Synthesis and Characterization of Soluble Polythiophene Derivatives Containing Electron-Transporting Moiety

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ABSTRACT: Soluble π-conjugated polythiophene derivatives containing the electron-transporting moiety were synthesized through $FeCl_3$-oxidative polymerization; poly(3-(2-benzotriazoloethyl)thiophene) (PBET) and poly(3-(2-(5-chlorobenzotriazolo)ethyl)thiophene) (PCBET). The structure of the polymers was verified by FT-IR, ^{1}H NMR, and element analysis. Introduction of the electron-transporting moiety, benzotriazole, on the side chain in poly(3-alkylthiophene) was an attempt to balance the injection rates of the electron and the hole from the opposite electrode into the light-emitting diodes (LEDs). This modification, therefore, would enhance electroluminescence (EL) efficiency. As the result, the external EL quantum efficiencies of PBET and PCBET were 7 and 3 times higher than that of poly(3-octylthiophene) (POT).

Introduction

Polymer light-emitting diodes (LEDs) exhibiting highly efficient and stable emission in the visible wavelength region are of great interest in optical applications such as color flat panel displays.[1−5] Since the first report by Burroughes et al. on the polymer LEDs made of the π-conjugated polymer, poly(*p*-phenylenevinylene),[1] a variety of π-conjugated polymers has been reported to exhibit electroluminescence (EL).[6−11] Polythiophenes are of a special class of π-conjugated polymeric materials for LEDs because of their excellent environmental stability, thermal stability, processability, and mechanical strength, as well as ease of fabrication.[12−16] However, their application has been limited due to the factors such as poor solubility in common organic solvents. The solubility problem is due to their rigid backbones.[17,18] This drawback can be overcome by attaching alkyl groups to a thiophene ring. Therefore, many kinds of poly(alkylthiophene)s have been studied for LEDs.[6,10] Poly(alkylthiophene)s exhibit good red color purity, but they tend to have rather low EL quantum efficiencies, typically $\sim 10^{-4}\%$.[13,14]

It is well-known in π-conjugated polymers that the electroluminescence is generated by recombination of electrons injected into the conduction band and holes in the valence band to form singlet exitons.[19] For the conjugated polymers investigated so far, it has been proved that the electron injection is more difficult than the hole injection.[20] With incorporation of an electron-transporting (ET) material between the cathode and the polymer layers in LEDs, the power efficiency can be improved through facilitated electron injection from the cathode in LEDs. Electron-deficient oxadiazo-, triazole-, quinoxaline-, and triazine-containing materials have been used as ET materials.[21−24] Among them, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) used to be widely employed.[25,26] However, attention has turned to nitrogen heterocycles such as 1,2,4-triazoles, 1,3,5-triazine, or quinoxalines because oxadialzoles have not been proved entirely successful as ET materials and because 1,2,4-triazole appears to block holes better than PBD.[27] However, the ET material has drawbacks such as crystallization and phase separation between cathode and polymer.[21]

To overcome this drawback, poly(3-(benzotriazolomethyl)thiophene) (PBMT) was synthesized by introducing the benzotriazole unit on the side chain in poly(3-alkylthiophene): as an ET moiety which can accept electrons efficiently. However, further structure modification of PBMT is necessary to make it soluble in common organic solvents. There are a few ways to modify polymer structures: either copolymerization with thiophene derivatives of good solubility in their homopolymers[8,28] or increasing alkyl-chain length from methylene to ethylene. With this reasoning, we have synthesized polythiophene copolymers, poly(3-(2-benzotriazoloethyl)thiophene) (PBET) and poly(3-(2-(5-chlorobenzotriazolo)ethyl)thiophene) (PCBET), which is more polar and electron-withdrawing than PBET. The HOMO and LUMO levels of PBET and PCBET were determined from ultraviolet photoelectron spectra (UPS) and UV−visible spectra. Their PL and EL characteristics were also investigated. To confirm the effect of ET moiety, all electronic properties of PBET and PCBET were compared with those of POT.

