Yellow Light-Emitting Poly(p-phenylenevinylene) Derivative with Balanced Charge Injection Property

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A new luminescent polymer, poly{1,4-phenylene-1,2-ethenediy1-2-[2''-(4''-octyloxyphenyl)-(5''-yl)-1''-3'',4''-oxadiazole]-1,4-phenylene-1,2-ethenediyl-2,5-bis-dodecyloxy-1,4-phenylene-1,2-ethenediy1} (Oxd-PPV), was synthesized by the Heck coupling reaction. Electron withdrawing pendant, conjugated 1,3,4-oxadiazole (Oxd), is on the vinylene unit. The band gap of the polymer figured out from the UV-visible spectrum was 2.23 eV and the polymer film shows bright yellow emission maximum at 552 nm. The electroluminescence (EL) maximum of double layer structured device (ITO/PEDOT:PSS/Oxd-PPV/Al) appeared at 553 nm. Relative PL quantum yield of Oxd-PPV film is 3.6 times higher than that of MEH-PPV film. The HOMO and LUMO energy levels of Oxd-PPV figured out from the cyclic voltammogram and the UV-visible spectrum are -5.32 and -3.09 eV, respectively, so that more balanced hole and electron injection efficiency can be expected compared to MEH-PPV. A double layer EL of Oxd-PPV has an maximum efficiency of 0.15 cd/A and maximum brightness of 464 cd/m².

Key Words : Eminescence, Poly(p-phenylenevinylene), 1,3,4-Oxadiazole (Oxd), Balanced charge injection

Introduction

Since the first report of the polymer light emitting diode (PLED) based on poly(p-phenylenevinylene) (PPV) by Cambridge group,1 many research groups have tried to improve the efficiency of LED. In order to improve the efficiency of light-emitting diodes (LEDs) based on PPV, it is necessary to reduce the energy gap between the LUMO energy level of the emissive polymer and the work function of the cathode (e.g. Al, Ca, Li). One of the strategies of improving the efficiency of PLED is to develop new polymers, which have the electron withdrawing groups such as cyano (-CN),2-4 1,3,4-oxadiazole (Oxd),5-7 fluoroaryl,8,9  or quinoline10 in the main chain or side chains. Such electron withdrawing groups can be used for enhancing the electron-injection rate from the cathode to polymer. In MEH-PPV based polymers, incorporation of Oxd units enhances the electron-injection rate while lowering the hole-injection rate, because their HOMO and LUMO energy levels are lower than those of MEH-PPV.

In this article, we report the synthesis, optical, electrochemical, and electroluminescent properties of poly{1,4-phenylene-1,2-ethenediy1-2-[2''-(4''-octyloxyphenyl)-(5''-yl)-1''-3'',4''-oxadiazole]-1,4-phenylene-1,2-ethenediyl-2,5-bis-dodecyloxy-1,4-phenylene-1,2-ethenediy1} (Oxd-PPV). We herein attempted to improve the EL efficiency by introducing Oxd units on the vinylene position of the polymer. The design of the polymer structure was intended to balance the rates of electron- and hole-injection in the EL device. Moreover, one can also expect that the chances of interactions between the main chains would be lower comparing to the case of polymers with the substituents on the phenyl ring.

Experimental Section

Materials. Tetrahydrofuran (THF) and diethyl ether were used after distillation over sodium/benzophenone. Acetonitrile and chloroform were used after distillation over P2O5 and potassium carbonate, respectively. Tributylamine and 1,1,2,2-tetrachloroethane (TCE) were distilled over calcium hydride. All other chemicals were purchased from Aldrich Chemical Co. and used as received unless otherwise described. 1,4-bis-dodecyloxy-2,5-divinylbenzene (6) were synthesized according to the literature procedures.2,11,12

