

Luminescence Properties of Poly[2-(4'-*t*-butylphenoxy)-1,4-phenylenevinylene]

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This article reports the photo-(PL) and electroluminescence (EL) properties of poly[2-(4'-*t*-butylphenoxy)-1,4-phenylenevinylene], **BPO-PPV** (Scheme 1). Although luminescence properties of many derivatives of poly(1,4-phenylenevinylene), PPV, have been reported by us¹ and others² since the Cambridge group's³ first report on the EL of PPV, electroluminescent properties of BPO-PPV has not been systematically reported yet, although there was a presentation on the optical properties of BPO-PPV.⁴ It was hoped that the presence of bulky 4'-*t*-butylphenoxy substituent will render the resulting polymer soluble in organic solvents and also improve EL performance owing to increased interchain distance that is known to hinder the formation of interchain exciton.⁵

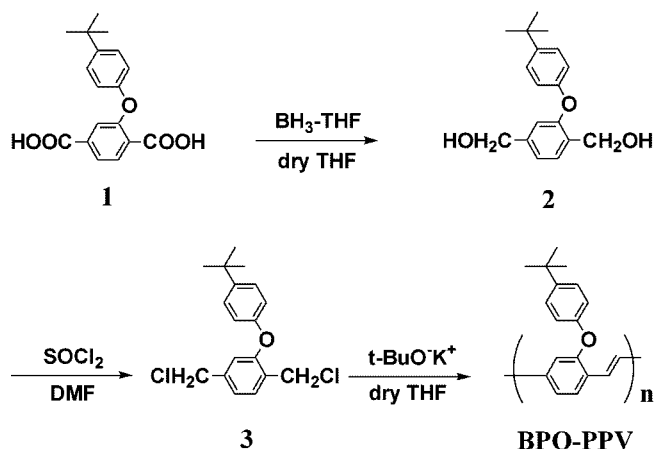
Results and Discussion

BPO-PPV was prepared at room temperature by Gilch polymerization⁶ of 1,4-bis(chloromethyl)-2-(4'-*t*-butyl) phenoxybenzene in THF using potassium *t*-butoxide. This compound was prepared by reacting 1,4-bis(hydroxymethyl)-2-(4'-*t*-butyl phenoxy)benzene with thionyl chloride. The bis-hydroxy compound could be obtained by reducing^{11c1} diethyl 2-(4'-*t*-butylphenoxy) terephthalate with LiAlH₄. **BPO-PPV** was found to be soluble in common solvents such as THF, methylene chloride, and chloroform. Its number average molecular weight was determined to be $\overline{M}_n = 32,200$ by gel-permeation chromatography using polystyrene standard. Its polydispersity index was 1.6.

Figure 1(a) shows the UV-Vis and PL spectra of a **BPO-**

PPV thin film (80 nm thick). The absorption at $\lambda_{\max} = 442$ nm is ascribed to the π - π^* transition of the backbone. PL emission occurs at *ca.* 500-650 nm with its maximum intensity being located at 538 nm corresponding to greenish yellow light. The PL spectrum was obtained at the excitation wavelength of 442 nm, and it exhibits multiple peaks arising from vibronic effect.^{7,8}

A light-emitting diode (LED) (device A) was constructed to have the configuration of ITO/PEDOT (30 nm)/**BPO-PPV** (80 nm)/Li:Al by spin coating of the two polymer layers consecutively onto an indium-tin oxide (ITO) coated glass followed by vacuum deposition of Li:Al alloy containing 0.26% Li. Here, PEDOT stands for poly(2,3-ethylenedioxythiophene) doped with sulfonated polystyrene (Bayer, $\sigma = 10 \text{ S cm}^{-1}$), which was utilized in order to enhance hole injection and transport from the ITO anode and also to improve interface contact. The second LED (device B) had the configuration of ITO/PEDOT (30 nm)/**BPO-PPV** (80 nm)/BBOT (3 nm)/Alq₃ (3 nm)/Li:Al. The 2,5-bis(5'-*t*-butylbenzoxazolyl) thiophene (BBOT) layer deposited by vacuum deposition, was employed as a hole blocker (HOMO: 6.29 eV against vacuum level)⁹ and the tris(8-hydroxyquinolate) aluminum (Alq₃) for an improved electron injection and transport. Alq₃ helps electron injection from the cathode due to its comparable LUMO level (2.84 eV)⁷ to the work function (2.9 eV) of lithium.^{10,11} Moreover, BBOT favors the electron transport because of its slightly lower LUMO level (3.16 eV) than the LUMO level of Alq₃. The higher HOMO



Scheme 1. Synthetic routes to BPO-PPV.

