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Red Light Emitting "Push−Pull" Disubstituted Poly(1,4-phenylenevinylenes)

Ronald M. Gurge,[†] Ananda Sarker,[†] Paul M. Lahti,*[,†] Bin Hu,[‡] and Frank E. Karasz[‡]

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01003, and Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: The "push−pull" electronically substituted systems poly(2[5]-chloro-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene) and poly(2[5]-bromo-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene)—**1** and **2**, respectively—were synthesized by a modified soluble precursor route. Thermal elimination of polyether precursors to **1** and **2** yields the final conjugated polymers as free-standing, flexible red films. The polyether precursors may be film-cast from methanol to make light emitting diode (LED) devices which have red light emission in the 620 nm region. The ease of synthesis and processibility of **1** and **2** make these promising candidates for red light emitting LEDs.

Introduction

Recent work has shown promise for the fabrication of light emitting diode (LED) devices that employ organic conjugated molecules and polymers as primary emitters.[1] Progress in organic LED research has been rapid and includes the development of multilayer devices to allow better matching of the work functions of the device electrodes to the emitter material, as well as development of an LED using alternating current.[2] The promise of such LEDs for flexible[3] and lightweight flat screen displays is such that they have been described even in the popular literature.[4] Given the multitude of possible organic conjugated structures, the breadth of work in this area is understandable as workers strive to find optimal properties for organic LED emission wavelengths, environmental stability, long-term emission stability, and emission intensity.

Among the organic materials that have been most promising are members of the poly(1,4-phenylenevinylene) (PPV) family of polymers.[5] PPVs have been much studied over the past 25 years for potential uses in a variety of electro-optical applications, with a marked acceleration in the number of studies since the development of soluble precursor methods that have allowed them to be more readily processed. For example, work by Burroughes, Bradley, *et al.* has shown that PPV and its copolymers with substituted analogues can be used to achieve variation in the emission wavelength of organic LEDs.[6,7] Where substitution with long-chain alkyl groups allows solubility in the final PPVs, traditional polymerization syntheses may be employed rather than the soluble precursor methods.[8]

The exact choice of PPV substitution in any putative device will be controlled by synthetic accessibility, ease of processing, and luminescent efficiency and lifetime. In this contribution, we wish to report synthetic details and some electroluminescence (EL) studies for members of the asymmetrically substituted, "push−pull" family of PPVs,[9] represented by poly(2[5]-chloro-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene) and poly(2[5]-bromo-5[2]-(*n*-hexyloxy)-1,4-phenylenevinylene), **1** and **2**, respectively. These polymers are of interest because they are easily made by a short synthetic sequence in multigram quantities, are readily film-cast from redissolvable precursors, and give encouragingly strong EL emission in the ≥620 nm (orange-red to red) spectral region even without fine-tuning of emission characteristics.

Experimental Section

General Methods. All new compounds were characterized by ^{1}H NMR, IR, and elemental analysis, the last of which was performed by the University of Massachusetts Microanalytical Laboratory. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker NR-80 (80 MHz), a Varian XL-200 spectrometer (200 MHz), or a Bruker MX-500 spectrometer (500 MHz). Unless otherwise stated, the solvents were deuteriochloroform ($CDCl_3$) and deuterium oxide (D_2O). All chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) or HOD (in D_2O) at 0.0 and 4.76 ppm, respectively, on the δ scale. Peak designations follow the standard notation: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Coupling constants, J, are reported in hertz (Hz). Infrared (IR) spectra were recorded from neat films, neat liquids, or potassium bromide (KBr) pellets, with absorption peaks reported in cm^{-1}, using a 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 notation: weak (w) or very strong (vs). Ultraviolet−visible (UV−vis) spectra were recorded on a Shimadzu UV-260 double-beam spectrometer or a Perkin-Elmer Lambda 9 spectrometer. All emission spectra (PL and EL) were recorded using LED samples cast on quartz plates, using a home-built emission spectrometer assembly that was calibrated against a Perkin-Elmer MPF-66 fluorescence spectrometer: all total luminance measurements were made using a calibrated commercial radiometer/photometer (International Light, Inc. Model IL 1400A).

Melting point determinations were made using a Fisher-Johns melting point apparatus; all temperatures are uncorrected. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGA-7 analyzer under a nitrogen atmosphere. Gel permeation chromatography (GPC) was carried out on a Waters GPC assembly consisting of a Model 590 pump, a Model 410 differential refractometer detector, and a Waters data module. Tetrahydrofuran (THF) was the eluent solvent, and polystyrene (M_w = 100 000) was used as a standard for GPC.

