Light Emitting Properties of Fluorine-Substituted Poly(1,4-phenylene vinylenes)

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ABSTRACT: Three fluorine-containing polymers, poly(2-fluoro-1,4-phenylene vinylene), poly(2,5-difluoro-1,4-phenylene vinylene), and poly(2[5]-(*n*-hexyloxy)-5[2]-fluoro-1,4-phenylene vinylene) (**1**−**3**, respectively) have been synthesized by the soluble precursor method and were used to fabricate light emitting diode (LED) devices. Monosubstituted **1** yielded an electroluminescent emission peaking at 560 nm (green-yellow); polymers **2** and **3** emitted in the 600−610 nm region (red). The result for **1** represents a blue shift in emission relative to emission from hompolymeric unsubstituted poly(1,4-phenylene vinylene) (PPV) LEDs fabricated by similar techniques, while the results for **2** and **3** represent a substantial red shift. These results may be compared to those obtained from LEDs fabricated from copolymers of PPV and poly(2,3,5,6-tetrafluoro-1,4-phenylene vinylene), which show a slightly blue shifted emission relative to homopolymeric PPV (Benjamin, I.; Faraggi, E. Z.; Avny, Y.; Davidov, D.; Neumann, R. *Chem. Mater.* **1996**, *8*, 352). The qualitative difference in EL emission for this work compared to that of Benjamin *et al.* is attributed to the fact that EL emission from **1**−**3** reflects the electronic effects of fluorine substitution upon the EL spectra, whereas the work of Benjamin *et al.* demonstrated the effects of changes in the average chain length of EL emitting homo-PPV blocks in PPV-*co*-PPVF4 copolymers.

Introduction

A large body of work has accumulated concerning the effects of chemical substitution on emissive efficiency, device longevity, and spectral behavior in conjugated organic compounds that can be used as chromophores in light-emitting diodes (LEDs).[1,2] Some success has been achieved in using both molecular and polymeric materials for such electrooptical uses.[3] While some qualitative guidelines have emerged for selecting molecules for testing, the search for the optimum LED materials still involves a certain empiricism in selecting the best design of conjugated materials, substituent choice, and position, as well as efficiency enhancements such as hole/electron injection layers and of electrodes with optimized work functions.

The electrooptical properties of the conjugated poly(1,4-phenylene vinylene) (PPV) family of polymers have been of particular interest.[4] We have been interested for a considerable time in the effects of ring-substitutents, especially those with electron-withdrawing properties.[5−8] In this regard the photoluminescence of halogenated PPVs which are promising candidates for LED investigations[8]—especially the fluorine-substituted variants[5,7]—are of interest. Fluorine substituents are unique because the element is a sterically small atom that bonds strongly to carbon while having a powerful electron-withdrawing effect in π-conjugated systems.[9] Fluorine thus could expected to have important electronic effects on PPV light emission, as well as possibly stabilizing the PPV backbone against oxidation and other degradative reactions.[10,11]

In this contribution, we describe the fabrication and luminescence testing of single-layer test LEDs containing poly(2-fluoro-1,4-phenylene vinylene), poly(2,5-difluoro-1,4-phenylene vinylene), and poly(2[5]-(*n*-hexyloxy)-5[2]-fluoro-1,4-phenylene vinylene), **1**−**3**, respectively. All are candidates as LED materials, despite their differences in electronic nature, with **1** and **2** being electronically deficient PPVs, and **3** being a “push−pull” substituted PPV (i.e., a system with electron-donor and electron-acceptor substituents attached in a *para*-connectivity). Finally, we compare light-emitting properties of **1**−**3** with those found in certain other PPV copolymers containing fluoroarene rings.

Experimental Section

General Methods. All new compounds were characterized by ^{1}H NMR, IR, and elemental analysis (University of Massachusetts Microanalytical Laboratory). Nuclear magnetic resonance (NMR) spectra were taken on Bruker NR-80 or Varian XL-200 spectrometers. All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) or HOD (in CD_3OD) at 0.0 and 4.76 ppm respectively on the d scale. Peak designations follow the standard notation; singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Coupling constants, *J*, are reported in hertz (Hz). Infrared (IR) spectra were recorded as neat films, neat liquids or potassium bromide (KBr) pellets, with absorption peaks reported in cm^{-1}, using an Nicolet FTIR spectrometer or a Perkin-Elmer 1420 ratio recording grating IR spectrometer. All peaks listed are strong (s), except those noted by the following notations: weak (w) or very strong (vs). Ultraviolet−visible (UV−vis) spectra were recorded on a Shimadzu UV-260 double beam spectrometer. All emission spectra (PL and EL) were recorded using samples cast on quartz plates, using a custom-built emission spectrometer assembly that was calibrated against a Perkin-Elmer MPF-66 fluorescence spectrometer.

Melting point determinations were made using a Fisher-Johns melting point apparatus; all temperatures are uncorrected. Reagent chemicals were obtained from Aldrich Chemical Co. unless otherwise stated. Thermo-gravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 analyzer under nitrogen atmosphere. Gel permeation chromatography (GPC) experiments were carried out on a Waters GPC consisting of a Model 590 pump, a Model 410 differential refractometer detector, and a Waters data module. Waters Ultrastyragel columns were used to measure molecular weights up to the 10^5 Da range. Tetrahydrofuran (THF) was used as the eluent solvent with 0.1% solutions of polymers, and calibration samples of polystyrene ($M_w = 100\,000$) were used as standards.

