Synthesis, photo- and electroluminescence properties of a PPV derivative with di(ethylene oxide) segment in the backone

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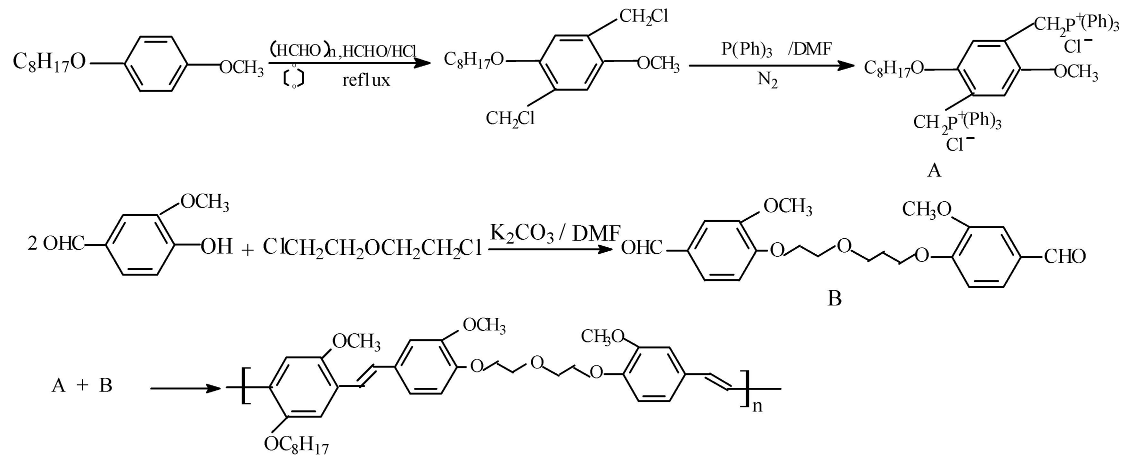
Electroluminescent (EL) devices based on conjugated polymers have been extensively studied owing to their potential advantages such as outstanding mechanical and optical properties, low-cost manufacture, and applicability to large area light displays [1, 2]. PPV and its derivatives are the most promising candidates for efficient light emitting diodes (LEDs), due to the high luminance and easy modification of the chemical structure to tune color [3]. Introduction of oligo(ethylene oxide) (OEO) spacers into the main chain is potentially attractive since this provides enhancement of the solubility and increases the necessary ionic conductivity. The polymers with the OEO spacers are also ideal materials for light emitting electrochemical cells (LECs) [4]. Early investigations were involved with the copolymers of distyrylbenzene and OEO [5]. More recent work by L. Duan *et al.* demonstrates blue emission for distyrylbenzene copolymer with tri(ethylene oxide) [6].

In this paper, we report on the synthesis of a new PPV derivative containing a flexible di(ethylene-oxide) segment in the main chain, poly(2-methoxy-5-octoxy)benzene)-block-di(ethylene oxide) (MOB-DEO). This may be a potential candidate material for light-emitting diodes (LEDs) and electroluminescent cells (LECs). The structures of the monomers and polymer were characterized by FT-IR, ^{1}H-NMR, and elemental analysis. The photo- and electroluminescence properties of the polymer were investigated. The project strategy is illustrated schematically in Scheme 1.

2-methoxy-5-octoxyl-1,4-xylenebis(triphenyl phosphonium chloride) (Monomer A) was synthesized by a procedure adapted from literature [7]. It was prepared in three steps from 4-methoxyphenol by etherification, followed by conversion to the chloromethylation and thereafter conversion to the triphenylphosphonium salt. ^{1}H-NMR (CDCl$_3$, TMS) δ (ppm): 0.85-0.83 (t, 3H), 1.30-0.97 (m, 12H), 2.85 (s, 3H), 3.04-3.12 (t, 2H), 5.31 (s, 2H), 5.34 (s, 2H), 6.75 (s, 1H), 6.78 (s, 1H), 7.86-7.57 (m, 30H). IR (KBr, cm^{-1}): 3020, 2925, 2854, 1586, 1513, 1437, 1223, 1111, 1027, 965, 874, 745, 690, 528, 491. Anal.Calcd. for $C_{53}H_{56}O_2P_2Cl_2$:C, 74.20; H, 6.58. Found: C, 74.15; H, 6.53.

