

New light-emitting poly{(9,9-di-*n*-octylfluorenediyl vinylene)-*alt*-[1,5-(2,6-dioctyloxy)naphthalene vinylene]}

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Abstract

A new conjugated light-emitting AB copolymer containing alternating fluorene and naphthalene units, poly{(9,9-di-*n*-octylfluorenediyl vinylene)-*alt*-[1,5-(2,6-dioctyloxy)naphthalene vinylene]} (PFV-*alt*-PNV), was synthesized via Horner-Emmons polymerization. The polymer is completely soluble in common organic solvents and exhibits good thermal stability up to 400 °C. UV-visible, fluorescence and photoluminescence measurements of the copolymer show peak maxima at 427, 500 and 526 nm, respectively. A light-emitting device containing the new polymer was fabricated using a simple indium tin oxide configuration: (ITO)/PEDOT:PSS/PFV-*alt*-PNV/Al. Measurements of current *versus* electric field were carried out, with an onset of light emission occurring at 2.5 V. The electroluminescence brightness was observed to reach a maximum of 5000 cd m⁻².

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Keywords: poly{(9,9-di-*n*-octylfluorenediyl vinylene)-*alt*-[1,5-(2,6-dioctyloxy)naphthalene vinylene]} (PFV-*alt*-PNV); Horner-Emmons polymerization; light-emitting polymer

INTRODUCTION

During the past decade, an explosive growth of activity in the area of organic electroluminescence has occurred in both academia and industry.^{1,2} As potential base materials in organic light-emitting diodes (OLEDs), conjugated polymers have been widely explored. For example, since the discovery of electroluminescence in poly(*p*-phenylene vinylene) (PPV),^{3,4} a wide variety of conjugated and semi-conjugated polymers have been used as the active emissive layer in OLED devices.^{5–8}

Studies have also shown that device efficiencies can be improved by various modifications, including the use of copolymers,^{3,4} variation of metal contacts⁹ and the use of heterostructures.^{4,5} With regard to polymer type, polyfluorenes (PFs) have been found to be particularly attractive active components in OLEDs because of their thermal and chemical stability and their exceptionally high solution and solid-state fluorescence quantum yields.^{10–13} Furthermore, facile substitution at the 9-position of monomeric fluorenes allows control over the physical properties of the corresponding polymer, including solubility, processability and thin-film morphology.^{14–16}

In efforts to enhance device lifetime and to allow tunability of the electronic properties of PFs, researchers have explored the introduction of comonomer units into the PF backbone.¹³ Others have explored the similar modification of 2,7-linked poly(fluorene vinylene)s (PFVs) by introducing phenylene vinylene units as the hole-transporting moiety, which leads to improved light-emitting efficiency compared to the parent PFs.^{17–19} Along these lines, we wished to explore the incorporation of naphthalene vinylene units into the conjugated backbone of defect-free PFVs.^{20,21} Naphthalene vinylene is an attractive component because it is bulky, electron rich and known to influence the band structure and

molecular conformation of PPVs in a predictable and systematic manner.^{22–24} For example, the presence of naphthalene vinylene units has been shown to cause a strong blue shift in the emission due to torsional twisting of the chain backbone induced by the bulky naphthalene ring, which reduces the planarity and leads to a reduction in the conjugation length.^{22–24} While there are multiple reports of the incorporation of 1,4-, 1,5- and 2,6-linked naphthalene vinylene units into PPVs,^{22–26} to our knowledge, there is only one report of the incorporation of naphthalene vinylene units into PFVs,²⁷ where three examples were prepared in which the conjugation proceeded through the 1,4-, 2,3- and 2,6-positions of the naphthalene ring.

