Synthesis and characterization of polyquinolines for light-emitting diodes

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A novel light-emitting polymer containing both a highly electron-affinitive segment, biquinoline, and a good hole transporting segment, dialkoxyphenylenevinylene, was synthesized and characterized. This polymer possessed excellent film-forming properties, good thermal stability, charge injection properties and electroluminescence efficiency. A greenish-yellow light emitting diode was fabricated using this copolymer as an emitter layer.

Introduction

Polymer light-emitting diodes (LEDs), based on conjugated polymers or polymers with conjugated segments or pendant groups, have been extensively studied recently due to their potential applications in large-area displays.[1–12] In principle, a polymer LED requires the injection of holes and electrons into the emitter layer. The recombination of the injected electrons and holes in the polymer layer generates singlet excitons whose radiative decay produces visible light. There are a number of factors that influence the performance of LEDs. Some factors are intrinsic to the device design and the methods of preparation. Other factors, such as the fluorescence quantum efficiency, charge carrier mobility, and thermal stability are inherent properties of the emitting materials. Since the first report of using poly(*p*-phenylenevinylene) (PPV) as an emissive layer in a LED, much effort has been put into the design and synthesis of suitable materials. It is known that balanced and efficient charge injection/transport for electrons and holes are crucial for achieving high device efficiency. However, most of the electroluminescent (EL) polymers investigated so far have unipolar character; there are rarely good conductors for both holes and electrons. Due to imbalanced charge injection and transport, the charge recombination in thin-film polymer LEDs often occurs close to the metal electrode. Thus, luminescence quenching by the metal usually results in a lower device efficiency. Bipolar types of EL polymers[13–15] are potential candidates that may achieve balanced charge injection in a single layer LED, since they combine all three desirable properties, electron transporting, hole transporting, and light emitting, in a single species.

Polyquinoline (PQ) has been studied as a blue light-emitting material in polymer LEDs. However, preliminary results from the literature[16] of a single layer LED device based on an electron-deficient, fluorinated PQ exhibited low levels of light emission and internal quantum efficiency (4×10^{-3}% using Ca as cathode) owing to poor hole injection. Recently, we have demonstrated that, by introducing tetraphenyldiaminobiphenyl (TPD) moieties into a PQ backbone, the hole injecting and transporting properties of the resulting polymer are significantly improved. A single layer LED with aluminum as the cathode showed a bright yellow light emission and had an external quantum efficiency of 1.8×10^{-2}%. Since TPD is a much more efficient hole injecting/transporting material compared to biquinoline for electron injecting/transporting, the overall light-emitting property of the polymer may still be affected by the imbalance of charge carriers. In this paper, we report a polymer (PQ-MEH-PPV) which contained a less electron-rich segment dialkoxyphenylenevinylene moiety and

an electron-deficient biquinoline unit that achieved much improved light-emitting performance (Chart 1).
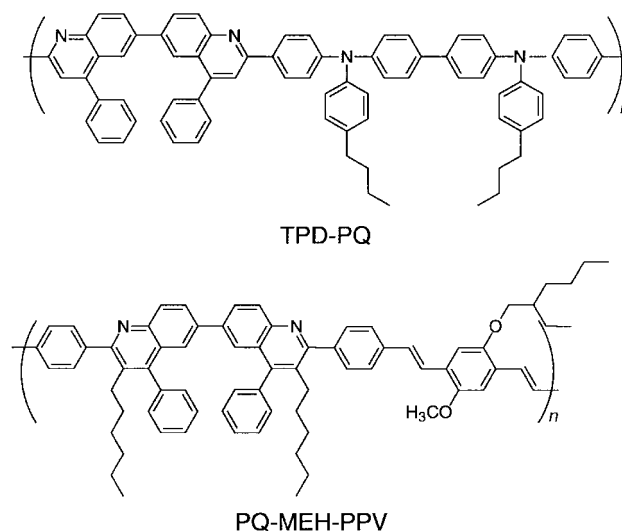

Chart 1 Structures of the polymers.