4,4-diforml-2,2-dimethoxy-di(ethylene oxide) diether (Monomer B) was synthesized from 4-hydroxy-3-methoxytenzaldehyde and 2,2-dichloro-ethyl ether according to the method described in literature [8].The 2,2-dichloro-ethyl ether(10 mmol) was added dropwise to a solution of 4-hydroxy-3-methoxytenzaldehyde (20 mmol) and anhydrous potassium carbonate (25 mmol) in DMF (50 mL) while stirring and then refluxed at 120 °C for 5 hr. The reaction mixture was cooled to the room temperature, then poured into the water, the precipitate was filtered, recrystallized from the ethanol, and dried under vacuum. A white solid was obtained. ^{1}H-NMR (CDCl$_3$, TMS) δ (ppm): 3.86 (s, 6H), 4.02-4.08 (t, 8H), 6.91(d, 2H), 7.42(d, 4H), 9.86 (s, 2H). IR (KBr, cm^{-1}): 2954, 2842, 1689, 1587, 1460, 1423, 1401, 1345, 1244, 1140, 1018, 745, 638, 580.



MOB—DEO

Scheme 1

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Anal.Calcd. for $C_{20}H_{22}O_7$: C, 64.16; H, 5.92. Found: C, 64.87; H, 6.02.

The synthesis of the polymer MOB-DEO was carried out by using a Wittig reaction between diphosphonium salt and dialdehyde. Monomer A (1 mmol) and monomer B (1 mmol) were dissolved in 10 mL chloroform, a mixture of ethanol (10 mL) and sodium methoxide (6 mmol) was carefully dripped into the solution of monomers at room temperature. A yellowish green solution was formed. After 1–2 days, 1 mL of 0.1 N aqueous HCl solution was added to stop the reaction. The polymer was isolated by filtration and purified by multiple precipitation from chloroform into methanol. After drying in a vacuum oven at room temperature, a yellowish green polymer was obtained. ^{1}H-NMR ($CDCl_3$, TMS) δ (ppm): 0.98 (m, 3H), 1.0–1.6 (m, 10H), 1.86 (m, 2H), 3.75 (s, 3H), 3.93 (s, 3H), 3.94 (s, 3H), 4.03–4.30 (m, 10H), 6.83–7.41 (m, 12H). IR (KBr, cm^{-1}): 2928, 2854, 1598, 1512, 1135, 1033, 963, 801. Anal. Calcd. for $(C_{37}H_{46}O_7)_n$: C, 73.72; H, 7.92. Found: C, 73.70; H, 7.89.

MOB-DEO is soluble in common solvents such as chloroform, methylene chloride, 1,1,2,2-tetrachloroethane, and tetrahydrofuran. Thus it can be spin-coated onto various substrates to give homogeneous transparent thin films. The weight-average molecular weight (M_w) of MOB-DEO was measured by gel permeation chromatography (GPC) with polystyrene as standard and THF as the eluent. A M_w of about 6600 and a polydispersity index (PDI) of 1.52 was obtained. The thermal stability of MOB-DEO was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The decomposition temperature (T_d) was about 347 °C, as determined at a 5 wt% loss.

UV-Vis spectra were recorded with a Lambda 25 UV-Vis spectrophotometer. The fluorescence spectrum measurements were conducted on a Perkin-Elmer LS55 luminescence spectrometer with a xenon lamp as the light source. Fig. 1 shows the UV-Vis and photoluminescence spectra of MOB-DEO in solution and solid film. The absorption maximum peaks are 350 nm and 401 nm, respectively in the solution and solid film state. Compared to the 451 nm in the solution, the emission peak in the solid film redshifted to 499 nm. This may be explained as follows: π–π^* interactions or aggregation of π-conjugated polymer chains in the solid state reduces the separation of ground and excited states, leading to more pronounced π–π stacking [9] and an increase in the conjugation length, causing the emission to be redshifted accordingly.

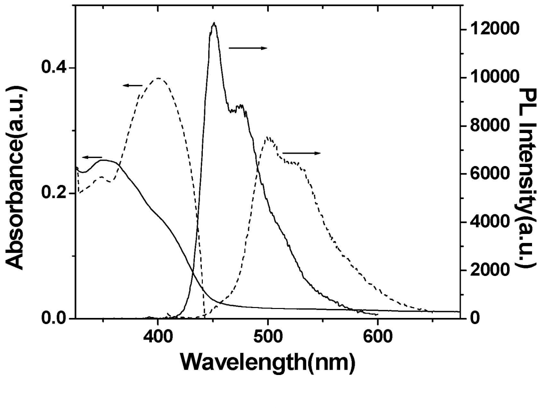

Figure 1 Absorption and photoluminescence spectra of MOB-DEO in 1×10^{-2} g/dL $CHCl_3$ (solid line) and film (dashed line).