Based on these considerations, we report here a new class of conjugated copolymer that incorporates alternating 2,7-linked fluorene vinylene units and 1,5-linked naphthalene

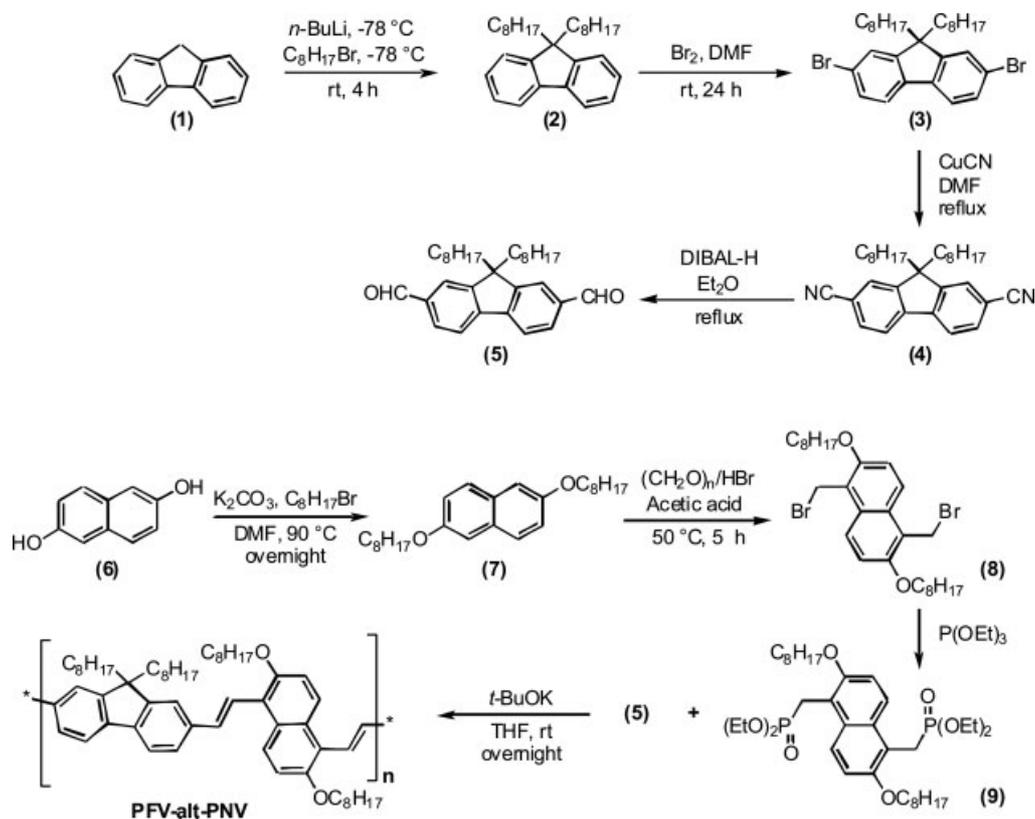
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Scheme 1. Strategy used to prepare monomers and polymer.

vinylene units. Specifically, we used Horner–Emmons coupling to prepare poly{[(9,9-di-*n*-octylfluorenyl vinylene)-*alt*-[1,5-(2,6-dioctyloxy)naphthalene vinylene]} (PFV-*alt*-PNV) as shown in Scheme 1. The structure and molecular weight of the polymer were characterized using ^1H NMR and ^{13}C NMR spectroscopy and gel permeation chromatography (GPC), respectively. The optical properties were characterized using UV-visible, fluorescence and photoluminescence measurements. We also fabricated a light-emitting device containing the new polymer and measured the current *versus* voltage characteristics and the electroluminescence brightness.

EXPERIMENTAL

Instrumentation

^1H NMR and ^{13}C NMR spectra were recorded using a General Electric QE-300 spectrometer (300 and 75 MHz, respectively). The data were processed and analyzed using NUTSNMR Utility Transform software (Acron NMR). Chemical shifts are reported in δ (ppm) relative to residual protons in the deuterated solvent. Molecular weights and dispersities ($D = M_w/M_n$) were measured using GPC with tetrahydrofuran (THF) as eluent and calibrated against polystyrene standards. Molecular weight chromatograms were collected using a Waters Styragel HR 5E column (7.8×300 mm) and analyzed using both a Waters 410 differential refractometer and a Waters 996 photodiode array detector. The data were processed using Waters Millennium 2010 Chromatography Manager GPC software (version 2.0). UV-visible spectra were measured in THF using a Varian Cary 50 Scan UV-visible spectrophotometer and normalized using Cary Scan software. Fluorescence spectra were collected in THF using a PerkinElmer LS 50B luminescence

spectrophotometer and processed using FL WinLab software (version 3.0). Photoluminescence spectra were collected from solid-state (powder) samples using a USB2000 Ocean Optics spectrometer and processed using OOIBase32 software.