4-Octyloxybenzoic acid methyl ester (I). A mixture of 15.21 g (100.0 mmol) of 4-hydroxy benzoic acid methyl ester, 20.73 g (150.0 mmol) of potassium carbonate (dried under vacuum at 80 °C for 12 hours prior to use) and 19.31 g (100.0 mmol) of 1-bromotetradecane in 150 mL of acetone was stirred and refluxed for 24 hours. After cooling the reaction mixture to room temperature, the solid particles were removed by filtration and successively washed with 100 mL of acetone and 100 mL of chloroform. After removal of the solvent from the combined filtrate, the crude liquid product was dissolved in 100 mL of chloroform. The solution was washed with aqueous NaOH and brine followed by drying over anhydrous magnesium sulfate and evaporating the solvent using a rotary evaporator. The product was purified by recrystallization from hexane/methanol at -5 °C. The yield of the product was 22.58 g (85.4%). MS [M+]: 264. 1H-NMR (CDCl3, ppm): δ 7.95-7.93 (d, J = 8.8, 2H),

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2.4-Octoxybenzoic acid hydrazide (2). A mixture of 21.15 g (80.00 mmol) of compound 1 and excess of hydrazine hydrate in 150 mL of methanol was refluxed for 24 hours. The reaction mixture was cooled to room temperature and the precipitate was filtered. The precipitate was washed with water then dried under vacuum. A white solid product yield was 86.1%. mp: 81-82 °C. 1H-NMR (CDCl3, ppm): δ 166.98, 162.90, 131.45, 122.10, 113.96, 66.11, 31.68, 29.20, 29.09, 28.99, 25.86, 22.52, 13.94. Anal. Calcd. for C16H24O3: C, 79.64; H, 7.98; N, 4.34. Found: C, 80.14; H, 8.32; N, 4.40.

4-Octoxybenzoic acid N’-[2’’-(4-bromophenyl)-acety]-hydrazide (3). A mixture of 3.22 g (15.0 mmol) of 4-bromophenylacetic acid, 3.97 g (15.0 mmol) of compound 2, and 2.91 g (15.0 mmol) of EDCI in 5 mL of DMAc was stirred for 5 hours under nitrogen atmosphere. The reaction mixture was poured into 200 mL of water and the precipitate was separated by filtration followed by washing with water. The crude solid product was purified by recrystallization from methanol. The yield of the white solid product yield was 0.798 g (65.4%). mp: 112-113 °C. 1H-NMR (CDCl3, ppm): δ 8.03-7.99 (d, J = 8.9, 2H), 7.66 (s, vinylene-H, 1H), 7.58-7.67 (d, J = 8.2, 2H), 7.37-7.35 (d, J = 8.5, 2H), 7.26-7.25 (d, J = 8.7, 2H), 7.00-6.99 (m, 4H), 4.04-4.01 (t, J = 6.6, 2H), 1.85-1.79 (m, 2H), 1.51-1.45 (m, 2H), 1.38-1.29 (m, 8H), 0.93-0.88 (t, J = 6.8, 3H). 13C-NMR (CDCl3, ppm): δ 165.15, 164.59, 162.08, 133.85, 133.37, 133.16, 132.33, 131.68, 131.62, 131.53, 128.77, 125.50, 123.19, 123.12, 115.86, 114.95, 68.28, 31.78, 29.30, 29.20, 29.09, 25.97, 22.63, 14.09. Anal. Calcd. for C23H27BrN2O2: C, 59.03; H, 4.95; N, 4.59. Found: C, 59.10; H, 4.90; N, 4.63.

