Synthesis and Characterization of Poly(fluorenylenevinylene-terphenylenevinylene) Containing Phenyl Pendant Group

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Abstract: Poly(fluorenylenevinylene-terphenylenevinylene) containing phenyl pendant group was synthesized by Suzuki coupling reaction and characterized by ^{1}H-NMR, ^{13}C-NMR, and IR-spectrum. The weight average molecular weight (M_w) of the obtained polymer was 31,000 with a polydispersity index of 1.9. The polymer showed good solubility in common organic solvents, and the solution and film emitted blue emission (λ_{max}=460 nm) on irradiation with UV light. The ITO/PEDOT/polymer/Al device fabricated using the polymer as an emitting layer emitted blue light with a maximum peak around 460 nm. The maximum efficiency of the device was 0.011%.

Keywords: light-emitting diode, poly(fluorenylenevinylene-terphenylenevinylene), blue emission.

Introduction

Light-emitting diode (LED) technologies that use conjugated polymers have shown substantial promise for electrooptical applications.[1-4] Important macromolecular structures for light emitting applications have been recently reviewed.[5,6] In the categories of conjugated polymers, polyfluorene and its derivatives occupy a significant position. Poly(fluorene)s (PFs) are attractive as active components of organic light emitting diodes because of their thermal and chemical stability and their exceptionally high solution and solid state fluorescence quantum yields (0.6-0.8).[7-10] Moreover, the facile substitution at the 9-position of the fluorene monomer allows control of polymer properties such as solubility, processability, and morphology. However, for most of the PFs investigated so far, relatively large band gaps and especially a high barrier to hole injection have limited their applications in PLEDs.[11,12]

Poly(p-phenylene) (PPP) and its derivatives have good thermal and oxidative stability, however, exhibit low solubility and high turn-on voltages. Low work function metals are required for efficient carrier injection into PPP derivatives. Furthermore, PPP and its derivatives are intrinsically violet blue emitters and present some difficulties in color tunability.[13]

Recently, we reported the synthesis and properties of poly(biphenylenevinylene) (PBPV) derivatives and poly(terphenylenevinylene) (PTPV) derivatives with a controlled conjation length of biphenylene vinylene unit or terphenylene vinylene unit, which are composed of alternating PPP and poly(phenylenevinylene) (PPV) units.[14-20]

In this article, we describe the synthesis and characterization of blue-light-emitting, poly(fluorenylenevinylene-terphenylenevinylene) containing phenyl pendant group, which is expected efficient pure blue emission resulted from fluorenylenevinylene and terphenylenevinylene backbone and the effect of introduced substituents into the vinyl bridge. Introducing phenyl pendant group to a vinyl bridge may expect to lead to enhanced solubility, oxidative and thermal stability, and reduced the formation of excimers owing to interchain interactions.

Experimental

Materials. Tetrahydrofuran (THF) and diethylether were distilled from sodium benzophenone ketyl. Toluene was purified by distillation from CaH_2 and used immediately. Triphenylphosphine was purchased from Aldrich, recrystallized from degassed ethanol, and sublimed under vacuum prior to use. 9,9-dihexylfluorene, benzoyl chloride, trimethylborate, n-BuLi (2.5 M in hexane), 2-ethylhexylbromide, 4-methoxyphenol, and tetrakis(triphenylphosphine) palladium (0) were purchased from Aldrich. Other chemicals were used without further purification.

Synthesis of 9,9-Dihexylfluorene. 60 g (361 mmol) of fluorene was stirred for 30 min in the 250 mL of THF, and 220 g (794.2 mmol) of n-BuLi was added. After stirring for 1 h, 131 g (794.2 mmol) of 1-bromohexene was added and

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stirred for 6 h. The reaction was terminated with water, and extracted with ether. The crude product was recrystallized in hexane. Mp: 34 °C, Yield: 91%. ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.3 (8H, m), aliphatic (C-H), 2.0 (4H, m), 1.0 (12H, m), 0.8 (6H, m), 0.6 (4H, m). FTIR (NaCl, cm⁻¹): 3047 (aromatic C-H), 2846 (aliphatic CH₂).

