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Defect-free Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-vinylene) for Polymer Light-Emitting Diode (PLED) Devices

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Abstract The π-conjugated light-emitting polymer poly (9,9-bis(2-ethylhexyl)fluorene-2,7-vinylene) (PEHFV), was synthesized in defect-free form via Horner-Emmons coupling. The structure and properties of the polymer were characterized by ^{1}H NMR, ^{13}C NMR, UV-vis, photo-luminescence (PL), and electroluminescence (EL) spectroscopies as well as gel permeation chromatography (GPC) and thermogravimetric analysis (TGA). The weight-average molecular weight (M_w) and polydispersity of the PEHFV were 34,000 g/mol and 2.3, respectively. The UV-vis spectra showed absorption maxima at 425 and 452 nm, and the PL emission spectra showed a maximum at 505 nm with a shoulder at 541 nm. The polymer was soluble in common organic solvents and easily spin-coated on indium-tin oxide (ITO)-coated glass substrates. A double-layer light-emitting device with an ITO/PEDOT:PSS/PFV/ Al configuration was fabricated. The turn-on voltage for the PEHFV device was observed at 3.0 V.

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Introduction

Polymer light-emitting diodes (PLEDs) are promising devices, especially for next generation active matrix displays. Solution deposition techniques, homogeneous large area thin films, reduced manufacturing process complexity, low-cost, high luminescence efficiency, large spectral range, and relatively simple device structures are some of the main reasons for an increased interest in polymer materials for LEDs [1]. Among the π-conjugated polymers, poly(*p*-phenylene vinylene) (PPV) [2] and poly(9,9-dialkylfluorene) (PF) [3] and their derivatives have been widely used for polymer LEDs. For PFs, few systematic studies have explored side-branching effects, [4] including possible effects of side-branching with respect to synthesis, MW and polydispersity, solubility, rheological properties, and end capping. This fact is surprising given that poly(2,7-fluorene)s with alkyl substituents attached to the C-9 position have been widely reported since 1989 [5–7]. In the case of PPV, different side-chain combinations of dialkoxy PPV derivatives showed an increase in EL efficiency with the length of the longest side chain [8]. The increase in efficiencies may be related to an increased chain-to-chain separation.

The goal of combining the attractive properties PF and PPV can be manifested in the study of polyfluorene vinylenes (PFVs). For both PPV and PFV, it is well known that the Gilch polymerization route has several advantages, including high yield, high molecular weight, low polydispersity, and facile design and availability of the monomers.

The Gilch route, however, suffers from the problem of having saturated defects along the chain backbone (predominantly tolane-bisbenzyl-type moieties analogous to those commonly found in samples of PPV) [9, 11]. Other published routes to PFVs are surprisingly few, although Heck coupling [10, 12, 14]. and acyclic diene metathesis (ADMET) polymerizations have been reported [15]. Both of these methods, however, require air-free conditions and the use of costly transition metal catalysts.

In the present study, we report the use of a simple Horner-Emmons reaction utilizing aromatic dialdehydes and diphosphonates to generate defect-free poly(9,9- bis (2-ethylhexyl) fluorene-2,7-vinylene) (PEHFV). The synthetic route [16, 17] and polymer structures are shown in Scheme 1 [18]. The samples obtained were of high molecular weight with no detectable saturated defects along the conjugated backbone [9, 11, 16, 17]. PLED devices with the defect-free PEHFV as the light-emitting layer were prepared and their electro-optical properties were characterized.

Experimental

Materials Fluorene, *n*-butyllithium (2.5 M in hexane), 1-bromooctane, potassium *tert*-butoxide (1 M solution in THF), bromine, copper cyanide, diisobutylaluminum hydride (DIBAL-H) in toluene, sodium borohydride, thionyl chloride, and triethyl phosphite were purchased from Aldrich Chemical Co. and used without further purification unless otherwise noted. THF was dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Dichloromethane and DMF were distilled over CaH$_2$, and column chromatography was performed using silica gel (Merck, 250–430 mesh).

Syntheses of monomers and polymers The strategy used to synthesize and polymerize the custom-designed monomers is illustrated graphically in Scheme 1. Details of analogous synthetic procedures can be found in a previous report [16].