Experimental Section

Materials. 3-Thiophenemethanol, 3-(2-thienyl)ethanol, 5-chlorobenzotriazole, benzotriazole, and iron chloride(III) from Aldrich Chemical Co. were used without any further purification. Phosphorus tribromide was purchased from Janssen Chimica. Pyridine and chloroform from Junsei Chemical Co. were dried over CaH_2, and tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), and 1,1,2,2,-tetrachloroethane (TCE) from Junsei Chemical Co. were used as received unless otherwise stated.

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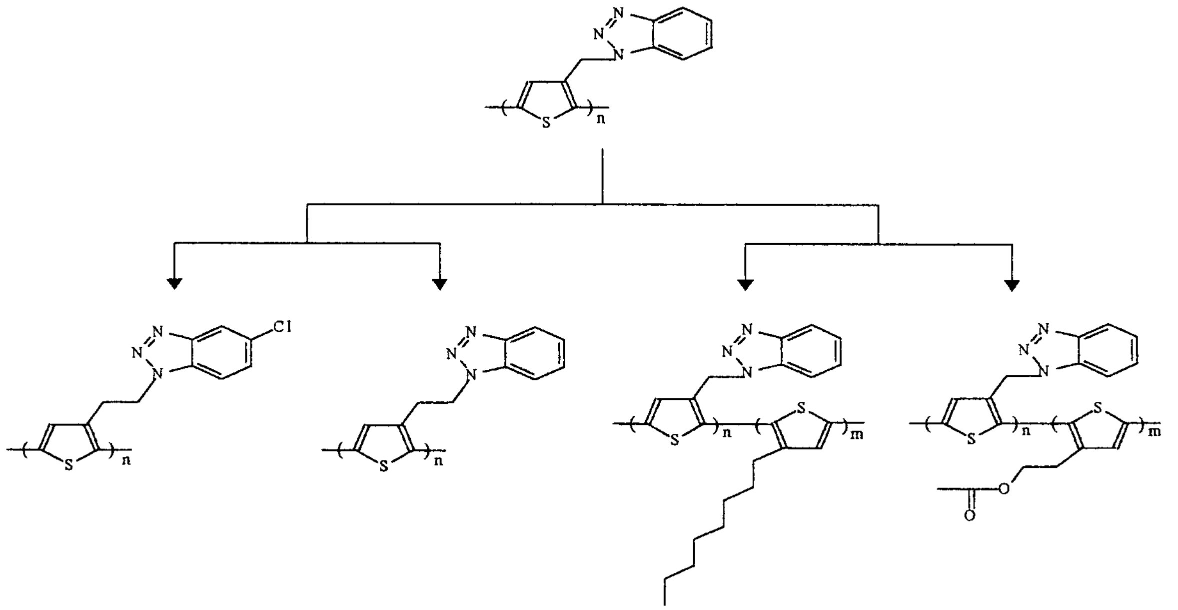
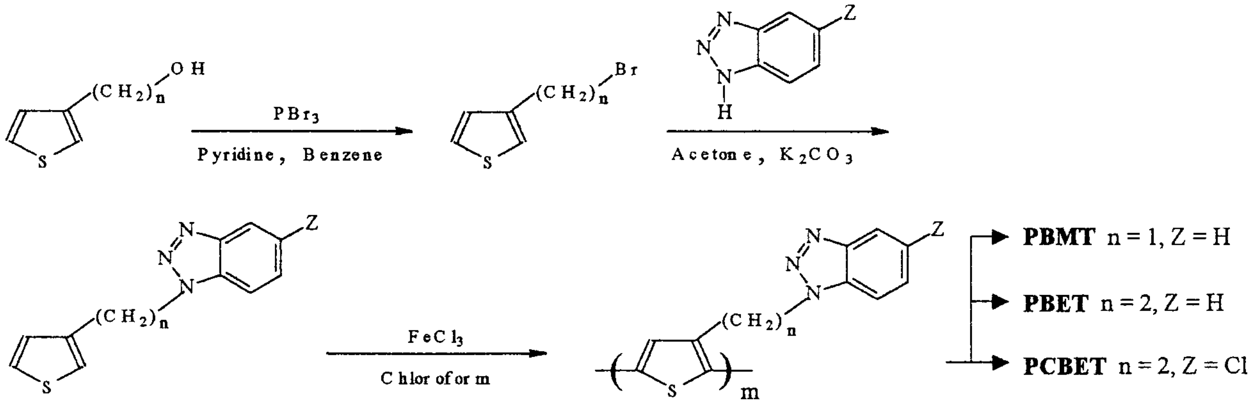


Figure 1. Concepts of polymer structure modifications.