Polymerization. The polymer was prepared by Heck coupling reaction between compound 5 and 1,4-bis-dodecyloxycyloxy-2,5-divinylbenzene (6). A mixture of 0.500 mmol of compound 5, 0.500 mmol of 1,4-bisdodecyloxycyloxy-2,5-divinylbenzene, 4.50 mg (0.0200 mmol) of Pd(OAc)2, 30.5 mg (0.100 mmol) of tri-o-tolyl-phosphine and 0.31 mL of tributylamine in 10 mL of DMF was stirred for 24 hours at 120 °C. The hot reaction mixture was poured into 500 mL of methanol then polymer precipitate was collected by filtration. The filtered polymer precipitate was redissolved in 100 mL of chloroform then washed with 400 mL of deionized water. The water layer was decanted carefully. The black catalyst particles in the polymer solution were removed by filtration followed by evaporation of the solvent using a rotary evaporator. The polymer was dissolved in small amount of THF then poured into methanol. The polymer precipitate was filtered and further purified by Soxhlet extraction in methanol for a day. The polymer was dried under vacuum at room temperature for a day. Anal. Calcd. for C58H112Br2N2O2: C, 79.76; H, 8.54; N, 4.24. Found: C, 79.46; H, 9.28; N, 4.34.

Instrumentation. The synthesized compounds were characterized by 1H-NMR and 13C-NMR spectra obtained using Varian Unity 500 MHz spectrometer. The elemental analysis was carried out with Carlo Erba elemental analyzer (CarloErba 1108). FT-IR spectrum was recorded by Nicolet 205 FT-IR spectrometer. Thermogravimetric analysis (TGA) of the polymer was carried out under nitrogen atmosphere at a heating rate of 20 °C/min with Thermogravimetric Analyzer (Thermal Analysis 2050, TA Instruments). The UV-Visible spectra of the polymer were measured using a Hewlett-Packard HP8453 with photodiode array detector. PL and EL
spectra of the polymers were obtained using a Photon Technology Spectrofluorophotometer. Cyclic voltammetry was carried out with EG&G 362 Scanning Potentiostat with a three electrode cell in a solution of Bu4NBF4 (0.2 M) in acetonitrile at a scan rate 100 mV/s. The polymer films were coated on a Pt wire by dipping the electrode into the polymer solutions in chloroform followed by drying in nitrogen stream. Pt gauze was used as the counter electrode and an Ag/AgCl electrode in 3 M NaCl was used as the reference electrode. Prior to each measurement the cell was deoxygenated with nitrogen. Gel permeation chromatography (GPC) measurements were conducted by a GPC system equipped with a Milton-Loy CM4000 pump, a 6-port sample injection valve (Rheodyne), a Waters Temperature Control Module, a LDC Analytical SpectroMonitor 3100 UV detector and two Waters Styragel linear columns using polystyrene as standard and chloroform as eluent.

**EL device fabrication and characterization.** EL devices were fabricated using ITO glass (resistance of ITO was about 10 Ω/square, Delta Technology) as an anode and aluminum (Al) as a cathode. The polymer film was prepared by spin casting from the solution in 1,1,2,2-tetrachloroethane (25 mg/mL, 1500 rpm), and then dried under vacuum for 2 hours. Prior to spin coating, the polymer solution was filtered through a 0.45-µm membrane filter. Al electrode was deposited (150 to 200 nm) onto the surface of the spin-coated polymer film by thermal evaporation technique at about 10⁻⁴ Pa. The typical active area of the LED device was 4 mm². The current density-voltage (J-V) and brightness (B-V) characteristics were measured using a source meter (KEITHLEY 2420) and a Luminometer (Minolta LS110). Evaluation of EL devices was performed under ambient conditions.

**Results and Discussion**

Synthetic route of the key monomer, compound 5, is shown in Scheme 1. The first step is a simple synthetic procedure of ether in which methyl 4-hydroxybenzoate reacts with 1-bromooctane to form 1 in a high yield of over 90%. Amidization of 1 with hydrazine leads to 2. Reaction of 2 with 4-bromophenylacetic acid in the presence of 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI), a well known amide coupling agent, gives 3. Cyclization of 3 by POCl3 leads to 4, which is a well-known method for the synthesis of oxadiazole. Figure 1 shows