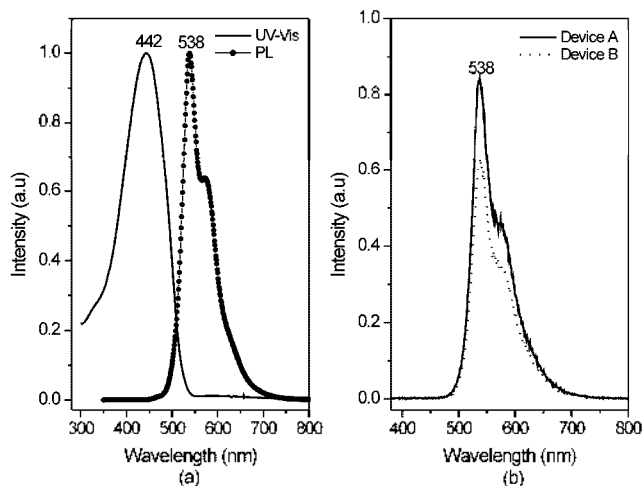


Figure 1. (a) Normalized UV-Vis and PL spectra of the thin film and (b) EL spectra of the devices.

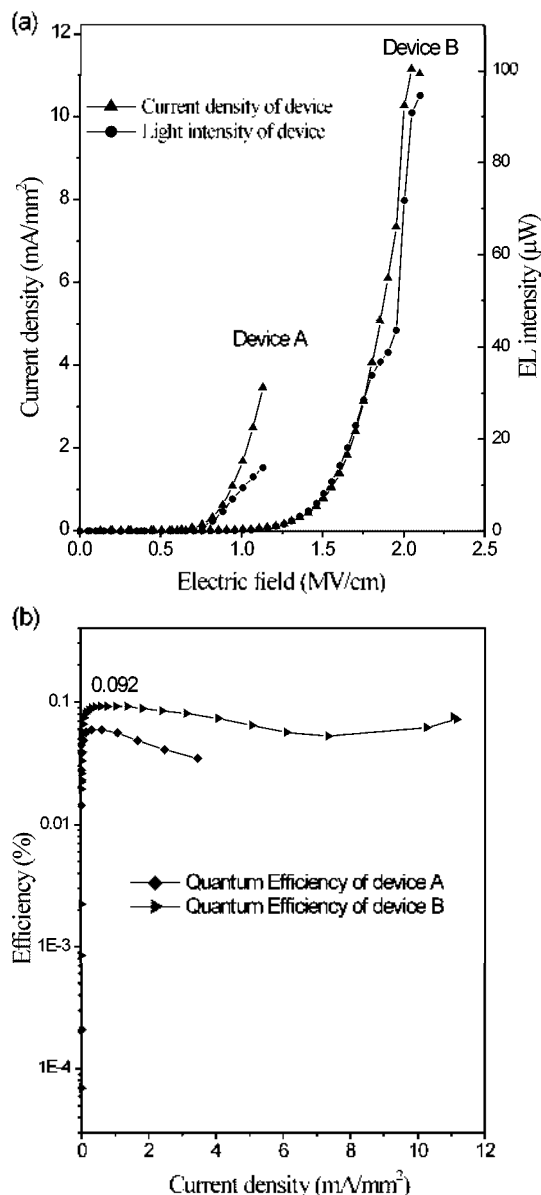


Figure 2. Current-EL intensity-electric field and efficiency of the devices.

level (5.81 eV) of Alq₃ than the HOMO level (6.29 eV) of BBOT effectively induce the formation of excitons mainly in the **BPO-PPV** layer due to the hole blocking ability of BBOT. Since the HOMO and LUMO levels of **BPO-PPV** determined by cyclovoltammetry¹² are 5.6 eV and 3.3 eV, respectively, both electrons and holes injected are expected to be confined in the layer of **BPO-PPV**.

