

Synthesis and characterization of a novel bipolar polymer for light-emitting diodes

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A novel bipolar light-emitting polymer containing both efficient hole and electron injecting/transporting segments exhibiting high thermal stability ($T_d = 445\text{ }^\circ\text{C}$), good electrochemical reversibility, excellent thin film-forming and light-emitting properties (bright yellow emission, a rectification ratio greater than 10^5 and a low turn-on voltage of 3.7 V) is reported.

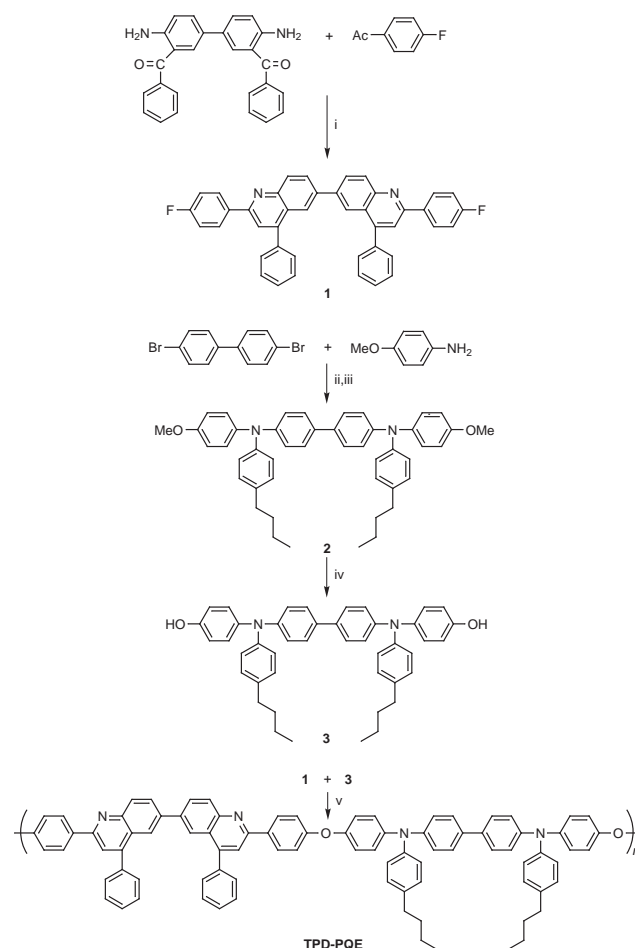
For most of the conjugated polymers that are reported in the literature, the hole injection/transport is more favorable than the electron injection/transport due to the electron-richness of the π -conjugated systems. To facilitate the electron injection, metals with low work functions, such as calcium and magnesium, have been used as cathodes. However, the stability of the resulting devices is severely compensated for by the sensitivity of these metals to both oxygen and moisture. To circumvent these problems, several approaches have been utilized, such as synthesizing highly electron-affinitive polymers,¹ inserting an additional electron injecting/transporting layer between the emitter and the cathode² and blending small molecules into the polymer matrix.³ Although some success has been achieved, several deficiencies are associated with these methods. For example, more tedious and complex multilayer structures were needed to offset the poor hole injection of the highly electron-affinitive polymers for achieving high device efficiency. In addition, phase separation often occurs when the dopant concentration is high. Recently, Bao *et al.*⁴ reported the results of light-emitting polymers containing both electron and hole transporting moieties that achieved efficient device performance. Thus, it is desirable to design and synthesize a bipolar polymer that possesses both a hole injecting/transporting segment and an electron-affinitive segment in order to enhance the charge injecting/transporting ability. Polyquinolines (PQs) are a class of heteroaromatic polymers that possess excellent thermal stability, good thin film processibility, high electron affinity and unique nonlinear optical properties.^{5,6} A blue electroluminescent (EL) device using a fluorinated polyquinoline (PQ-100) as the emitting layer has been reported that possessed a very high turn-on voltage (50 V) due to difficulties achieving efficient/balanced charge injection.⁷ On the other hand, tetraphenyldiaminobiphenyl (TPD) has been widely used as an excellent hole-transport material in fabricating small molecule EL devices.⁸ In the hope of combining both the blue light-emitting and good electron-affinitive properties of the bisquinoline and the efficient hole-injecting/transporting 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* a nucleophilic replacement reaction/polycondensation. Here we report the excellent thermal, electrochemical and EL results obtained from this polymer.