2-(Hexyloxy)-*p*-xylene. In a three-necked flask equipped with a magnetic stirrer, a condenser, an addition funnel, and a nitrogen inlet was put 80 mL of absolute ethanol. The ethanol was cooled on an ice bath (0 °C) while 3.8 g (0.16 mol)

[†] Department of Chemistry, University of Massachusetts.

[‡] Department of Polymer Science and Engineering, University of Massachusetts.

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of sodium metal was added to the stirred solution in small portions. Next, 4.0 g (0.27 mol) of sodium iodide was added, and the mixture was stirred until a clear solution was achieved. 2,5-Dimethylphenol (20.0 g, 0.164 mol) was added, and the mixture was stirred for 10–15 min to give a colorless solution. 1-Bromohexane (27.2 g, 0.164 mol) in 30 mL of ethanol was added dropwise over 30 min under an argon atmosphere, and the reaction mixture was heated at reflux for 12 h. After 12 h, the reaction was allowed to cool to room temperature. Distilled water (100 mL) was added to the flask. The solution was extracted with diethyl ether (2 × 75 mL). The combined ether layers were washed with 10% sodium hydroxide (2 × 75 mL), distilled water (2 × 75 mL), and brine (2 × 75 mL) and then dried ($MgSO_4$), and the ether was distilled. The crude product was vacuum distilled (bp 122 °C/5 mmHg) to give 29.9 g (88% yield) of colorless liquid 2-(hexyloxy)-*p*-xylene. Anal. Calcd for $C_{14}H_{22}O$: C, 81.57; H, 10.67. Found: C, 81.23; H, 10.68. ^{1}H NMR (80 MHz, $CDCl_3$): δ 6.99 (1 H, d, $J = 7.8$ Hz), 6.65 (2 H, m), 3.94 (2 H, t, $J = 6.1$ Hz), 2.30 (3 H, s), 2.17 (3 H, s), 1.2–1.8 (8 H, m), 0.97 (3 H, t, $J = 5.8$ Hz).

1-Chloro-2,5-dimethyl-4-(hexyloxy)benzene (3). To a stirred solution of 20.0 g (0.164 mol) of 2-(hexyloxy)-*p*-xylene in 160 mL of dry carbon tetrachloride were added 100 mg of 2,2′-azobis(isobutyronitrile) (AIBN) and 24.1 g (0.180 mol) of *N*-chlorosuccinimide under nitrogen at room temperature. One drop of concentrated HCl was added, and the mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, the succinimide was filtered and the solvent was distilled away. The resulting viscous liquid was cooled to 0 °C to crystallize the product. The crude product was recrystallized from hexane to give 9.6 g of **3** as white crystals, mp 45–47 °C, yield 37%. Anal. Calcd for $C_{14}H_{21}ClO$: C, 69.84; H, 8.79; Cl, 14.72. Found: C, 69.92; H, 8.67; Cl, 14.52. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.07 (1 H, s), 6.65 (1 H, s), 3.92 (2 H, t, $J = 6.0$ Hz), 2.31 (3 H, s), 2.15 (3 H, s), 1.2–1.8 (8 H, m), 0.90 (3 H, t, $J = 5.8$ Hz).

1-Bromo-2,5-dimethyl-4-(hexyloxy)benzene (4). 2-(Hexyloxy)-*p*-xylene (9.86 g, 0.048 mol) was dissolved in 100 mL of CCl_4. *N*-Bromosuccinimide (8.60 g, 0.048 mol) was added along with 0.1 g of AIBN as initiator. The mixture was heated under reflux under a nitrogen atmosphere overnight, and the resulting suspension was gravity filtered to remove succinimide byproduct. The solvent was then removed from the filtrate under reduced pressure, and the liquid crude product crystallized after 1 h of cooling in a refrigerator. Finally, crude solid was recrystallized from hexane to give 9.30 g (68%) of **4** with mp 45–45.5 °C. Anal. Calcd for $C_{14}H_{21}OBr$: C, 58.98; H, 7.37; Br, 28.03. Found: C, 58.21; H, 7.85; Br, 29.10. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.24 (s, 1 H), 6.66 (s, 1 H), 3.91 (t, 2 H, $J = 6.1$ Hz), 2.33 (s, 3 H), 2.14 (s, 3 H), 1.38 (m, 8 H), 0.90 (t, 3 H, $J = 5.8$ Hz).