Figure 1(b) includes the EL spectra of the first and the second devices, and they are very similar to the PL spectrum of the **BPO-PPV** shown in Figure 1(a). This again tells us that the EL emission is from the **BPO-PPV** layer. Figure 2 compares the electric field (*E*) – current density (*I*) and electric field (*E*) – light intensity curves of the two devices.

According to Figure 2(a), maximum intensity of emitted light was about 18 μW (750 cdm⁻²) at 1.18 MVcm⁻¹ for the device A and 98 μW (3800 cdm⁻²) at 2.13 MVcm⁻¹ for the

device B. This result implies that the device stability is improved by the utilization of BBOT and Alq₃ layers. As alluded above, facilitated injection and transport of electrons by the aid of the two layers together with an efficient hole blocking by the BBOT layer improves the exciton formation in the emitting layer of device B. Moreover, Figure 2(a) shows that the current density and emitted light intensity exhibit a parallel dependence on the applied electric field, which implies an efficient utilization of injected carriers.

Finally, external quantum efficiencies, or the ratio between the number of photons emitted and the number of electrons injected, of the two devices are plotted against current density in Figure 2(b). The device A's initial maximum external efficiency is 0.06% that decreases to 0.04% as the current density increases, whereas the device B's maximum efficiency was higher (0.09-0.07%). Although we do not have any information on the carrier mobilities of **BPO-PPV**, the results of the present investigation suggest that **BPO-PPV** is a better hole transporter than electron transporter, as to be the case for PPV¹³ and many of its derivatives.^{14,15} We^{1(e-f)}, however, reported recently that attachment of proper pendants on PPV backbone can achieve a balance in carrier mobilities.

In summary, this article describes the PL and EL properties of a new soluble PPV derivative, **BPO-PPV**. This polymer is found to be an emitter of greenish yellow light and the LED devices fabricated with this polymer revealed external quantum efficiencies of *ca.* 0.05-0.1%. Although the performance of the two devices described in this work still requires a significant improvement to be of practical importance, it is conjectured that better device structures and fabrication methods would be able to provide us with a strong possibility of developing devices based on **BPO-PPV** for practical applications.

Experimental Section

Synthesis of the BPO-PPV polymer. The **BPO-PPV** polymer was synthesized by the so-called Gilch-Wheeler polymerization⁶ of 1,4-bis(chloromethyl)-2-(4'-*t*-butylphenoxy)benzene (**3**), which was prepared from 2-(4'-*t*-butylphenoxy)terephthalic acid (**1**) as described below.

1,4-Bis(hydroxymethyl)-2-(4'-*t*-butylphenoxy)benzene (2). 2-(4'-*t*-Butylphenoxy)terephthalic acid (**1**) (3.14 g, 0.01 mol) was dissolved in dry THF (30 mL) taken in a 250 mL two-necked round-bottomed flask fitted with a nitrogen balloon and a dropping funnel. The reaction mixture was cooled (0 °C) while stirring in an ice-salt bath. Added BH₃-THF solution (2.58 g, 0.03 mol) drop-wise, over a period of one hour, through the dropping funnel. The reaction mixture was further stirred at room temperature, for a period of 6 hours. Cooled the reaction mixture using ice-salt bath, destroyed the excess borane (if remaining any) by adding THF-water (20 mL, 1 : 1 by vol.) mixture, slowly through the dropping funnel. To this was then added, K₂CO₃ (10 g) and stirred well. Filtered the reaction mixture, collected the filtrate and the crude product obtained on evaporation of the

same was chromatographed to obtain pure product 1,4-bis(hydroxymethyl)-2-(4'-*t*-butylphenoxy)benzene in the solid form. Yield: 1.8 g (63%).

