Synthesis and Characterization of a Bipolar Light-Emitting Copolymer Consisting of Tetraphenyldiaminobiphenyl and Bis-Quinoline Units

Yunqi Liu, Hong Ma, and Alex K-Y. Jen*

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

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Since the discovery of a electroluminescent (EL) polymer in 1990,[1] a great number of polymers have been synthesized and investigated because of their potential application in large-area flat panel displays. However, the search for new polymers that possess the combined desirable properties, such as high brightness and EL efficiency, low turn-on voltage, long operating lifetime, and good processibility, remains a big challenge in this area.[2−6] It is well-established that high quantum efficiency EL devices can be obtained by achieving both efficient charge injection and balanced mobility of both charge carriers inside the EL materials. In general, most of the EL polymers are more favorable to the hole injection or p-doping than the electron injection or n-doping due to their inherent richness of π electrons. Recently, Adachi reported the generation of highly efficient organic light-emitting diodes (LEDs) using bipolar emitters which combine both an electron transport unit and a hole transport unit on an emitter molecule. The diodes exhibited both high luminance (19 000 cd/m^2) and high quantum efficiencies (as high as $\phi_{EL} \sim 4\%$).[7] More recently, Bao[8] and Galvin[9] reported the use of light-emitting polymers containing both electron- and hole-transporting moieties to achieve efficient device performance. Thus, it is desirable to design and synthesize a bipolar polymer that possesses both a hole-injection/-transport segment and an electron-affinitive segment in order to enhance the charge injection/transport ability. Polyquinolines (PQ) have outstanding thermal stability, low dielectric constants, low moisture absorption, very high glass-transition temperature (T_g), and good film-forming properties.[10−12] A blue EL device using a fluorinated polyquinoline (PQ-100) as the emitting layer has been reported.[13] However, this device possessed a very high turn-on voltage (50 V) due to the difficulty in achieving efficient/balanced charge injection. Tetraphenyldiaminobiphenyl (TPD) has been widely used as an excellent hole-transport material in fabricating small molecule EL devices.[14,15] In hope of combining both the blue light-emitting and good electron-affinitive properties of the bis-quinoline and the efficient hole-injection/-transport properties of the TPD into a single bipolar material to enhance the overall performance of an EL device, we have copolymerized these two functional moieties via the Friedländer condensation reaction. In this paper, we report the excellent thermal, electrochemical, and EL results obtained from this polymer.

The synthesis of the copolymer (TPD−PQ) was shown in Scheme 1. Compound **1** was synthesized (55% yield) from the modified Buchwald coupling reaction[16] between aniline and 4,4′-dibromobiphenyl in the presence of tris(dibenzylideneacetone) dipalladium [$Pd_2(dba)_3$], 1,1′-bis(diphenylphosphino)ferrocene (dppf), and sodium *tert*-butoxide (NaO-*t*-Bu), followed by the addition of 1-bromo-4-butylbenzene and additional NaO-*t*-Bu. Monomer **2** was obtained (70% yield) from the Friedel−Crafts reaction between compound **1** and acetyl chloride in carbon disulfide. Compound **3**, 4,4′-diamino-3,3′-dibenzoyldiphenyl, was prepared (75% yield) using the procedure that was reported by Stille.[17] The copolymer was prepared by the acid-catalyzed Friedländer condensation reaction between **2** and **3** in diphenyl phosphate and *m*-cresol at 135−140 °C for 48 h under nitrogen.[18] The resulting viscous polymer solution was precipitated into methanol containing 10% triethylamine, followed by Soxhlet extraction with the same solution for 24 h to give a pale-yellow fibrous solid (yield 97%). The chemical structures of the monomers and polymer were confirmed by ^{1}H NMR and elemental analysis.[19]

The synthesized copolymer was very soluble in common organic solvents, such as chloroform, tetrahydrofuran (THF), and cyclopentanone. This was partially due to the two *n*-butyl side chains that were attached on the TPD moiety, which greatly enhanced the solubility of the polymer. The molecular weight of this polymer was determined by gel permeation chromatography (GPC) with THF as eluent and polystyrene as the standard. TPD−PQ had a weight average molecular weight $M_w = 99\,900$, with a polydispersity index of 1.56. A pinhole-free thin film was obtained easily by the spin-coating technique.

