Synthesis and Light-Emitting Properties of a Novel π-Conjugated Poly[di(*p*-phenyleneethynylene)-*alt*-(*p*-phenylenecyanovinylene)] Containing *n*-Octyloxy Side Branches

Jun Ho Chi,[1] Chang-Lyoul Lee,[2,3] Jang-Joo Kim,[4] Jin Chul Jung[1]

[1]*PC Group, Chemical R&D Center, Cheil Industries Inc., Gocheon-dong, Uiwang-Si, Gyeonggi-Do, 437–711, Korea*
[2]*Optoelectronics Group, Cavendish Laboratory, Cambridge University, United Kingdom*
[3]*Optical Materials and Device Laboratory, Advanced Photonics Research Institute, Gwangju Institute of Science and Technology, Gwangju 500-712, Korea*
[4]*School of Materials Science and Engineering, Seoul National University, Seoul 151-744, Korea*

ABSTRACT: A novel π-conjugated poly[di(*p*-phenyleneethynylene)-*alt*-(*p*-phenylenecyanovinylene)] having *n*-octyloxy side chains (PPE-C$_8$PPE-PPV) was prepared by polymerization of the monomer DEDB with BCN. Chemical structure of the polymer obtained was confirmed by ^{1}H NMR, FTIR, and EA. PPE-C$_8$PPE-PPV had a molecular weight enough to fabricate the electroluminescent (EL) device, and showed a good organosolubility, excellent thermal stability, and film-forming property. In UV absorption and PL spectra in film it showed a maximum at 430 and 543 nm, respectively, which appeared 5 and 41 nm longer wavelengths than that of the solution, respectively. HOMO, LUMO energy levels and band gap were determined to be −5.70, −3.29, and 2.41 eV, respectively. Two EL devices with low-work function cathodes were fabricated with the structures of ITO/PEDOT/PPE-C$_8$PPE-PPV/cathodes (LiF/Al and Mg:Ag/Ag). The both devices exhibited a bright green light emission at 545 nm and the maximum luminescence of 197 cd/cm^2 (LiF/Al) and 158 cd/cm^2 (Mg:Ag/Ag). © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 914–922, 2008

Key words: poly(*p*-phenyleneethynylenecyanovinylene)]; poly(*p*-phenylenecyanovinylene); poly[di(*p*-phenyleneethynylene)-*alt*-(*p*-phenylene-1-cyanovinylene)]; electroluminescent poly(*p*-phenyleneethynylenecyanovinylene); light-emitting polymer

INTRODUCTION

Since the first discovery of the electroluminescent (EL) properties using a conjugated poly(*p*-phenylenevinylene) (PPV) by Cambridge group in 1990,[1] the performance of polymer light-emitting diodes (PLEDs) has been steadily improved not only in the emitting light intensity but also in the device lifetime. Today, a very wide variety of polymer materials is being investigated in search of higher efficiency and performance of PLEDs by the pertaining scientific and technological community.[2]

To make efficient LEDs, a good balance should be fulfilled between rates of charge injection and transportation. Most conjugated EL polymers show a greater tendency for transporting holes than electrons, and this difference leads to the recombination zone closer to the cathode and thereby quenching of the excitons. This is one of the main sources of reduced performance and efficiency of LEDs, and many researches have been focused on elevating electron transporting ability of EL polymers.[3,4] One strategy to improve the ability was first demonstrated by Greenham et al.[5] They synthesized poly(*p*-phenylene-1-cyanovinylene)s and found that the electron-withdrawing cyano group contributes greatly to accelerate electron mobility. Since then many PPV derivatives containing various electron withdrawing groups such as halo,[6] trifluoromethyl,[7] trifluoromethanesulfonyl,[8] oxadiazole,[9] and pyridyl[10] substituents were developed and their device efficiencies have been investigated.

The alternative strategy was to use cathode metals with lower work functions such as Li, Ca, and Mg in fabricating devices. Such metals facilitate electron injection into organic materials, but they are so highly sensitive to air oxidation that they should be appropriately passivated. Recently, use of alloy electrodes made of Mg/Ag or insulating layer like LiF has appeared very promising in achieving high-performance devices.[11,12]

An ethynylene group is a π-electron system highly capable of transporting π-electrons like a vinylene group, but a *p*-phenyleneethynylene unit is known to be slightly lower in effective π-conjugation length than a *p*-phenylenevinylene unit.[13] Therefore poly(*p*-phenyleneethynylene)s (PPEs) seem to be more advantageous in designing blue-light emitting polymers than PPVs with corresponding chain structure,[3,14] and many PPEs have been modified by incorporating some electron-withdrawing groups such as oxadiazole,[4] nitropyridyl,[15] and benzothiadiazolyl unit[16] onto their backbones. Recently, PPE derivatives containing cyano group have attracted a lot of attention among the pertaining researchers.[17,18]

EL performance of PLEDs is strongly affected also by their device structure. For instance, to lower turn-on voltage, the device should be so fabricated that the HOMO or LUMO of each material and the work functions of the electrodes should be well matched. The single-layer structure is rarely used for fabricating high-performance diodes because the cumulative function of the emitter results in a low efficiency and a short lifetime. More elaborate diodes have a multilayer structure in which several layers are overlapped for specific functions.[19,20] To facilitate the movement of holes or electrons, an injection layer and a transport layer are inserted between the emitter and the corresponding electrode.[21,22]

