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LETTER

Synthesis, characteristics of blue electroluminescent copolymers containing fluorene unit and aliphatic non-conjugated segments

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Polyfluorenes (PFs) have been intensively studied as the blue light-emitting materials due to their high photoluminescence (PL) quantum yields in the solid-state, thermal stability, suitable solubility, and good charge transport properties [1–5], and various fluorene-based copolymers have been synthesized for their benefits such as having the nature of two monomers, tuning the optical properties and improving device performance. Recently, Sung-Ho Jin et al. [6] reported a new poly(9,9-dialkylfluorene-2,7-vinylene) (PFV), and its copolymers with various ratios of MEHPV units, efficiently tuning HOMO and LUMO binding energy levels. However, these PFV fully conjugated homopolymer or copolymers all emitted greenish-blue or green light due to the introduction of the double bond in the main chain, which increased the π–π^* conjugated length. On the other hand, the application of PFs in light emitting diodes has been hampered by the appearance of green electroluminescence (ca. 530 nm); this green electroluminescence has been attributed to either intermolecular interactions [7], which lead to the formation of aggregates, or to the presence of emissive keto defect sites that arise as a result of thermo- or electro-oxidative degradation of the polyfluorene backbone [8].

In this study, we introduced saturated aliphatic soft segments (non-conjugated) into the fluorene-co-phenylenevinylene main chain through the easier-realized Wittig polycondensation reaction. The short conjugated segments provide short emission wavelengths, and the non-conjugated segments tend to limit formation of undesirable long-wavelength solid state emission bands. The fabricated LEDs with the two synthesized copolymers showed good color purity and high EL brightness. The synthetic route and details are given in Scheme 1.

9,9-Diethylfluorene (**1**) and 2,7-bis(bromomethyl)-9,9-diethylfluorene (**2**) were synthesized following the procedures reported in reference [9] and [10], respectively. 1,6-Bis(4-formylphenoxy)hexane (**4-I**) and 1,8-bis(4-formylphenoxy)octane (**4-II**) were synthesized according to the procedures reported in literature [11]. All the chemical structures were verified by FTIR and ^{1}H-NMR spectra.

The synthesis of 2,7-bis(bromomethyl)-9,9-diethylfluorene triphenylphosphonium salt (**3**) was carried out by heating a mixture of triphenylphosphine (0.932 g) and compound **2** (0.653 g) in DMF (1.0×10^{-5} m^3) at 140 °C overnight. The crude product was obtained as a precipitate in diethyl ether solution and then recrystallized from ethanol to give the phosphonium salt as a white powder. Yield: 60%; mp: > 400 °C. ^{1}H-NMR ($CDCl_3$, ppm, δ): 7.79–7.71 (m, 30H, P-ArH), 7.50 (d, 2H, ArH), 7.10 (d, 2H, ArH), 6.94 (s, 2H, ArH), 5.44 (d, 4H, CH_2-P), 1.54 (q, 4H, CH_2), 0.07 (t, 6H, CH_3).

The polymerization of **P1** and **P2** were through the Wittig polycondensation reaction. For **P1**, a solution of 0.5596 g of diphosphonate **3** and 0.1956 g of dialdehyde **4-I** in 1.0×10^{-5} m^3 of chloroform was prepared. Sodium methoxide (0.1844 g) was dissolved in 1.0×10^{-5} m^3 ethanol and then carefully dropped into the solution of monomers. After 24 h, the polymer product was precipitated from methanol. The crude polymer was filtered and then purified by a Soxhlet extraction in methanol for 2 days to yield a yellow powder (0.13 g, 39 % yield). ^{1}H-NMR ($CDCl_3$, ppm, δ):

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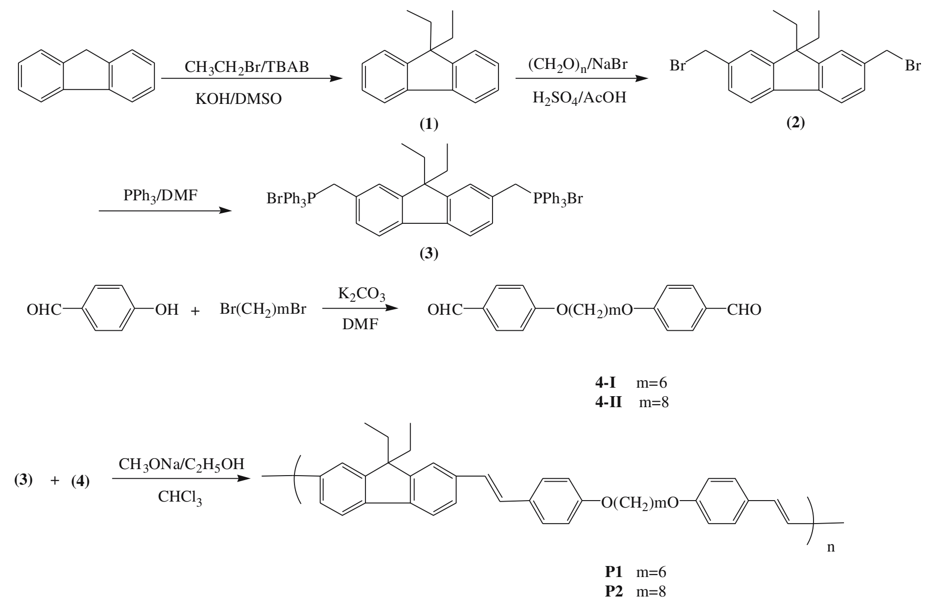