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2-(*n*-Hexyloxy)-5-nitro-*p*-xylene (8). Sodium nitrate (45.0 g, 0.65 mol) was dissolved in 400 mL of ice cold 70 v/v % nitric acid. To this solution was added dropwise 25.0 g (0.21 mol) of 2-(*n*-hexyloxy)-*p*-xylene.[8] The mixture was stirred for 7 h at 0 °C in an ice/water bath. At the end of the reaction, the mixture was poured into 1 L of distilled water. The precipitated product was collected on a Buchner funnel, washed with copious amounts of water, and recrystallized from 95% ethanol to give 26.3 g (77%) of **8** as white needles, mp 70−72 °C. Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.68; H, 8.30; N, 5.46. ^1H NMR (80 MHz, $CDCl_3$): δ 7.92 (s, 1 H), 6.37 (s, 1 H), 4.03 (t, 2 H, $J = 6.1$ Hz), 2.62 (s, 3 H), 2.22 (s, 3 H), 1.2−1.8 (m, 8 H), 0.92 (t, 3 H, $J = 5.9$ Hz).

2-Amino-5-(hexyloxy)-*p*-xylene (9). Compound **8** (10.1 g, 60.5 mmol) was dissolved in about 50 mL of 2:1 v:v ethanol/tetrahydrofuran. The solution was transferred to a Pyrex heavy-walled pressure bottle and charged with 0.18 g of platinum (IV) oxide catalyst. The solution was hydrogenated for 12 h at room temperature (55 psi). After the hydrogenation was complete, the solution was filtered through a glass frit to remove the catalyst. The solvent was then removed by distillation to give 8.3 g (97%) of colorless liquid **9**, bp 92−93 °C, at atmospheric pressure. Anal. Calcd for $C_{14}H_{23}$ NO: C, 75.97; H, 10.47; N, 6.33. Found: C, 76.11; H, 10.68; N, 5.29. ^1H NMR (80 MHz, $CDCl_3$): δ 6.57 (s, 1 H), 6.49 (s, 1 H), 3.66 (t, 2 H, $J = 6.3$ Hz), 3.09 (broad s, 2 H), 2.13 (s, 6 H), 1.2−1.8 (m, 8 H), 0.90 (t, 3 H, $J = 5.9$ Hz).

2-Fluoro-5-(*n*-hexyloxy)-*p*-xylene (11). A 13.8 g (0.10 mol) sample of **9** was dissolved in 97 mL of 6 M hydrochloric acid in a 300 mL beaker. The mixture was kept in an ice/water bath and brought to 0 °C. Next, a solution of 7.5 g (0.11 mol) of sodium nitrite in 30 mL of distilled water was added dropwise to the vigorously stirred solution. A gray precipitate, presumably the benzenediazonium chloride salt, soon disappeared after the final addition of the sodium nitrite. Next, a solution of 12.2 g (0.11 mol) of sodium tetrafluoroborate in 50 mL of distilled water was added dropwise to the cold reaction. Immediately, a beige precipitate began to appear. After the addition of the sodium tetrafluoroborate, the solution was allowed to stir for 15 min. The beige precipitate was filtered, and washed with copious amounts of ice−water. After 24 h of drying under vacuum at room temperature, 2-(*n*-hexyloxy)-5-*p*-xylenediazonium tetrafluoroborate (**10**) was isolated (21.1 g, 89%, mp 100−102 °C dec). ^1H NMR (80 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 6.96 (s, 1 H), 4.20 (t, 2 H, $J = 6.0$ Hz), 2.73 (s, 3 H), 2.25 (s, 3 H), 1.2−1.8 (m, 8 H), 0.92 (t, 3 H, $J = 5.9$ Hz). This material was pure enough to use in the subsequent step.

The salt **10** (19.4 g, 82 mmol) obtained as described above was subjected to thermal decomposition in small quantities (2−3 g). *CAUTION! Although we had no problems with decompositions carried out as described below, we recommend the use of safety precautions appropriate to potentially explosive reactions, including: small reaction scale, use of blast protection, and extra facial protection!* In a typical procedure, 2.5 g (10.1 mmol) portions of **10** were added dry to a 250 mL three necked round-bottom flask with a distillation head and condenser attached. The reaction was placed behind a Plexiglas shield in the hood and was heated slowly to 110 °C in an oil bath. The heating was continued until the visible evolution of nitrogen had ceased. The crude black oil was cooled, dissolved in dichloromethane, and placed in an Erlenmeyer flask. Next, the dichloromethane extracts were washed with 10% sodium hydroxide, brine, and distilled water and then dried ($MgSO_4$), and the methylene chloride was distilled away. The crude product was vacuum distilled (bp 102−104 °C/5 mmHg) to give 6.8 g (60% yield) of yellow liquid **11** from a total of 19.4 g (82 mmol) of **10**. Anal. Calcd for $C_{14}H_{21}FO$: C, 74.96; H, 9.44; F, 8.47. Found: C, 74.93; H, 9.43; F, 8.50. ^1H NMR (80 MHz, $CDCl_3$): δ 6.77 (d, 1 H, $J = 9.9$ Hz), 6.58 (d, 1 H, $J = 6.5$ Hz), 3.89 (t, 2 H, $J = 6.0$ Hz), 2.20 (s, 3 H), 2.15 (s, 3 H), 1.2−1.8 (m, 8 H), 0.91 (t, 3 H, $J = 5.8$ Hz).

