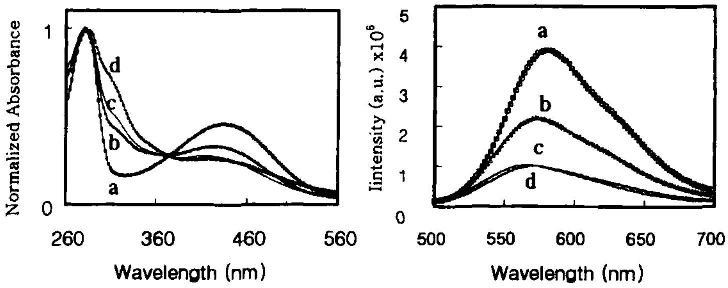


FIGURE 1. Structures of PBET and $[(BET)_m\text{-}OcCz_2]_n$.

RESULTS AND DISCUSSION

TABLE 1. Composition ratio of BET and OcCz in copolymers, average molecular weight (M_w), weight decrease, and optical properties of polymers

	Ratio (BET:OcCz$_2$)	M_w	T_{id} (°C) (loss 5%)	λ_{max} (nm)	Emissive Wavelength (nm)
A	PBET	68000	412	438	582
B	11 : 1	39000	312	426	572
C	7 : 1	25000	297	414	570
D	4 : 1	19000	312	412	568



(A) (B)

FIGURE 2. (A) UV-VIS absorption spectra of spin-coated films (B) PL emission spectra (a : PBET , b: $[(BET)_{11}\text{-}OcCz_2]_n$, c: $[(BET)_7\text{-}OcCz_2]_n$, d : $[(BET)_4\text{-}OcCz_2]_n$).

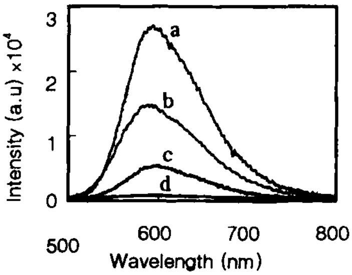


FIGURE 3. EL emission spectra of ITO/polymer/Al Device (a : PBET , b: $[(BET)_{11}\text{-}OcCz_2]_n$, c: $[(BET)_7\text{-}OcCz_2]_n$, d : $[(BET)_4\text{-}OcCz_2]_n$).

As shown in Table 1, average molecular weight of the polymers was decreased from 68,000 (only PBET) to 19,000 ($[(BET)_m$- $OcCz_2]_n$). the weights decrease appeared in the polymers were less than 5 % when heated up to 300 ℃ under N_2. The small decrease in their weights indicates that these polymers are thermally stable. Figure 2(A) showed the normalized UV spectra of PBET and copolymers. The absorption peak was blue-shifted from λ_{max} = 440 nm with PBET to λ_{max} = 412 nm with increase of carbazole composition ratio. And carbazole dimer peak was appeared at 310 nm. In PL emission spectra as shown Figure 2(B), maximum emission peaks of a, b, c and d appeared at 582 nm, 572 nm, 570 nm, and 568 nm respectively and the PL intensity of polymers was decreased with introduction of carbazole moieties. EL emission spectra of the device of ITO/polymer/Al were shown in figure 3. The EL intensity of polymers also was decreased with increase of carbazole composition ratio. In spite of ability of carbazole to improve the recombination of holes and electrons, increase of carbazole composition worked as the hindrance in enhancement of EL intensity [4], because carbazole blocked the conjugation length of polymers.

CONCLUSIONS

Novel luminescent copolymers, $[(BET)_m$-$OcCz_2]_n$ containing both electron transporting benzotriazole and hole transporting octylcarbazole moiety were synthesized. In spite of ability of carbazole to improve the recombination of holes and electrons, increase of carbazole composition ratio worked as the hindrance in enhancement of EL intensity, because carbazole interrupted the conjugation of polymers and decreased molecular weight.

ACKNOWLEDGMENT

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