The thermal properties of TPD−PQ were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TPD−PQ possessed

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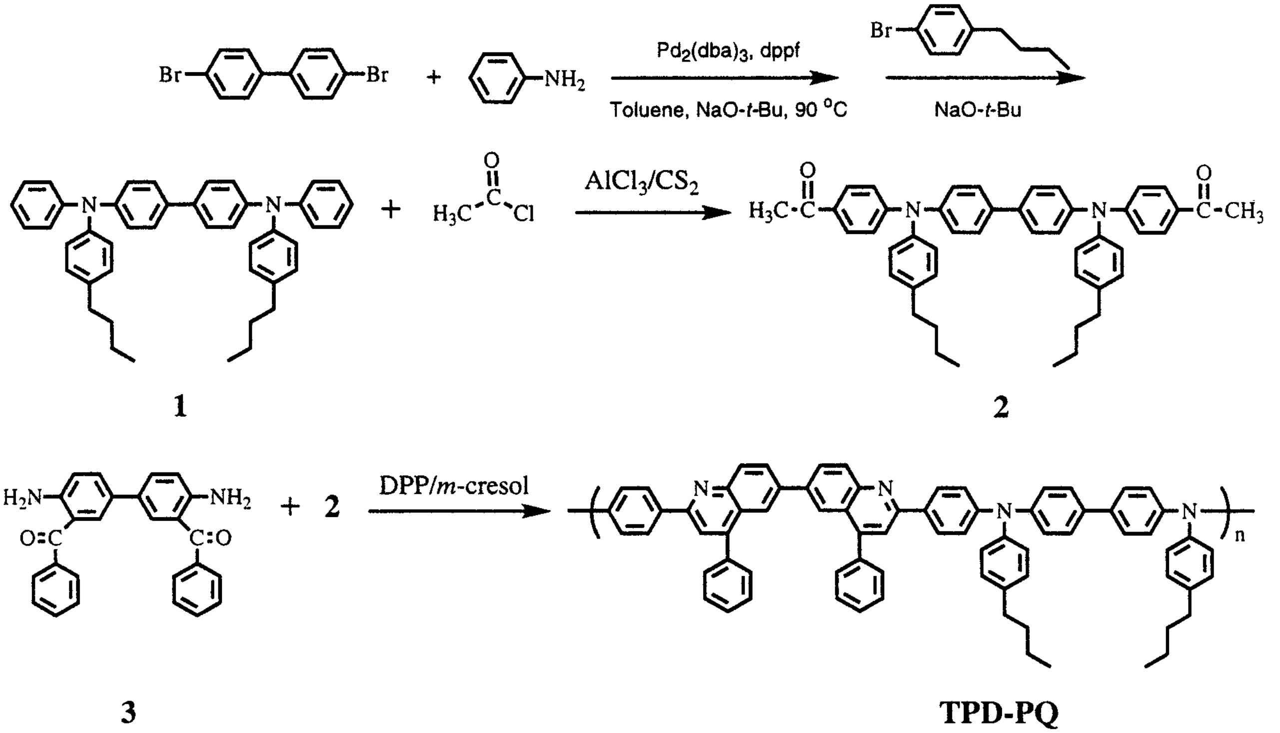
Scheme 1. Synthesis of TPD−PQ



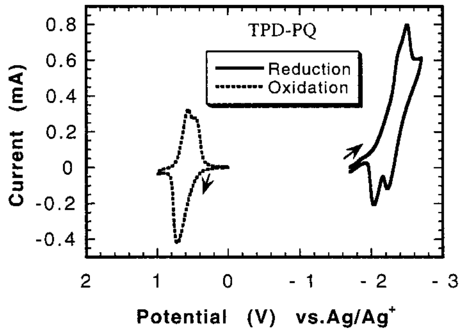


Figure 1. Cyclic voltammetry of TPD−PQ spin-coated on ITO glass in an acetonitrile solution of TBAP (0.1 M) at a scan rate of 40 mV/s.

excellent thermal stability with a glass-transition temperature (T_g) of 215 °C and a decomposition temperature (T_d) of 461 °C.