1,4-Bis(bromomethyl)-2-fluoro-5-(*n*-hexyloxy)benzene (12). To a stirred solution of 3.52 g (15.7 mmol) of **11** in 125 mL of dry carbon tetrachloride were added 100 mg of azoisobutyronitrile and 5.95 g (33.2 mmol) of *N*-bromosuccinimide, under nitrogen, at room temperature. The mixture was heated at reflux for 24 h. Irradiation with a 500 W tungsten lamp was used to facilitate the completion of the reaction. After the reaction was cooled, the floating solid succinimide byproduct was filtered away, and the solvent was distilled from the filtrate. The resulting viscous liquid was cooled to 0 °C to crystallize the crude product, which was recrystallized from 95% ethanol to give 1.76 g (29%) of **12** as white crystals, mp 39−40 °C. Anal. Calcd for $C_{14}H_{19}Br_2FO$: C, 44.01; H, 5.01; Br, 41.82; F, 4.97. Found: C, 44.18; H, 4.84; Br, 42.10; F, 4.70. ^1H NMR (80 Mhz, $CDCl_3$): δ 6.79 (d, 1 H, $J = 10$ Hz), 6.59 (d, 1 H, $J = 6.5$ Hz), 4.47 (s, 4 H), 3.93 (t, 2 H, $J = 5.8$ Hz), 1.2−1.8 (m, 8 H), 0.91 (t, 3 H, $J = 5.9$ Hz).

2-Fluoro-5-(hexyloxy)-1,4-bis(tetrahydrothiophenio-methyl)benzene Dibromide (13). Compound **12** (1.22 g, 3.19 mmol) was suspended in a solution of tetrahydrothiophene (1.4 g, 15.9 mmol) in 35 mL of dry methanol. The mixture was stirred at 55 °C for 24 h. The solvent and excess tetrahydrothiophene were removed by distillation to give an off-white residue which was dissolved in a minimum amount of methanol and precipitated into 200 mL of dry acetone. After vacuum drying, white powder **13** (1.25 g, 70%) was obtained with mp 163−166 °C dec. This compound is stable in a freezer under inert atmosphere. An analytical sample was obtained by 3-fold precipitation from methanol into acetone. Anal. Calcd for $C_{22}H_{35}Br_2FOS_2$: C, 47.32; H, 6.31; Br, 28.62; F, 3.40, S, 11.48. Found: C, 47.38; H, 6.27; Br, 29.1; F, 3.50; S, 11.52. ^1H NMR (80 Mhz, CD_3OD): δ 7.64 (d, 1 H, $J = 8.8$ Hz), 7.52 (d, 1 H, $J = 4.5$ Hz), 4.77 (s, 2 H), 4.67 (s, 2 H), 4.29 (t, 2 H, $J = 6.2$ Hz), 3.66 (m, 8 H), 2.48 (m, 8 H), 1.54 (m, 8 H), 1.02 (asym t, 3 H, $J = 7.5$ Hz).

Polyelectrolyte 14. The bis(sulfonium) salt **13** (600 mg, 1.08 mmol) was dissolved in 25 mL of distilled water. The solution was filtered through a glass frit and placed in a 100 mL round-bottom flask. An equal volume of pentane was added to the flask, and the two-phase system was cooled to 0 °C under argon. A solution of tetramethylammonium hydroxide was also cooled to 0 °C under argon/pentane. Both solutions were thoroughly purged with argon gas for 1 h. Then, the base (0.47 mL, 1.30 mmol) was added swiftly by syringe. The polymerization was allowed to proceed for 1 h at 0 °C. The excess base was neutralized with 6 M HCl solution to a phenolphthalein end point. The resulting yellow-green solution was dialyzed against distilled water (Spectropore 1 filters, M_w cutoff 6000−8000) for 3 days to give a uniform green solution. This solution was used to cast films which are soluble in methanol but insoluble in THF and $CHCl_3$. This material is appropriate for conversion to polyether **15**.

Polyether 15. The sulfonium polyelectrolyte **14** was dissolved in a minimal amount of methanol. The solution was stirred for 1 week under argon, during which pendant polyether **15** precipitated from the solution. The tacky yellow material was completely soluble in $CHCl_3$ and THF. **15** can be dissolved in THF and passed through a 0.2 mm filter for gel permeation chromatography or for use in film casting and device fabrication. Cast films can be completely redissolved into $CHCl_3$ or THF. Gel permeation chromatography in tetrahydrofuran (polystryrene standards) gave $M_w = 91\,500$ and $M_n = 33\,800$.

Poly(2-fluoro-1,4-phenylene vinylene) (1). The synthesis and characterization of this polymer from polyelectrolyte **6** via precursor **4** has been fully described elsewhere.[5] Anal. Calcd for C_8H_5F: C, 79.99; H, 4.20; F, 15.82; S, 0.0. Found: C, 79.04; H, 4.29; F, 14.05; S, 0.44. IR (neat film, cm^{-1}): 961 (*trans* HC=CH). UV−vis (neat film on quartz, λ_{max}): 422 nm. PL (neat film on quartz, λ_{max}, excitation at 360 nm): 560 nm. EL (ITO/(**1**)/Ca(Al), 10 V(pulsed), λ_{max}): 560 nm.

Poly(2,5-difluoro-1,4-phenylene vinylene) (2). The synthesis and characterization of this polymer from polyelectrolyte **7** via precursor **5** has been fully described elsewhere.[5] Anal. Calcd for $C_8H_4F_2$: C, 69.57; H, 2.92; F, 27.51; S, 0.0. Found: C, 69.35; H, 2.89; F, 27.28; S, 1.08. IR (neat film, cm^{-1}): 962 (*trans* HC=CH). UV−vis (neat film on quartz, λ_{max}): 420 nm. PL (neat film on quartz, λ_{max}, excitation at 390 nm): 605 nm. EL (ITO/(**2**)/Ca(Al), 10 V(pulsed), λ_{max}): 600 nm.