In this study it was motivated to develop a new PPE derivative for EL device application by combining attractive aspects of PPEs and PPVs. For this a new π-conjugated polymer having the structure of (PPE)₂-*alt*-(PPV) that contains an electron-withdrawing cyano group on PPV unit and two solubility-enhancing (*n*-octyloxy) side branches on a PPE unit was designed and prepared. As such a polymer poly[*p*-phenyleneethynylene-2,5-di(*n*-octyloxy)-*p*-phenyneneethynylene-*p*-phenylene-1-cyanovinylene] (PPE-C₈PPE-PPV) was prepared by the Pd(0)/CuI-catalyzed Heck reaction of 2,5-di(*n*-octyloxy)-1,4-diethynylbenzene (DEDB) with 1,2-bis(4-bromophenyl)-1-cyanovinylene (BCN), and its photoluminescent (PL) and EL properties were investigated. The monomer DEDB was prepared by deacetonating 2,5-di(*n*-octyloxy)-1,4-bis(3-methyl-3-hydroxybut-1-ynyl)benzene (OMHB), which had been obtained by Pd(0)/CuI-catalyzed coupling of 2,5-di(*n*-octyloxy)-1,4-dibromobenzene (DODB) with 3-methylbut-1-yn-3-ol at 90°C.

To study the EL properties of PPE-C₈PPE-PPV, two devices were fabricated with the multilayer structures of ITO/PEDOT/PPE-C₈PPE-PPV/LiF/Al and ITO/PEDOT/PPE-C₈PPE-PPV/Mg:Ag/Ag. In the devices PPE-C₈PPE-PPV and PEDOT function as light-emitting layer and hole-transporting layer, respectively.

EXPERIMENTAL

Materials

Pd(PPh₃)₄, 3-methylbut-1-yn-3-ol, 4-bromobenzaldehyde, and 4-bromophenylacetonitrile (Acros), CuI (Junsei), and NaH (Aldrich) were used without purification. 1,4-Di(*n*-octyloxy)benzene was prepared from *p*-hydroquinone and 1-bromooctane.[23] Et₃N (Junsei) was distilled over CaH₂ under reduced pressure, and toluene (Acros) was dried with P₂O₅ before distillation. Poly(3,4-ethylenedioxythiophene-2,5-dyl) (PEDOT), Mg, Ag, LiF, and Al were purchased from Aldrich and used as received. Other inorganic reagents and organic solvents of chemical grade were used as received unless otherwise stated.

Measurements

^{1}H and ^{13}C NMR spectra were recorded on 300-MHz Bruker AM 300 spectrometer using tetramethylsilane as internal standard. Chemical shifts are given in ppm unit, and FTIR spectra were measured using Infinite Gold Mattson Spectroscopy in KBr pellet. Melting points were determined using Haake-Büchler melting point apparatus. Elemental analysis (EA) was performed using Elemental Vario EL microanalyzer (The Korea Basic Science Institute, Daegu, Korea), and the phase transitions were determined by DSC using Perkin-Elmer PC series DSC 7 thermal analyzer at 10°C/min scan rate in nitrogen atmosphere. The number- (M_n) and weight-average molecular weights (M_w) were measured on a GPC with two mixed-bed columns (Polymer Lab, Mixed C, 300 × 8.0 mm I.D.) at 40°C using THF as eluent and standard polystyrene as reference. TGA was carried out under nitrogen at 20°C/min heating rate. UV–vis spectra were recorded on Scinco UV S-2100 spectrophotometer and PL spectra were taken from fluorescence spectrophotometer (DM 151i, DongWoo Optron) upon irradiating 325-nm light from He/Cd laser (IK series, KIMMON Co.). X-ray diffractogram was obtained in a transmission mode using Ni-filtered Cu/Kα-radiation on a Rigaku Geiger Flex D-Max X-ray diffractometer. Cyclic voltammogram (CV) (Prinston Applied Research, Model 263A) was measured in a conventional three-electrode cell using a polymer thin film (spin-coated onto ITO glass) as the working electrode, Pt gauze as the counter electrode, Ag/AgNO₃ as the reference electrode, and 0.1*M* Bu₄NClO₄ in acetonitrile as electrolyte. Cathodes (LiF/Al and Mg:Ag/Ag) were fabricated by vacuum deposition of the substances from a thermal evaporation system (VEV-303, VTS). Film thicknesses were measured using alpha step (ALPHA-STEP 500, KLA Tencor.). The current density-voltage characteristics were determined on a photocurrentmeter (Model 2400 series, Keithley). All

measurements of the EL devices were carried out in ambient conditions.

Synthesis

2,5-Di(n-octyloxy)-1,4-dibromobenzene

DODB was prepared from 1,4-di(n-octyloxy)benzene in accordance with the literature procedure.[23] Yield: 97%. mp: 57°C.

2,5-Di(n-octyloxy)-1,4-bis(3-methyl-3-hydroxybut-1-ynyl)benzene

In a 500-mL three-necked round-bottom flask equipped with a reflux condenser, a thermometer, a N_2 gas inlet, and a dropping funnel DODB (14.7 g, 30 mmol), Pd(PPh$_3$)$_4$ (0.55 g, 0.48 mmol), and CuI (0.18 g, 0.96 mmol) were added to dry Et$_3$N (300 mL). After stirring in N_2 flow at room temperature for 30 min, 3-methylbut-1-yn-3-ol (10.86 mL, 0.15 mol) was dropped over 15 min at room temperature and the mixture was heated at 90°C for 24 h. After cooling to room temperature, the reaction mixture was filtered and the filtrate was evaporated to obtain ivory solids. They were purified by recrystallization from 95% ethanol/H_2O (9/1 v/v).