Scheme 1. Synthetic Scheme of Polythiophene Derivatives



Instruments. ^1H NMR spectra were obtained on a Varian Unit Inova 300 (300 MHz) spectrometer. The NMR spectra were recorded in ppm relative to tetramethylsilane (δ 0.00) as an internal standard. Infrared spectra were obtained on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Mass spectra were taken on a VG Trio 2000 spectrometer with the electron beam energy of 70 eV and on a Finnigan MH95S (high resolution). Elemental analyses were performed with Carlo-Erba 1108. Melting points were determined using an Electrothermal model 9100 digital analyzer. UV−visible spectra were recorded with a HP 8452A diode array spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) on a Waters with polystyrene standard calibration. Thermal properties were analyzed with a Rheometric Scientific System (TGA1000, DSC PLUS) at a heating rate of 10 °C/min under nitrogen gas flow. Spin-cast films were prepared by Brewer Science CEE 100. Film thickness was measured by Rudolph Auto EL2 ellipsometer. Aluminum layer was deposited with Vacuum TM 100R thermal evaporator. Photoluminescence spectra were recorded on an ISS PC1 spectrofluorometer. EL spectra were recorded by employing a Jobin Yvon U-1000 double monochromator with a Stanford Research SR 400 photon counter. $I-V-L$ characteristics were recorded on a Kethley 236 source/measure unit for voltage−current relationship and by a Newport 818-SL photodiode for voltage-electroluminescence intensity. Ultraviolet photoelectron spectroscopic (UPS) measurements were made with a surface analysis instrument AC-1 (RIKEN KEIKI, Japan). All of the measurements mentioned above were performed in air and at room temperature.

Film and LED Fabrication. Films of the polymers were obtained by spin-coating on glass substrate at 3000 rpm for 30 s from TCE solution (0.02 g/mL). The spin-coated films were ca. 500 Å thick. To measure HOMO level of polymer from UPS, polymer solutions for film preparation were made by dissolving 20 mg of a polymer into chloroform of 1 mL, and films were then prepared to the thickness of 200 nm using a spin coater. The films were dried to remove chloroform solvent in a vacuum oven at room temperature for 6 h before UPS measurements. Single layer LEDs were fabricated with emissive layer sandwiched between an indium tin oxide (ITO) anode and an aluminum cathode. Light emitting polymer solution (0.02 g/mL in TCE) was spin-coated onto precleaned ITO/glass substrates at a spin speed of 3000 rpm for 30 s. These emissive layers were ca. 500 Å thick. On top of these, a 1000 Å thick Al layers were vacuum evaporated at pressure below 10^{-6} Torr.

Thiophene Derivatives Preparations. Synthetic routes and polymer structures are shown in Scheme 1, and Figure 1 shows the concepts of polymer structure modifications.

3-Octylthiophene (**OT**) was synthesized from 3-bromothiophene according to the procedure outlined by Kumada et al.,[29] and 3-(2-acetoxyethyl)thiophene (**AcET**) was prepared from 3-(2-thienyl)ethanol following the literature procedure.[30] 3-(Bromomethyl)thiophene and 3-(2-Bromoethyl)thiophene were synthesized from 3-thiophenemethanol and 2-(3-thienyl)-ethanol following the procedure described in the literature, respectively.[31−33]

3-(Benzotriazolomethyl)thiophene (BMT). Potassium carbonate (11.4 g, 104.9 mmol) was added to a solution of 3-(bromomethyl)thiophene (10.0 g, 56.4 mmol) and benzotriazole (8.0 g, 67.2 mmol) in 150 mL of acetone. The reaction mixture was heated to reflux for 15 h. After cooling, the resulting mixture was filtered and the solvent in the filterate was removed. The residue was chromatographed on silica gel using ethyl acetate−hexane (1:10) as eluent to yield the white solid **BMT** (4.3 g, 35.1%). Mp: 55−57 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 5.90 (2H, s, CH_2), δ 7.14−7.17 (2H, m, Th−H), δ 7.28−7.32 (1H, m, Th−H), δ 7.34−7.42 (2H, m, Ar−H), δ 7.82−7.90 (2H, m, Ar−H). FT-IR (KBr pellet, cm^{-1}): 3104, 2952, 1432, 1273, 741. EI MS *m/e* (relative intensity): 215 (1, $C_{11}H_9N_3S_1^+$), 97 (3, $C_5H_5S_1^+$). High-resolution MS: *m/e* = 215.0523 (calculated 215.0517) for $C_{11}H_9N_3S_1$.

