Novel copolymers containing triphenylamine and alkylfluorene moiety in the main chain

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Since the first successful demonstration of polymer light emitting diodes (PLEDs) from a conjugated polymer in 1990, PLEDs have attracted worldwide attention as a candidate for the next generation of emissive flat panel displays [1, 2]. However, there are several disadvantages associated with conjugated polymers as the active materials for the emissive display. The emission spectra from conjugated polymers are often too broad for the application as a full color display, since the resulting emission is typically not saturated [3]. Moreover, the majority of PLEDs reported to date emit from a fluorescent transition, severely limiting the quantum efficiency. The quantum efficiency of a device emitting from a fluorescent material is limited by the low theoretical ratio of singlet excitons (25%) compared to triplet excitons (75%), which are formed upon electron-hole recombination in the electroluminescent process [4, 5]. Polymer-based electroluminescent materials offer the advantage of being directly processible from solution, permitting deposition through spin and blade coating under atmospheric conditions. Further, novel deposition processes such as ink-jetting will allow the volume production of full colour displays on large area applications. In order that polymer materials can be used for red-green-blue (R.G.B.) display applications there are a number of criteria that must be satisfied [6, 7]. Triphenylamine (TPA) has been by far the most widely used hole-transporting layer (HTL) in the preparation of organic LEDs [8] even though problems such as surface diffusion and relatively low thermal stability retarded practical applications. Incorporation of TPA into the polymer is expected to overcome these weaknesses. We attempted synthesis of stable new polymers possessing TPA, alkylfluorene and PPV linkage in the main chain and investigated their properties. UV-vis spectra were recorded using a Hewlett Packard 8452A Diode Array Spectrophotometer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were conducted on TA Instruments (TGA 2050, DSC 2010) at a heating rate of 10 °C/min. PL-spectra were recorded using a spectrofluorophotometer (PTI).^{1}H-NMR spectra were measured by 300-MHz (Varian Gemini) and 500-MHz (Varian Unity INOVA 500) Spectrometer. IR-spectra were recorded using FT-IR spectrometer (Nicolet Model 205).

Polymer Synthesis was conducted as follows: The TPA-containing TFPPV (poly({4-[2-(9,9-dihexyl-7-propenyl-9H-fluoren-2-yl)vinyl]phenyl}phenyl-*p*-tolyl-amine)) and TFCN-PPV (poly(2-(7-{1-cyano-2-[4-(phenyl-*p*-tolyl-amino)phenyl]vinyl}-9,9-dihexyl-9H-fluoren-2-yl)but-2-enenitrile))copolymers under investigation have been prepared by the wittig reaction [9]. In a three-neck flask, 1.96 g (2 mmol) of 2,7-bis (chloromethyl)-9,9'-n-hexylfluorene triphenylphosphonium salt (1) and 0.6 g (2 mmol) of 4,4-phenyliminobisbenzenaldehyde (2) were dissolved in a mixture of 60 $\times 10^{-6}$ m^3 of anhydrous ethyl alcohol and 20 $\times$ 10^{-6} m^3 of chloroform. Then 2.3 g of 5% solution of sodium metal in anhydrous ethyl alcohol was added to the mixture dropwisely with a syringe. The mixture was kept at room temperature for 12 h. The precipitated yellow solid, TFPPV and TFCNPPV were washed thoroughly with water and methanol and then with methanol in a Soxhlet extractor for 2 days.

The structures of TFPPV and TFCNPPV were confirmed by means of FT-IR and NMR spectra as well as elemental analyses. TFCNPPV showed a sharp absorption peak at 2200 cm^{-1} corresponding to CN stretching band in the vinylene linkages. TFPPV showed an absorption peak at 900–950 cm^{-1} region assigned to the out of plane vibration of the trans-vinylene in the vinylene linkages. In the NMR spectrum of TFPPV and TFCNPPV, the peak at 9.8 ppm is assigned to the terminal aldehyde groups in the monomer and the peak around at 6.8–7.8 ppm is ascribed to the aromatic hydrogens in the triphenylamine and alkylfluorene unit. All the polymers prepared exhibit good thermal stability with a high decomposition temperature and high T_g as supported by TGA and DSC data under nitrogen atmosphere. The polymers TFPPV and TFCNPPV were soluble in chloroform. In the DSC thermograms, the glass-transition temperature (T_g) of TFPPV and TFCNPPV appeared at 153 and 160 °C, respectively. The T_g of TFCNPPV, which has cyano groups in the backbone, appeared at a higher temperature which was higher than