Materials

The starting materials and reagents bromine, 1-bromooctane, *n*-butyllithium (2.5 mol L^{-1} in hexane), copper cyanide, 2,6-dihydroxynaphthalene, diisobutylaluminium hydride (DIBAL-H; 1.5 mol L^{-1} solution in toluene), fluorene, potassium *tert*-butoxide (1 mol L^{-1} solution in THF), sodium borohydride and thionyl chloride were purchased from either Acros or Aldrich Chemical Co. and used without further purification unless otherwise noted. In synthetic manipulations, the solvents diethyl ether and THF were dried by distillation from sodium/benzophenone under argon. The solvents *N,N*-dimethylformamide (DMF) and dichloromethane were similarly distilled from CaH_2 under argon. Column chromatography was performed using 250–430 mesh silica gel (Merck).

Device fabrication and testing

The configuration of our testing device is shown schematically in Fig. 1. Glass substrates coated with indium tin oxide (ITO) and with an initial resistance of ca $0.3 \Omega \text{ sq}^{-1}$ were obtained from SPI Supplies. After partitioning into 2.54×2.54 cm squares, the ITO pieces were sonicated sequentially for 15 min in detergent followed by repeated rinsing with deionized water, acetone and isopropanol. The ITO was then covered with two strips of Scotch brand tape as a mask against acid etching, which was performed by placing the slides in a 1 : 1 solution of H_2O and HCl for 20 min. After etching, the substrates were sonicated

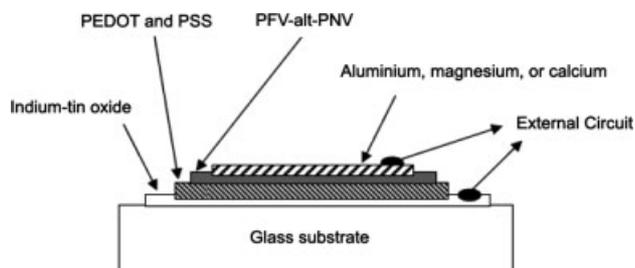


Figure 1. Configuration of our double-layer PLED devices.

for 15 min in deionized water, acetone and isopropanol. The substrates were then plasma-cleaned under oxygen for 5 min. An aqueous solution of poly[3,4-(ethylenedioxy)thiophene]-*co*-poly(vinylbenzenesulfonic acid) (PEDOT:PSS; Baytron P, Bayer Corp.) was filtered through a 0.45 μm poly(vinylidene fluoride) syringe filter prior to use. The PEDOT:PSS solution was spin-coated onto the substrates at 1500 rpm using a Speedline Technologies P6204 spin-coater. After spin coating, the PEDOT:PSS-coated substrates were baked at 60 °C for 2 h in a vacuum oven to remove any traces of water, which can lead to degradation of the device. A solution of PFV-*alt*-PNV (0.5 mg mL⁻¹ in THF) was spin-coated on top of the PEDOT:PSS layer. The substrates were placed under vacuum with no heat for 1 h. Thermal evaporation of aluminium was performed below 10⁻⁶ torr using an Edwards E306 thermal evaporator. The active sections of the devices were then covered with an epoxy resin and allowed to dry so that these regions were shielded from exposure to oxygen during the testing of the devices.