3-(2-Benzotriazoloethyl)thiophene (BET). BET was obtained from 3-(2-bromoethyl)thiophene and benzotriazole following a procedure similar to that described for **BMT**. The yield of the white solid **BET** was 41.7%. Mp: 67−68 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.49 (2H, t, J = 7.57 Hz, CH_2), δ 4.96 (2H, t, J = 7.57 Hz, CH_2), δ 6.90−7.01 (2H, m, Th−H), δ 7.25−7.28 (1H, m, Th−H), δ 7.37−7.40 (2H, m, Ar−H), δ 7.85−7.88 (m, 2H). FT-IR (KBr pellet, cm^{-1}): 3098, 2964, 1452, 1278, 747. EI MS *m/e* (relative intensity): 229 (1, $C_{12}H_{11}N_3S_1^+$), 110 (13, $C_6H_7S_1^+$). High-resolution MS: *m/e* = 229.0683 (calculated 229.0674) for $C_{12}H_{11}N_3S_1$.

3-(2-(5-Chlorobenzotriazolo)ethyl)thiophene (CBET). CBET was obtained from 3-(2-bromoethyl)thiophene and 5-chlorobenzotriazole following a procedure similar to that described for **BMT**. The yield of the white solid **CBET** was 49.8%. Mp: 80−82 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.48 (2H, t, J = 7.51 Hz, CH_2), δ 4.97 (2H, t, J = 7.51 Hz, CH_2), δ 6.85−7.05 (2H, m, Th−H), δ 7.20−7.30 (1H, m, Th−H), δ 7.30−7.40 (1H, m, Ar−H), δ 7.75−7.90 (2H, m, Ar−H). FT-IR (KBr pellet, cm^{-1}): 3098, 2964, 1452, 1281, 755. EI MS *m/e* (relative intensity): 263 (1, $C_{12}H_{10}N_3S_1Cl_1^+$), 110 (33, $C_6H_7S_1^+$). High-resolution MS: *m/e* = 263.0286 (calculated 263.0284) for $C_{12}H_{10}N_3S_1Cl_1$.

Polythiophene Derivatives Preparation. All polymers were synthesized by chemical oxidation of the monomers using $FeCl_3$ in chloroform according to a procedure similar to that described in the literature.[34−36]

Poly(3-(benzotriazolomethyl)thiophene) (PBMT). A solution of anhydrous ferric chloride (2.46 g, 15.2 mmol) in 100 mL of dry chloroform was added dropwise to a stirred solution of **BMT** (1.00 g, 4.6 mmol) in 80 mL of dry chloroform over 5 h at room temperature. The mixture was stirred for 12 h at room temperature. The black suspension was poured into stirred methanol (500 mL). The solid was collected by filtration and washed with methanol. After being dried in a vacuum, a light green solid was obtained. FT-IR (KBr pellet, cm^{-1}): 3098, 2952, 1737, 1432, 1367, 1236, 1038, 845, 750, 601.

Poly(BMT-AcET) (P(BMT-AcET)). A solution of anhydrous ferric chloride (2.46 g, 15.2 mmol) in 100 mL of dry chloroform was added dropwise to a stirred solution of **BMT** (0.50 g, 2.3 mmol) and **AcET** (0.39 g, 2.3 mmol) in 80 mL of dry chloroform over 5 h at room temperature. The mixture was stirred for 12 h at room temperature. The black suspension was poured into stirred methanol (500 mL). The solid was collected by filtration and washed with methanol. The solid was redissolved in chloroform (50 mL) and filtrated. The copolymer dissolved in chloroform was dedoped by refluxing in concentrated ammonia overnight. The chloroform phase was separated from the ammonia phase and washed with fresh ammonia four times and with deionized water five times. The copolymer was precipitated again in methanol. After this was dried in a vacuum, a light orange solid was obtained (yield: 14%). FT-IR (KBr pellet, cm^{-1}): 2952, 1739, 1435, 1362, 1239, 1074, 1041, 842.

