Chem. Mater. **1998,** *10,* 3301−3304

Synthesis and Characterization of a Novel Light-Emitting Polymer Containing Highly Efficient Hole-Transporting Aromatic Diamine

Yunqi Liu, Michelle S. Liu, Xiao-chang Li, and Alex K-Y. Jen*

Department of Chemistry, Northeastern University, 360 Huntington Avenue, Boston, Massachusetts 02115

Received July 15, 1998
Revised Manuscript Received September 18, 1998

Recently, polymeric light-emitting materials have attracted much attention for their potential applications in large-area displays.[1] Following the discovery of poly(*p*-phenylene vinylene) (PPV),[2] a wide range of polymers, for example, polythiophene,[3,4] poly(*p*-phenylene),[5] poly(vinylcarbazole),[6,7] and polyfluorene,[8] have been reported in the literature as potential candidates for polymeric light-emitting diodes (LEDs). One of the greatest advantages of these devices over molecular LEDs is the ease of processing of the polymers into high-quality thin films. In particular, organic-soluble conjugated polymers, such as poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV), have received considerable attention.[9−12] Although MEH-PPV can be fabricated into a LED possessing a high quantum efficiency ($\eta_{\text{ext}} = 1\%$), there are several deficiencies, such as the polymer's synthesis. The polymer uses the 2-(2′-ethylhexyloxy)-5-methoxy-1,4-bis(chloromethyl)benzene monomer, which often results in a significant amount of insoluble polymer gel due to the cross-linking of the polymer chains. In addition, an inherent thermal property, its low glass-transition temperature ($T_g = 65$ °C), may prohibit the long-term use of the device. In this paper, we report the synthesis and characterization of a novel copolymer (TPD-MEH-PPV) consisting of tetraphenyldiaminobiphenyl (TPD) and MEH-PPV moieties. The design of the polymer was based on the motivation (1) to improve both the hole-transporting property and oxidative stability of the MEH-PPV by inserting into the polymer chain an easily p-dopable and electrochemically reversible TPD moiety; (2) to raise the T_g of the MEH-PPV by inserting the TPD moiety which has more rigid biphenyl structure; and (3) to improve simultaneously both the synthetic procedure and the solublity of the polymer[13] by using the Wittig−Horner condensation reaction to avoid potential cross-linking problems and to enhance the solubility of the polymer in common organic solvents by attaching two *n*-butyl groups onto the benzene rings of the TPD.

The method for preparing the copolymer is outlined in Scheme 1. Monomer **2** was synthesized from 4,4-dibromobiphenyl by a three-step reaction[14−16] (overall yield, 33%). Alkylation of 4-methoxyphenol, followed by chloromethylation of **3**, gave 2-(2′-ethylhexyloxy)-5-methoxy-1,4-bis(chloromethyl)benzene **4** in 60% yield. The condensation reaction between **4** and triethyl phosphite afforded the diphosphonate **5** in quantitative yield.[17] The TPD-MEH-PPV was prepared by the Wittig−Horner condensation reaction[18] between the dialdehyde **2** and 2-(2′-ethylhexyloxy)-5-methoxy-1,4-xylene tetraethyl diphosphonate **5** in tetrahydrofuran (THF).[19] The chemical structure of the resulting polymer was confirmed by ^{1}H NMR and elemental analysis. It is worth pointing out that polymer gels were not formed during this polymerization process.

TPD-MEH-PPV was a yellow powder which dissolved easily in common organic solvents such as chloroform, tetrahydrofuran, and xylene. The molecular weight of the polymer was determined using gel permeation chromatography (GPC) with polystyrene as the calibration standard. The number average (M_n) and the weight average (M_w) molecular weight of the polymer was 15 000 and 37 000, respectively. A uniform and pinhole-free thin film of the polymer was obtained by spin-coating from its chloroform solution.

The thermal properties of TPD-MEH-PPV and MEH-PPV were analyzed using thermal gravimetric analysis

---

(1) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed*. **1998**, *37*, 403.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(3) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1994**, *372*, 444.

(4) Liu, Y. Q.; Jiang, X. Z.; Li, Q. L.; Zhu, D. B. *Synth. Met.* **1997**, *85*, 1285.

(5) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater*. **1992**, *4*, 36.