Testing was performed using a Keithley 236 source meter unit, a Hamamatsu photonics photomultiplier, and a home-written LabView program. Current–voltage–luminescence data were collected from 0 to 10 V in steps of 0.10 V. To provide balanced charge injection and to improve the efficiency of the devices, double-layer polymer light-emitting diodes (PLEDs) were constructed in which a hole-transporting and an electron-transporting/emitting layer were successively deposited onto the ITO anode as shown in Fig. 1. This configuration affords control over the electron and hole injection rates by creating barriers to charge transport at the heterojunction between the two semiconducting layers.²⁸

Syntheses of monomers and polymer

The target polymer (PFV-*alt*-PNV) was prepared using the strategy shown in Scheme 1. While the preparation of compounds 2–5 has been described,^{20,21} and compound 6 is commercially available, we provide in the following paragraphs experimental details of the synthesis of compounds 7–9 as well as that of the final coupling step leading to PFV-*alt*-PNV.

Synthesis of 2,6-bis(octyloxy)naphthalene (7)

Potassium carbonate (81.6 g, 0.590 mol) was added to a mixture of 2,6-dihydroxynaphthalene (30.0 g, 0.190 mol) and octyl bromide (97.5 g, 0.505 mol) in 400 mL of DMF, and the resulting solution was stirred at 90 °C overnight. The solution was poured into 700 mL of water, and the resulting precipitate was collected by filtration, washed with water and methanol, and then dried. The crude product was recrystallized from methanol to give compound 7 as a light gray solid (41.3 g, 0.107 mol, 67% yield).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 7.60–7.63 (d, J = 8.8 Hz, 2H, naphthyl), 7.06–7.12 (m, 4H, naphthyl), 4.04 (t, J = 6.7 Hz, 4H, OCH₂), 1.83 (m, 4H, OCH₂CH₂), 1.41–1.56 (m, 4H, OCH₂CH₂CH₂), 1.23–1.41 (m, 16H, alkyl), 0.89 (t, J = 7.2 Hz, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃; δ , ppm): 156.1, 130.2, 128.5, 119.7, 107.4, 68.6, 32.4, 29.9, 29.84, 29.79, 26.6, 23.2, 14.6.

Synthesis of 1,5-bis(bromomethyl)-2,6-bis(octyloxy)naphthalene (8)

Compound 7 (9.0 g, 0.023 mol), paraformaldehyde (1.87 g, 0.0623 mol) and a 12.4 mL aliquot of 33% HBr in acetic acid (0.210 mol) were added to 40 mL of acetic acid. The mixture was heated to 50 °C for 5 h and then cooled to room temperature. The resulting light purple precipitate was filtered, washed with water and methanol, and then dried. The crude product was recrystallized from hexane to give compound 8 as off-white needle-like crystals (9.0 g, 0.016 mol, 58% yield).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 8.00–8.03 (d, J = 9.4 Hz, 2H, naphthyl), 7.25–7.30 (d, J = 9.4 Hz, 2H, naphthyl), 5.05 (s, 4H, CH₂Br), 4.16 (t, J = 6.6 Hz, 4H, OCH₂), 1.87 (m, 4H, OCH₂CH₂), 1.46–1.59 (m, 4H, OCH₂CH₂CH₂), 1.21–1.43 (m, 16H, alkyl), 0.88 (t, J = 6.7 Hz, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃; δ , ppm): 153.8, 128.3, 126.0, 119.5, 116.1, 70.0, 32.4, 30.1, 29.9, 29.8, 26.6, 25.8, 23.2, 14.7.

Synthesis of 2,6-bis(octyloxy)-1,5-bis(methylenediethyl phosphate)naphthalene (9)