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 counterelectrode and Ag/Ag$^+$ was used as the reference electrode, with 0.1 M tetrabutylammonium perchlorate (TBAP) in acetonitrile as the electrolyte. A typical CV curve is shown in Figure 1. Two redox-active moieties were revealed for the copolymers. Under a positive scan, a two-electron-transfer step was observed due to the oxidation of the unbonded electrons on the nitrogen atom of the TPD group. Consequently, under a negative scan, another two-electron-transfer step, due to the reduction of the unbonded electrons on the nitrogen atom of bis-quinoline, was also observed. It is worthwhile to point out that both the oxidative (p-doping) and the reductive (n-doping) processes were highly reversible for the TPD−PQ.

The energy levels of TPD−PQ were calculated using the ferrocence (FOC) value of −4.8 eV as the standard.[20] The onset potentials of the oxidation and the reduction (Figure 1) were determined to be 0.36 and −2.18 V vs FOC (E_{FOC} = 0.12 V vs Ag/Ag$^+$). Therefore, the HOMO, LUMO energy levels and the band gap (E_g) were −5.16, −2.62, and 2.54 eV, respectively. The band gap obtained from the electrochemical measurement is in excellent agreement with the result determined by the absorption spectrum of the polymer (λ_{onset} = 488 nm, E_g = 2.54 eV).

Three types of LEDs with the structure of ITO/copper phthalocyanine (CuPc)/TPD−PQ/Al (A), ITO/poly(9-vinylcarbazole) (PVK)/TPD−PQ/aluminum tris(8-hydroxyquinoline) (Alq$_3$)/Al (B), and ITO/TPD−PQ/Alq$_3$/Al (C) were fabricated. The CuPc, Alq$_3$, and Al layers were evaporated under vacuum (10^{-6} Torr). Thin films of PVK and TPD−PQ were spin-coated from a 1,2-dichloroethane solution and from a cyclopentanone solution at 2000 rpm for 20 s. PVK is insoluble in cyclopentanone. As a result, we were able to spin-coat TPD−PQ on top of PVK without distorting the polymer interface. The thickness of CuPc, PVK, and TPD−PQ were ~40 nm and the active areas of the resulted devices were 7.07 mm^2.

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(19) ^{1}H NMR (300 MHz) for monomer **1** (CD_2Cl_2): 0.95 (t, *J* = 7.3 Hz, 6H), 1.40 (m, 4H), 1.58 (m, 4H), 2.59 (t, *J* = 7.7 Hz, 4H), 6.92−7.41 (m, 10H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H). For monomer **2** (CD_2Cl_2): 7.78 (d, *J* = 8.8 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H), 7.20 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 8.6 Hz, 4H), 7.10 (d, *J* = 8.3 Hz, 4H), 7.00 (d, *J* = 8.7 Hz, 4H), 2.62 (t, *J* = 7.7 Hz, 4H), 1.61(m, 4H), 1.39(m, 4H), 0.95(t, *J* = 7.3 Hz, 6H). For monomer **3** ($CDCl_3$): 7.63 (d, *J* = 7.3 Hz, 4H), 7.54 (q, 4H), 7.41 (d, *J* = 2.0 Hz, 2H), 7.39 (dd, *J* = 3.0 Hz, 2.0 Hz, 2H), 7.37 (d, *J* = 3.0 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 6.0 (br, 4H). For polymer TPD−PQ (THF-d_8): 8.39 (br, 4H), 8.30 (br, 4H), 8.19 (br, 2H), 8.08 (br, 2H), 7.54−7.84 (m, 16H), 7.10−7.44 (m, 22H), 2.75(t, 4H), 1.77 (m, 4H), 1.54 (m, 4H), 1.09 (t, 6H). Anal. Calcd for $(C_{74}H_{60}N_4)_n$: C, 88.41; H, 6.02. Found: C, 87.98; H, 6.45.