(6) Kido, J.; Hongawa, K.; Okuyama, K.; Nagai, K. *Appl. Phys. Lett.* **1993**, *63*, 2627.

(7) Jiang, X. Z.; Liu, Y. Q.; Song, X. Q.; Zhu, D. B. *Synth. Met.* **1997**, *87*, 175.

(8) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.

(9) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(10) Brown, A. R.; Greenham, N. C.; Burroughes, J. H.; Bradley, D. D. C.; Friend, R. H.; Burn, P. L.; Kraft, A.; Holmes, A. B. *Chem. Phys. Lett*. **1992**, *200*, 46.

(11) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(12) Yu, G. *Synth. Met.* **1996**, *80*, 143.

(13) Rost, H.; Teuschel, A.; Pfeiffer, S.; Hörhold, H.-H. *Synth. Met.* **1997**, *84*, 269.

(14) Thayumanavan, S.; Barlow, S.; Marder, S. R. *Chem. Mater.* **1997**, *9*, 3231.

(15) Campaigne, E.; Archer, W. L. *Organic Syntheses*; John Wiley & Sons: New York, 1963; Collect. Vol. IV, 331.

(16) Compound **2** was obtained by a three-step reaction (overall yield, 33%). ^{1}H NMR (300 MHz, CD_2Cl_2): 0.96 (t, $J = 7.6$ Hz, 6H), 1.41 (dd, $J = 7.3$ Hz, 4H), 1.61 (dd, $J = 7.3$ Hz, 4H), 2.63 (t, $J = 7.6$ Hz, 4H), 7.03 (d, $J = 8.3$ Hz, 4H), 7.11 (d, $J = 8.2$ Hz, 4H), 7.20 (m, 8H), 7.57 (d, $J = 7.9$ Hz, 4H), 7.67 (d, $J = 8.3$ Hz, 4H); MS (EI) found MH^+ 657.5, $C_{46}H_{45}N_2O_2$ calcd for MH^+ 657.3.

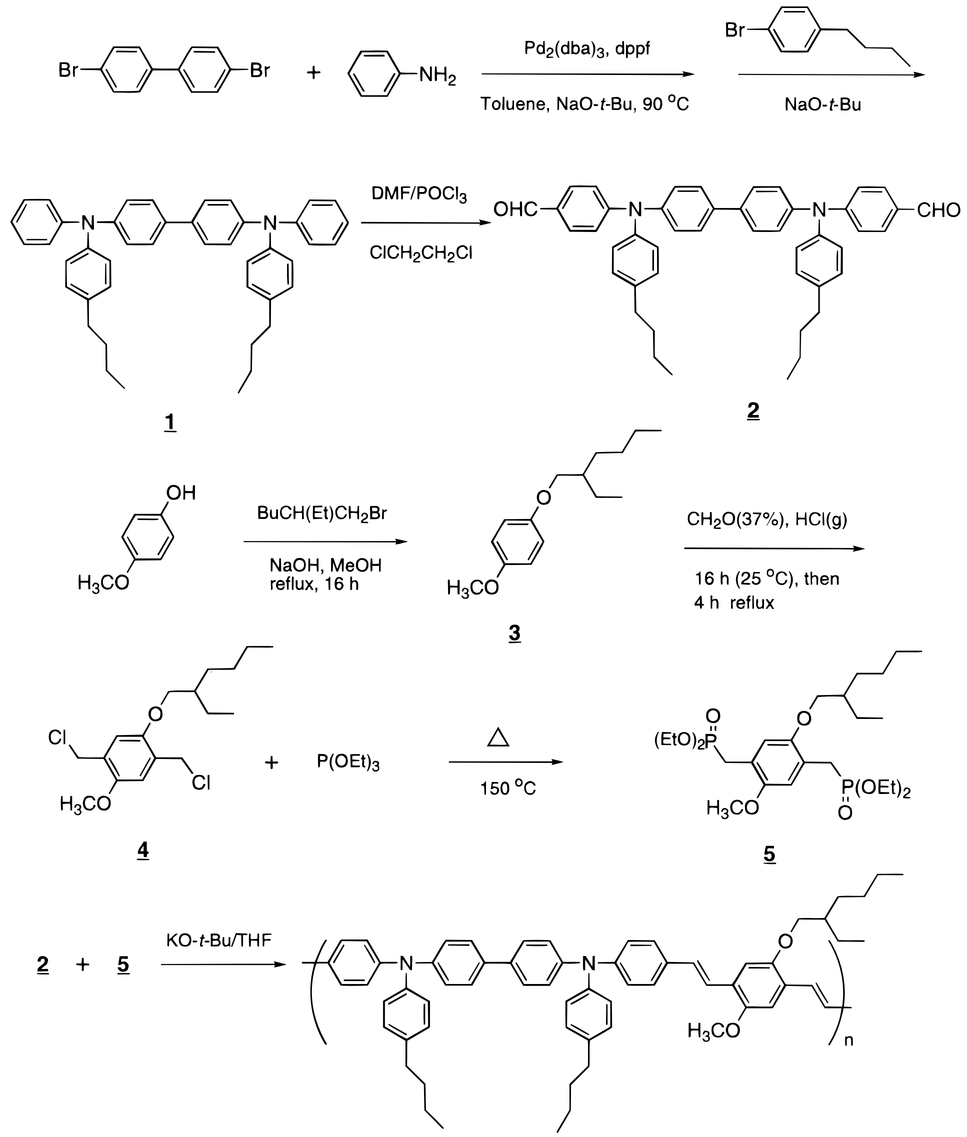
(17) Wadsworth, W. S., Jr. *Org. React*. **1977**, *25*, 73.