Poly(BMT-OT) (P(BMT-OT)). BMT (0.50 g, 2.3 mmol) and **OT** (0.45 g, 2.3 mmol) were copolymerized according to the procedure described for **poly(BMT-AcET)**. A light orange solid was obtained (yield: 14%). FT-IR (KBr pellet, cm^{-1}): 2924, 2857, 1685, 1460, 1373, 1186, 1083, 836, 721.

Poly(3-(2-benzotriazoloethyl)thiophene) (PBET). A solution of anhydrous ferric chloride (2.46 g, 15.2 mmol) in 100 mL of dry chloroform was added dropwise to a stirred solution of **BET** (1.00 g, 4.4 mmol) in 80 mL of dry chloroform over 5 h at room temperature. The mixture was stirred for 12 h at room temperature. The black suspension was poured into stirred methanol (500 mL) to generate green precipitate. The solid was collected by filtration and washed with methanol. The polymer was redissolved in chloroform (50 mL) and dedoped by refluxing in concentrated ammonia overnight. The chloroform phase was separated from the ammonia phase and washed with fresh ammonia four times and with deionized water five times. The polymer was precipitated again in methanol. After being dried in a vacuum, a light orange solid was obtained (yield: 55%). Anal. Calcd for $(C_{12}H_9N_3S)_n$: C, 63.41; H, 3.99; N, 18.49. Found: C, 63.14; H, 3.21; N, 18.13. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.43 (0.4H, s, HH−CH_2), δ 3.56 (0.6H, s, HT-CH_2), δ 4.96 (2H, s, CH_2), δ 6.82 (1H, s, Th−H), δ 7.27−7.34 (2H, m, Ar−H), δ 7.73−7.92 (2H, m, Ar−H). FT-IR (KBr pellet, cm^{-1}): 3098, 3008, 2901, 1748, 1558, 1516, 1298, 1222, 1108, 1052, 778, 724.

Table 1. Solubilities in Organic Solvents[a] and Average Molecular Weights of Polythiophene Derivatives

polymer	solvent CHCl$_3$	THF	DMF	TCE	GPC M_w	M_n	PDI
PBMT	X	X	X	X			
P(BMT-OT)	△	△	△	△	3323	1796	1.85
P(BMT-AcET)	△	△	△	△	3105	1688	1.84
PBET	○	○	○	○	35138	17010	2.07
PCBET	○	○	○	○	37954	20043	1.89
POT	○	○	○	○	104174	16756	6.22

[a] Solubility: ○, soluble; △, partially soluble; X, insoluble.

Poly(3-(2-(5-chlorobenzotriazolo)ethyl)thiophene) (PCBET). CBET was polymerized according to the procedure described in the previous section for synthesis of the polymer **PBET**. The yield of **PCBET** was 63%. Anal. Calcd for $(C_{12}H_8N_3SCl)_n$: C, 55.07; H, 3.08; N, 16.05. Found: C, 55.12; H, 2.94; N, 16.00. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 3.42 (0.4H, s, HH−CH_2), δ 3.56 (0.6H, s, HT-CH_2), δ 4.96 (2H, s, CH_2), δ 6.82 (1H, s, Th−H), δ 7.25−7.34 (1H, m, Ar−H), δ 7.73−7.92 (2H, m, Ar−H). FT-IR (KBr pellet, cm^{-1}): 3021, 2928, 1524, 1476, 1424, 1215, 930, 758, 669.

Poly(3-octylthiophene) (POT). OT was polymerized according to the procedure described in the literature.[36] The yield of **POT** was 72%.