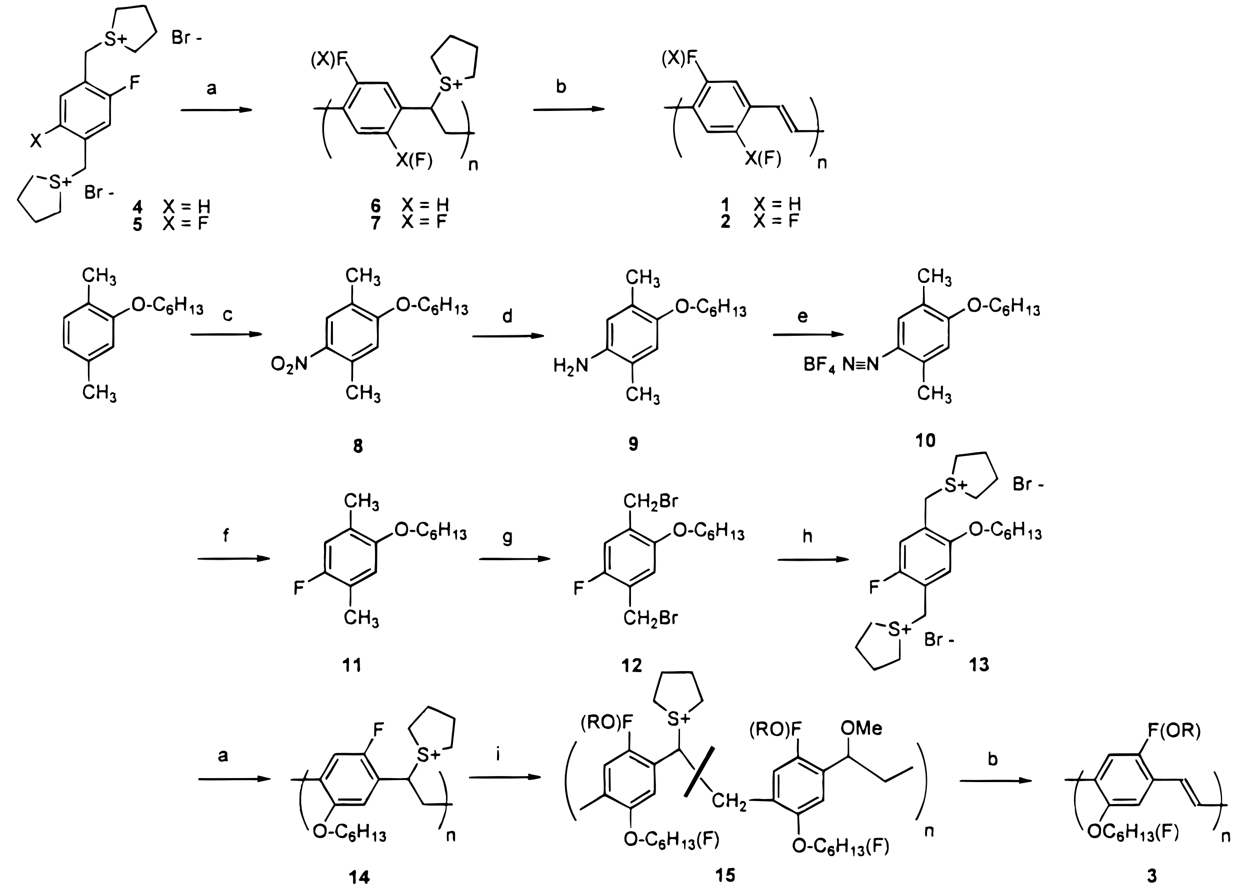


Figure 1. Syntheses of polymers **1**−**3**: (a) Bu_4NOH/H_2O-pentane/0 °C; (b) >230 °C, vacuum; (c) $NaNO_3/HNO_3$/0 °C; (d) H_2/EtOH−THF/catalytic PtO_2; (e) $NaNO_2$/aqueous HCl/0 °C and then aqueous $NaBF_4$; (f) dry pyrolysis; (g) *N*-bromosuccinimide/CCl_4/AIBN/Δ; (h) $C_5H_{10}S$/MeOH/Δ; (i) MeOH/room temperature/7 days.

Poly(2[5]-fluoro-5[2]-(*n*-hexyloxy)-1,4-phenylene vinylene) (3). A film of polyether **15** was clamped between two 0.125 in-thick Teflon plates, and then heated at 230 °C for 6 h under vacuum (<0.01 mmHg) to give a red film of PPV **3**. The final polymer films are insoluble in $CHCl_3$, THF, and MeOH. Anal. Calcd for $C_{14}H_{17}OF$: C, 76.33; H, 7.78; F, 8.62; S, 0.0. Found: C, 72.02; H, 7.44; F, 8.3; S, 0.30. IR (neat film, cm^{-1}): 962 (*trans* HC=CH). UV−vis (neat film on quartz, λ_{max}): 455 nm. PL (neat film on quartz, λ_{max}, excitation at 390 nm): 630 nm. EL (ITO/(**3**)/Ca(Al), 10 V(pulsed), λ_{max}): 626 nm.