Results and discussion

The design and synthesis of the monomers and PQ-MEH-PPV polymer are outlined in Scheme 1. The bis(*o*-aminophenyl ketone) **1** was synthesized (75% yield) according to a literature procedure.[17] Compound **2** was obtained from a Friedel–Crafts reaction between bromobenzene and octanoyl chloride in carbon disulfide (80% yield). A condensation reaction between **1** and **2** under acidic conditions afforded compound **3** (71% yield). Monomer **4** was obtained (48% yield) by lithiation of **3** with *n*-BuLi (2.1 equiv.) at $-78\ ^\circ$C and then quenching with dimethylformamide. The Wittig–Horner polycondensation reaction[18] between **4** and **5** was carried out in THF using potassium *tert*-butoxide as base and afforded polymer **6** as a yellow powder. The ^{1}H NMR spectrum of the polymer in THF-d$_8$ and elemental analysis demonstrated the expected polymer structure. The introduction of dialkoxy and hexyl side chains helped prevent early precipitation during the polymerization process. The polymer was soluble in common organic solvents, such as tetrahydrofuran, chloroform, and toluene. Pinhole-free, homogeneous, thin films could be formed by spin-coating from a CHCl$_3$ solution of the polymer. The weight average molecular weight of this polymer ($M_w = 40\,200$ with a polydispersity of 1.4) was determined by gel permeation chromatography (GPC) using polystyrene standards. The ther-
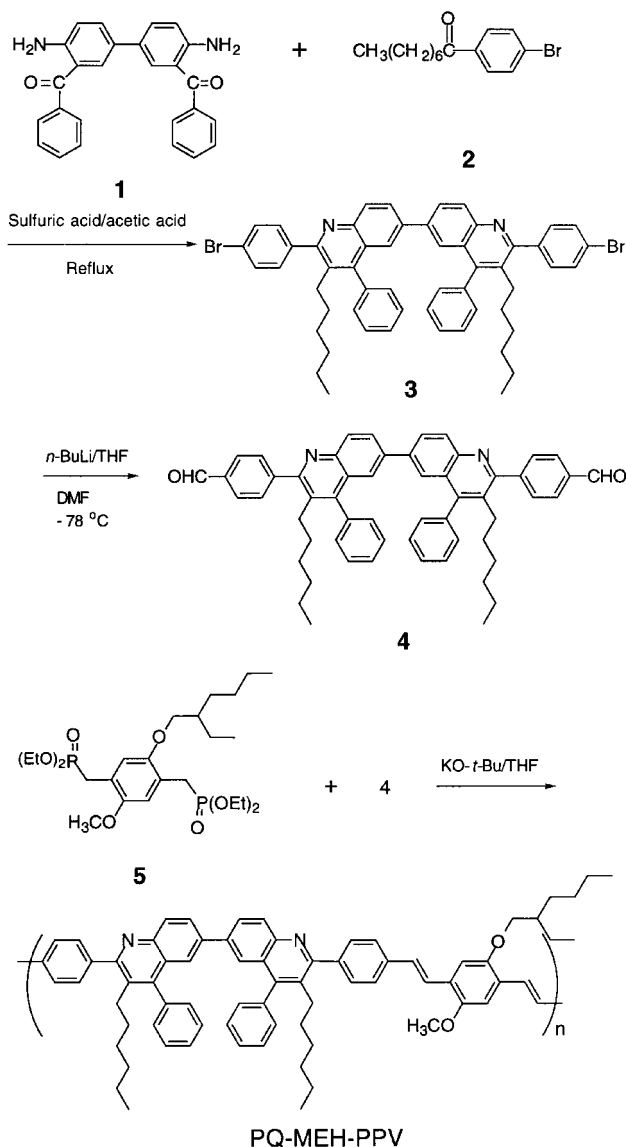
Scheme 1 Synthesis of PQ-MEH-PPV.