Synthesis of 2,7-Dibenzoyl-9,9-dihexylfluorene. In the mixture of 20 g (60 mmol) of 9,9-dihexylfluorene, 32 g (240 mmol) of AlCl₃ and 100 mL of CS₂, 33.7 g (240 mmol) of benzoyl chloride was added and stirred for 48 h. The reaction was terminated with ice and 100 mL of HCl, and extracted with CH₂Cl₂. The crude product was recrystallized in hexane. MP: 54 °C, Yield: 40%. ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.8-7.7 (10H, m), 7.6 (2H, m), 7.5 (4H, m) aliphatic (C-H), 2.0 (4H, m), 1.0 (12H, m), 0.8 (6H, m), 0.6 (4H, m). FTIR (NaCl, cm⁻¹): 3047 (aromatic C-H), 2846 (aliphatic CH₂), 1750 (C=O).

Synthesis of 2,7-Bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene. After stirring of 14.1 g (27.6 mmol) of 4-bromobenzyl phosphonium salt, 1.56 g (64.4 mmol) of NaH and 80 mL of toluene, 5 g (9.2 mmol) of 2,7-dibenzoyl-9,9-dihexylfluorene was added in the mixture. After stirring for 35 h, the reaction was terminated with 80 mL of 2 N-HCl. The crude product was recrystallized in hexane. Mp: 158 °C, Yield: 38%. ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.7-6.8 (26H, m), aliphatic (C-H), 1.8 (4H, m), 1.0 (12H, m), 0.8 (6H, m), 0.6 (4H, m). FTIR (NaCl, cm⁻¹): 3040 (aromatic C-H), 2950 (aliphatic CH₂), 1065 (C-Br).

Preparation of 1-Methoxy-[4-(2′-ethylhexyl)oxybenzene]. One-neck flask equipped with a nitrogen inlet, dean-stark trap and reflux condenser was charged with 4-methoxyphenol (22.4 g, 0.19 mol), potassium hydroxide (10.6 g, 0.19 mol) and benzene (200 mL). The reaction mixture was refluxed at 80 °C and was removed water for 24 h. Then, the mixture was cooled to room temperature and benzene solvent was evaporated. 2-Ethylhexylbromide (36.7 g, 0.19 mol), copper (0.3 g, 4.72 mmol) and NMP 100 mL were charged in the reaction mixtures. After the reaction mixture was refluxed at 160 °C for 48 h, the mixture was cooled to room temperature. The organic layer was extracted, washed with water, dried over MgSO₄ and filtered. The solution was evaporated and distilled under reduced pressure (Bp: 108 °C/1 mmHg, Yield: 95%). ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 6.9 (4H, s), -OCH₂- and -OCH₃ 3.8 (5H, m), aliphatic (C-H) 1.8-0.9 (15H, m). FTIR (NaCl, cm⁻¹): 3047 (aromatic C-H), 2846 (aliphatic CH₂), 1200 (C-O-C).

Preparation of 2,5-Dibromo-1-methoxy-[4-(2′-ethylhexyl) oxy]benzene. Bromine (64.9 g, 0.406 mol) was added dropwise over 30 min, to a stirred and ice-cooled solution of the 1-methoxy-[4-(2′-ethylhexyl)oxy]benzene (40.0 g, 0.169 mol) and iodine (0.3 g, 1.8 mmol) under rigorous exclusion of light at room temperature for 8 h. 20% aqueous KOH solution (200 mL) was added and the mixture was stirred until the color disappeared. After the reaction mixture was

extracted with dichloromethane, organic layer was washed with water, dried over MgSO₄ and filtered. The solution was evaporated and the crude product was distillated under reduced pressure (Bp: 134 °C/1 mmHg, Yield: 85%). ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), δ 7.1 (2H, s), -OCH₂- and -OCH₃ 3.8 (5H, m), aliphatic (C-H) 1.8-0.9 (15H, m). FTIR (NaCl, cm⁻¹): 3047 (aromatic C-H), 2846 (aliphatic CH₂), 1200 (C-O-C), 1065 (aromatic C-Br).