Results

Synthesis. The synthesis of polymer **1** by polymerization of the bis(sulfonium) salt **4** to polyelectrolyte **6** and subsequent thermolysis followed the methodology originally described by Wessling[12−14] that has previously been described by us.[5] Polymer **2** was synthesized by the same method via salt **5** and polyelectrolyte **7**, also previously described.[5] "Push−pull" polymer **3** was synthesized by an analogous route. Nitration of 2-(*n*-hexyloxy)-*p*-xylene gave **8**, followed by reduction to amine **9**, which as treated with sodium nitrite and precipitated with fluoroboric acid to give the stable diazonium tetrafluoroborate salt **10**, which can be stored indefinitely. This salt can be thermally decomposed to give the ring-fluorinated compound **11**, and converted to the bis(bromomethyl)benzene derivative **12** by Ziegler bromination. Formation of the corresponding bis(sulfonium) salt **13** is conveniently achieved by treatment with tetrahydrothiophene in methanol. The syntheses of **1**−**3** are shown in Figure 1.

With the bis salt **13** in hand, aqueous base was used to produce polyelectrolyte **14** as a greenish solution from which free-standing films could be cast. We converted polyelectrolyte **14** to organic-soluble, backbone-pendant polyether precursor **15**, which upon thermal elimination under vacuum yielded red films of polymer **3**. The films of all polymers **1**−**3** were fairly tough and had some flexibility but were not elastic at ambient temperatures. Thermogravimetric analysis (TGA) showed that temperatures of 210−250 °C were suitable for elimination from the precursors **5**, **7**, and **15** at reasonable rates. The eliminated hexyloxy-substituted polymer **3** decomposes at temperatures above 490 °C, but polymers **1** and **2** are stable in nitrogen atmosphere to temperatures above 500 °C.

Preparation of LEDs. LEDs were prepared using commercially available plates (Standish) having three indium-tin oxide (ITO) electrodes on each plate. All fabrication and measurement manipulations were performed under inert atmosphere at room temperature. The ITO electrodes are 1600 Å thin films coated on to the glass squares (about 1.2 cm × 1.2 cm); each device has a resistance of 100 W. The plates were cleaned using chloroform and dried under vacuum for 5 h before use. Polyether **15** was spin cast under nitrogen atmosphere as a 20 mg/mL solution in chloroform at 4000 rpm onto the ITO coated plates. Polyelectrolytes **5** and **7** were spin cast under the same conditions from 30 mg/mL solutions in methanol. The precursor films on the plates were then heated under vacuum at 250 °C to yield the conjugated PPVs. This was followed by evaporation deposition of an aluminum or calcium cathode through a mask (about 2 mm × 2 mm) at <2 mmHg onto the device. The overall pixel areas are 6 mm^2 in area. The thickness of the emissive layer of **1, 2**, or **3** used in each

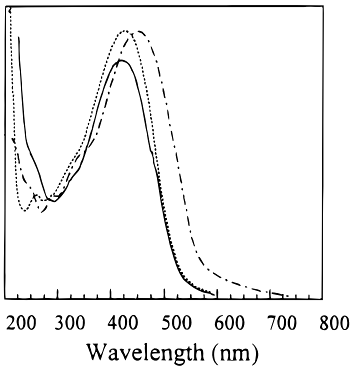


Figure 2. Comparative UV–vis spectra from neat films of **1** (—), **2** (···), and **3** (– ·). Absorbances were arbitrarily scaled relative to one another for ease in comparison.

device was about 90 nm (900 Å). The LEDs were stored in a glovebox at room temperature under nitrogen or argon.

Double layer LEDs were made by the same procedure described above, but with an additional step in which a layer of poly(1,4-phenylenevinylene) (PPV) was deposited onto the ITO plate before the appropriate layer of **1**, **2**, or **3**. In this process, after cleaning of the ITO plate, a 30 mg/mL solution in methanol of the tetrahydrothiophenium chloride precursor for unsubstituted PPV[13] was spin-coated onto the plate. The precursor coated plate was then baked at 220 °C for 3 h under vacuum to yield a conjugated PPV layer that was about 60 nm (600 Å) thick. The selected layers of **6**, **7**, or **15** were then spin-coated and eliminated on top of the PPV layer as described above. All subsequent steps in the two-layer LEDs were carried out in the manner described above for the single layer LEDs.

Absorption and Luminescence Spectral Results. Thin film UV–vis, fluorescence (FL), and electroluminescence (EL) spectra were obtained using the single-layer device samples described above. Band pass filters were used to select the 360 or 390 nm region for excitation to measure PL spectra. Pulsed voltage (rather than dc) was used to observe the EL spectra at room temperature under argon atmosphere. For EL emission/current vs voltage studies, the EL and current emission intensities were measured with a monochromator, photomultiplier, and ammeter using dc forward current injection. Total luminescence measurements were made using a calibrated commercial radiometer/photometer (International Light, Inc. Model IL 1400A). Figures 2–4 compare the various spectra for **1**–**3**. The ordinates of the spectra are arbitrarily scaled so that the spectral maxima are of similar height to compare more readily the line shape and wavelength maxima.