(18) Maercker, A. *Org. React*. **1965**, *14*, 270.

(19) To a stirred solution of **5** (134.2 mg, 0.25 mmol) and dialdehyde **2** (164.2 mg, 0.25 mmol) in dry THF (35 mL) at room temperature (N_2) was added dropwise a 1.0 M potassium *tert*-butoxide/THF solution (0.5 mL, 0.5 mmol) by a syringe until no red color was formed. The reaction mixture was stirred for 2 h, after which the THF was evaporated in a vacuum. The resulting solid was washed with a solution of methanol, water, and acetone (3:1:1) to remove any inorganic byproducts. The yellow polymer was then Soxhlet extracted with acetone for 12 h to remove any low molecular weight products. The polymer was collected by filtration and dried under vacuum at 50 °C for 1 day to give 190 mg of product (86% yield). ^{1}H NMR ($CDCl_3$): δ 0.95 (t, $J = 7.5$ Hz, 12 H), 1.38 (m, 6H), 1.6 (m, 11H), 2.6 (t, $J = 7.5$ Hz, 4H), 3.9 (s, 3H), 3.95 (br, 2H), 7.09 (br, 20H), 7.45 (br, 10H). Anal. Calcd. for $(C_{63}H_{68}N_2O_2)_n$: C, 85.48; H, 7.74; N, 3.17; O, 3.61. Found: C, 85.01; H, 7.33; N, 3.01; O, 3.19.

10.1021/cm980498s CCC: $15.00

Scheme 1. Synthesis of TPD-MEH-PPV



TPD-MEH-PPV

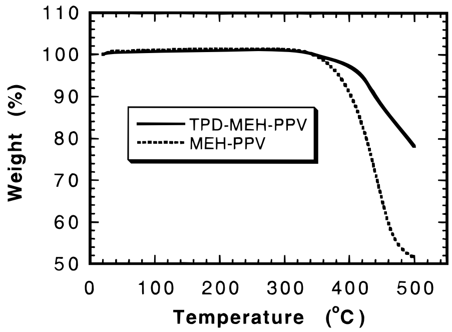


Figure 1. Thermal gravimetric analysis thermograms of MEH-PPV and TPD-MEH-PPV.

(TGA) and differential scanning calometry (DSC) under a nitrogen atmosphere. Both TGA thermograms for TPD-MEH-PPV and for MEH-PPV are shown in Figure 1. The TPD-MEH-PPV started to show weight loss at 308 °C and had lost 22.8% of its original weight by 500 °C. In comparison, MEH-PPV began showing weight loss at 295 °C and had lost 49.9% of its original weight by 500 °C. Recently, Tokito et al.[20] had found that the thermal stability of the EL device was directly related to the T_g and the thermal stability of the materials used. TPD-MEH-PPV had a much higher T_g (146 °C) as compared to MEH-PPV (65 °C), indicating that the incorporation of the more rigid TPD moiety into the polymer chain significantly enhanced the thermal stability of the polymer; this may in turn improve the operating lifetime of the electroluminescent (EL) device.