   Yield: 89%. mp: 105°C. IR (KBr pellet, cm^{-1}): 3200–3500 (—OH), 2850–2960 (aliphatic CH), 2205 (—C≡C—), 1276 (aryl-alkyl ether), ^{1}H NMR (CDCl$_3$, ppm): 0.87 (t, 6H, —OC$_7$H$_{14}$CH$_3$), 1.29 (m, 16H, —OC$_2$H$_4$C$_4$H$_8$C$_2$H$_5$), 1.49 (m, 4H, —OC$_6$H$_{12}$CH$_2$CH$_3$), 1.61 (s, 12H, C—CH$_3$ bonded to ethynyl), 1.76 (m, 4H, —OCH$_2$CH$_2$C$_6$H$_{13}$), 2.05 (s, 2H, OH), 3.93 (t, 4H, —OCH$_2$C$_7$H$_{15}$), 6.84 (s, 2H, ArH), ^{13}C NMR(CDCl$_3$, ppm): 14.7 (—OC$_7$H$_{14}$CH$_3$), 23.3 (—OC$_6$H$_{12}$CH$_2$CH$_3$), 26.7 (—OC$_2$H$_4$CH$_2$C$_5$H$_{11}$), 29.9 (HO—C—CH$_3$), 30.0 (—OC$_3$H$_6$CH$_2$C$_4$H$_9$), 30.2 (—OC$_4$H$_8$CH$_2$C$_3$H$_7$), 32.1 (—OCH$_2$CH$_2$C$_6$H$_{13}$), 32.4 (—OC$_5$H$_{10}$CH$_2$C$_2$H$_5$), 66.4 (C—OH), 70.2 (—OCH$_2$C$_7$H$_{15}$), 79.1 (ArC—C), 99.7 (C≡C—OH), 114.1 (ArC bonded to C≡C), 117.8 (ArC), 154.2 (ArC bonded to OC$_8$H$_{17}$).

2,5-Di(n-octyloxy)-1,4-diethynylbenzene

In a 250-mL three-necked round-bottom flask equipped with a reflux condenser, a thermometer, and a N_2 gas inlet, OMHB (4.98 g, 10 mmol), NaH (0.825 g, 30 mmol), and dry toluene (100 mL) were placed. The mixture was magnetically stirred at 120°C for 18 h in N_2 stream. After cooling to room temperature, the reaction mixture was filtered and evaporated to dryness. Recrystallization of the residue from 95% ethanol afforded yellow crystals.

   Yield: 89%. mp: 63°C. IR (KBr pellet, cm^{-1}): 3280 (≡CH), 2850–2960 (aliphatic CH), 2205 (—C≡C—), 1276 (aryl-alkyl ether). ^{1}H NMR (CDCl$_3$, ppm): δ =

0.86 (t, 6H, —OC$_7$H$_{14}$CH$_3$), 1.28 (m, 16H, —OC$_2$H$_4$C$_4$H$_8$C$_2$H$_5$), 1.44 (m, 4H, —OC$_6$H$_{12}$CH$_2$CH$_3$), 1.77 (m, 4H, —OCH$_2$CH$_2$C$_6$H$_{13}$), 3.30 (s, 2H, ≡CH), 3.94 (t, 4H, —OCH$_2$C$_7$H$_{15}$), 6.93 (s, 2H, ArH). ^{13}C NMR (CDCl$_3$, ppm): δ = 14.3 (—OC$_7$H$_{14}$CH$_3$), 22.8 (—OC$_6$H$_{12}$CH$_2$CH$_3$), 26.1 (—OC$_2$H$_4$CH$_2$C$_5$H$_{11}$), 29.3 (—OC$_3$H$_6$CH$_2$C$_4$H$_9$), 29.4 (—OC$_4$H$_8$CH$_2$C$_3$H$_7$), 29.6 (—OCH$_2$CH$_2$C$_6$H$_{13}$), 32.0 (—OC$_5$H$_{10}$CH$_2$C$_2$H$_5$), 69.8 (—OCH$_2$C$_7$H$_{15}$), 79.9 (Ar—C≡C), 82.6 (ArC—C), 113.4 (ArC bonded to C≡C), 117.9 (ArC), 154.1 (ArC bonded to OC$_8$H$_{17}$).

1,2-Bis(4-bromophenyl)-1-cyanovinylene

BCN was prepared from 4-bromophenylacetonitrile and 4-bromobenzaldehyde and characterized in accordance with the literature procedure.[24] Yield: 87%. mp: 127°C.

Poly[1,4-phenyleneethynylene-2,5-di(n-octyloxy)-1,4-phenyneneethynylene-1,4-phenylene-1-cyanovinylene]

In thoroughly dried polymerization tube equipped with a reflux condenser and a thermometer DEDB (0.6121 g, 1.6 mmol), BCN (0.5809 g, 1.6 mmol), Pd(PPh$_3$)$_4$ (0.074 g, 0.064 mmol), and CuI (0.012 g, 0.064 mmol) were suspended in dry toluene (20 mL) and Et$_3$N (5 mL) under bubbling of argon gas. The suspension was made homogeneous by raising the temperature to 80°C and reacted for 24 h at that temperature. After cooling to room temperature, the reaction mixture was filtered and then the filtrate was dropped into excess ethanol (100 mL) under vigorous stirring for precipitation. The precipitates were isolated by filtration and then purified by redissolving in toluene and reprecipitating from ethanol. The reprecipitates were washed thoroughly with water, methanol, and acetone in sequence and dried in vacuum at 50°C to constant weight.

   FTIR (KBr pellet, cm^{-1}): 2960–2850 (aliphatic CH), 2220 (—CN), 2205 (—C≡C—), 1586 (—C=C—), 1276 (aryl-alkyl ether). ^{1}H NMR (CDCl$_3$, ppm; Fig. 1): 0.87 (t, 6H, H-1), 1.22 (m, 16H, H-2–5), 1.52 (m, 4H, H-6), 1.84 (m, 4H, H-7), 4.02 (t, 4H, H-8), 7.02 (s, 2H, H-9), 7.47 (s, 1H, H-12), 7.57–7.87 (m, 8H, H-10,11,13,14). EA[wt %, repeat unit = C$_{43}$H$_{49}$NO$_2$ (611.85)]: Calc. C 84.41, H 8.07, N 2.29, O 5.23 and found C 84.26, H 8.11, N 2.32, O 5.31.