Discussion

The syntheses of the precursor bis(sulfonium) salts **1**–**3** were straightforward, but required a number of extra steps and precautions due to the necessity of introducing the fluorine substituents via diazonium salt decomposition. For example, in the synthesis of **2**, we could not satisfactorily introduce both fluorine atoms by simultaneous, double diazonium decomposition and had instead to carry out the same synthetic sequence twice to introduce them sequentially.[5] The need to use diazotization chemistry and its attendant safety precautions (see Experimental Section) renders **1**–**3** synthetically less convenient than some other halogenated PPVs, although we felt that the added stability of the carbon–fluorine bond relative to other carbon–halogen bonds made fluorinated PPVs attractive for a possible extension of LED lifetime. It is possible that the use of recently described, selective aryl-fluorinating reagents such as Selectafluor[15] would allow synthesis of appropriate fluoroarene intermediates in larger quantities; however, this remains to be determined.

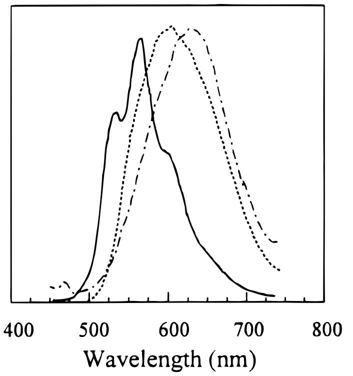


Figure 3. Comparative photoluminescence spectra from neat films of **1** (—), **2** (···), and **3** (– ·). Emission ordinates were arbitrarily scaled relative to one another for ease in comparison. Excitation wavelengths were 360, 390, and 390 nm, respectively.

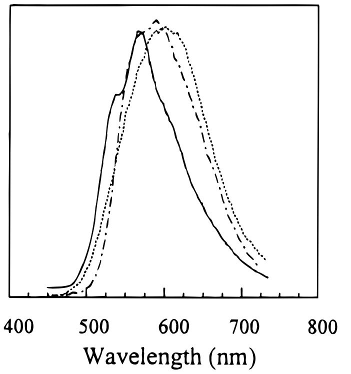


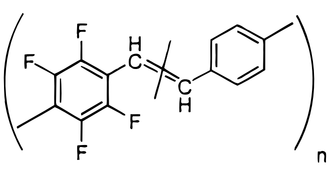
Figure 4. Comparative electroluminescence spectra from neat films of **1** (—), **2** (···), and **3** (– ·). Emission ordinates were arbitrarily scaled relative to one another for ease in comparison.

The bis salts **4**, **6**, and **13** are quite stable in the dry form at <0 °C. All three polymerize in straightforward fashion under aqueous conditions to give solutions of precursor polyelectrolytes **5**, **7**, and **14**. The polyelectrolytes may be dialyzed against deionized water, film-cast into yellow-green free-standing films, and subjected to direct thermal elimination to give the final, conjugated PPVs **1** and **2**. We chose to follow a procedure that we have previously employed[8] for substituted PPVs and converted polyelectrolyte **14** to polyether **15** by room temperature methanolysis. Polyether **15** is soluble in organic solvents such as chloroform and tetrahydrofuran and may be easily film cast and then readily be eliminated to give **3**.

Polymers **1**–**3** contained 0.4, 1.1, and 0.3% residual sulfur, respectively, showing that elimination was not complete, even when sulfonium displacement by methanol was employed. Such residues have been observed in other PPVs produced by *in vacuo* elimination from sulfonium-based polyelectrolytes[5–8,16] and do not appear to have a strong effect on the emission wavelength, although the residues may affect the electroluminescent efficiency and device longevity. Recent studies demonstrate that it is possible to improve[10,17] the original vacuum thermolytic[12,13] elimination procedures for making PPVs by this general route. We attempted elimination of precursor polymer **6** to polymer **1** by thermolysis in an HCl/argon atmosphere, but obtained essentially the same elemental composition for **1** as before. In this study we were most concerned with specific effects of substitution upon the emission wavelengths for PPVs; hence, we have left the optimization of elimination conditions for future study.

Figures 2−4 show the UV−vis, photoluminescence (PL), and electroluminescence (EL) spectra for **1**−**3**. Fluoropolymer **1** in film form has a UV−vis absorption maximum at 422 nm, with PL and EL maxima at about 560 nm to give a greenish-yellow emission color. Difluoro-PPV **2** has a UV−vis maximum in the film very similar to that of monofluoro **1**, at 420 nm. However, **2** has a PL emission at about 590 nm and a EL maximum at about 600 nm, considerably red-shifted relative to those of **1** and yielding an overall reddish-orange emission color in both types of spectroscopy. Push−pull polymer **3** shows a UV−vis absorption maximum at 445 nm that is somewhat red-shifted relative to those of **1** and **2**. The PL and EL maxima for **3** are also red-shifted at 630 and 610 nm to give a red to reddish-orange color. By comparison, unsubstituted PPV has a UV−vis absorption maximum at about 450 nm and PL and EL emission maxima at about 560 nm (yellow-green).[18] In summary, the monofluoro-PPV **1** has a UV absorption peak that is blue-shifted relative to that of unsubstituted PPV, with EL and PL spectra virtually the same as those of PPV. Difluoro-PPV **2** exhibits a blue-shift in the UV spectrum relative to PPV but has PL and single-layer EL emissions that are substantially red-shifted relative to those of PPV. "Push−pull" disubstituted PPV **3** has PL and EL maxima that are all red-shifted relative to those of PPV.