mal stability of the polymer was measured by thermogravimetric analysis (TGA) under a nitrogen atmosphere. Its decomposition temperature was above 400 °C, as shown in Fig. 1. The glass-transition temperature (T_g) of 147 °C was determined by differential scanning calometry (DSC) analysis. These results are consistent with the thermal properties of a typical rigid structure parent polymer with flexible side-chains

The UV–VIS spectra of PQ-MEH-PPV are shown in Fig. 2. The polymer had an absorption peak (λ_{max}) at 406 nm, which was derived from the π–π^* transition of the conjugated system.
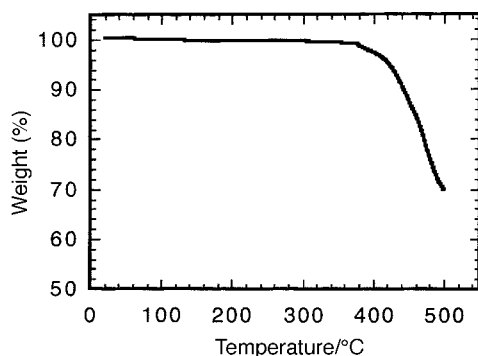

Fig. 1 Thermogravimetric analysis of PQ-MEH-PPV.
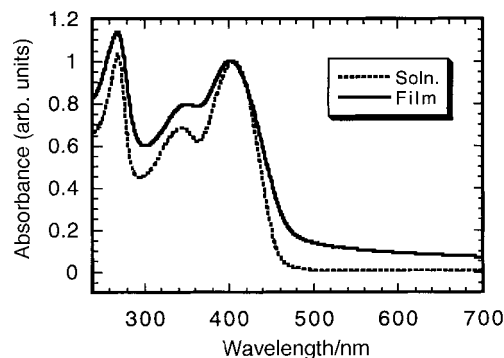
Fig. 2 UV–VIS spectra of polymer in chloroform solution and as solid film.

The relatively sharp absorption edge indicated that the formation of the aggregates was minimal due to the long alkyl chains attached to the polymer that prevented the polymer chains from packing. The bandgap of the polymer (2.70 eV) was determined by extrapolation to its absorption band edge.

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 perchlorate (TBAP) in acetonitrile as the electrolyte. Fig. 3 shows the cyclic voltammogram of the PQ-MEH-PPV. The polymer exhibited a reversible reduction peak under cathodic sweep. However, the oxidative sweeping only produced an irreversible peak, which is similar to that of the MEH-PPV during an anodic sweep. The onset potentials of the reduction and oxidation were located at -2.08 V and $+0.67$ V vs. FOC ($E_{FOC}+0.12$ V vs. Ag/Ag$^+$). Regarding the energy level of the ferrocene/ferrocenium reference (-4.8 eV), the HOMO and LUMO energy levels of PQ-MEH-PPV were -5.47 eV and -2.72 eV, respectively (Fig. 4). Compared with the HOMO and LUMO energy levels of TPD-PQ, the larger energy barrier between the PQ-MEH-PPV/ITO interface made the injection of holes more difficult, while the smaller energy gap between the polymer and Al cathode facilitated the injection of electrons. Therefore, a more balanced charge injection could be achieved.