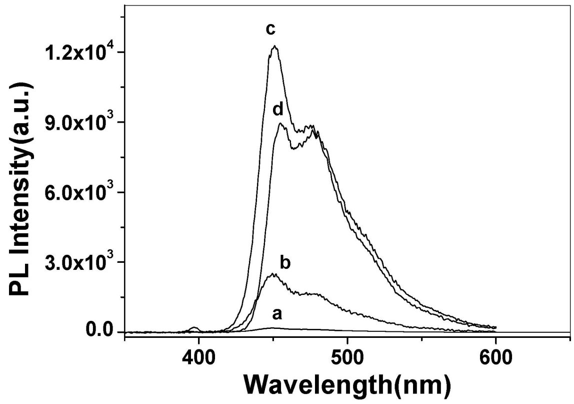

Figure 2 PL spectra of MOB-DEO in different concentrations in $CHCl_3$ at room temperature (a. 1×10^{-4}; b. 1×10^{-3}; c. 1×10^{-2}; d. 1×10^{-1} g/dL).

The relationship between the concentration and the emission intensity is shown in Fig. 2. The fluorescence emission spectra of a freshly prepared chloroform solution of MOB-DEO were obtained at 30 °C over a wide range of concentration, from 1×10^{-4}g/dL to 1×10^{-1} g/dL. The PL spectrum shows a peak at 451 nm with a shoulder peak around 478 nm in $CHCl_3$ solution and the intensity ratio of the two emission bands varies with concentration. The intensity of the shoulder peak becomes more pronounced with increased concentration because of the couple of the excitons and the interactions of the polymer chains in the conjugated system. The new excimer emission is contributed to the redshift of emission bands for the polymer in a relative concentrated solution [10]. At low concentrations (curves a, b, and c), the emission intensity increases with the concentration increasing. In this concentration region, the molecules act as individuals or isolated chains independent from each other, and the emission intensity is the sum of the individual concentrations. At higher concentrations (d), the emission intensity decreases as the concentration increases. Once the concentration reaches 1×10^{-2} g/dL and beyond, self-quenching and other factors increase the probability for energy losses and cause a decrease in fluorescence efficiency and emission intensity.

A LED device with an ITO/PEDOT-PSS/MOB-DEO/Ba/Al configuration was fabricated to examine the EL properties. The PEDOT-PSS was used as a hole transporting layer; MOB-DEO was used as the emitting layer and a thin layer of Ba (5 nm) was used as the cathode. The Ba layer was coated with a 200 nm layer of Al, the thickness of the emissive layer was about 80 nm. The EL spectrum and Current-brightness-voltage curves are shown in Figs 3 and 4. The forward current increases with forward bias voltage while the reverse bias current remains small. The peak of EL emission is at 528 nm with a turn on voltage of 7.1 V which is significantly lower than the 15 V for the PPV and exhibits a luminance of 330 cd/m^2 with a driving

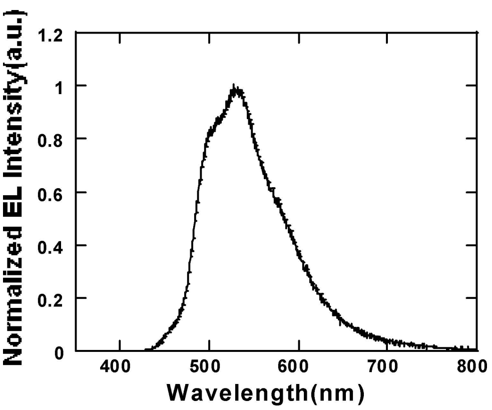

Figure 3 EL spectrum of ITO/PEDOT-PSS/ MOB-DEO /Ba/Al device.

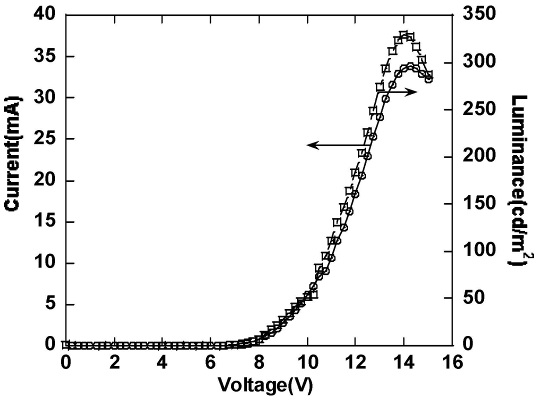

Figure 4 Current-brightness-voltage characteristics of ITO/PEDOT-PSS/ MOB-DEO /Ba/Al device.

voltage of 14 V. The highest external quantum efficiency of the double-layer LED was 2.78%. Compared to the photoluminescence spectrum, the EL emission shifted to the longer wavelength. A possible explanation [11] is that under the additional electric field, the emitting molecule was partially polarized to be orientated, the degree of the order was improved, so the π–π conjugation length increased, and the energy gap was reduced, the EL emission redshifts. The LECs of MOB-DEO is under further investigation.

Acknowledgment

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