Recently, Benjamin *et al.*[19] reported EL emission wavelengths for several PPV-*co*-(2,3,5,6-tetrafluoro-1,4-phenylenevinylene) copolymers (PPV-*co*-PPVF4). Overall, there was a slight EL blue shift in PPV-*co*-PPVF4 by comparison to homo-PPV. Benjamin *et al.* attributed this behavior to the presence of oligomeric blocks of PPV of reduced length in their copolymers. They noted that PPVF4 blocks apparently have an EL efficiency similar to that of the PPV blocks, but the higher threshold function for PPVF4 blocks makes these weak EL emitting chromophores in the copolymer.[19] The net effect for PPV-*co*-PPVF4 with increasing PPVF4 content was a blue shift of about 60 nm in the UV absorption maximum relative to PPV but only about 5 nm in the EL spectrum. Thus, the behavior of this copolymer is dominated by PPV EL behavior and only indirectly affected by the PPVF4 blocks.



By contrast, homopolymers **1**−**3** are effective EL emitting polymers despite their fluorine substituents; hence, the wavelength maxima shifts in **1**−**3** relative to PPV are caused by actual substitution electronic effects and not by a variation in conjugation length of the emitting chromophore. Steric effects on the conformations **1** and **2** relative to unsubstituted PPV should be minor, because the C−F bonds will not occupy greatly more volume in the polymer than will C−H bonds. The alkoxy substituent on **3** should disrupt the solid state planarity relative to PPV.[20] Molecular mechanics geometry optimizations were carried out using the Unified Force Field (version 1.01) in the Molecular Simulations Inc. Cerius^2 program suite,[21] assuming a randomized head-to-head, head-to-tail, and tail-to-tail regioconnectivity in a decamer of **3**. The calculations show that the alkoxy substituents can form a "halo" (Figure 5) around a slightly deplanarized PPV conjugated backbone. The surrounding layer of substituents can possibly shield the main polymer chain from oxidation and other reactions. The lowest energy conformers still allow reasonable conjugation of the PPV framework, in accord with the experimental finding that the UV−vis maximum of **3** is somewhat red shifted relative to PPV, rather than exhibiting a considerable blue shift that would indicate twisting and reduced conjugation. The emission wavelengths of 600−610 nm for 2,5-disubstituted **2** and **3** are quite similar to those recently reported by us for the 2,5-disubstituted PPVs poly(2[5]-chloro-5[2]-(*n*-hexyloxy)phenylene vinylene) and poly(2[5]-bromo-5[2]-(*n*-hexyloxy)phenylene vinylene), **16** and **17** respectively.[8] The reddish electroluminescent polymer MEH-PPV,[22] **18**, has an EL emission at about 600 nm (2.07 eV), very similar to that of difluoro PPV **2**. All the PPV derivatives with 2,5-disubstitution of π-donating, inductive-withdrawing substituents have a considerable red shift relative to parent PPV in the solid state PL and EL. Difluoro PPV **2** has the longest wavelength luminescence of the series of 2,5-disubstituted PPVs with bromine, chlorine, and fluorine atoms attached to the aryl ring; the photoluminescence maxima for **19**, **20**, and **2** are 560, 580, and 600 nm, respectively.[7]

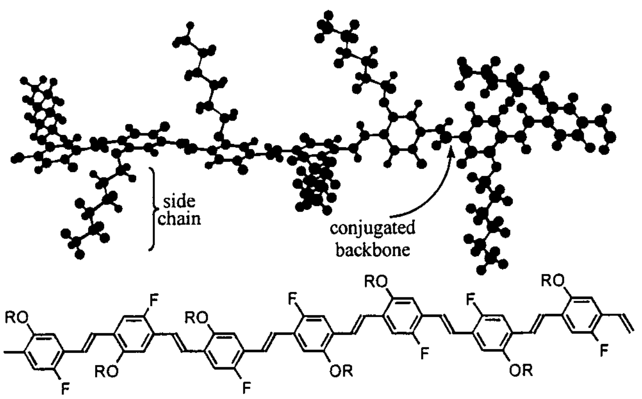
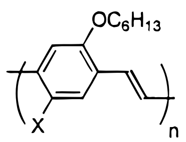
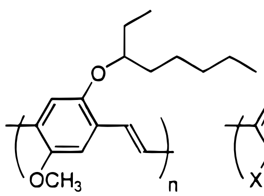


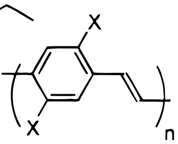
Figure 5. Force field optimized structure for the regiorandomized oligomer of **3**. Details of the computation are described in the text.



16 X = Cl
17 X = Br



18



19 X = Br
20 X = Cl

The emissive output for **1**−**3** was also studied as a function of drive voltage. We found it convenient to pursue the studies for **1** and **2** in double layer devices using PPV as a putative hole-injection layer, *i.e.*, in an ITO/PPV/(**1** or **2**)/Ca(Al) configuration. This was not necessary for "push−pull" polymer **3**, which gave very good results in single layer devices. Figure 6 shows the

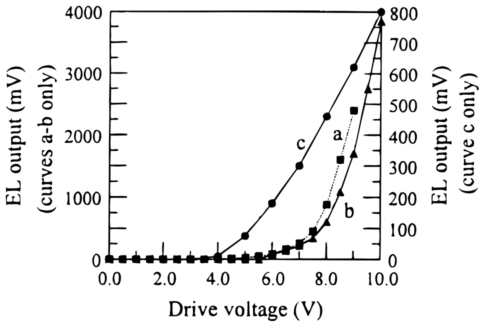


Figure 6. Emission vs voltage plots for polymers **1**−**3**, curves a−c respectively. EL emission intensity is given in millivolts (mV) and drive voltage in volts (V). Curves a and b for the double layer device with PPV are represented by the left ordinate; curve c for single layer device is represented by the right ordinate—details on device preparation are given in the text. For these curves, divide the ordinate by 90 to convert to units of cd/m^2.