Device fabrication

ITO-coated glass substrates were thoroughly cleaned by washing with acetone, ultrasonication in water for 10 min, dipping in boiling isopropanol, and finally treating with UV-O$_3$. PEDOT solution (5 wt %) in isopropanol was spin-coated onto the cleaned
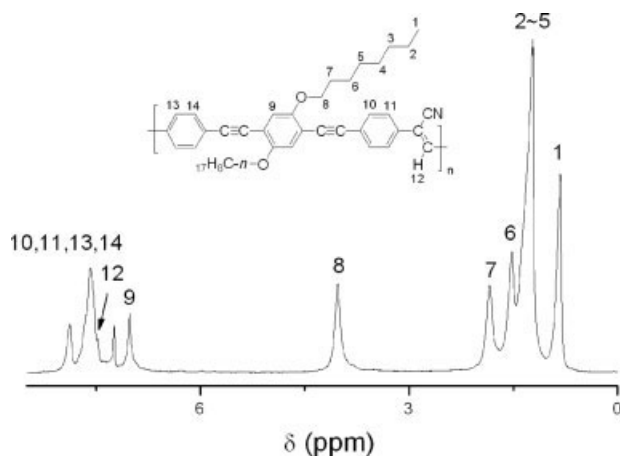
Figure 1 ¹H NMR spectrum of PPE-C₈PPE-PPV (CDCl₃, 25°C).

ITO plates (1.3 × 1.3 cm²) at 4000 rpm for 40 s, and annealed at 150°C for 10 min to remove the isopropanol. The polymer solutions (3 wt %) in toluene were spin-coated onto the PEDOT layer at 2500 rpm for 40 s and then dried in vacuum at 80°C. The polymer-coated substrates were then put into a vacuum chamber and cathode materials comprising LiF/Al or Mg: Ag/Ag were deposited onto them. To construct device with ITO/PEDOT/PPE-C₈PPE-PPV/ LiF/Al structure 7-Å thick LiF was deposited onto polymer-coated substrates at a rate of 0.1 Å/s, and then 600 Å thick Al was subsequently deposited onto LiF layer at a rate of 1.5 Å/s using an electric heater controlled at 5 V and 90 mA at room temperature and a pressure below 3×10^{-6} Torr.

The other device with Mg:Ag/Ag cathode was fabricated at the same pressure. The 1000 Å thick Mg:Ag (10/1 w/w) alloy layer was deposited at room temperature by coevaporation of Mg and Ag from different sources at a rate of 2.0 and 0.5 Å/s, respectively. Then Ag (∼ 200 Å) was evaporated onto Mg:Ag layer at the same conditions. The thickness of organic and cathode layers was monitored using a quartz crystal thickness monitor placed near the substrate.

RESULTS AND DISCUSSION

Monomer synthesis

The monomer DEDB was prepared by Pd(0)/CuI-catalyzed coupling of DODB with 3-methylbut-1-yn-3-ol and subsequent deacetonation of the dibutynol intermediate, as shown in Scheme 1. In the coupling reaction Et₃N was used simultaneously as HBr absorber and reaction solvent, and large amounts of triethylammonium hydrobromide salt were by-produced. This salt as well as the Pd(0)/CuI catalyst residues were insoluble in the reaction medium at ambient temperature and readily removed by simple filtration. In the dibutynol intermediate the 2-hydroxyisopropyl moiety functions as an ethynyl-protecting group that can be readily deprotected by eliminating a molecule of acetone using NaH. Overall yield of DEDB monomer based on DODB as starting material was around 80%.

Chemical structure of the monomer DEDB was confirmed by ¹H and ¹³C NMR and FTIR spectroscopy. In the Experimental section all the spectral data are summarized. In its ¹H NMR spectrum it was clear to see that the hydroxy proton to observe from OMHB at 2.05 ppm disappeared completely and instead the ethynyl proton originating from HC≡C— triple bond of DEDB were newly observable at 3.35 ppm. In FTIR spectrum the characteristic
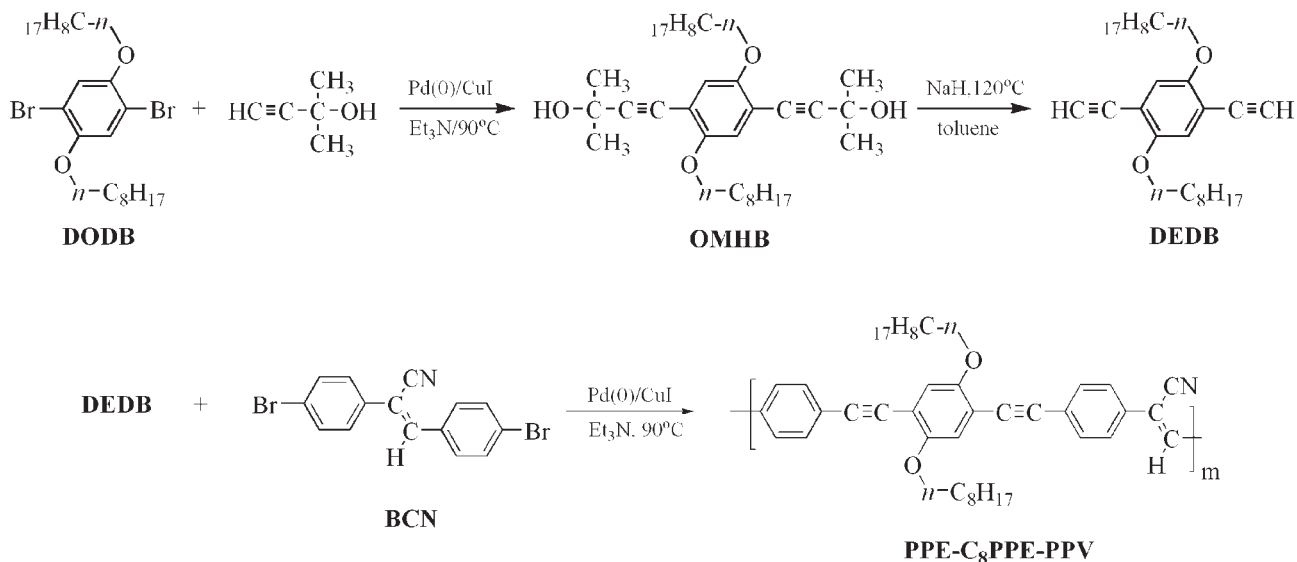
Scheme 1 Synthesis of monomer and polymer.