9,9-Bis(2-ethylhexyl)fluorene (1). Compound **1** was obtained as a pale brown oil (99%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.72 (d, J=7.3 Hz, 2H, aromatic), 7.41 (d, 2H, J=7.3 Hz, 2H, aromatic), 7.23–7.37 (m, 4H, aromatic), 2.03 (m, 4H, α-CH$_2$), 1.28 (m, 2H, β-CH), 0.60–0.97 (m, 16H, alkyl), 0.54 (t, J=7.4 Hz, 12H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.1, 141.9, 127.2, 126.9, 124.6, 120.1, 55.4, 45.1, 34.2, 28.7, 27.4, 23.2, 14.5, 10.8.

2,7-Dibromo-9,9-bis(2-ethylhexyl)fluorene (2). Under argon, 39 g (0.10 mol) of 9,9-bis(2-ethylhexyl)fluorene was

placed in a 500 mL round-bottomed flask. After the addition of 300 mL of dry DMF, 15 mL (0.30 mol) of bromine was added slowly. The mixture was allowed to react for 20 h at rt, and then saturated NaHSO$_3$ was added until the red color disappeared. The mixture was extracted three times with 200 mL of diethyl ether. The organic extracts were combined, washed with brine, and dried with magnesium sulfate. Upon filtering the solution and evaporating the solvent, a viscous yellow oil was obtained and used without further purification or analysis.

2,7-Dicyano-9,9-bis(2-ethylhexyl)fluorene (3). Pale yellow crystalline **3** (0.43 g, 54%) was obtained upon removal of the solvent under vacuum. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.85 (d, J=8.2 Hz, 2H, aromatic), 7.67–7.73 (m, 4H, aromatic), 2.03 (m, 4H, α-CH$_2$), 0.58–1.00 (m, 22H, alkyl), 0.26–0.56 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 152.5, 144.1, 132.1, 128.4, 121.9, 119.6, 111.9, 56.3, 44.8, 35.3, 34.1, 28.5, 27.4, 23.1, 14.4, 10.7.

9,9-Bis(2-ethylhexyl)fluorene-2,7-dicarboxaldehyde (4). Compound **4** was obtained as a yellow oil (0.76 g, 85%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 10.09 (s, 2H, –CHO), 7.89–8.00 (m, 6H, aromatic), 2.10 (m, 4H, α-CH$_2$), 0.57–0.94 (m, 22H, alkyl), 0.36–0.52 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 192.5, 153.3, 146.2, 136.4, 130.5, 125.3, 121.8, 55.9, 44.8, 35.3, 34.1, 28.5, 27.5, 23.1, 14.4, 10.7.

2,7-Bis(hydroxymethyl)-9,9-bis(2-ethylhexyl)fluorene (5). Compound **5** was obtained as colorless crystals (0.78 g, 87%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.65 (d, J=7.7 Hz, 2H), 7.38 (s, 2H), 7.30 (d, J=7.7 Hz, 2H), 4.74 (s, 4H, CH$_2$OH), 1.97 (m, 4H), 1.59 (s, 2H, CH$_2$OH), 0.59–0.98 (m, 22H, alkyl), 0.42–0.56 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.9, 141.4, 136.3, 128.3, 125.1, 120.2, 55.5, 47.5, 44.8, 35.2, 34.5, 28.7, 27.5, 23.1, 14.5, 10.7.

2,7-Bis(chloromethyl)-9,9-bis(2-ethylhexyl)fluorene (6). Compound **6** was obtained as a white crystalline solid (31.5 g, 93%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.65 (d, J=7.7 Hz, 2H), 7.41 (s, 2H), 7.32 (d, J=7.7 Hz, 2H), 4.66 (s, 4H, CH$_2$Cl), 1.99 (m, 4H), 0.62–0.99 (m, 22H, alkyl), 0.37–0.56 (m, 8H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.9, 141.4, 136.5, 128.0, 125.1, 120.4, 55.5, 47.4, 44.8, 35.2, 34.5, 28.7, 27.5, 23.2, 14.5, 10.8.