Electrochemical measurements were performed using cyclic voltammetry (CV) at room temperature in a conventional three-electrode cell with a polymer thin film spin-coated onto indium tin oxide (ITO) glass as the working electrode (~ 3 cm^2). Pt gauze was used as the counter electrode and Ag/Ag$^+$ was used as the reference electrode, with 0.1 M tetrabutylammonium

---

(20) Tokito S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.

Table 1. Electronic Parameters for MEH-PPV and TPD-MEH-PPV

	E^{ox} vs Ag/Ag$^+$ (V)	E^{red} vs Ag/Ag$^+$ (V)	EC E_g (eV)	$E^{ox\ a}$ vs E_{FOC} (V)	E^{red} vs E_{FOC} (V)	HOMO (eV)	LUMO (eV)
MEH-PPV	0.36	−2.09	2.45	0.24	−2.21	−5.04	−2.59
TPD-MEH-PPV	0.47	−2.10	2.57	0.35	−2.22	−5.15	−2.58

[a] E_{FOC} = 0.12 V vs Ag/Ag$^+$.

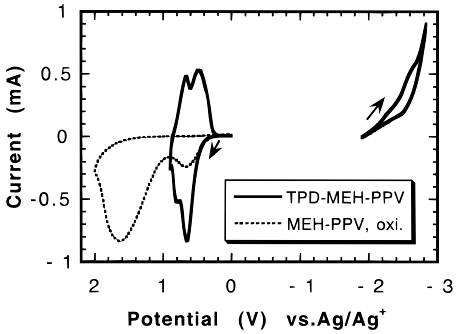


Figure 2. Cyclic voltammograms of MEH-PPV and TPD-MEH-PPV films on ITO glass in an acetonitrile solution of TBAP (0.1 M) at a scan rate of 40 mV/s. Solid line, TPD-MEH-PPV film; dotted line, MEH-PPV film.

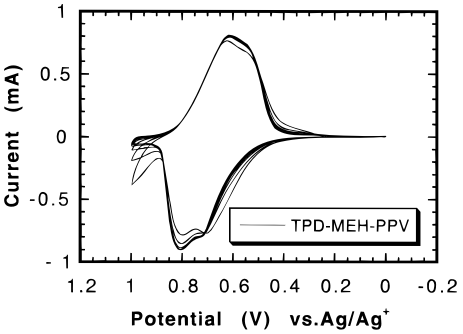


Figure 3. Cyclic voltammogram of 10 cycles of repetitive scans of TPD-MEH-PPV.

perchlorate (TBAP) in acetonitrile as the electrolyte. Figure 3 shows the cyclic voltamogramms of both TPD-MEH-PPV and MEH-PPV. The TPD-MEH-PPV exhibited two reversible waves (formal potentials $E^{I}_{1/2}$ = 0.57 V, $E^{II}_{1/2}$ = 0.72 V vs Ag/Ag$^+$) under an anodic sweep. In contrast, the MEH-PPV exhibited only two irreversible waves (dotted line). Moreover, the anodic peak current, $I_{p,a}$, for TPD-MEH-PPV increased gradually with an increase in the scan cycles, reaching a constant maximum after four cycles (Figure 3). In comparison, the oxidation waves for MEH-PPV disappeared after a few repetitive scans. This indicated that TPD-MEH-PPV possessed excellent electrochemical reversibility and stability. However, the reduction of this polymer was shown to have an ireversible wave during the first cycle, which indicated that TPD-MEH-PPV may have a very high electron injection barrier. This may lead to the imbalance of charge injection and transporting for single layer LED made by this polymer.

The redox potentials obtained from CV measurements for both TPD-MEH-PPV and MEH-PPV under the same conditions are listed in Table 1. The HOMO and LUMO values are calculated by assuming the energy level of ferrocene/ferrocenium (E_{FOC}) at −4.8 eV.[15,21] The band gap (E_g= 2.57 eV) can be derived from the difference

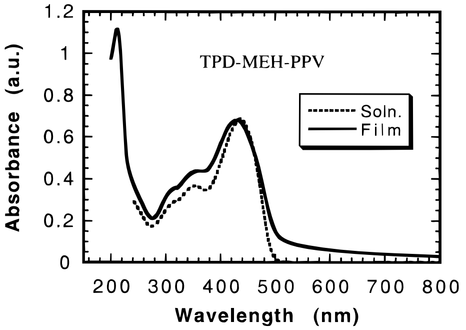


Figure 4. UV−vis absorption spectra of TPD-MEH-PPV. Solid line, as a film; dotted line, in chloroform solution.