The synthesis of the copolymer (TPD-PQE) is outlined in Scheme 1. Compound **1** was synthesized (80% yield) from 4,4'-diamino-3,3'-dibenzoyldiphenyl ether and 4-fluoroacetophenone.⁹ Compound **2** was synthesized (50% yield) from the modified Buchwald coupling reaction^{10,11} between 4-anisidine and 4,4'-dibromobiphenyl in the presence of tris(dibenzylideneacetone)dipalladium [$\text{Pd}_2(\text{dba})_3$], 1,1'-bis(diphenylphosphi-

no)ferrocene (dppf) and NaOBu^t , followed by the addition of 1-bromo-4-butylbenzene and additional NaOBu^t . Compound **3** was obtained (72% yield) from **2** by a demethylation reaction.¹² Polymerization between **1** and **3** was carried out in the presence of K_2CO_3 in a NMP-toluene solvent mixture.¹³ The resulting viscous polymer solution was precipitated into MeOH, followed by Soxhlet extraction with MeOH to afford polymer **4** (78% yield). The chemical structures of monomers and polymer were confirmed by ^1H NMR and elemental analyses.

TPD-PQE was a pale-grey fibrous solid. As a result of the two n-butyl groups attached on the TPD moiety, the TPD-PQE was readily soluble in common organic solvents, such as CHCl_3 , THF and cyclopentanone. The weight average molecular weight ($M_w = 58400$ with a polydispersity index of 5.76) was determined by gel permeation chromatography using THF as eluent and polystyrene as standard.

The thermal properties of TPD-PQE were determined by thermal gravimetric analysis (TGA) and differential scanning



Scheme 1 Reagents and conditions: i, conc. H_2SO_4 , AcOH; ii, $\text{Pd}_2(\text{dba})_3$, dppf, toluene, NaOBu^t , $90\text{ }^\circ\text{C}$; iii, 4- $\text{BrC}_6\text{H}_4\text{Bu}$, NaOBu^t ; iv, $\text{BBr}_3\cdot\text{SMe}_2$, $\text{ClCH}_2\text{CH}_2\text{Cl}$; v, K_2CO_3 , toluene, NMP.

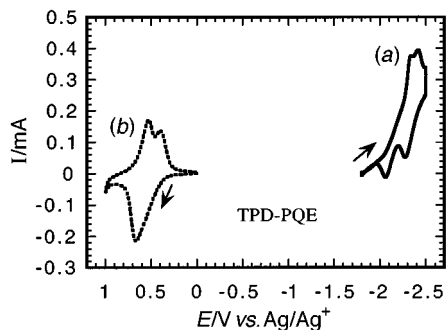


Fig. 1 Cyclic voltammety of TPD-PQE spun-coated on ITO glass in an MeCN solution of TBAP (0.1 M) at a scan rate of 40 mV s⁻¹: (a) reduction and (b) oxidation.

calometry (DSC). The TPD-PQE possessed excellent thermal stability with a glass transition temperature (T_g) of 196 °C, and a T_d (onset of the decomposition temperature) of 445 °C.

The energy levels of TPD-PQE were investigated by cyclic voltammety (CV). A thin film of the polymer was spin-coated onto pre-cleaned indium-tin-oxide (ITO) glass as a working electrode ($\sim 3 \text{ cm}^2$) from a cyclopentanone solution (concentration $\sim 3 \text{ mg ml}^{-1}$). The reference and counter electrodes were Ag/Ag⁺ (non-aqueous) and Pt gauze, respectively. The experiment was carried out under nitrogen with tetrabutylammonium perchlorate in anhydrous MeCN (TBAP, 0.1 M) as the supporting electrolyte. A typical CV curve is shown in Fig. 1. Two redox-active moieties were revealed for the copolymers. It is worth pointing out that the oxidative (*p*-doping) process was highly reversible and the reductive (*n*-doping) process was quasi-reversible for TPD-PQE. As a matter of fact, such a bipolar ability is beneficial to the performance of LEDs. The energy values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) for TPD-PQE were calculated using the ferrocene (FOC) value of -4.8 eV below the vacuum level.¹⁴ The onset potentials of oxidation and reduction of TPD-PQE (Fig. 1) were determined as +0.39 and $-2.07 \text{ V vs. Ag/Ag}^+$, corresponding to +0.27 and -2.19 V vs. FOC (EFOC = $0.12 \text{ V vs. Ag/Ag}^+$). Thus, the HOMO and LUMO levels and the HOMO–LUMO gap should be -5.07 , -2.61 and 2.46 eV , respectively. The optical E_g calculated from the onset (426 nm) of the UV–VIS absorption spectra of the spin-coated films for TPD-PQE was 2.91 eV .