Scheme 1 Synthetic routes to the monomers and copolymers

7.84–7.26 (m, 8H, ArH), 7.23–7.00 (m, 6H, ArH), 6.98–6.76 (m, 4H, HC=CH), 4.00 (t, 4H, OCH_2), 2.08–1.26 (m, 12H, CH_2), 0.33 (s, 6H, CH_3). FTIR (KBr, cm^{-1}): 961 (trans HC=CH), 880 (cis HC=CH).

For **P2,** yield: 43%. ^{1}H-NMR ($CDCl_3$, ppm, δ): 7.84–7.26 (m, 8H, ArH), 7.23–7.00 (m, 6H, ArH), 6.98–6.72 (m, 4H, HC=CH), 4.03 (t, 4H, OCH_2), 2.08–1.26 (m, 16H, CH_2), 0.35 (s, 6H, CH_3). FTIR (KBr, cm^{-1}): 961 (trans HC=CH), 882 (cis HC=CH).

Both of the two synthesized copolymers were highly soluble in common organic solvents such as chloroform, tetrahydrofuran and toluene. They could be spin-coated onto ITO-glass giving highly transparent and homogeneous thin films. The weight-average molecular weights (*M*w), determined by gel permeation chromatography using polystyrene standards, were 6200 and 6100 with polydispersity index of 2.46 and 2.91 for **P1** and **P2**, respectively. Thermal properties of the polymers were evaluated by the means of TGA and DSC under nitrogen atmosphere. TGA measurements demonstrated that the two polymers possessed good thermal stability and the weight loss temperatures for **P1** and **P2** were 405 and 398 °C, respectively. The DSC showed glass transitions at 75 °C and 65 °C for **P1** and **P2**, respectively. For both of the two copolymers, neither a melting point nor any liquid crystal transition was observed in either the heating or cooling cycles, indicating that the polymers were amorphous.

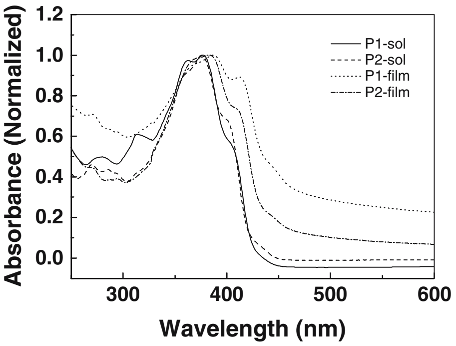


Fig. 1 UV absorption spectra of **P1**, **P2** in solution and as thin films

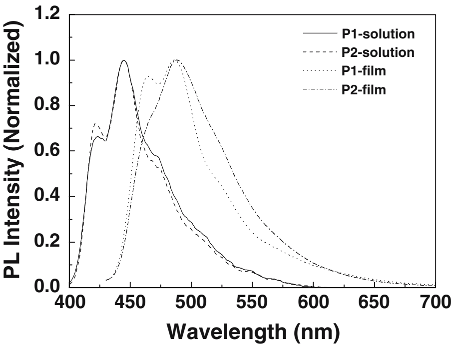


Fig. 2 PL spectra of **P1**, **P2** in solution and as thin films

The UV–visible absorption spectra and PL spectra of polymers both in dilute chloroform solutions and as thin films were measured. Figure 1 shows that the maximum UV–visible absorptions of **P1** and **P2** in solutions appear at approximately 377 nm and 379 nm, respectively. The absorption of the film samples show similar absorption profiles compared to those in solutions and the maxima are slightly red-shifted. Figure 2 shows the PL spectrum of **P1** in solution exhibit a

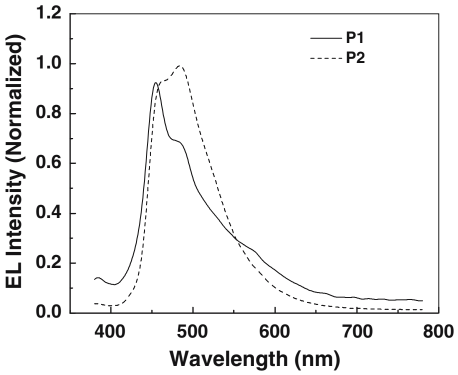


Fig. 3 Electroluminescene (EL) spectra of **P1** and **P2** with a configuration of ITO/PEDOT /copolymer/Ca/Al