Preparation of 1-Methoxy-[4-(2′-ethylhexyl)oxy]benzene diboronic acid. 2,5-Dibromo-1-methoxy-[4-(2′-ethylhexyl) oxy]benzene (40.0 g, 0.10 mol) was added drop-wise to magnesium powders (7.4 g, 0.30 mol) in boiling THF (250 mL). After the reaction mixture was refluxed for 2 h, the reaction mixture was cooled to -70 °C using liquid nitrogen. Then, the undiluted trimethylborate (42.0 g, 0.40 mol) was added and stirred for 12 h at room temperature. After 2 M H₂SO₄ aqueous solution was added, the organic layer was extracted with ether, washed with water, dried over MgSO₄ and filtered. The solvent was evaporated and crude product was recrystallized in hexane to give product of white crystal (Yield: 20%). ¹H NMR (CDCl₃, 500 MHz) (ppm): aromatic (C-H), 7.1(2H, s), -OCH₂- and -OCH₃ 3.8 (5H, m), aliphatic (C-H) 1.8-0.9 (15H, m). FTIR (KBr, cm⁻¹): 3500-3150 (O-H), 2846 (aliphatic CH₂), 1200 (C-O-C).

Polymerization. All handling of catalysts and polymerization was done in a nitrogen atmosphere. To a stirred solution of 1-methoxy [4-(2′-ethylhexyl)oxy]benzene diboronic acid (0.578 g, 1.786 mmol), 2,7-bis[(4-bromophenyl)-1-phenyl-ethylene]-9,9-dihexylfluorene (1.5 g, 1.786 mmol) in 10 mL THF and 4 mL 2 M K₂CO₃ solution in water was added catalysts, Pd(PPh₃)₄ (8.4 mg, 0.6 mol%). The reaction mixture was heated at 80 °C under nitrogen atmosphere for 8 h. Bromobenzene (0.05 g, 0.318 mmol) was added and then phenyl boronic acid (0.05 g, 0.41 mmol) was added with small amounts of catalysts for end-capping. After 2 h, the reaction mixture was poured into methanol (50 mL) and filtered with glass filter. The residue was dissolved in CHCl₃ and washed with water. After being dried over MgSO₄, precipitation was twice repeated with chloroform/methanol (Yield: 65%). ¹³C NMR (CDCl₃, 500 MHz) (ppm): 153, 151, 144, 143, 142, 141, 140, 139, 137, 136, 135, 132, 131, 130, 129, 129.5 128, 128.5, 127.5, 126, 125, 124, 120, 119, 116, 114, 71, 56, 54, 41, 39, 32, 32.5 30, 29, 28, 23, 22, 21, 12, 11.

Fabrication of the LED. Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on, an indium-tin oxide coated glass substrate which had been washed with water, acetone, and isopropyl alcohol sequentially. A tin polymer film was spin coated (3,000 rpm, 50 s) from a filtered (0.2 m filter) 1.0 wt% polymer solution in chlorobenzene on a PEDOT layer. An aluminium electrode was deposited on top of the device at a high vacuum (below 1 × 10⁻⁵ Torr). Wires were attached to the respective electrodes with a con-

ductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Instrument. Melting points were determined using an Electrothermal Mode 1307 digital analyzer. ¹H-NMR and ¹³C-NMR spectral data were expressed in ppm relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FTIR spectra were obtained with a Bomem Michelson series FTIR spectrometer and the UV-visible absorption spectra were obtained in chloroform on a Shimadzu UV-3100 spectrophotometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly Model M590 pump, μ-styrngel columns of 105, 104, 103, 500 and 100 Å, refractive index detectors, solvent THF). Elemental analyses were performed by Leco Co. CHNS-932. TGA measurments were performed on a Perkin-Elmer Series 7 analysis system under N_2 at a heating rate of 10 °C/min. Cyclic voltammetry measurements of the polymer films were performed on a BAS 100 B/W electrochemical analyzer in acetonitrile with 0.1 M tetrabutylammonium perchlorate (Bu_4NClO_4) as the supporting electrolyte at a scan rate of 100 mV/s. The potentials were measured against an Ag/AgCl reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising current and background current of the cyclic voltammogram. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluorometer utilizing a lock-in amplifier system with a chopping fre-

quency of 150 Hz. Thickness of films was determined with a Sloan Dektak.

Results and Discussion

The synthesis of the monomer and polymer is outlined in Scheme I. 4-Methoxyphenol was used as a starting material for the synthesis of 1-methoxy-[4-(2'-ethylhexyl)oxy]benzene diboronic acid. In a separate reaction, fluorene was reacted with 2.5 equiv of butyllithium in diethyl ether at -78 °C. The resulting 9,9'-dilithiofluorene was reacted with 2.5 equiv of hexyl bromide at -78 °C, yielding 9,9'-dihexylfluorene. 2,7-Dibenzoyl-9,9-dihexylfluorene was obtained by Friedel-crafts acylation of n-hexylfluorene. 4-Bromobenzylphosphonium salt was obtained from the reaction between triphenyl-phosphine and 4-bromobenzyl bromide. The monomer, 2,7-bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene was synthesized by Wittig reaction of 4-bromobenzylphosphonium salt and 2,7-dibenzoyl-9,9-dihexylfluorene. The polymerization was carried out by Suzuki coupling reaction following termination with bromobenzene and phenyl boronic acid. The ¹H-NMR and IR spectra of the polymer and elemental analysis confirmed the expected polymer structure. The resonance for the boronic acid was absent in the ¹H-NMR spectrum of polymer, showing that no monomeric residues remained in the polymer (Figure 1). In the IR spectrum of the obtained polymer, the O-H stretching for boronic acid and aromatic C-Br stretching for 2,7-bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene were disappeared. The obtained polymer was readily soluble in common organic
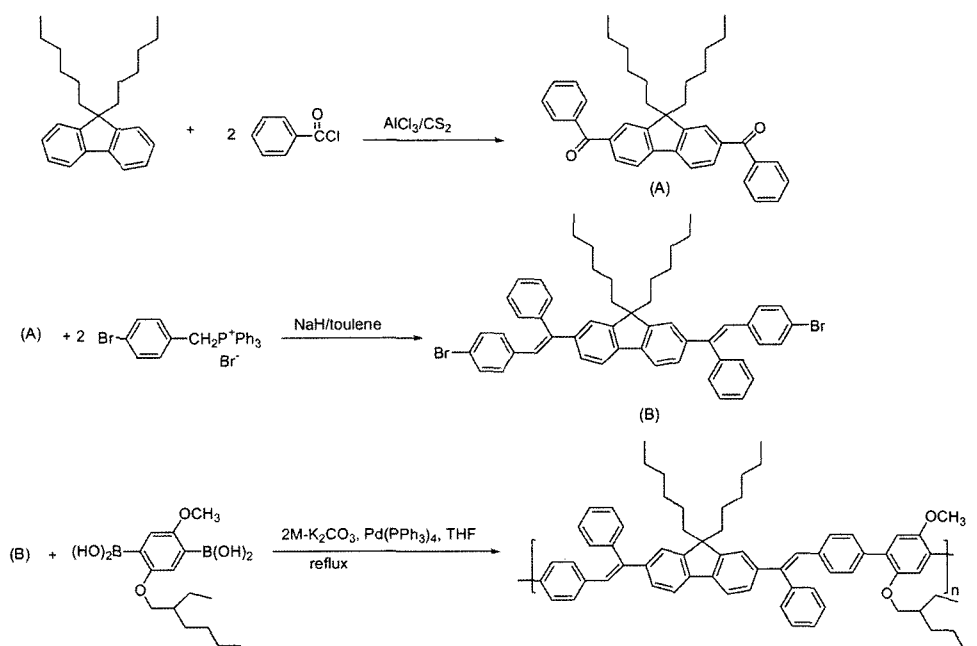