2,7-Bis(methylenediethylphosphate)-9,9-bis(2-ethylhexyl)fluorene (7). Compound **7** was obtained in crude form (2.2 g, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.58 (d, J=7.7 Hz, 2H), 9.29 (s, 2H), 7.23 (d, J=7.7 Hz, 2H), 3.87–4.19 (m, 8H, OCH$_2$CH$_3$), 3.20 (d, J_{PH} = 21.8 Hz, CH$_2$P), 1.95 (m, 4H), 1.25 (m, 12H, OCH$_2$CH$_3$), 0.59–0.98 (m, 22H, alkyl), 0.40–0.58 (m, 8H) ^{13}C NMR (75 MHz, CDCl$_3$): δ 151.6, 140.3, 130.2, 128.9, 126.0, 120.0, 62.5, 55.3, 45.5, 35.5, 35.1, 33.8, 28.6, 27.2, 23.2, 16.9, 14.5, 10.6.

Poly(9,9-bis(2-ethylhexyl)fluorene-2,7-vinylene) via Horner-Emmons Coupling. As shown in Scheme 1, the
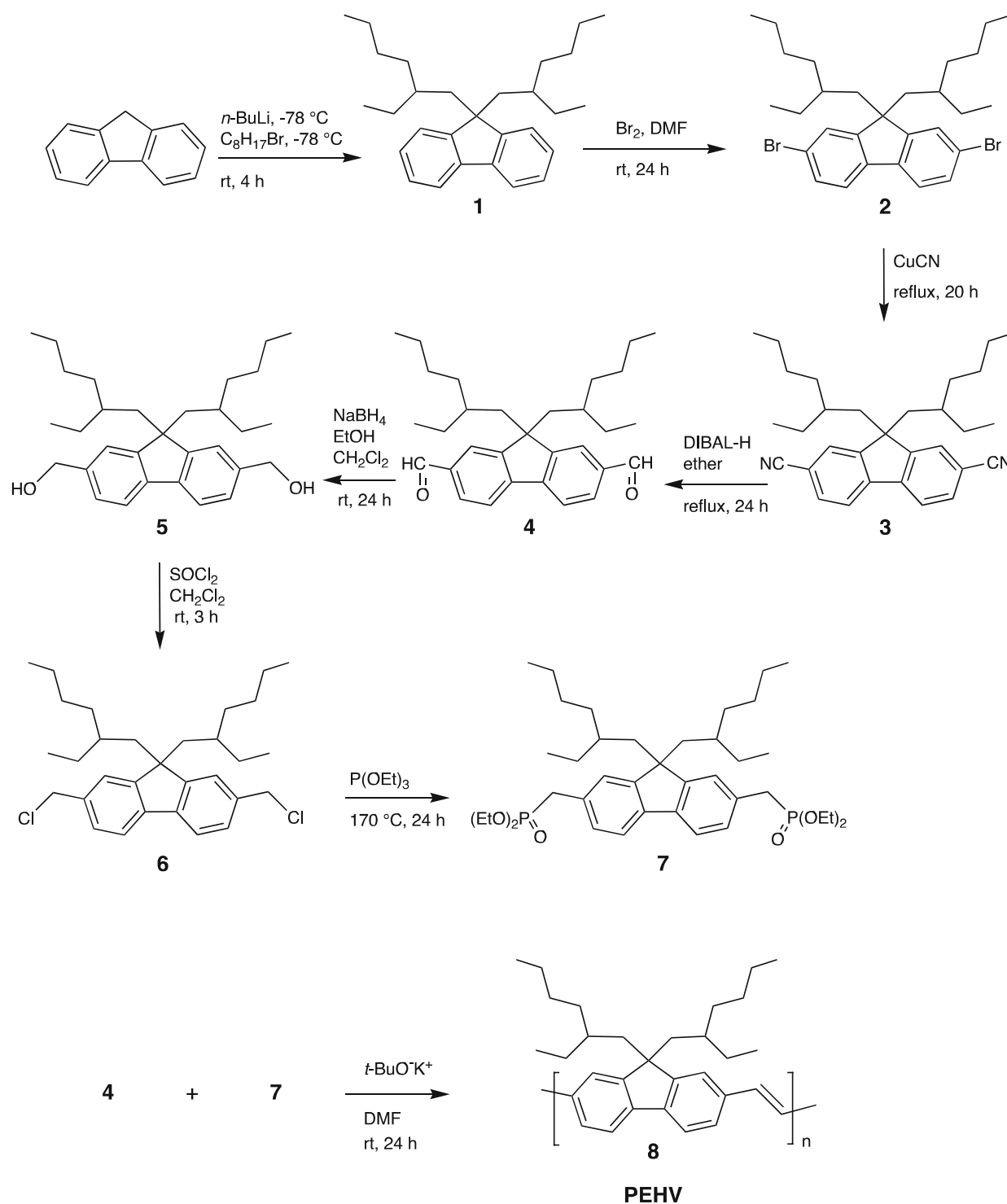
Scheme 1 Strategy for synthesizing monomers and polymers