Results and Discussion

Preparation and Characterization. The solubilities and the molecular weights of the polymers are shown in Table 1. **PBMT** was insoluble in organic solvents such as chloroform, THF, DMF, and TCE. By introducing alkyl and polar group at the thiophene ring, the solubility of **poly(BMT-AcET)** and **poly(BMT-OT)** was increased more than that of **PBMT**. Nevertheless, only their oligomer fractions were turned out to be soluble; those with a molecular weight of a few thousand. However, **PBET** and **PCBET** were completely soluble in many organic solvents due to ethylene groups in polymer structure. The number-average molecular weights (M_n) of **PBET**, **PCBET** and the **POT** were determined by GPC and found to be 16 000−20 000 against the polystyrene standards. The weight-average molecular weights (M_w) of **PBET** and **PCBET** were ca. 35 000 and 38 000 with polydispersibilities of 2.07 and 1.89, respectively. The weight-average molecular weight (M_w) of POT was 1×10^5 with a polydispersibility of 6.22 similar to that found in the literature.[36] The chemical structures of **PBET** and **PCBET** were studied by ^{1}H NMR. The results proved that **BET** and **CBET** were polymerized into **PBET** and **PCBET** with low regioregularity. The head-to-tail contents of **PBET** and **PCBET** were found to be ca. 60%.

Thermal Properties of Polymers. The DSC thermograms obtained from the second heating of polymers

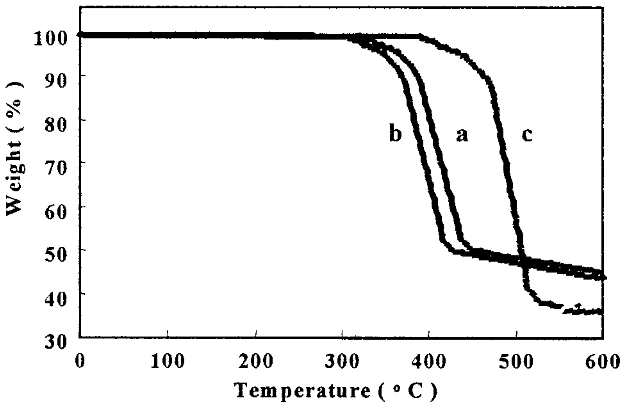


Figure 2. TGA curves of (a) **PBET**, (b) **PCBET**, and (c) **POT**.

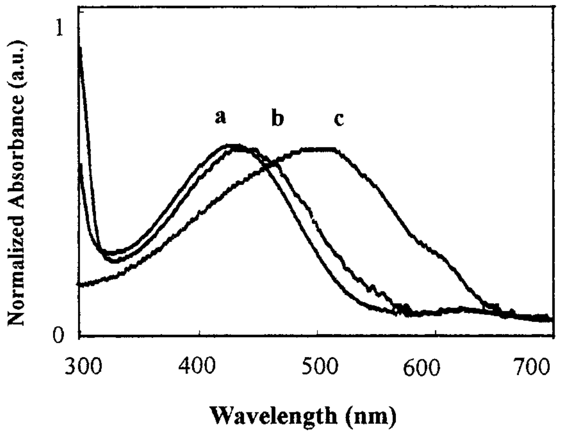


Figure 3. UV–vis spectra of (a) **PBET**, (b) **PCBET**, and (c) **POT** in the solid state.

PBET and **PCBET** showed the glass transition temperature (T_g) at 107 and 105 °C, respectively. The TGA curves of the three 3-substituted polythiophene derivatives are shown in Figure 2. The onset temperatures of weight loss are 320, 300, and 400 °C for **PBET**, **PCBET** and **POT**, respectively. The onset temperature of **POT** is higher than the others because of higher molecular weight.

UV–Vis Spectroscopy of Films. Solid-state UV–vis spectra gave further insight into the extent of the polymer conjugation and structure, as well as the solid-state electronic effects of the polymeric materials. As shown in Figure 3, a $\pi-\pi^*$ transition energy of polythiophene backbone was observed in the spectra of **PBET**, **PCBET**, and **POT**. Their $\pi-\pi^*$ transitions are exhibited by the absorption with maximum wavelength (λmax) at around 444, 446, and 500 nm for **PBET**, **PCBET**, and **POT**, respectively. The band-gaps calculated from UV band edge of polymer were 2.21, 2.14, and 1.96 eV for **PBET**, **PCBET**, and **POT**, respectively.