PQ-MEH-PPV was used as an emitter layer in a single layer LED device using aluminum as the cathode. The polymer layer was spin-coated from a chloroform solution onto an ITO-coated glass substrate. The aluminum layer was then deposited under vacuum (10^{-6} Torr) onto the polymer film as the cathode. Fig. 5 shows the photoluminescence spectra of a thin film of PQ-MEH-PPV and the electroluminescence spectrum of an ITO/PQ-MEH-PPV/Al device. The two spectra are
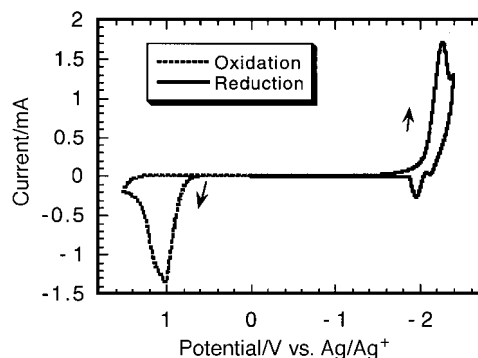
Fig. 3 Cyclic voltammogram of polymer film on ITO glass (Measured in acetonitrile solution of TBAP (0.1 M) at 40 mV s^{-1}, referenced vs. Ag/Ag$^+$).
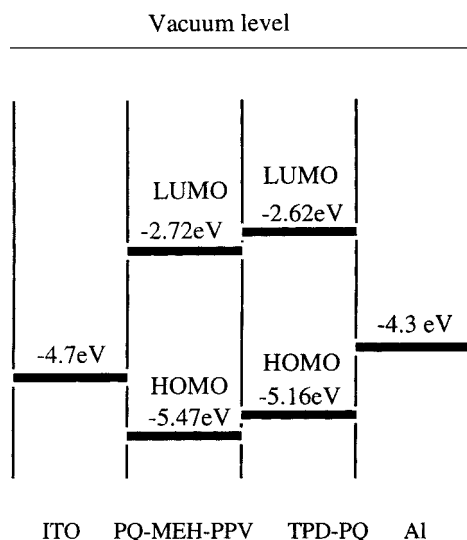
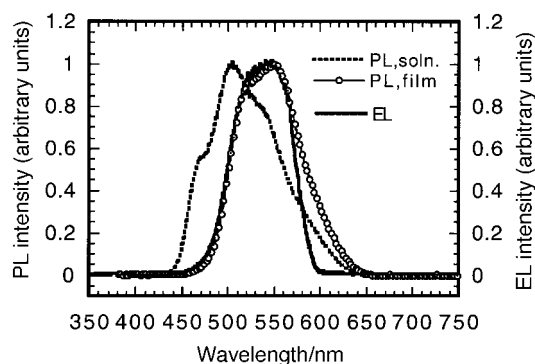**Fig. 4** Energy level diagrams of PQ-MEH-PPV and TPD-PQ.

Fig. 5 Photoluminescence and electroluminescence spectra of the polymer.

almost identical. This indicates that electron–hole recombination occurs in the polymer layer, resulting in the excitation of the polymer. The emission peak was centered at 550 nm, which was slightly red-shifted when compared to the photoluminescence of the solution.

The typical current–voltage and light–voltage curves of this device are shown in Fig. 6. Bright greenish-yellow light emission can be seen easily under normal light conditions and is relatively stable at room temperature. Current and light arose at the same voltage, and the two curves matched very well. The turn-on voltage (18 V) was almost the same as that of TPD-PQ (17 V). However, an external quantum efficiency of 0.06% was obtained, which was more than three times higher than the device made by using the TPD-PQ and thirty times
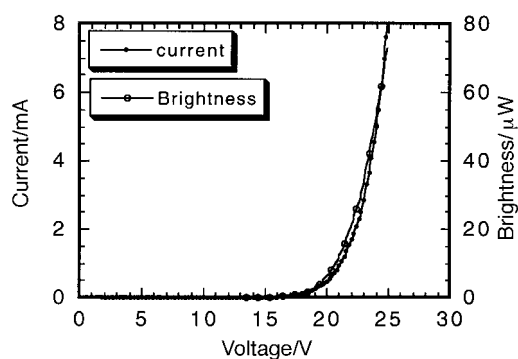

Fig. 6 Current/light–voltage characteristics of an ITO/PQ-MEH-PPV/Al device.

higher than that using MEH-PPV[12] as emitting layer with the same device configuration. This result indicated that a better match of electron and hole injection from opposite electrodes was achieved in this polymer. However, further work on studying the mechanisms of charge transport in bipolar types of polymers is still needed.