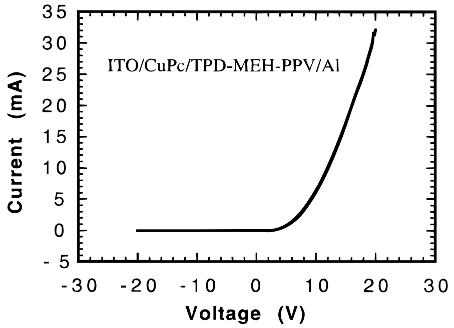


Figure 5. Current−voltage characteristic for the ITO/CuPc/TPD-MEH-PPV/Al light-emitting diodes.

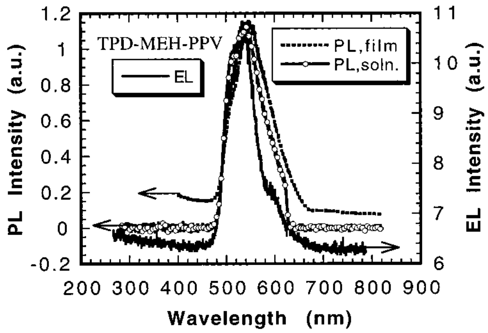


Figure 6. Photoluminescence and electroluminescence spectra of TPD-MEH-PPV. Solid line with circles, PL, in chloroform solution; dotted line, PL, as film; solid line, EL of the device.

between the onset of the first oxidation potential and the onset of the first reduction potential. This value is in good agreement with the E_g value obtained from the absorption data (2.47 eV) (Figure 4).

A LED device (with 2 mm diameter dots) was fabricated using a two-layer structure in this study. A layer of copper phthalocyanine (CuPc), with a thickness of 50 nm, was evaporated onto an ITO glass substrate (anode) in a vacuum (2 × 10^{-6} Torr), then a polymer film, with a thickness of 50 nm, was spin-coated onto the CuPc layer. The Al electrode (cathode) was finally evaporated onto the polymer film under the same vacuum condition used for CuPc.

The current−voltage (*I*−*V*) characteristics of the device, illustrated in Figure 6, show a typical diode

---

(21) Pommerehne, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porch, M.; Daub, J. *Adv. Mater.* **1995**, *7*, 551.

behavior with a high rectification ratio of 1.1×10^6 at ± 3.75 V. When increasing the forward bias, both the current and the intensity of the emitting light increased superlinearly after the turn-on voltage of 4.5 V. No light was observed under reversed bias up to -20 V. The device emitted bright yellow light ($\lambda_{max} = 540$ nm), which could be seen clearly in daylight. The wavelength of the emitted light had a significant blue-shift when compared to that of MEH-PPV. This may be explained by the shorter conjugation length of the copolymer which introduces a larger gap between the HOMO and the LUMO energy states. The EL spectrum was almost identical with the photoluminescent (PL) spectra (solution and thin film) of the polymer (Figure 6), indicating that the same excitation state was involved. However, the shape of the EL spectrum was slightly different from that of the PL spectra. The EL spectrum was much steeper on the long-wavelength side. This was due to the partial absorption caused by the CuPc layer, since CuPc has a strong absorption band in the region between 520 and 680 nm.

In conclusion, we have synthesized a new electroluminescent polymer by incorporating both a highly efficient hole-transporting moiety, TPD, and a light-emitting moiety, MEH-PPV, into the polymer chain. This facile method provides the synthesis of light-emitting polymers with a broad variation of polymer backbones. The resulting polymer possesses high thermal stability, good electrochemical reversibility and stability, an excellent thin-film-forming property, and a bright light-emitting property. Double-layer LED devices with relatively air-stable aluminum electrodes based on the TPD-MEH-PPV polymer show a rectification ratio greater than 10^6 and a low turn-on voltage of 4.5 V.

Acknowledgment. The authors would like to thank S. Liu for the molecular weight measurements. Financial support from Office of Naval Research (ONR) through the MURI Center (CAMP) and Air Force Office of Scientific Research (AFOSR) through the DURIP program is gratefully acknowledged.

CM980498S