![Scheme 1](image-url)
1HMR-spectrum of 4 and 5. As the 1H-NMR peak of the benzyl proton in 4 appeared at 4.13 ppm and the benzyl proton in phenylacetonitrile appears approximately at 3.7 ppm, one can assume that the acidity of the two protons is comparable. It is well known that phenylacetonitrile undergo condensation reaction with 4-bromobenzaldehyde. Thus, it is expected that 4 can also undergo condensation reaction with 4-bromoaldehyde. In fact, it was possible to obtain 5 by condensation reaction between compound 4 and 4-bromobenzaldehyde in the presence of catalytic amount (10 mole%) of tetrabutylammonium hydroxide in relatively high yield (85.3%) and purity. The chemical structure of compound 5 can be confirmed by the 1H-NMR spectrum in Figure 1(b). Polymerization was conducted by the well known palladium-catalyzed Heck coupling reaction between 5 and 1,4-bis-dodecyloxy-2,5-divinylbenzene in DMF at 140 °C (Scheme 1). In the FT-IR spectrum of the polymer (Figure 2), the weak peak at 3040 cm⁻¹ and the relatively strong absorption at 965 cm⁻¹ correspond to C-H stretching and out-of-plane bending motions of trans vinylene, respectively.  The FT-IR spectra of the polymers show 1612 cm⁻¹ (C=N stretch), which is characteristic band of Oxd ring stretch. The number average molecular weight of the polymer was 9.3 x 10³ with a polydispersity index of 4.70 as determined by GPC. The point of 5%−weight loss in the TGA thermogram of Oxd-PPV appeared at 373 °C. The polymer was readily soluble in chloroform, THF, or toluene and it was possible to make smooth and optically clear film by spin coating.

Figure 3 shows the UV-visible and PL spectra of the polymer solution in chloroform and film. The π−π* transition of the Oxd pendant appeared at 365 nm in solution or film. The additional absorption maximum at 415 (solution) and 421 nm (film) correspond to π−π* transition of the main chain of the polymer. 5,11 The band gap energies figured out from the absorption edge of the UV-visible spectrum of the polymer is 2.23 eV. The tail appearing in the long wavelength region of PL spectra of 2,5-dialkoxy-1,4-phenylenevinylene (DROPPV) derivative is attributable to the inter-chain interactions, i.e. excimer. 14 It is known that inter-chain interactions tend to lower PL efficiency. 14-17 However, no such tail was observed in the PL spectrum of Oxd-PPV indicating no appreciable amount of excimer formation. It is because,
when the the Oxd unit is attached to the vinylene unit in the main chain, the dihedral angle between the phenyl ring in the main chain and the vinylene group is greater than that in MEH-PPV. As a result, the possibility of chain stacking between polymer chains is lower than in MEH-PPV. Moreover, Oxd units would stick out almost perpendicularly to the phenyl ring in the main chain. In this case, chances of interactions between the main chains would be extremely low comparing to the case of polymers with the substituents on the phenyl ring. The PL quantum yield of Oxd-PPV is low comparing to the case of polymers with the substituents withdrawing and bulky Oxd groups lead to increase in polymerization reaction. The incorporation of electron-withdrawing and bulky Oxd groups lead to increase in electron affinity so that the charge injection rates are more balanced compared to those in MEH-PPV. In addition, the presence of the rigid and bulky Oxd unit on the vinylene unit suppresses the inter-chain interactions leading to enhancement of radiative relaxation. The double layer EL device based on the polymer fabricated with Al cathode shows bright yellow emission and high efficiency with a relatively low turn on voltage.

Conclusions

A new polymer with Oxd units on the vinylene unit was synthesized by the palladium-catalyzed Heck coupling polymerization reaction. The incorporation of electron-withdrawing and bulky Oxd groups lead to increase in electron affinity so that the charge injection rates are more balanced compared to those in MEH-PPV. In addition, the presence of the rigid and bulky Oxd unit on the vinylene unit suppresses the inter-chain interactions leading to enhancement of radiative relaxation. The double layer EL device based on the polymer fabricated with Al cathode shows bright yellow emission and high efficiency with a relatively low turn on voltage.

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