Luminescence Properties. Photoluminescence (PL) spectra were recorded with an excitation wavelength corresponding to the absorption maximum wavelength of the polymer as shown in Figure 4. The PL spectrum of **POT** showed that the emission maximum is 655 nm and emission peaks of **PBET** and **PCBET** appeared at around 580 and 588 nm, respectively. The emission of **PBET** and **PCBET** were blue-shifted about 70 nm because of sterically induced backbone distortion resulting from benzotriazole group.[14] The PL intensity of polymer **PBET** was similar to that of **PCBET** and 40 times higher than that of **POT**.

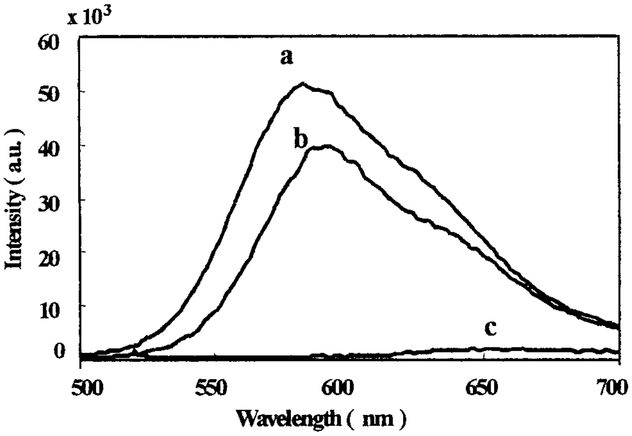


Figure 4. PL spectra of (a) **PBET**, (b) **PCBET**, and (c) **POT** in the solid state.

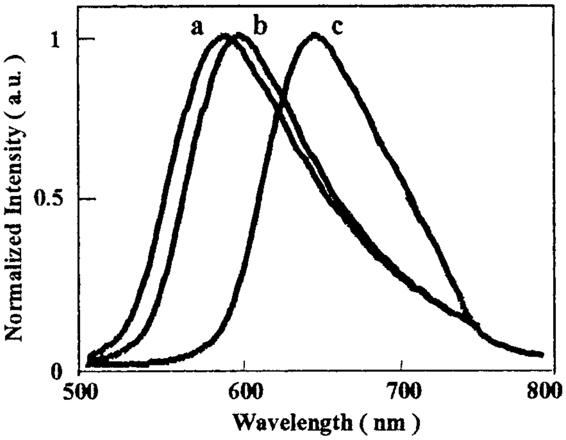
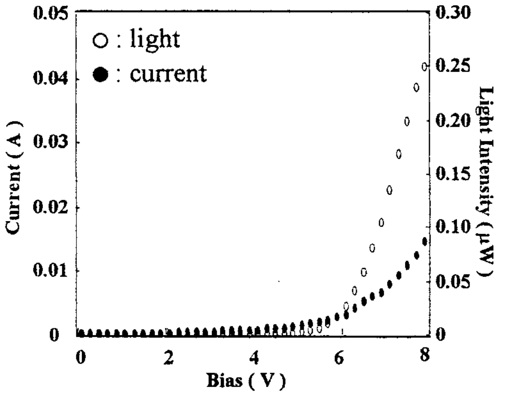


Figure 5. EL spectra of (a) **PBET**, (b) **PCBET**, and (c) **POT** in ITO/polymer/Al devices.

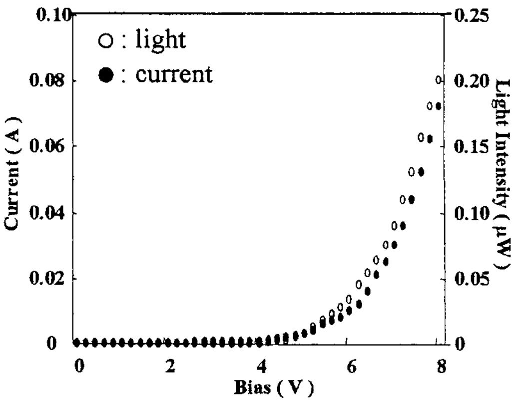
All processing steps for EL characteristic measurements were carried out in air and at room temperature. EL spectra of the devices of ITO/polymer/Al are shown in Figure 5. The maximum emission peaks of **PBET**, **PCBET** and **POT** appeared at 580, 600, and 650 nm, respectively.