In conclusion, a new polymer composed of regularly alternating biquinoline and dialkoxyphenylene vinylene moieties has been prepared by the Wittig–Horner polycondensation. The polymer possesses excellent thermal stability and solubility, and good charge transport and emissive capabilities. A single layer LED device with the relatively air-stable aluminum electrode using this polymer as an emitter layer showed a respectable external quantum efficiency of 0.06%.

Experimental

NMR spectra were recorded on a Varian WM-300 (300 MHz) spectrometer using deutero solvent as reference or internal deuterium lock. The chemical shift data for each signal were given in units of δ relative to tetramethylsilane (TMS) where δ (TMS)=0. Differential scanning calometry (DSC) and thermogravimetric analysis (TGA) for the polymers were carried out under nitrogen at a rate of 10 °C per minute using the Shimadzu instrument. UV–VIS spectra were recorded on a Perkin-Elmer spectrophotometer (Lambda 9 UV/VIS/NIR). Gel permeation chromatography (GPC) measurements were carried out using a Waters Styragel (HR 4E, 7.8×300 mm) column with polystyrene as the standard, and THF as the solvent.

Cyclic voltammograms of the polymer films (spin-coated onto indium-tin oxide coated glass, ITO glass) were recorded at room temperature in a typical three electrode cell with a working electrode (ITO glass), a reference electrode (Ag/Ag$^+$, externally referenced against Fc/Fc$^+$, 0.12 V), and a counter electrode (Pt gauze) under a nitrogen atmosphere at a sweeping rate of 40 mV s^{-1} (CV-50W Voltammetric Analyzer, BAS). A solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile was used as the electrolyte.

LEDs fabrication and measurement

For the single layer devices, polymer solutions in chloroform (8 mg mL^{-1}) were used to spin-cast on top of the anodic electrode, ITO glass (100 $\Omega/\square$, Delta Techn. Ltd.). The cathode Al electrode (*ca.* 200 nm) was deposited by thermal evaporation under vacuum (2×10^{-6} Torr). The film thickness was measured with a Dektak surface profilometer (Model 3030). The active emissive area defined by the cathode was about 8 mm^2.

Photoluminescent spectra of the neat films (coated on quartz glass) or solutions of the polymers were recorded by a CCD system (Instaspec IV CCD, Oriel) under UV light excitation (366 nm). Electroluminescence spectra of LEDs were recorded with the same CCD system. I–V–L curves of the LEDs were recorded by a semiconductor analyzer (4155B Semiconductor Parameter Analyzer, Hewlett Packard) with a calibrated multi-functional optical meter (model 2835-C, Newport).

Syntheses

Commercially available chemicals (Aldrich) were used without further purification. Bis(*o*-aminophenyl ketone) **1**[17] and diphosphonate **5**[18] were prepared according to the procedures from the literature. All reactions were performed under a dry nitrogen atmosphere.

Compound 2. To a 100 ml 3-necked flask with aluminum chloride (14.66 g, 110 mmol) was added dropwise octanoyl chloride (17.07 mL, 100 mmol). The resulting solution was stirred at room temperature for 15 min, to which was added

dropwise bromobenzene (34.29 g, 218.4 mmol). The reaction mixture was stirred at room temperature for another 5.5 h, and then poured into a mixture of crushed ice (50 g) and hydrochloric acid (25 mL). The product was filtered, washed sequentially with 2% hydrochloric acid, 5% sodium hydroxide solution and water, and dried to afford a white solid (22.6 g, 80%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.88 (t, $J=8.6$ Hz, 3H), 1.29–1.34 (m, 8H), 1.72 (quintet, 2H), 2.92 (t, $J=7.6$ Hz, 2H), 7.59 (d, $J=8.6$ Hz, 2H), 7.82 (d, $J=8.6$ Hz, 2H).