ethynyl absorption band of DEDB was observed at 2205 cm^{-1}. In addition, the hydroxy absorption originally observable in OMHB at 3500 cm^{-1} could not be detected in DEDB at all. Therefore it could be assured that the monomer DEDB was successfully prepared with the structure as shown in Scheme 1.

Synthesis and characterization of polymer

As shown in Scheme 1, the poly[1,4-phenyleneethynylene-2,5-di(*n*-octyloxy)-1,4-phenyneneethynylene-1,4-phenylene-1-cyanovinylene] (PPE-C$_8$PPE-PPV) was prepared in Et$_3$N by the Pd(PPh$_3$)$_4$/CuI-catalyzed Heck reaction[25] of DEDB with 1,2-di(4-bromophenyl)-1-cyanovinylene (BCN), which had been derived by the Knoevenagel condensation of 4-bromophenylacetonitrile with 4-bromobenzaldehyde. The Heck coupling reaction between an aromatic bromide and an acetylene derivative is a dehydrobromination reaction conducted in Et$_3$N, and Et$_3$N hydrobromide is by-produced. This ammonium salt is and the catalyst residues were removed in the same way as in monomer preparation.

As to see from Scheme 1, PPE-C$_8$PPE-PPV can be considered an alternating poly[di(1,4-phenyleneethynylene)-*alt*-(1,4-phenylene-1-cyanovinylene)] [(PPE)$_2$-*alt*-(PPV)], on which two *n*-octyloxy side branches are affixed to a PPE unit. The cyano group-containing PPV unit was incorporated to modify PPE backbone structure for enhanced electron affinity, and the side branches are aimed to enhance organosolubility of the polymer.

The average molecular weights of polymer were determined to be M_n = 9100 and M_w = 19,000 with a polydispersity index (PDI) of 2.1 by GPC in THF using a polystyrene standard. The M_n value corresponds to ∼ 15 repeating units in a chain, which means that PPE-C$_8$PPE-PPV prepared is not very high in molecular weight. Such low molecularity of PPE-C$_8$PPE-PPV seems to arise from the inherently low reactivity of the Heck coupling reaction.[26] However, this chain length is not disappointing in EL application of the PPE-C$_8$PPE-PPV because the value lies sufficiently higher than the effective π-conjugation length of conventional EL polymers, which is known to be about 10 repeat units.[27]

The chemical structure of the PPE-C$_8$PPE-PPV thus prepared was characterized by ^{1}H NMR, FTIR spectroscopy, and EA. In the Experimental section all the spectral data are summarized, and in Figure 1 the ^{1}H NMR spectrum is reproduced with interpretation of each peak. In Figure 1 it is to see that the ethynyl proton to observe from DEDB at 3.35 ppm disappeared completely and instead the vinyl and aromatic protons originating from BCN are newly observable at 7.47 and 7.6–7.9 ppm, respectively. In FTIR it is to confirm that the absorption bands characteristic of cyano-
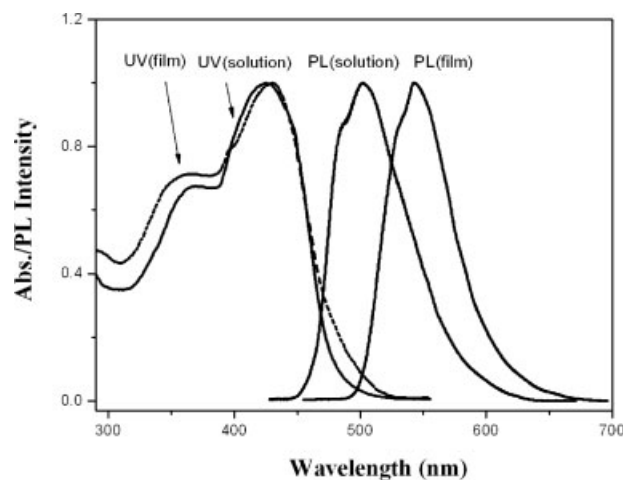
Figure 2 Normalized UV absorption and PL emission spectra of PPE-C$_8$PPE-PPV.

vinylene and ethynylene are observed at 2220 (—CN), 1586 (—C=C—), and 2205 cm^{-1} (—C≡C—), respectively, while the absorption of alkyne group to appear at 3280 cm^{-1} vanished completely. In addition to the FTIR spectroscopic characterization, the high coincidence between measured and calculated EA data supports that prepared polymer was successfully synthesized with the structure as shown in Scheme 1.

In fabricating an EL device with economic competitiveness it is required that polymer thin films should be made readily by means of spin coating or solvent casting. For the filming processes a polymer should be freely soluble in an organic solvent, and our PPE-C$_8$PPE-PPV was molecularly designed to improve the solubility by incorporating flexible *n*-octyloxy side groups onto rigid backbone. Solubility test revealed that PPE-C$_8$PPE-PPV was freely soluble at room temperature in common solvents such as toluene, CHCl$_3$, and THF. This result indicates that the *n*-octyloxy side chains made a great contribution to enhancing solubility of the polymer.