A 50 mL round-bottomed flask containing compound 8 (8.0 g, 0.014 mol) and triethyl phosphite (13 mL, 0.076 mol) was heated to 100 °C for 4 h. The excess triethyl phosphite was then removed by distillation. The crude product was purified by column chromatography on silica gel using 10:90 acetone:methylene chloride as the eluent to give a light orange solid, which was recrystallized from hexane to give pure compound 9 as off-white needle-like crystals (5.0 g, 0.0073 mol, 51% yield).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 8.00–8.03 (d, J = 9.6 Hz, 2H, naphthyl), 7.26–7.32 (d, J = 9.6 Hz, 2H, naphthyl), 4.10 (t, J = 6.6 Hz, 4H, OCH₂), 3.86–4.01 (m, 8H, OCH₂CH₃), 3.67–3.75 (d, J = 22.0 Hz, 4H, PCH₂), 1.84 (m, 4H, OCH₂CH₂), 1.43–1.57 (m, 4H, OCH₂CH₂CH₂), 1.21–1.42 (m, 16H, alkyl), 1.15 (t, J = 7.2 Hz, 12H, OCH₂CH₃), 0.89 (t, J = 7.2 Hz, 6H, CH₃). ¹³C NMR (75 MHz, CDCl₃; δ , ppm): 153.3, 129.4, 125.7, 115.3, 114.3, 114.2, 69.9, 62.4, 32.3, 30.2, 30.0, 29.8, 29.4, 26.6, 25.3, 23.5, 23.2, 16.9, 16.8, 14.6.

Synthesis of PFV-*alt*-PNV

Dicarboxyaldehyde 4 (0.11 g, 0.25 mmol) and diphosphate 9 (0.16 g, 0.23 mmol) were dissolved in 50 mL of anhydrous THF under nitrogen, and a 2 mL aliquot of a 1 mol L⁻¹ THF solution of potassium *tert*-butoxide (2 mmol) was added. The mixture was stirred overnight at room temperature under nitrogen. The resulting polymer was precipitated into 200 mL of methanol, and the mixture was centrifuged. The supernatant was decanted, and the residue was re-dissolved in a minimum amount of THF. The crude polymer was then successively re-precipitated into methanol and propanol. The purified polymer was dried under vacuum overnight to afford PFV-*alt*-PNV as a bright yellow solid (0.064 g, 0.078 mmol, 34% yield).

¹H NMR (300 MHz, CDCl₃; δ , ppm): 8.2–8.4 (d, J = 9.8 Hz, 2H, naphthyl), 7.5–7.8 (m, 8H, fluorenyl and vinyl), 7.3–7.4 (m, 4H, naphthyl and fluorenyl or vinyl), 4.18 (t, J = 6.4 Hz, 4H, OCH₂), 2.05 (m, 4H, fluorene α -CH₂), 1.89 (m, 4H, OCH₂CH₂), 1.04–1.45 (m, 36H, alkyl), 0.72–0.95 (m, 16H, CH₃ and fluorene β -CH₂). ¹³C NMR

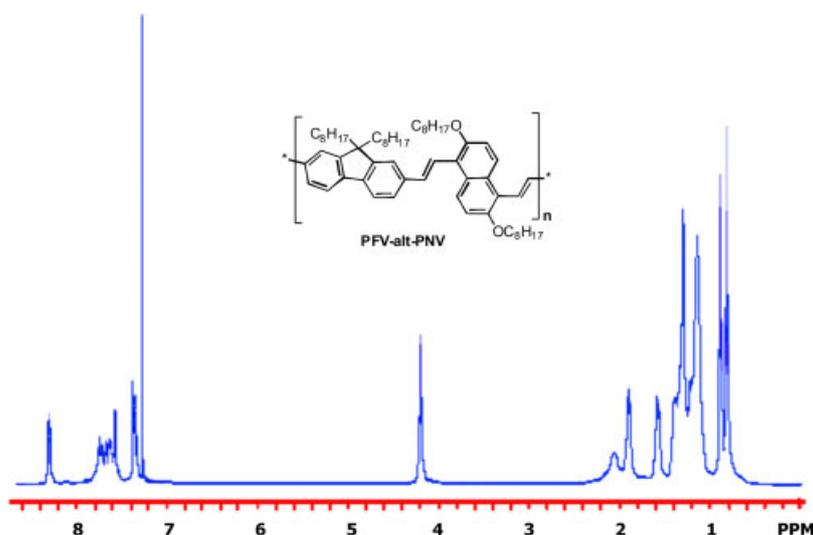


Figure 2. ^1H NMR spectrum in CDCl_3 of PFV-*alt*-PNV prepared by Horner–Emmons polymerization.