Scheme I. Synthetic scheme of monomer and polymer.

solvents such as chloroform, toluene, chlorobenzene, etc. Pinhole-free and homogeneous thin film could be formed by spin-coating from chloroform solution. GPC analysis yielded weight average molecular weight of polymer of 31,000 with polydispersity index of 1.9. Thermal stability of the polymer measured by thermogravimetric analysis (TGA) under a nitrogen atmosphere showed stability in the 400 °C range. The weight loss of the polymer was less than 5% on heating to 400 °C (Figure 2). The glass transition temperature (T_g) of 76 °C was determined by differential scanning calorimetry (DSC) analysis in a nitrogen atmosphere at a heating rate of 20 °C/min. The absorption and emission spectra of polymer in chloroform solution and in solid film are shown in Figure 3. The UV spectrum of a dilute solution and a film of polymer showed λ_{max} at 370 and 375 nm, respectively with a
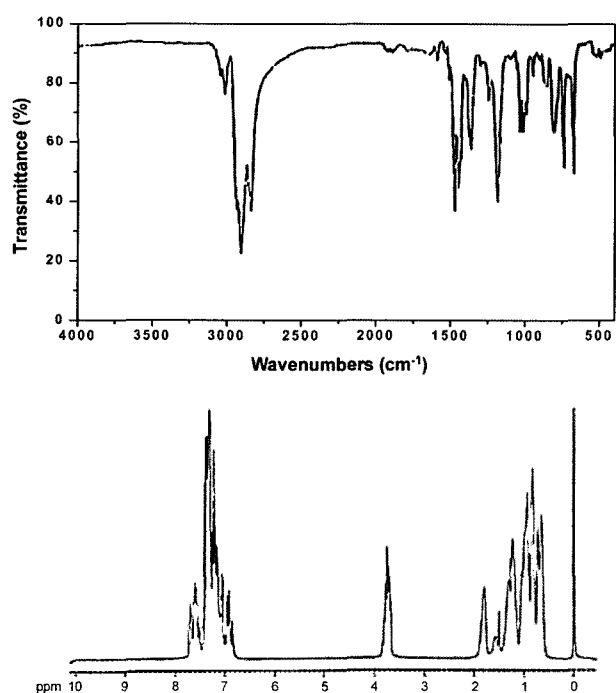
Figure 1. ^{1}H-NMR and IR spectrum of the polymer.
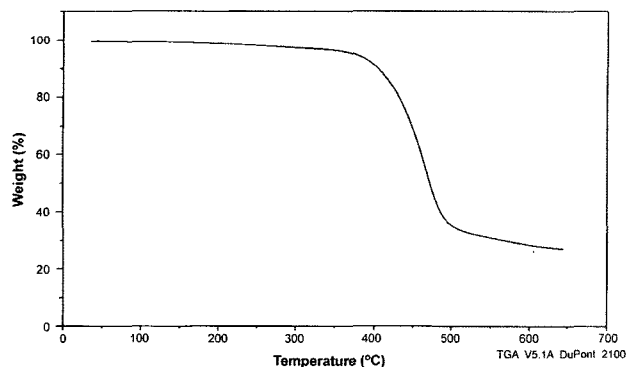
Figure 2. TGA thermogram of the polymer.

small bathochromic shift in the film. The maximum emission in the photoluminescence spectrum of the solution and a film of polymer was observed at 454 and 460 nm, respectively. The red shift relative to solution which is attributed to packing effects in the local geometry is very small.[21] It may be due to inhibited intermolecular interaction by introduced phenyl pendant.