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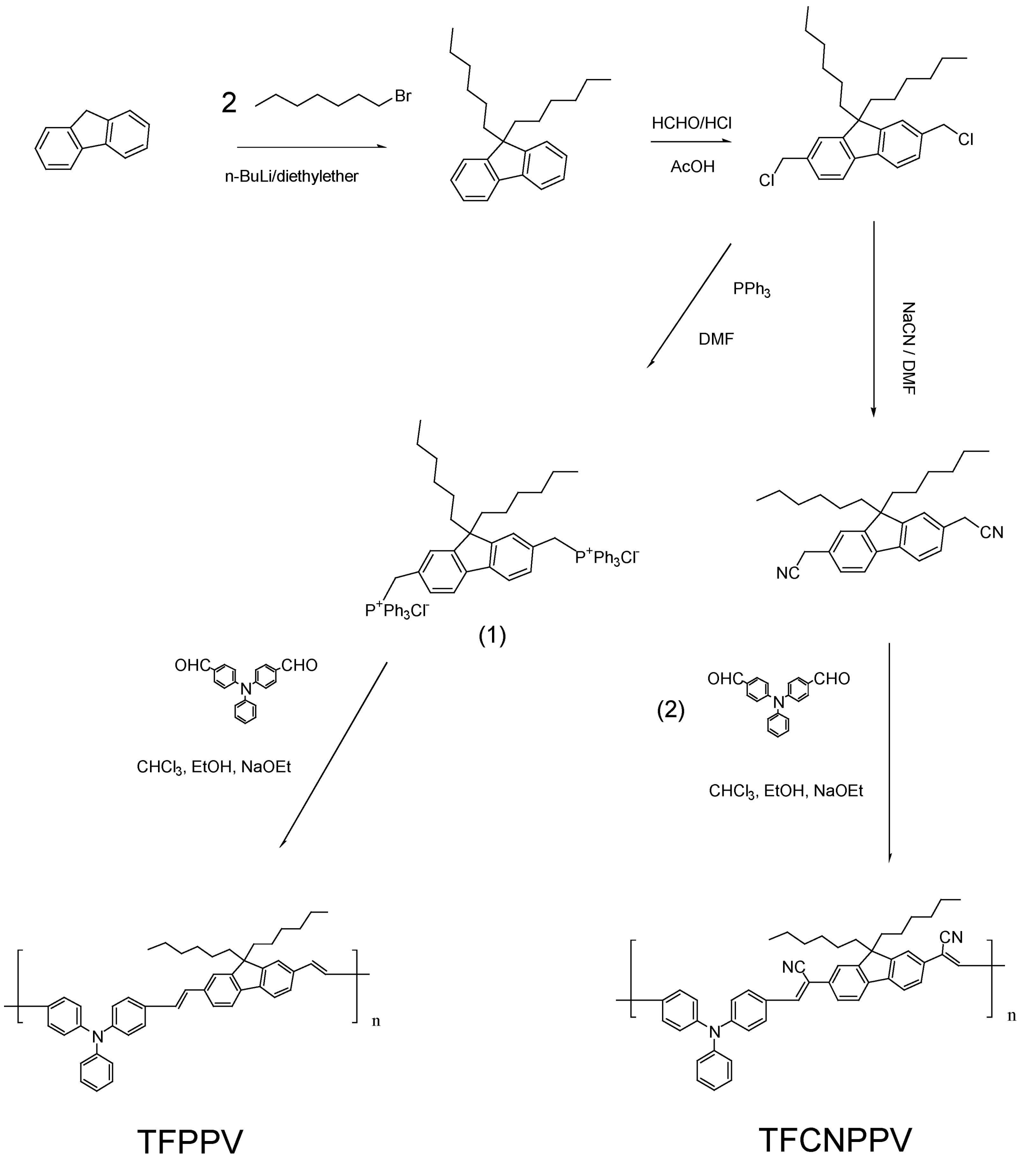

Scheme 1 Synthetic route of TFPPV and TFCNPPV.