dicarboxyaldehyde (0.99 g, 1.4 mmol) and crude **7** were dissolved in 50 mL of anhydrous DMF under nitrogen. To this solution, potassium *tert*-butoxide (10 mL of a 1 M solution in THF) was added. The reaction was stirred overnight at rt under nitrogen. The polymer was precipitated into 400 mL of methanol, and the mixture was centrifuged. The supernatant was decanted, and the poly-mer residue was re-dissolved in a minimum amount of THF. The crude polymer was then successively re-precipitated using methanol, isopropyl alcohol, and hexane to remove small molecule impurities and/or oligomers. The final product was dried under vacuum overnight to afford PFV as a bright yellow-green solid (79%). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 7.16–7.83 (m, 8H, aromatic &

vinylic), 1.94–2.21 (m, 4H, α-CH_2), 0.74–1.13 (m, 18H, alkyl), 0.62–0.75 (m, 6H), 0.43–0.62 (m, 6H).

Measurements ^{1}H and ^{13}C NMR spectra were recorded using a General Electric QE-300 spectrometer (300 MHz), and chemical shifts were recorded in ppm. The data were processed using NUTSNMR Utility Transform Software (Acron NMR). The UV-vis spectra were recorded on a Perkin Elmer Lambda 19 UV-VIS-NIR spectrophotometer with baseline corrections and normalizations carried out using WinLab software. Photoluminescence spectra were collected on a USB2000 Miniature Fiber Optic Spectrometer. We used OOIBase32 Spectrometer Operating Software to collect and display data obtained from the USB2000 instrument.

Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) relative to calibrated polystyrene standards using a Waters Styragel HR 5E column (7.8×300 mm) and both a Waters 410 Differential Refractometer and a Waters 996 Photodiode Array Detector. Thermogravimetric analysis (TGA) data were collected using a Perkin-Elmer TGA-7 under nitrogen, while differential scanning calorimetry (DSC) data were collected using a Perkin-Elmer DSC-7 under nitrogen at a heating rate of 10 °C/min. Clean ITO was treated with O_2 plasma for 100 to 210 s before use. Films of PEDOT:PSS (Baytron) were prepared by spin casting a solution containing 0.5% by weight of the polymer in THF at a speed of 1,500 rpm for 120 s under ambient conditions. A film of aluminum was then deposited on top of the polymer film through a shadow mask by vacuum evaporation at a pressure of less than 4×10^{-6} Torr. For characterization of the device performance, current-voltage (I–V) curves were measured with a Keithley 236 programmable source meter.