Compound 3. To a stirred solution of 3,3′-dibenzoylbenzidine **1** (0.78 g, 2 mmol) and 4′-bromoacetophenone **2** (1.70 g, 6 mmol) in glacial acetic acid (4.0 mL) was added concentrated sulfuric acid (0.04 mL). The reaction mixture was refluxed for 50 h. During this period of time, additional acetic acid and sulfuric acid were added to drive the dehydration to completion. After that, the reaction mixture was cooled down and poured slowly into ice-cold water. Concentrated ammonium hydroxide was added to neutralize the mixture. The resultant pale yellow suspension was suction filtered, then washed with water, methanol, and methylene chloride to get rid of the starting materials. The product was a pale yellow powder (1.25 g, 71%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.73 (t, $J=7.1$ Hz, 6H), 0.84–1.17 (m, 16H), 2.53 (t, $J=8.0$ Hz, 4H), 7.26 (dd, $J=8.3$ Hz, $J=2.3$ Hz 4H), 7.43–7.54 (m, 12H), 7.63 (d, $J=8.4$ Hz, 4H), 7.85 (dd, $J=8.8$ Hz, $J=2.0$ Hz, 2H), 8.17 (d, $J=8.4$ Hz, 2H).

Compound 4. *n*-Butyllithium (0.84 mL of a 2.5 M solution in hexane, 2.1 mmol) was added dropwise into a solution of **3** (884.5 mg, 1 mmol) in THF (50 mL) at −78 °C. After stirring for 0.5 h, excess dimethylformamide (0.5 mL) was added and the mixture was stirred at room temperature for 45 min. Water was then added to quench the reaction. After removal of the solvent, the mixture was poured into water and extracted twice with methylene chloride. The organic layer was collected and dried over Na$_2$SO$_4$. The solvent was evaporated and the residue was purified through a short silica gel column with methylene chloride–ethyl acetate=9:1 as eluent. The product was a yellow powder (424.56 mg, 48%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.69 (t, $J=7.1$ Hz, 6H), 0.84–1.25 (m, 16H), 2.53 (t, $J=7.8$ Hz, 4H), 7.27 (dd, $J=8.8$ Hz, $J=2.9$. Hz 4H), 7.46–7.55 (m, 8H), 7.77 (d, $J=8.0$ Hz, 4H), 7.86 (dd, $J=8.7$ Hz, $J=1.9$ Hz, 2H), 8.03 (d, $J=7.9$ Hz, 4H), 8.19 (d, $J=8.94$ Hz, 2H), 10.12 (s, 2H). Anal. Calcd for C$_{56}$H$_{52}$N$_2$O$_2$: C, 85.68; H, 6.68; N, 3.60. Found: C, 85.51; H, 6.43; N, 3.55%.

PQ-MEH-PPV. To a stirred solution of **5** (235.5 mg, 0.3 mmol) and dialdehyde **4** (161.0 mg, 0.3 mmol) in dry THF (50 mL) at room temperature was added dropwise a solution of potassium *tert*-butoxide in THF (0.6 mL, 0.6 mmol) by syringe until no red color was formed. The reaction mixture was stirred for 2.5 h, after which the THF was evaporated *in vacuo*. The resulting solid was washed with a solution of methanol, water, and acetone (3:1:1) to remove any inorganic by-products. The yellow color 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 for 1 day to give 150 mg of product (50%). ^{1}H NMR (300 MHz, THF-d_8) δ 0.73 (t, $J=7.0$ Hz, 12H), 0.87–0.97 (m, 17H), 1.00–1.07 (m, 8H), 2.56 (br, 4H, α-CH$_2$), 3.96–4.07 (br, 5H), 7.32–7.57 (m, 30H, vinyl and aromatic). Anal. Calcd for C$_{73}$H$_{76}$N$_2$O$_2$: C, 86.52; H, 7.56; N, 2.76. Found: C, 85.77; H, 7.48; N, 2.55%.

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