the T_g of TFPPV by approximately 7 °C. The results indicate that T_g can be increased through incorporation of cyano moieties in the main chain. The decomposition temperatures (10% weight loss) of TFPPV and TFCNPPV measured by TGA were 388.5 and 383 °C, respectively (Fig. 1). In conjugated polymers, the extent of conjugation length directly affects the band gap of the π-$\pi*$ transition. The UV/Vis absorption spectra of the TFPPV and TFCNPPV in chlorofoform solution showed the maximum absorptions corresponding to the π-$\pi*$ transition at 398 nm and 425 nm, respectively. The difference is due to the presence of the cyano groups in TFCNPPV (Fig. 2). The maximum in the photoluminescence spectrum of the conjugated polymers depends on both the degree of conjugation and the effective conjugation length. The solution of TFPPV and TFCNPPV show very intense yellow light peaked at 467 and 511 nm (Fig. 3). The absorption and emission of the conjugated polymers are closely related with their chemical structures. Compared with their TPA-containing analogues, the cyano group-containing copolymers (TFCNPPV) have at least 27 nm and 44 nm red shift in the absorption and the emission spectra, respectively.

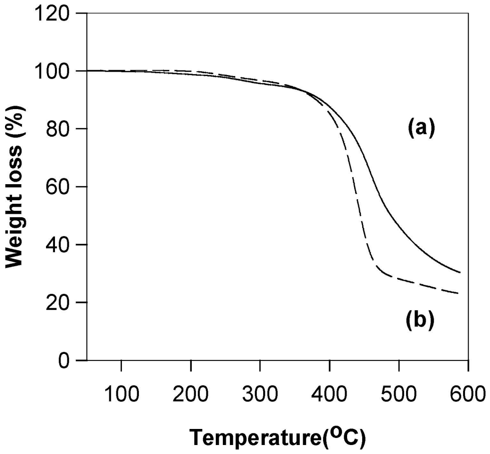

Figure 1 TGA thermogram of (a) TFPPV and (b) TFCNPPV at a heating rate of 10 °C/min under nitrogen atmosphere.

In summary, TFPPV and TFCNPPV copolymers containing alkylfluorene and triphenylamine were successfully synthesized by the Wittig reaction. The wavelength of maximum absorption of TFPPV and TFCNPPV appeared at 398 and 425 nm, respectively. The

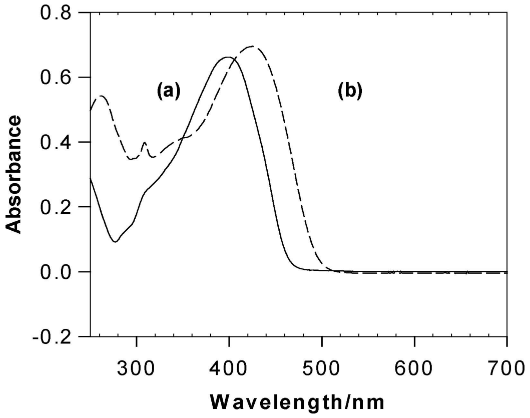

Figure 2 UV/Vis absorption spectra of (a) TFPPV and (b) TFCNPPV in $CHCl_3$.

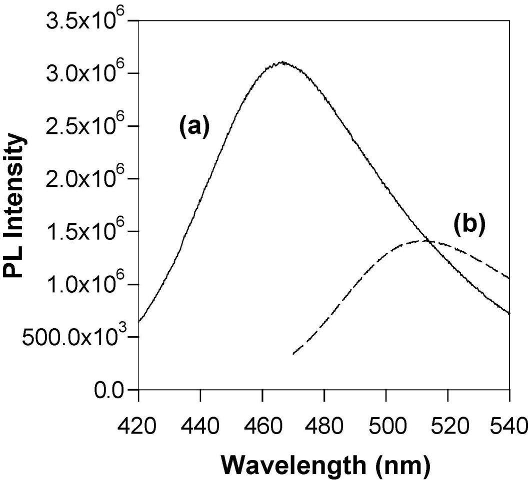

Figure 3 PL spectra of TFPPV (λ_{max} = 467 nm) and TFCNPPV (λ_{max} = 511 nm) in $CHCl_3$ solution.

photoluminescence (PL) spectra of TFPPV and TFCNPPV showed maximum emission at 467 nm and 511 nm in chloroform solution, respectively. The decomposition temperatures (10% weight loss) of TFPPV and TFCNPPV were 388.5 and 383 °C, respectively. These polymers showed high T_g and good thermal stability.

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