(75 MHz, CDCl_3 ; δ , ppm): 153.4, 152.1, 141.1, 137.7, 136.0, 129.2, 125.9, 122.1, 121.3, 120.4, 115.9, 70.2, 55.5, 41.0, 32.3, 30.7, 30.2, 29.9, 26.8, 23.1, 14.6.

RESULTS AND DISCUSSION

The molecular structure and purity of the monomers and product polymer were evaluated using ^1H NMR and ^{13}C NMR spectroscopy. Figure 2 shows the ^1H NMR spectrum of PFV-*alt*-PNV in CDCl_3 , which demonstrates that the Horner–Emmons methodology leaves no residual monomeric species and produces no saturated defects along the conjugated polymer backbone (i.e. there are no resonances at *ca* 3.1 ppm, which have been assigned to $\text{Ar}-\text{CH}_2-\text{CH}_2-\text{Ar}$ defects along the conjugated backbones of related polymers).^{20,21,29} The aromatic naphthyl resonances appear as a doublet at 8.2–8.4 ppm and a doublet within a multiplet at 7.3–7.4 ppm; furthermore, integration over the ranges 7.3–7.4 and 7.5–7.8 ppm totals four and eight protons, respectively, which argues for the formation of vinylic groups connecting the naphthyl and fluorenyl moieties. There are also two sets of peaks for four protons each appearing at 4.18 and 1.89 ppm, which arise from the α and β methylenes, respectively, of the naphthyl side chains. Similarly, we assign the resonance at 2.05 ppm to the α methylenes of the fluorenyl side chains. Finally, integration of the region below 1.0 ppm, which includes all four methyl group resonances and the β methylenes of the fluorenyl group, gives the expected 16 protons.

GPC indicates that M_n and \bar{D} are $14\,000\text{ g mol}^{-1}$ and 1.4, respectively. These values are typical for polymers prepared using the types of reactions and experimental conditions employed here.²⁷ The polymer is completely soluble in a variety of common organic solvents, including chloroform, chlorobenzene, methylene chloride and THF.

The UV-visible absorption spectrum of the copolymer in dilute THF solution was measured (Fig. 3). The single broad absorbance maximum centered at 427 nm arises from a π to π^* transition along the conjugated backbone.³⁰ This band is somewhat blue-shifted when compared to that for PFVs, which exhibit dual absorption maxima at *ca* 430 and 455 nm (due to vibrational splitting).^{20,21,31,32} While there are no published examples of poly(2,6-bis-alkoxy-1,

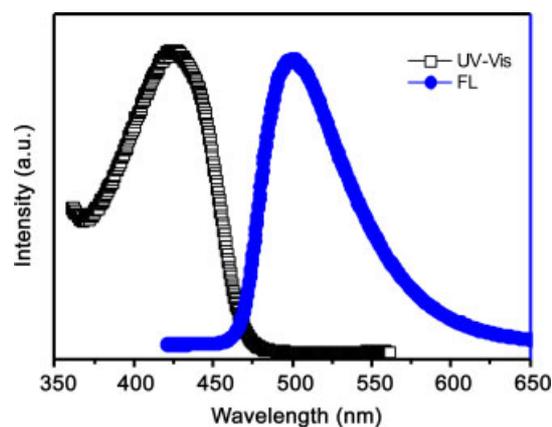


Figure 3. UV-visible absorption ($1.0 \times 10^{-5}\text{ mol L}^{-1}$) and fluorescence spectra ($4.8 \times 10^{-5}\text{ mol L}^{-1}$) in THF at room temperature of PFV-*alt*-PNV prepared by Horner–Emmons polymerization.