The main emission peak of the polymer is blue shifted with respect to poly(9,9-dihexylfluorenediylvinylene-alt-1,4-phenylenevinylene) which shows PL maxima for the solution and the film at 477 and 482 nm, respectively, indicating that the effective conjugation of polymer is partially interrupted, resulting in 9,9-dihexylfluorenediylvinylene-1,4-phenylene chromophores connected to each other by non-coplanar phenylene groups as well as introduced phenyl pendant group in the vinyl bridge.[22] It has been suggested that isolated unsubstituted oligophenylenes are nonplanar, presumably due to ortho-hydrogen interactions. Substitution with methoxy and ethylhexyloxy groups in the middle phenyl ring results in a larger torsional angle between the two consecutive aryl units because of the increased steric interactions. Moreover, the introduced phenyl pendant groups in the vinyl bridge inhibited the coplanarity although the vinyl bridge can develop a high degree of coplanarity with fluorene unit in copolymer.

Cyclic voltammetry (CV) was employed to estimate its HOMO and LUMO energy level. The electrochemical process probed by cyclic voltammetry is similar to it involved in the charge injection and transport process in LED devices. The polymer film was coated onto a Pt electrode and scanned positively and negatively at a scan rate of 100 mVs^{-1} in a 0.1 M solution of Bu$_4$NClO$_4$ in anhydrous acetonitrile. The onset potential for reduction and oxidation was observed at about -1.6 and 1.2 V, respectively. From the onset potential of the oxidation and reduction processes, the band gap of the polymer was estimated to be 2.8 eV, which is consistent with the result of absorption edge (λ_{edg} = 440 nm : 2.84 eV). According to the equations, the LUMO and HOMO of polymer was estimated to be -2.8 and -5.6 eV, respectively.

Double layer LED with structure ITO/PEDOT/polymer/Al utilizing obtained polymer as emissive layer was fabricated. The blue electroluminescence (λ_{max} = 460 nm) was obtained (Figure 4). The electroluminescent spectrum was similar to the PL spectrum of polymer except a small shoulder appeared around 530 nm. The tailing in the long wavelength region is largely due to defects in the emissive polymer layer which act as new recombination centers in which excitons radiatively decay giving emissions different from those given by excitons decaying on the pristine polymer main chain.[10,23-25] The emitting color of device showed the blue emission (x,y) = (0.16, 0.16) for polymer in CIE (Commission Internationale de l'Eclairage) chromaticity coordinates.

Figure 5 represents typical current-voltage and luminescence-voltage measurements in a device. Current and light
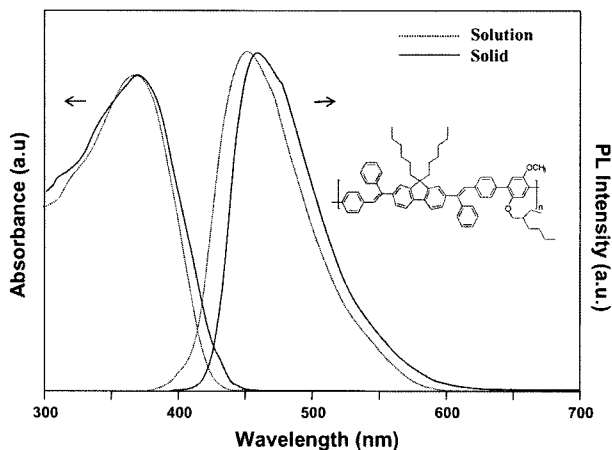
Figure 3. The absorption and emission spectra of polymer in chloroform solution and in solid film.
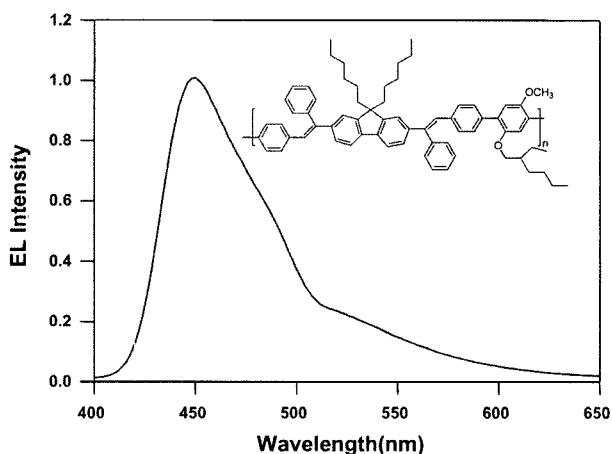