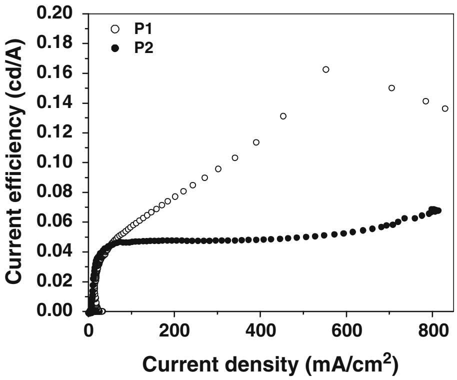


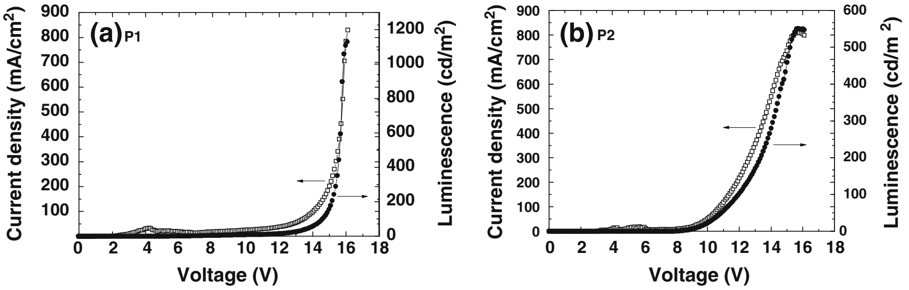
Fig. 5 Current-luminescence efficiency of PLEDs of P1 and P2 with a configuration of ITO/PEDOT/copolymer/Ca/Al

maximum at 444 nm and a shoulder at 420 nm, which red-shift to 487 and 459 nm in film, respectively, and become characteristically broader than those of solution spectrum. The PL spectrum of **P2** shows similar PL emission profiles in solution and in film state as compared to **P1**. As expected, the introduction of the non-conjugated aliphatic spacer interrupt the π–π* conjugated length of the backbone and cause the emission shift to blue region compared to the PFV homopolymer ($\lambda_{\max}$ = 507 nm) and copolymers ($\lambda_{\max}$ = 576–593 nm) in reference [6]. In addition, the long wavelength emission (about 530 nm) which usually appears in rigid PF derivatives [7, 8] is not observed in these two copolymers, indicating that the non-conjugated spacer reduces formation of aggregates or excimers in solid state. The quantum efficiency of two copolymers in chloroform solution was determined more than twice using dilute quinine sulfate as a standard [12]. The PL quantum yields of **P1** and **P2** in solution were determined as Φ_{sol} = 0.43 and 0.36, respectively.

The HOMO and the LUMO energy levels of the copolymers were measured by electrochemical cyclic voltammetry (CV) using SCE electrode as the reference electrode. All the copolymers exhibited irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.97 and 1.03 eV (vs SCE) for **P1** and **P2**, respectively, which correspond to HOMO energy levels of 5.71 and 5.77 eV. The band gaps of **P1** and **P2**, taken from the onset of the absorption spectrum, were 2.80 and 2.83 eV, respectively. The LUMO energy level was approximated by subtracting the optical band gap from the HOMO binding energy to be 2.91 and 2.94 for **P1** and **P2**, respectively. In comparison with PFV (E_{HOMO} = 5.34, E_{LUMO} = 2.75 eV) [6], the LUMO energy levels of the copolymers were reduced, indicating copolymers have improved electron-injection and transport properties.

The polymers light-emitting diodes (PLEDs) with the configuration ITO/PEDOT/copolymer/Ca/Al were fabricated to investigate the electroluminescent properties and the current-voltage-luminance characteristics of **P1** and **P2**. A PEDOT layer was spin-coated on top of the ITO and dried at 100 °C for 1 h under vacuum. A 90 nm layer of copolymers were spin-coated from their toluene solutions onto the PEDOT layer under nitrogen. A 10 nm thick calcium electron-injecting cathode was deposited on the polymer film through a mask by vacuum evaporation at a pressure less than 2.6×10^{-4} Pa, followed by a protective coating of aluminum for 180 nm. As shown in Fig. 3, the EL spectra of **P1** and **P2** are similar to PL emission in the solid state film with emission peaks at 459 nm and 486 nm, which blue shifts compared to the PFV copolymer in

Fig. 4 Current–voltage–luminescence (*I-V-L*) characteristics of PLEDs of **P1** (**a**) and **P2** (**b**) with a configuration of ITO/PEDOT /copolymer/Ca/Al



reference [6] due to the introduction of aliphatic non-conjugated segments into the main chain to confine the conjugated length. The voltage-current density and luminescence characteristics of the devices for copolymer **P1** and **P2** are shown in Fig. 4. In the forward bias, the turn-on voltages of **P1** and **P2** are 6.2 and 8.2 V, both are relatively higher than the PFV homopolymer and copolymers [6] due to the non-conjugated segments in the main chain. The maximum brightness and highest efficiency of **P1** were observed to be 1130 cd/m^2 and 0.16 cd/A, both are relatively higher than those of the PFV homopolymer and copolymers in reference [6]. The EL efficiency of **P2** shows good stability at high current density region. It should be noted that the present work has not attempted to modify the configurations and fabrication conditions of the devices. After the optimization of such parameters, higher emission efficiency of PLEDs are expected (Fig. 5).

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