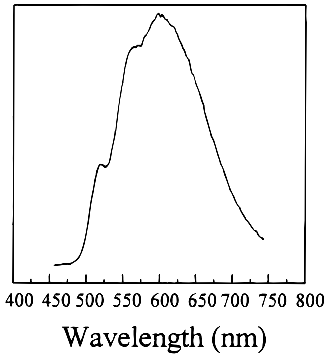


Figure 7. EL spectrum for an ITO/PPV/(**2**)/Ca(Al) device. Details on device preparation are given in the text.

voltage vs luminance behavior for the three polymer containing LEDs.

The ITO/PPV/(**1**)/Ca(Al) device using monofluoro PPV gave a yellow-green emission at about 560 nm that is quite similar to that of both ITO/PPV/Ca(Al) and ITO/(**1**)/Ca(Al) single layer devices.[23] Thus, it is possible that both **1** and PPV are emitting in the double layer device. The fact that the single layer ITO/(**1**)/Ca(Al) device has the same EL spectrum as the double layer device suggests that **1** alone can also be used as an emissive layer. However, Figure 6a shows that a moderately high turn-on voltage—at least 7 V—is required for the emission from **1**. The double layer ITO/PPV/(**1**)/Ca(Al) LED has an output of about 100 cd/m^2 at 30 V(pulsed).

An ITO/PPV/(**2**)/Ca(Al) device with the difluoro PPV **2** chromophore gives an orangish-yellow emission above its turn-on voltage of 7 V that is considerably less red than the emission color produced by ITO/(**3**)/Ca(Al) or ITO/PPV/(**3**)/Ca(Al) devices incorporating "push−pull" polymer **3**. The spectra in Figure 3 show that difluoro **2** can act as an emitting layer in a single layer device with a emission wavelength of about 600 nm, which appears orange-red to the eye. Figure 7 shows the emission spectrum from a double layer ITO/PPV/(**2**)/Ca-(Al) LED, with maxima at about 520 and 560 nm as well as the expected 600 nm. The presence of multiple peaks suggests that the PPV layer as well as the layer of **2** is emitting in the multilayer device. The use of the configuration ITO/PPV/(**2**)/Ca(Al) leads to a total luminance of 100 cd/m^2 at 30 V(pulsed). However, this enhancement relative to the single layer LED is achieved at the cost of broadening the emission spectrum and a consequent yellow appearance in this device due to emission from the PPV layer. In addition, the double layer LED still requires a turn-on voltage of over 7 V.

The EL spectrum of the single layer ITO/(**3**)/Ca(Al) device was the same as that of a ITO/PPV/(**3**)/Ca(Al) device that was tested for comparison. This shows that **3** is the emitting layer even in a PPV/(**3**) double layer device. Using a pulsed voltage of 10 V for emission in the single layer device of ITO/(**3**)/Ca(Al), a luminance level up to 20 cd/m^2 was obtained. The use of a hole-injecting PPV layer in a ITO/PPV/(**3**)/Ca(Al) enhances the total luminance, yielding an output of 120 cd/m^2 at 30 V(pulsed). This compares to a luminance level of 5 cd/m^2 obtained at drive voltages of ~25 V for PPV used as an emissive layer in an earlier multilayer device enhanced by use of a 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole electron injection layer.[24] We found that LEDs incorporating **3** exhibited a linear increase of emission as current increases, but required relatively high currents while operating at low voltages. The luminance/current density for the ITO/(**3**)/Ca(Al) LED is 2.25×10^{-3} cd/A, compared to a value of 17.0×10^{-3} cd/A for the multilayer PPV-based device previously described.[24] This appears to be consistent[25] with the effect of electron withdrawal by the fluorine substituent in **3**. The turn-on voltage of the single layer LED of **3** was just over 4 V, lower than the 6−7 V turn-on voltage for the LEDs fabricated using the more electron-deficient PPVs **1** and **2**.

Polymer **3** has color and stability characteristics similar to those of the previously reported chloro and bromo analogues **16** and **17**, and is a candidate as a red-light-emitting polymer, despite its higher current densities at low voltages. The results for the fluorinated PPVs are interesting, but the problems in obtaining red light emission from difluoro PPV **2** make this polymer less desirable for use as an emissive layer. As described above, these studies provide useful information about fluorine electronic effects upon band gap and emission behavior for the PPVs. Fluorinated derivatives of related conjugated polymers may provide equally interesting electrooptic behavior relative to their unsubstituted parent systems.

Summary

PPV derivatives **1**−**3** with fluorine substituents on the aryl rings both show PL and EL shifts in emission wavelength relative to unsubstituted PPV. While in monofluoro PPV **1** ring-substitution yields electronic spectra that are similar to those of PPV itself, 2,5-disubstitution in **2** and **3** results in considerably red-shifted emission maxima. These results demonstrate the electronic effects of fluorine aryl-ring substitution on the EL emission for the PPVs, which contrast with the slight blue EL shifts observed by Benjamin *et al.* through shortening the effective conjugation length in homo-PPV by copolymerization with tetrafluoro-PPV comonomers. The very different qualitative effects achievable with similar substitution patterns demonstrates the tunability can be achieved in the EL emission wavelengths of the PPVs. Work is in progress to optimize the use of **1**−**3** in multilayer LEDs, to decide whether enhancement of EL capabilities is sufficient to warrant the synthetic efforts of placing fluorine on the aryl units of PPV.

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