IR. (KBr, ν_{\max} , cm^{-1}): 3320 (O-H stretching), 2962 and 2870 (C-H stretching), 1610, 1575, 1508 (aromatic C=C stretching), 1247 and 1216 (C-O stretching), 1012, 835. ^1H NMR (CDCl_3) δ : 7.53 (d, 1H, ArH), 7.38 (d, 2H, ArH), 7.13 (d, 1H, ArH), 6.88 (m, 3H, ArH), 4.66 (d, 2H, $-\text{CH}_2\text{OH}$), 4.57 (d, 2H, $-\text{CH}_2\text{OH}$), 4.20 (br t, 1H, $-\text{CH}_2\text{OH}$), 4.10 (br t, 1H, $-\text{CH}_2\text{OH}$), 1.30 (s, 9H, $-\text{C}(\text{CH}_3)_3$).

1,4-Bis(chloromethyl)-2-(4'-*t*-butylphenoxy)benzene (3). The bis-hydroxymethyl compound (2) (1.72 g, 0.6×10^{-2} mol) was dissolved in DMF (5 mL) in a 100 mL 2-necked round-bottomed flask fitted with a CaCl_2 guard tube and a dropping funnel. Cooled the mixture, added thionyl chloride (2.85 g, 0.024 mol) drop wise. The reaction mixture was stirred at room temperature for a period of four hours. Then it was poured into cold water and the product was extracted by using methylene chloride. The crude product obtained on evaporation of the solvent was chromatographed to obtain pure 1,4-bis(chloromethyl)-2-(4'-*t*-butylphenoxy)benzene (3) in the form of liquid. Yield: 1.56 g (80%).

IR. (KBr, ν_{\max} , cm^{-1}): 2962 and 2869 (C-H stretching), 1610 (aromatic C=C stretching), 1255 and 1174 (C-O stretching). ^1H NMR (CDCl_3) δ : 6.87-7.47 (m, 7H, ArH), 4.69 (s, 2H, $-\text{CH}_2\text{Cl}$), 4.46 (s, 2H, $-\text{CH}_2\text{Cl}$), 1.33 (s, 9H, $-\text{C}(\text{CH}_3)_3$).

BPO-PPV. The monomer (3) (0.91 g , 0.28×10^{-2} mol), was taken in a 250 mL two-necked flask. To one neck was connected the nitrogen balloon and the other neck was closed with a septum. To this was then added, dry THF (100 mL). The mixture was stirred at room temperature for about 5 min. Added *t*-BuOK (17 mL, 0.017 mol) slowly to this solution using a syringe. Stirred the reaction mixture overnight. Prepared a solvent mixture of methanol (450 mL) and water (30 mL), and poured the reaction mixture into it slowly while stirring and continued the stirring for a further period of two hours. Then it was filtered under suction. The precipitate was collected and re-dissolved in minimum quantity of THF (150 mL), which was then filtered. The clear filtrate was collected and poured slowly into a beaker containing methanol (800 mL), while stirring. The solid precipitated out was collected by filtration. The polymer thus obtained was further purified by the Soxhlet extraction for three days. Finally, it was dried in vacuum oven.

Yield: 0.425 g (61%). The number (\overline{M}_n) and weight average molecular weights (\overline{M}_w) of this polymer were measured by the gel-permeation chromatography using THF as the eluent and polystyrene as standard. And the \overline{M}_n and \overline{M}_w values were found to be 32,200 and 51,800, respectively.

IR. (KBr, ν_{\max} , cm^{-1}): 3035 (=C-H stretching), 2960 and 2856 (C-H stretching), 1600 and 1500 (C=C stretching), 1217 and 1170 (C-O stretching), 958 (=C-H out-of-plane bending). ^1H NMR (CDCl_3) δ : 6.75 (br m, 11H, ArH and $-\text{CH}=\text{CH}-$), 1.30 (br s, 9H, $-\text{C}(\text{CH}_3)_3$).

Characterization and PL and EL properties. The methods for the characterization of the polymer and measurement of PL and EL properties are the same as described earlier in detail by us.^{1(d),e)}

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