Thermal stability of the polymer was investigated by TGA in N$_2$ atmosphere. TGA thermogram showed that PPE-C$_8$PPE-PPV began to degrade at 345°C with a one-step pyrolysis pattern, indicating that it possesses high-thermal stability and its main chain and *n*-octyloxy side chains decompose away simultaneously. Phase behaviors of the polymer were studied by DSC in N$_2$ flow at 10°C/min scan rate in the temperature range just below degradation temperature, but no phase transition could be detected at all in spite of repeated scans. This result suggests that phase transition temperature of PPE-C$_8$PPE-PPV might lie higher than the degradation temperature of the polymer, which is frequently the case in many rigid-rod polymers.[28]

In X-ray diffractogram the polymer showed no sharp peak in the wide-angle region but only very

TABLE I
Optoelectrical Properties of PPE-C$_8$PPE-PPV

UV (nm)		PL (nm)[a]						
Solution[c]	Film	Solution[c]	Film	EL (nm)	HOMO (eV)	LUMO (eV)	E_g (eV)	E_g^{opt} (eV)[b]
425	430	502	543	545	−5.70	−3.29	2.41	2.38

[a] Excited at He-Cd 325 nm.
[b] Band gap estimated from edge of UV absorption.
[c] In toluene solution.

broad halo at about $q = 15$ nm^{-1}, indicating that it is entirely amorphous. In the small-angle region the polymer showed a broad peak at around $q = 4.3$ nm^{-1}, corresponding to the Bragg spacing of 14.6 Å. This peak was characteristic of a typical layer structure,[29] in which the main chains form rigid backbone layers and the flexible side chains form a separate crystal region.

UV–vis absorption and photoluminescence

To investigate optical properties of PPE-C$_8$PPE-PPV their UV–vis absorption and PL emission spectra were taken both in toluene solution and in thin film. The normalized spectra are reproduced in Figure 2 and their spectral data are summarized in Table I.

In UV–vis spectrum taken in toluene PPE-C$_8$PPE-PPV shows a small maximum at 360 nm and a large peak at 425 nm. In thin film, PPE-C$_8$PPE-PPV exhibits the respective maxima at 355 nm and at 430 nm as well as a discernible shoulder at 396 nm. Presumably the small maximum corresponds to $\pi \rightarrow \pi^*$ transition of the π-electrons of PPV unit and the large maximum does to that of the delocalized π-electrons of polymer main chain. Based on the absorption edge of film, optical band gap of PPE-C$_8$PPE-PPV was determined to be 2.38 eV.

In PL spectrum, in solution, PPE-C$_8$PPE-PPV exhibited bluish-green light in the wide wavelength range (444–635 nm) with a maximum at 502 nm and a shoulder at 487 nm. This shoulder might correspond to the shoulder observed in UV–vis absorption spectrum in solution at 396 nm. In PL spectrum, taken in film, the polymer showed emission with a discernible shoulder at 532 nm and a maximum at 543 nm, which appeared 41 nm red-shifted compared with that of PL spectrum taken in solution. The red shift is attributable to an excimer[30] formed by intermolecular interaction between neighboring chains of the polymer, which is remarkably higher in solid state than in dilute solution.

Electrochemical properties

To gather information on the oxidation–reduction potentials of PPE-C$_8$PPE-PPV, cyclic voltammographic measurement was performed at room tem-perature and 30 mV/s scan rate using a conventional three-electrode cell filled with dilute Bu$_4$NClO$_4$ in acetonitrile as electrolyte, and a cyclic voltammogram (CV) obtained is reproduced in Figure 3. From the onset potentials of oxidation and reduction of the CV of PPE-C$_8$PPE-PPV, HOMO and LUMO energy levels and band gap energy (E_g) relative to the ferrocene (Fc) value of −4.8 eV as standard ($E_{Fc} = E_{Ag} - 0.09$ eV)[31] were determined and listed in Table I.

In Figure 3, it is seen that on applying positive potential PPE-C$_8$PPE-PPV shows the onset potential of oxidation at 0.99 V and a maximum at 1.17 V. On applying negative potential it begins to reduce at −1.42 V and reaches a maximum at −1.77 V. From the potential values HOMO and LUMO energy levels of PPE-C$_8$PPE-PPV relative to Fc and E_g were calculated to be −5.70 and −3.29 and 2.41 eV, respectively. The E_g value (2.41 eV) measured from CV scan was well coincident with the value (2.38 eV) determined from the UV–vis absorption edge at 518 nm of thin film.