Current–Voltage–Luminance (*I*–*V*–*L*) Characteristics. Figure 6 shows the current–bias–luminance (*I*–*V*–*L*) characteristics of the ITO/polymer/Al devices. The turn-on voltages of **PBET**, **PCBET** and **POT** were about 4 V, and their external EL quantum efficiencies (QE) were 9×10^{-4}%, 4×10^{-4}% and 1.2×10^{-4}%, respectively. The external EL QE of **PBET** and **PCBET** were 7 and 3 times higher than that of **POT**, respectively. The external EL QE of POT (1.22×10^{-4} %) was measured and found to be similar to or better than that of poly(3-alkylthiophenes) described in the literature.[13,14] There was no dramatic enhancement of external EL QE for **PBET** and **PCBET** with respect to that of **POT**, less than we had expected. The reason it did not increase as much as we had expected can be explained in the energy diagrams of polymers in Figure 7.

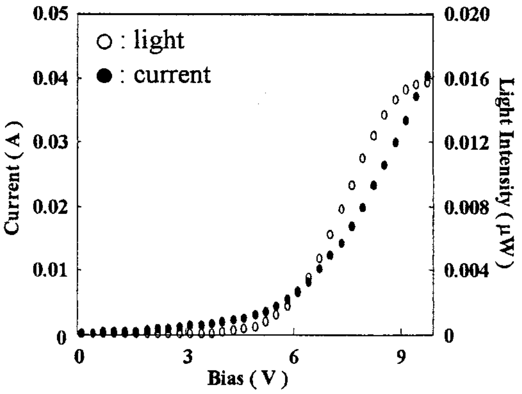
Ultraviolet Photoelectron Spectroscopy (UPS). Figure 7 shows the HOMO and LUMO levels of polymers. The HOMO levels of polymers obtained from UPS data and were 5.45, 5.62, and 4.57 eV for **PBET**, **PCBET**, and **POT**, respectively. The LUMO levels were evaluated from the optical band gaps estimated from UV–vis spectra and the HOMO levels. As we had



(a) **PBET**



(b) **PCBET**



(c) **POT**

Figure 6. $I-V-L$ curves of (a) **PBET**, (b) **PCBET**, and (c) **POT**.

expected, the LUMO and HOMO levels were lowered about 0.8 eV for **PBET** and **PCBET** with respect to that of **POT**. Therefore, the enhancement of external EL QE can be rationalized by the reduction of imbalance in carrier injection. However, there was no dramatic enhancement of external EL QE. For an ideal device, the LUMO and HOMO of the polymer are so matched to the electrodes, that the barrier heights are zero.[37] In this work, however, the increment of barrier height of hole injection by the effect of ET unit caused the slight enhancement of external EL QE.

Conclusions

A series of polythiophene derivatives was synthesized to investigate their electroluminescent properties. They contain a ET moiety on the side chain, which makes them to accept the electrons more efficiently. In the UV–visible and luminescence spectra, the maximum absorption and emission spectra of **PBET** and **PCBET** were about 70 nm blue-shifted with respect to that of **POT** because of steric hindrance. The LUMO and HOMO levels of **PBET** and **PCBET** were lowered by introducing the ET moiety, compared with those of **POT**, but the total barrier height of charge injection was not reduced significantly. Nevertheless, the external EL quantum efficiencies of **PBET** and **PCBET** were enhanced more than that of **POT**, because the injection rates of both carriers might be in better balance due to the effect of ET material in ITO/polymer/Al devices.

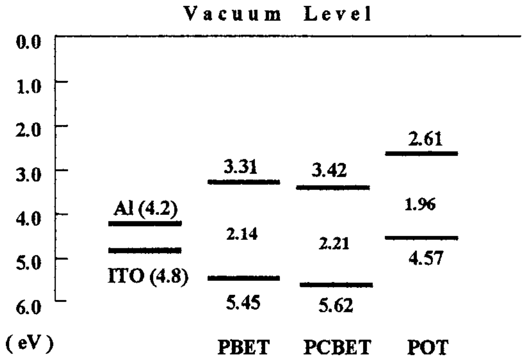


Figure 7. Energy diagrams of polythiophene derivatives.

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