Results and discussion

Synthesis and characterization of monomers and polymers Fluorene-based polymers can be easily functionalized with substituents at the C-9 position. The electronic and optical properties of the conjugated polymer can then be tuned by modifying the structure of the polymer backbone, which can shift the energy levels of the HOMO and LUMO. For poly(9,9-bis(2-ethylhexyl)fluorene-2, 7-vinylene), we adjusted the energy levels by introducing a vinylene group via Horner-Emmons coupling of the aromatic dialdehydes and diphosphonates shown in Scheme 1. The Horner-Emmons reaction was used because we wished to generate an alternating fluorene vinylene homopolymer with no saturated defects along the conju-
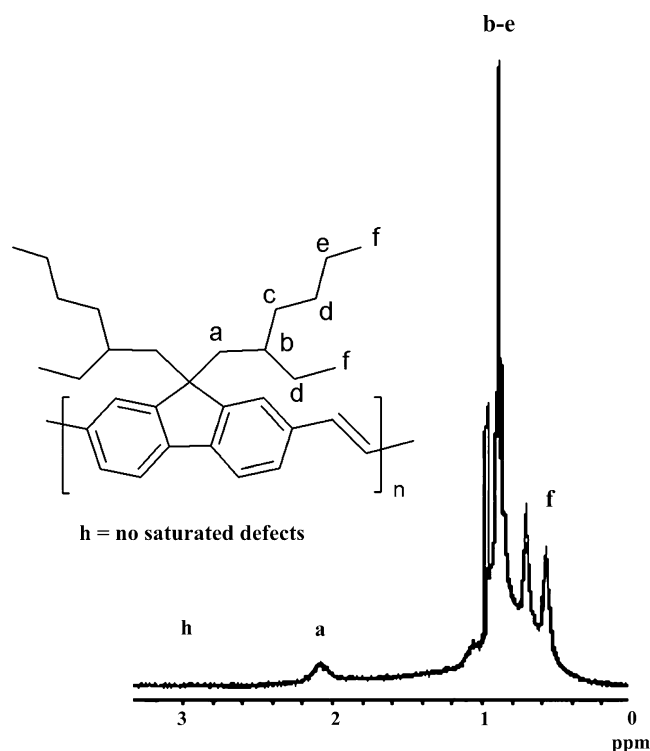
Fig. 1 ^{1}H-NMR spectrum of PEHFV prepared by Horner-Emmons coupling

gated backbone [16, 17]. The molecular structures of the monomer and the corresponding polymer were identified by ^{1}H-NMR spectroscopy. Figure 1 highlights the region between 0.0 and 3.5 ppm for PEHFV, showing no detectable resonances near 3.1 ppm that are characteristic of saturated defects [9, 11, 16]. We thus conclude that our synthesis strategy gives PEHFV with no detectable saturated defect along the conjugated backbone. In the case of Gilch polymerization [16], a small resonance at 3.1 ppm is typically observed [11, 16]; this resonance has been assigned to Ar–CH_2–CH_2–Ar defects along the chain backbone. The PEHFV also showed a monomodal distri-
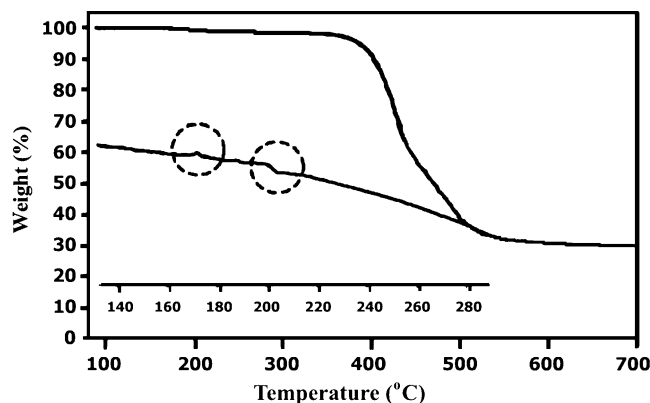

Fig. 2 TGA and DSC thermograms of PEHFV prepared by Horner-Emmons coupling

bution with a number-average molecular weight (M_n) of ~34,000 and a weight-average molecular weight (M_w) of ~78,000 to give a PDI=2.3 as determined by GPC with THF as the eluent.

The thermal behavior of the resulting polymers was investigated by TGA. Shown in Fig. 2 are the TGA thermograms of the synthesized polymers obtained under nitrogen. The PEHFV samples exhibited good thermal stabilities, losing their weight at less than 3% on heating to approximately 400 °C under nitrogen, but lose about 68% of their weight at 450–480 °C. The high thermal stability of the present polymers should prevent chain deformation and degradation of the emitting layer by current-induced heating during the operation of EL devices. On the basis of these results, it might be expected that the PEHFV synthesized in the present work, which has a highly rigid backbone and long flexible alkyl groups on the side chain, would form liquid crystalline structures. The DSC measurements showed glass transitions at around 170–230 °C for this PFV with a branched-chain substituent at the C-9 position. However, we found no evidence of a significant mesophase or liquid crystalline texture in the analyses by DSC and polarized microscopy.