5-naphthalene vinylene) to provide baseline comparison (although two reports describe the synthesis and study of poly(2,6-bis-octyloxy-1,5-naphthalene vinylene), the actual polymer examined according to our nomenclature was poly(1,5-bis-alkoxy-2,6-naphthalene vinylene)^{25,33}), we have recently prepared such a derivative as part of a separate study, and λ_{max} appears at 387 nm,³⁴ which is red-shifted compared to that of unsubstituted poly(1,5-naphthylene vinylene) in the solid state ($\lambda_{\text{max}} = 361\text{ nm}$).²⁵ Furthermore, compared to the PFV-*alt*-PNVs linked through the 1,4-, 2,3- and 2,6-naphthyl positions (where $\lambda_{\text{max}} = 357, 360$ and 381 nm , respectively),²⁷ λ_{max} of PFV-*alt*-1,5-PNV is strongly red-shifted by $\geq 46\text{ nm}$. Notably, the 1,4-PNV variant is even more strongly red-shifted ($\lambda_{\text{max}} \approx 443\text{ nm}$).³⁵ Given that the literature provides no consistent ordering of the λ_{max} values with regard to the substitution pattern in PNVs,^{27,35,36} we refrain from drawing any structural correlations.

Figure 3 also shows the fluorescence (FL) spectrum of PFV-*alt*-PNV obtained upon excitation at 428 nm in THF. The emission band of PFV-*alt*-PNV peaks at 500 nm; correspondingly, the solution appears to emit green light. The emission band is intensified and red-shifted when compared to PFVs, which show a major band at

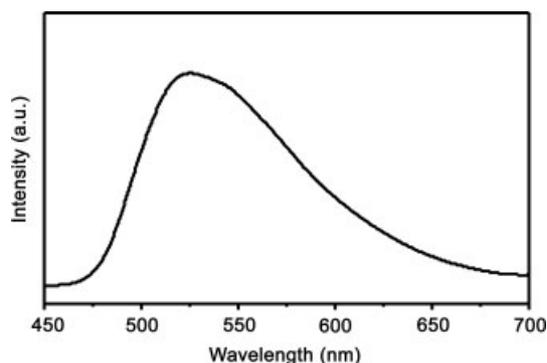


Figure 4. Photoluminescence spectrum at room temperature (excitation at 370 nm) of PFV-*alt*-PNV prepared by Horner–Emmons polymerization.

ca 466 nm with weaker bands at longer wavelength intervals that can be attributed to vibrational splitting.^{20,21,37–39} Interestingly, the FL_{max} of 500 nm for our PFV-*alt*-PNV is identical to that reported for the PFV-*alt*-1,4-PNV isomer.²⁷ However, as with the absorption data discussed in the preceding paragraph, we are unable to correlate the FL_{max} values with the various substitution patterns in the PNV moieties.^{27,35,36} Notably, the Stokes shift observed for our PFV-*alt*-PNV (ca 73 nm) is lower than that reported for the 1, 4-, 2,3- and 2,6-naphthyl-substituted PFV-*alt*-PNV analogs.

The photoluminescence (PL) spectrum of a solid (powder) sample of PFV-*alt*-PNV was recorded at room temperature using an excitation wavelength of 370 nm (Fig. 4). The major PL emission band is centered at ca 526 nm, which is red-shifted by ca 26 nm relative to that in dilute solution. The red shift might arise due to a change from a coiled conformation in solution to a more extended conformation in the solid state.⁴⁰ We also note that the PL emission band for PFV-*alt*-PNV is red-shifted by ca 16 nm when compared to the corresponding 9,9-dialkyl-PFVs. Moreover, compared to the PFV-*alt*-PNVs linked through the 1,4-, 2,3- and 2,6-naphthyl positions (where PL_{max} = 514, 465 and 477 nm, respectively),²⁷ the PL_{max} of PFV-*alt*-PNV is red-shifted by ≥ 12 nm. With regard to device applications, the PL_{max} of PFV-*alt*-PNV (ca 526 nm) approaches that of 1,4-PNV, where PL_{max} = 577 nm.³⁵

Cyclic voltammetry was employed to investigate the electrochemical behavior of the polymer as well as estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The HOMO and LUMO energy levels of polymers can be calculated from the onset oxidation potential and the absorption edge of the UV-visible spectrum.^{41–43} From our electrochemistry measurements (not shown), we determined the HOMO energy level of PFV-*alt*-PNV to be -4.70 eV. From the UV-visible spectrum in Fig. 3, the absorption edge is 475 nm, and thus the energy gap (E_G) is 2.61 eV, which gives a LUMO energy level of -2.09 eV. It should be noted, however, that the E_G and LUMO values are only estimates because the electrochemical data were collected from thin-film polymer samples in the solid state, while the UV data were collected from polymer samples dissolved in solution.