If CV scans are repeated, the electrical conduction usually decreases more or less because of the interface barrier formed between polymer film and electrode surface[32] and/or by the insulating effect of nonconducting moieties contained in the polymer molecule,[33] and the decrease results in elevating the
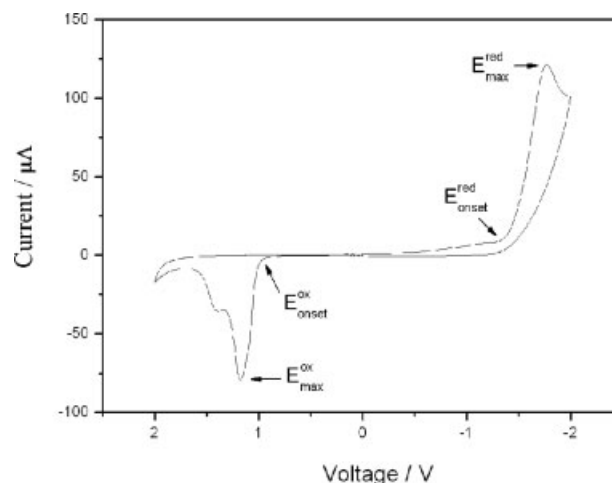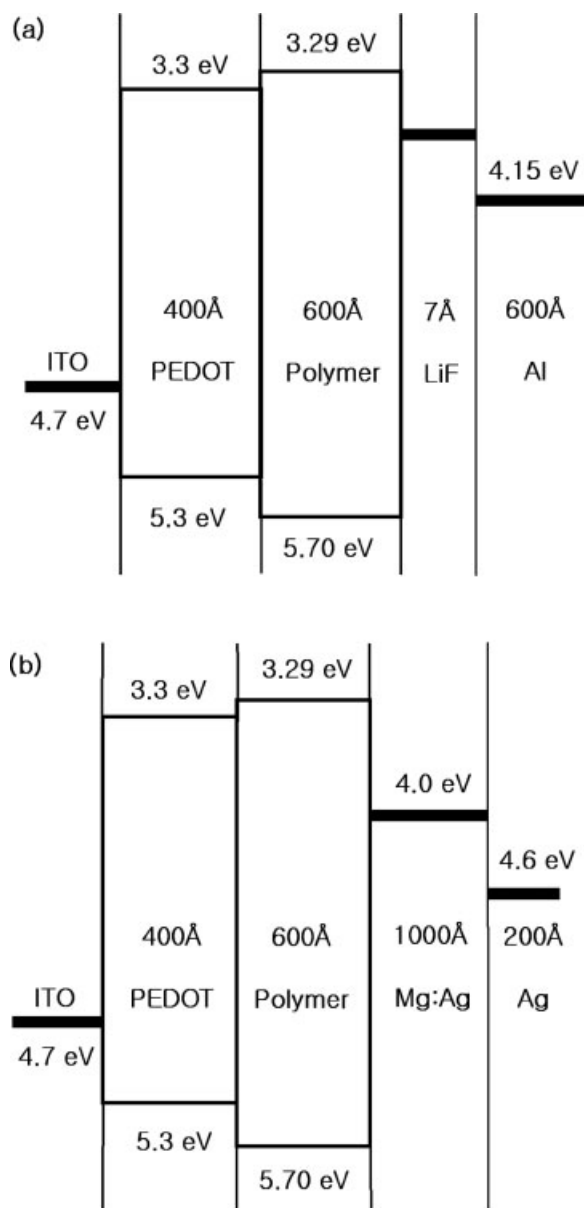

Figure 3 Cyclic voltammogram of PPE-C$_8$PPE-PPV film coated on ITO glass.

Figure 4 Construction and energy level of two devices, ITO/PEDOT/PPE-C$_8$PPE-PPV/LiF/Al (a) and ITO/PEDOT/PPE-C$_8$PPE-PPV/Mg:Ag/Ag (b).

band gap energy. However, in our experimental result for PPE-C$_8$PPE-PPV no difference between the two E_g values was noticed in repeated CV scans, signifying that the insulating *n*-octyloxy side groups did not shield any electrical conduction. This deduction indicates further that in CV scans the electrical conduction takes place little along the side chain but mainly across and along the main chain.

EL and I-V-L characteristics

To measure EL performance and density-voltage-luminescence (I-V-L) characteristics of PPE-C$_8$PPE-PPV two devices with the multilayer structure of ITO/
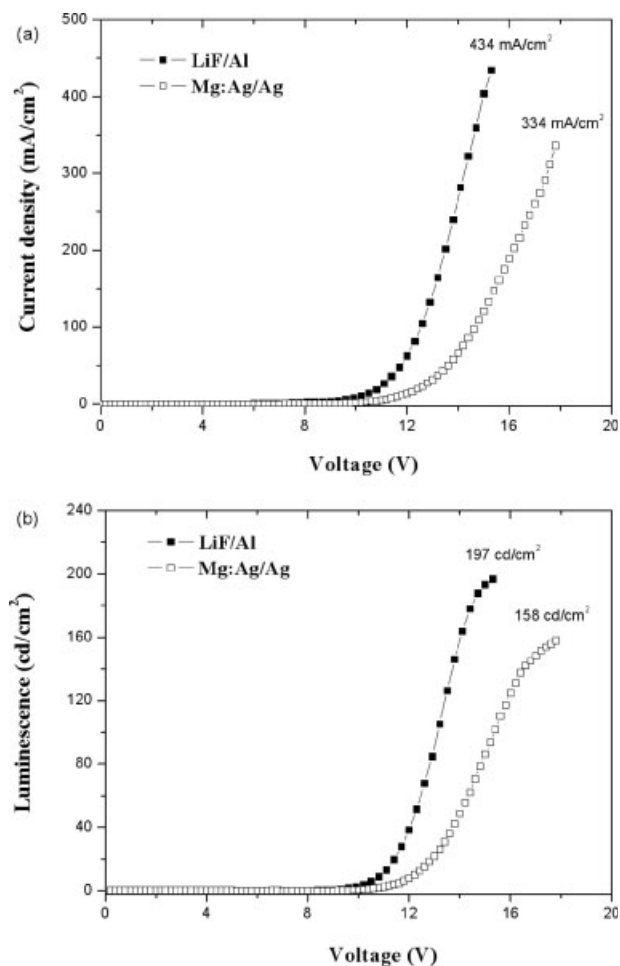
PEDOT/PPE-C$_8$PPE-PPV/LiF/Al and ITO/PEDOT/PPE-C$_8$PPE-PPV/Mg:Ag/Ag were fabricated, as shown in Figure 4, in which for PPE-C$_8$PPE-PPV the band energy levels determined from the CV were used. EL spectrum was measured on applying 15 V from a pulse DC voltage source and reproduced in Figure 5 after normalized.