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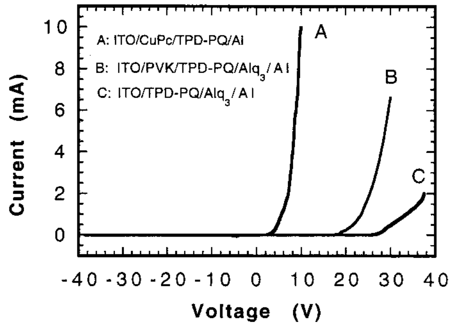

Figure 2. Current–voltage characteristic for the light emitting devices. (A) ITO/CuPc/TPD–PQ/Al, (B) ITO/PVK/TPD–PQ/Alq_3/Al, (C) ITO/TPD–PQ/Alq_3/Al.

Figure 2 shows the current–voltage ($I-V$) characteristics for the three LEDs. All of the devices revealed an excellent diode behavior, i.e., under the forward bias (a positive voltage that was applied to the ITO electrode), the current increased superlinearly with the increase of applied voltage after exceeding the turn-on voltage. Moreover, under reverse bias, no obvious increase of current was observed when the applied voltage was increased. The turn-on voltage and rectification ratio were determined to be 3.8 V and 6.8×10^3 (at ±8.5 V) for type A, 20.0 V and 1.1×10^5 (at ±30.0 V) for type B, and 28.0 V and 3.1×10^5 (at ±33.0 V) for type C, respectively. The most significant feature derived from the $I-V$ curves was that the turn-on voltages for the type A and B devices were significantly decreased when CuPc and PVK were used as the hole-injection/-transport layer. This suggests that the TPD–PQ polymer may possess very good electron-transporting properties and it needs the CuPc or PVK layer to balance the device's overall charge-injection/-transport properties in order to optimize the performance of the multilayer LEDs.

The photoluminescence (PL) spectrum of TPD–PQ and the EL spectra of the LEDs are shown in Figure 3. The thin film of TPD–PQ emitted yellow light (λ_{max} = 550 nm) when it was excited at 366 nm. The EL spectra for type B and C devices were almost identical to the PL spectrum (λ_{max} = 550 nm for type B and λ_{max} = 540 nm for type C). However, due to the partial absorption by CuPc in the region of 520–680 nm, the EL spectrum for the type A device was blue-shifted to 515 nm, with its long-wavelength side having become much steeper. Bright yellow light emission was observed in daylight under forward bias for all three types of LEDs.

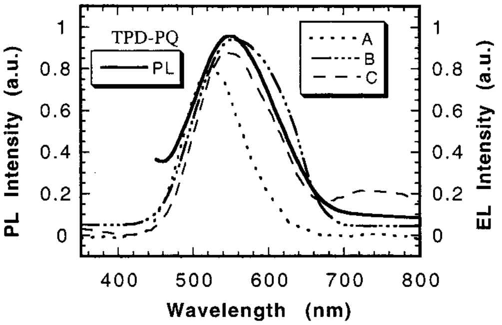

Figure 3. Photoluminescence and electroluminescence spectra of TPD–PQ: (A) ITO/CuPc/TPD–PQ/Al, (B) ITO/PVK/TPD–PQ/Alq_3/Al, (C) ITO/TPD–PQ/Alq_3/Al.

In conclusion, a bipolar light-emitting polymer was synthesized via a simple Friedländer condensation reaction. This polymer possessed high thermal stability, good electrochemical reversibility, and excellent thin-film-forming properties. In addition, bright light emission, high rectification ratio, and low turn-on voltage were achieved for the LEDs fabricated with this bipolar polymer.

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