Optical and photoluminescence properties The UV-vis absorption spectra of the PEHFV prepared via Horner-Emmons polymerization at a concentration of 4.8×10^{-5} M is shown in Fig. 3. The sample of PEHFV exhibits a broad absorption with three discernable λ_{max} bands having increasing intensities at ~400 nm, 425 nm, and 452 nm, respectively. These bands can be attributed to π-π* transitions of the conjugated backbone that are vibrationally split and consistent with extended delocalization between the fluorene and vinylene units [11, 12, 14, 19].
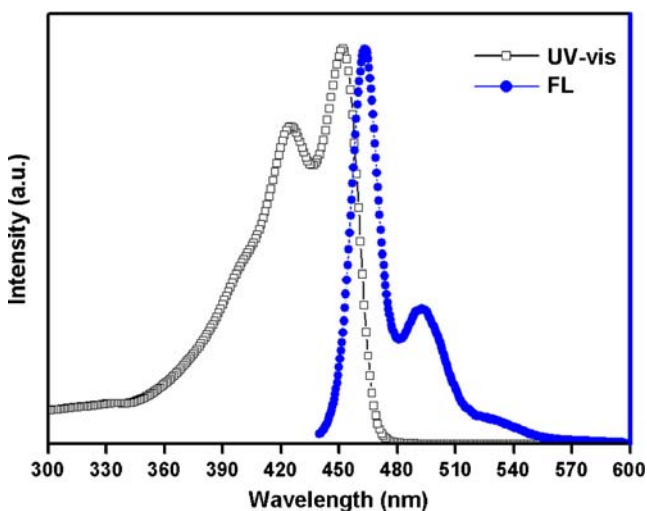
Fig. 3 Absorption spectra and fluorescence (1.0×10^{-6} M, excitation at 428 nm) in THF at room temperature of PEHFV prepared by Horner-Emmons coupling
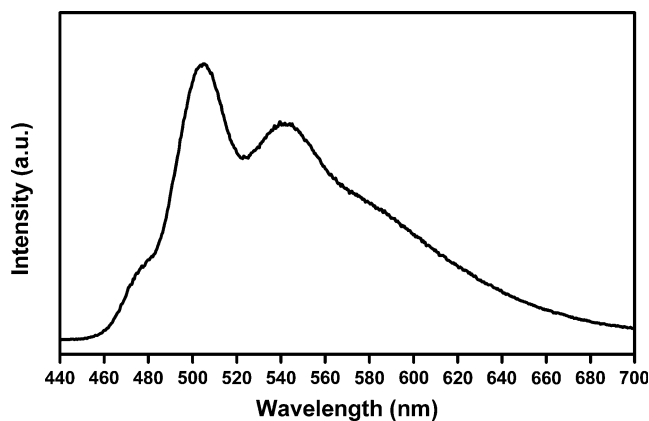

Fig. 4 Photoluminescence of PEHFV in solid form (powder) at room temperature (excitation at 370 nm)

We note further that the absorption spectrum for the PEHFV produced here is identical to that reported for other PFVs prepared via ADMET [15] and Horner-Emmons coupling [16, 17]. Taken together with the NMR data above, we conclude that PFVs prepared via Horner-Emmons coupling and ADMET polymerization afford polymers that are free of saturated defects along the backbone.

The fluorescence (FL) spectrum is characterized by three discernable emission bands having decreasing intensities at 453 nm, 483 nm, and ~515 nm, respectively; the pattern of these bands also reflects the influence of vibronic coupling [12, 14, 19]. The photoluminescence (PL) spectrum obtained for the sample of PEHFV deposited as a film is shown in Fig. 4. The major emission bands in the spectrum appear at ~475 nm, 505 nm, 540 nm, and ~575 nm. The red shift of these vibronically coupled maxima relative to those in solution is consistent with previous studies of PFVs and related materials [12, 14, 19].