Figure 4. Electroluminescent spectrum of ITO/PEDOT/polymer/Al device.

Figure 5. Current-voltage and brightness-voltage characteristics of ITO/PEDOT/polymer/Al device.

packing effect due to inhibited intermolecular interaction. The blue electroluminescene ($\lambda_{max}=460$ nm) was obtained by ITO/PEDOT/polymer/Al structured device. The maximum efficiency of device was 0.011%.

arise at almost the same voltage at 10 V, indicating a balance of hole and electron injection. The maximum brightness is 11.5 μW at 17 V and 48 mA/cm^2. In the quantum efficiency-voltage curve, the maximum quantum efficiency of device was 0.011% at 16 V.

Conclusions

The new blue-light-emitting, poly(fluorenylenevinylene-terphenylenevinylene) containing phenyl pendant group, was synthesized by Suzuki coupling reaction with 2,7-bis[(4-bromophenyl)-1-phenylethylene]-9,9-dihexylfluorene and 1-methoxy-[4-(2'-ethylhexyl)oxy]benzene diboronic acid. The polymer showed good solubility and good thermal stability up to 400 °C. The maximum emission in the photoluminescence spectrum of the solution and a film of polymer was observed at 454 and 460 nm, respectively, indicating reduced
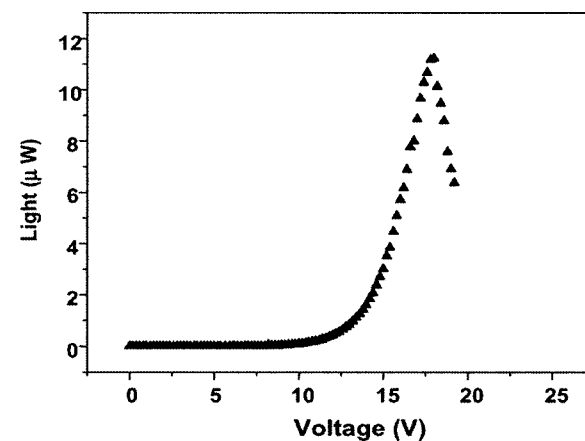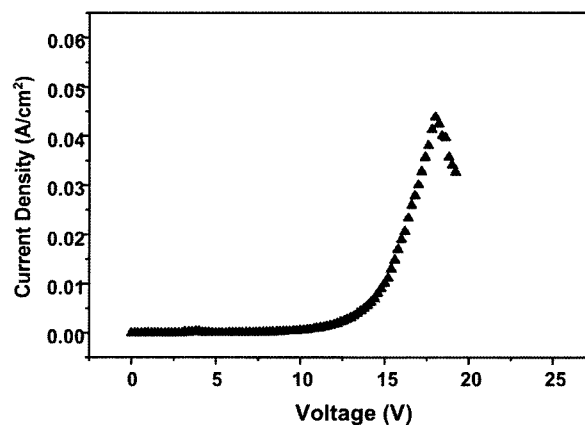
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