When EL spectrum is compared with film-state PL spectrum presented in Figure 2, it is to confirm that both spectra have a maximum peak at almost the same wavelength, indicating that both EL and PL involve the same excited state, although the EL peak was slightly broader compared with the corresponding PL spectrum. The weak and broad emission at >700 nm might arise from the excimers.[30,34]

The current I-V-L characteristics of two devices with LiF/Al and Mg:Ag/Ag cathodes are reproduced in Figure 6. The characteristics of the current density against the applied voltage exhibited an excellent diode behavior. Once the device is turned on at a critical voltage, the current density increased strictly linearly with increasing applied voltage, as shown in Figure 6(a). The turn-on voltages of two devices with LiF/Al and Mg:Ag/Ag cathodes were determined to be 9 and 10 V, respectively. Figure 6(b) shows the V-L characteristic of two devices. Maximum luminescence of the device with the structure ITO/PEDOT/PPE-C$_8$PPE-PPV/LiF/Al was measured to be about 197 cd/cm^2 at a current density of 434 mA/cm^2 and at a voltage of 15 V, while the maximum was measured to be about 158 cd/cm^2 for the ITO/PEDOT/PPE-C$_8$PPE-PPV/Mg:Ag/Ag at a current density of 334 mA/cm^2 and at a voltage of 18 V. As shown in Figure 6, the lower turn-on voltage and higher luminescence of the device with LiF/Al cathode than those of the device with Mg:Ag/Ag cathode could be attributed to the thin LiF layer inserted between emitting polymer
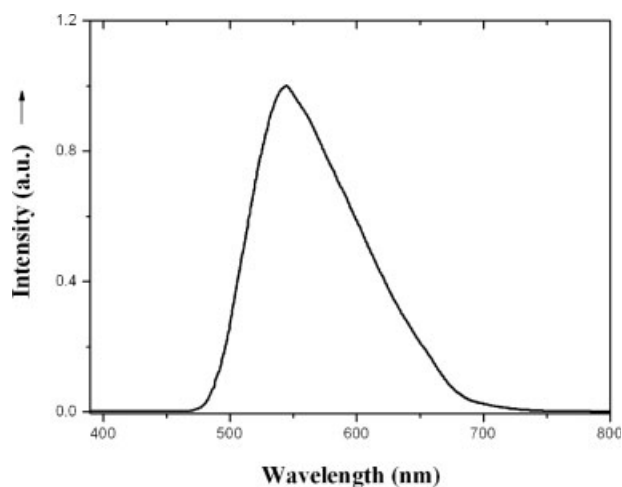
Figure 5 EL spectrum of PPE-C$_8$PPE-PPV in thin film.

Figure 6 I-V (a) and V-L (b) characteristic curves for the devices of ITO/PEDOT/PPE-C$_8$PPE-PPV/cathodes.

and Al electrode. It was reported[11,35] that a thin LiF layer used as an insulator greatly lowers the work function of cathode and subsequently improves the device performance.

The external quantum efficiency for the device with ITO/PEDOT/PPE-C$_8$PPE-PPV/LiF/Al configuration was about 0.06% at a voltage of 15 V and a current density of 434 mA/cm^2, while the external quantum efficiency for the ITO/PEDOT/PPE-C$_8$PPE-PPV/Mg:Ag/Ag was about 0.03% at a voltage of 18 V and a current density of 334 mA/cm^2. The higher quantum efficiency of the former device than that of the latter device manifests the advantage of the device with LiF used as cathode material.

CONCLUSIONS

As a new π-conjugated poly[di(*p*-phenyleneethynylene)-*alt*-(*p*-phenylenecyanovinylene)] containing two *n*-octyloxy side branches poly[*p*-phenyleneethynylene-2,5-di(*n*-octyloxy)-*p*-phenyleneethynylene-*p*-

phenylene-1-cyanovinylene] (PPE-C$_8$PPE-PPV) was synthesized by the Pd(0)/CuI-catalyzed Heck reaction of DEDB with BCN and its PL and EL properties were investigated. The monomer DEDB was prepared by deacetonation of OMHB, which had been synthesized by Pd(0)/CuI-catalyzed coupling of DODB with 3-methylbut-1-yn-3-ol. Chemical structure of PPE-C$_8$PPE-PPV was characterized by ^{1}H NMR, FTIR, and EA. The polymer was highly soluble in toluene, CHCl$_3$, and THF, and showed M_n = 9100, M_w = 19,000, and polydispersity index = 2.1 in GPC. In wide-angle X-ray diffractometry, PPE-C$_8$PPE-PPV exhibited loosely-developed layer structure. Thermal stability was confirmed up to 345°C in TGA and it showed excellent film-forming properties. In UV–vis absorption spectra in solution and in film PPE-C$_8$PPE-PPV exhibited its maximum at 425 and 430 nm, respectively, while PL maximum in film appeared at 543 nm, about 41 nm red-shifted relative to that at 502 nm in the solution. The HOMO, LUMO energy levels and band gap of PPE-C$_8$PPE-PPV were determined to be −5.70, −3.29, and 2.41 eV, respectively. This result indicates that the polymer was electrochemically active in both the oxidation and reduction region. EL characteristics were investigated using two multilayer EL devices with the structure of ITO/PEDOT/PPE-C$_8$PPE-PPV/cathodes (LiF/Al and Mg:Ag/Ag). The EL devices emitted bright green light with a maximum at almost the same wavelength of 545 nm as the PL emission spectrum. The device with the structure of ITO/PEDOT/PPE-C$_8$PPE-PPV/LiF/Al showed slightly lower turn-on voltage (9 V vs. 10 V) and higher luminescence (197 cd/cm^2 vs. 158 cd/cm^2) than that with the structure of ITO/PEDOT/PPE-C$_8$PPE-PPV/Mg:Ag/Ag.

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