Electroluminescence and current-voltage-luminescence (I-V-L) characteristics The LED structure consisted of an
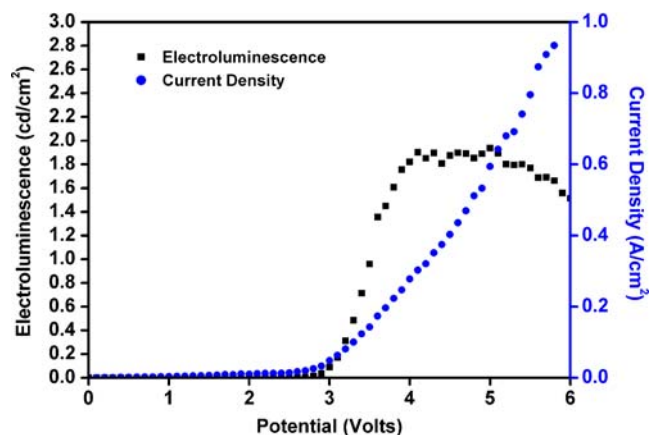
Fig. 5 Current and electroluminescence versus voltage profile of the ITO/PEDOT:PSS/PEHFV emitting layer/Al device

aluminum contact on the surface of the polymer, which was spun-cast on the ITO surface from a solution of PEHFV in THF. Aluminum was then deposited on the surface by vacuum evaporation at pressures of $\sim 10^{-6}$ Torr, yielding a circular active layer with a diameter of 0.075 cm^2. Figure 5 show the current-electric field strength (*I-V-L*) and the luminescence-electric field strength (*L-V-L*) characteristics, respectively, of a single-layer light-emitting diode consisting of ITO/PEDOT:PSS/PFV/Al. The current was observed to increase with increasing forward bias voltage, which indicated typical rectifying characteristics. The I–V data consisted of a linear plot, but for the 0–6 V range only. The plot in Fig. 5 shows that the device is a typical diode because the I–V curve increases exponentially with voltage. The turn-on voltage is readily apparent at $\sim$3.0 V collected with a photomultiplier tube (PMT) simultaneously with the collection of the I–V data. The EL was measured for a PEHFV polymer LED over the full range of voltages, including the turn-on voltage and the breakdown voltage. Figure 5 also shows the EL–V data, but again for the 0–6 V range only. The EL–V curve increases exponentially with voltage and then levels off at higher voltages (and correspondingly higher current densities), which is consistent with the behavior reported for related OLED devices [20]. The turn-on voltage is again readily apparent at $\sim$3.0 V, which is relatively low (good), considering that the device was prepared under ambient conditions. The PEHFV showed high EL power at low threshold voltage due to the enhanced *p*-electron delocalization of the fluorene group. Finally, we calculated the luminous efficiency to be 6.5 cd/A at an operating voltage of 4 V. Importantly, the magnitude of the observed electroluminescence is more than 100 times greater that found in commercial OLED-based displays [21].

It is known that the contacts between the polymer and the electrodes strongly influence device efficiency. One optimization strategy is to modify the ITO surface with a thin layer of conducting polymer such as polyaniline [22] or poly(3,4-ethylene dioxythiophene) (PEDOT) [23]. The presence of a thin PEDOT interlayer can improve the device efficiency by an order of magnitude or more. The fluorene and vinylene repeat units influence both the HOMO and the LUMO energy levels. These energy levels realize efficient hole and electron injection from both electrodes [24].

Conclusions

Horner-Emmons coupling proved to be an efficient synthetic route for the preparation of electroluminescent PEHFV. UV-vis absorption spectra in THF of the PEHFV showed dual absorption maxima at 425 and 452 nm attributed to π-π* transitions of the conjugated backbone. Upon excitation in THF, the polymer exhibited a greenish fluorescence (λ_{max} emission = 463 nm with shoulder at 496 nm). Similarly, photoluminescence spectra of powder samples showed λ_{max} emission = 505 nm with a shoulder at 540 nm. The PEHFV samples showed high thermal stability up to 400 °C and exhibited a high glass transition temperature, which might be key in preventing deformation and degradation of the emitting layer by current-induced joule heating during the operation of PEHFV-based electroluminescence devices.

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