To fabricate LED devices, copper phthalocyanine (CuPc), tris(8-hydroxyquinoline)aluminium (Alq₃) and Al layers were evaporated in a vacuum (10^{-6} Torr). Thin films of poly(9-vinylcarbazole) (PVK) and TPD-PQE were spin-coated from a 1,2-dichloroethane solution and from a CHCl₃ solution, which were filtered through a $0.2 \mu\text{m}$ Teflon filter before spin-coating. Three types of LEDs with the structure of ITO/CuPc/TPD-PQE/Al (A), ITO/PVK/TPD-PQE/Alq₃/Al (B) and ITO/TPD-PQE/Alq₃/Al (C) were employed in this study. The thickness of the TPD-PQE was the same ($\sim 35 \text{ nm}$) for all three types of LEDs, while the thickness of CuPc, PVK, Alq₃ and Al were ~ 35 , ~ 40 , ~ 50 and $\sim 100 \text{ nm}$, respectively. The active area of the resulting devices was 7.07 mm^2 . All of the fabrication processes

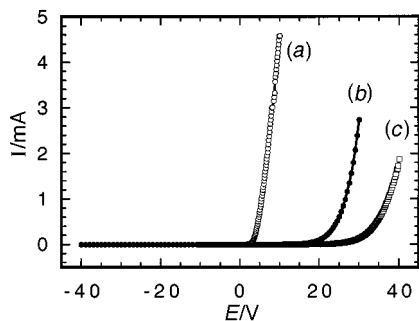


Fig. 2 Current–voltage characteristic for the light emitting devices. (a) ITO/CuPc/TPD-PQE/Al A, (b) ITO/PVK/TPD-PQE/Alq₃/Al B and (c) ITO/TPD-PQE/Alq₃/Al C.

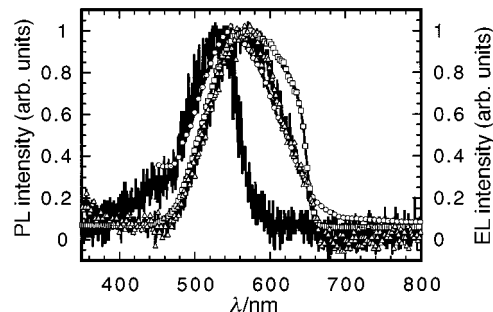


Fig. 3 (○) Photoluminescence spectrum of TPD-PQE and electroluminescence spectra of (—) ITO/CuPc/TPD-PQE/Al A, (□) ITO/PVK/TPD-PQE/Alq₃/Al B and (△) ITO/TPD-PQE/Alq₃/Al C.

(except for vacuum evaporation) and measurements were performed in air and at room temperature.

Fig. 2 shows the current–voltage characteristics of the LEDs. Excellent diode behavior was found for these devices. The turn-on voltage and rectification ratio were determined to be 3.7 V, and 5.1×10^4 (at 4.5 V) for A, 21.0 V and 4.2×10^5 (at 30.0 V) for B, and 30.1 V and 6.0×10^4 (at 36.0 V) for C, respectively. It is worth noting that, for these devices using PVK or CuPc as hole injecting/transporting layers, the turn-on voltages were decreased, while using Alq₃ as an electron injecting/transporting layer, the turn-on voltages were increased. This indicated that the TPD-PQE polymer has a good electron injecting/transporting ability. When the hole injecting/transporting (PVK or CuPc) layers were introduced, the overall charge injection/transport of the devices were balanced, which led to the decrease of the turn-on voltages.

Fig. 3 shows the photoluminescence (PL) spectrum of a TPD-PQE film and EL spectra of the LEDs. The PL spectrum of TPD-PQE had an emission peak at 547 nm when it was excited at 366 nm. The EL spectrum from device A is blue-shifted ($\lambda_{\text{max}} = 530 \text{ nm}$) compared to the PL spectrum of the TPD-PQE. In particular, its long wavelength side became much steeper. This was due to partial absorption by CuPc in the 520–680 nm region.¹⁵ The shape of the EL spectrum from device C is similar to the PL spectrum of TPD-PQE, however, it is red-shifted to 568 nm. In the case of device B, the EL emission shows a peak at 570 nm with a shoulder at $\sim 620 \text{ nm}$. The shoulder is probably due to emission from aggregates of carbazole groups.¹⁹ Bright light emission can clearly be seen under room light at forward bias for all three types of LEDs.

In conclusion, a bipolar copolymer was synthesized and characterized. This polymer showed high thermal stability, good electrochemical reversibility and excellent thin film-forming ability. In addition, very good LED performance was obtained with a low turn-on voltage, high rectification ratio, and bright light emission.

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