Figure 5 shows the current–voltage (I – V) and luminescence–voltage (L – V) characteristics of the light-emitting diodes of ITO/PEDOT : PSS/PFV-*alt*-PNV/Al configured device. The LED structure consists of an evaporated aluminium contact on the surface of the copolymer that was spun-cast on the ITO glass from the solution of PFV-*alt*-1,5-PNV in THF. The I – V plot in Fig. 5 shows that the current increases linearly with increasing forward bias voltage over the range 0–10 V, which is consistent with typical rectifying

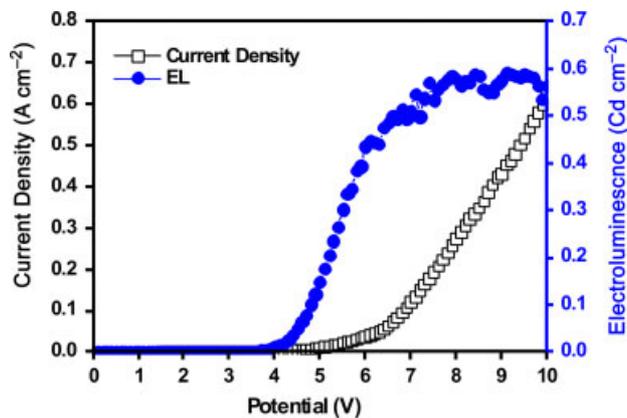


Figure 5. Current–voltage (I – V) and luminescence–voltage (L – V) characteristics of the light-emitting diode of ITO/PEDOT : PSS/PFV-*alt*-PNV/Al.

characteristics. Further, the exponential increase in current as a function of voltage is consistent with typical diode behavior.

Simultaneous with the collection of the I – V data, electroluminescence (EL) *versus* voltage data were collected with a photomultiplier tube added to the equipment used to record the I – V data. The EL data were collected for a PFV-*alt*-1,5-PNV polymer LED over the full range of voltages, including the turn-on voltage and the breakdown voltage. Figure 5 shows the EL *versus* V data over the range 0–10 V, where the EL *versus* 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 polymer-based OLED devices.⁴⁴ The turn-on voltage is relatively low (ca 2.5 V) compared to that of PFV-based LEDs (typically >3.0 V).^{17,45} The lower turn-on voltage of the PFV-*alt*-PNV device might arise from enhanced π -electron delocalization through the naphthalene units along the conjugated backbone, which leads to a lowering of the HOMO energy level.²²

Finally, we calculated the luminous efficiency to be 12.9 cd A^{-1} at an operating voltage of 5 V. Importantly, the magnitude of the observed EL is markedly greater than that typically found in commercial OLED-based displays.¹ Despite these encouraging results, a side-by-side comparison of the performance of this new polymer and related light-emitting polymers in a device architecture is needed before its true utility can be unequivocally established.

CONCLUSIONS

A modified Horner–Emmons strategy was used to prepare PFV-*alt*-PNV. The polymer showed good thermal stability and was readily soluble in common organic solvents. The UV-visible spectrum showed a broad absorption band at 427 nm for PFV-*alt*-PNV. The solution-phase fluorescence spectra showed FL_{max} at 500 nm, and the solid-state photoluminescence spectra showed PL_{max} at 526 nm. A two-layer light-emitting device having a simple ITO/PEDOT : PSS/polymer/Al configuration was fabricated. Measurements of current and luminescence *versus* voltage showed onset voltages for these two-layer PLEDs to be 2.5 V with a maximum brightness of 5000 cd m^{-2} . These characteristics suggest that PFV-*alt*-PNV is an attractive candidate for use in polymer-based OLED devices.

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