1,4-Bis(bromomethyl)-2-chloro-5-(hexyloxy)benzene (5). To a stirred solution of 7.5 g (48 mmol) of **3** in 70 mL of dry carbon tetrachloride were added 100 mg of AIBN and 18 g (0.100 mol) of *N*-bromosuccinimide, under nitrogen, at room temperature. The mixture was heated at reflux for 24 h. Irradiation with a 1000 W lamp was used to facilitate the completion of the reaction. After the mixture was cooled, the succinimide was filtered, and the solvent was distilled away to give crude **5** as a thick oil. ^{1}H NMR indicated that the desired product was the major component in the reaction mixture, with varying amounts of partially brominated product, as shown by the presence of Ar-CH_3 groups at about δ 2.2 ppm. We did not distill crude **5**, in order to avoid thermal decomposition. The crude material is suitable to make compound **7**. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.00 (1 H, s), 6.88 (1 H, s), 4.53 (2 H, s), 4.45 (2 H, s), 4.04 (2 H, t, $J = 6.0$ Hz), 1.85–1.20 (8 H, m), 0.92 (3 H, t, $J = 5.5$ Hz).

1,4-Bis(bromomethyl)-2-bromo-5-(hexyloxy)benzene (6). Compound **6** was obtained from 2-bromo-5-(hexyloxy)-*p*-xylene (9.7 g, 0.034 mol) by the procedure described above for **5**, using 2 equiv of *N*-bromosuccinimide (12.7 g, 0.071 mol) in carbon tetrachloride solvent. Recrystallization of the crude solid product from hexane gave 6.2 g (42%) of white crystalline solid **6** with mp 70–71 °C. Anal. Calcd for $C_{14}H_{19}OBr_3$: C, 38.0; H, 4.40; Br, 54.20. Found: C, 38.02; H, 4.25; Br, 54.20. ^{1}H NMR (80 MHz, $CDCl_3$): δ 7.49 (s, 1 H), 6.93 (s, 1 H), 4.54 (s, 2 H), 4.45 (s, 2 H), 4.02 (t, 2 H, $J = 5.7$ Hz), 1.2–1.9 (8 H, m), 0.90 (3 H, t, $J = 5.7$ Hz).

2-Chloro-5-(hexyloxy)-1,4-bis(tetrahydrothiopheniomethyl)benzene Dibromide (7). To a solution of 6.0 g (19.1 mmol) of crude **3** in 50 mL of methanol was added 8.4 g (95 mmol) of tetrahydrothiophene. The mixture was warmed to 60 °C, stirred for 24 h, and cooled to room temperature. Excess methanol and tetrahydrothiophene were removed by distillation, and the resulting solid product was dissolved in a minimal amount of methanol and reprecipitated twice into 500 mL of spectral grade acetone. The precipitate was filtered and washed with acetone to afford 6.8 g (73%) of **7**, a white powder with mp 173–176 °C (dec). The compound is quite hygroscopic and must be stored under argon. Anal. Calcd for $C_{22}H_{35}S_2Br_2ClO$: C, 45.96; G, 6.14; S, 11.15. Calcd for $C_{22}H_{35}S_2Br_2ClO\cdot 3H_2O$: C, 42.01; H, 6.57; S, 10.19. Found: C, 42.28; H, 5.63; S, 10.24. ^{1}H NMR (200 MHz, D_2O): δ 7.84 (s, 1 H), 7.34 (s, 1 H), 4.69 (s, 2 H), 4.54 (s, 2 H), 4.20 (t, 2 H, $J = 6.3$ Hz), 3.55 (m, 8 H), 2.40 (m, 8 H), 1.36 (m, 8 H), 0.90 (asym t, 3 H, $J = 7.3$ Hz).

2-Bromo-5-(hexyloxy)-1,4-bis(tetrahydrothiopheniomethyl)benzene Dibromide (8). **6** (2.34 g, 5.34 mmol) was suspended in a solution of tetrahydrothiophene (2.50 mL, 28.40 mmol) plus 15 mL of methanol. The mixture was stirred at 50 °C for 48 h. Next, solvent and excess tetrahydrothiophene were removed from the reaction mixture under reduced pressure to give a white residue. It was dissolved again in a minimal amount of methanol at 45 °C and precipitated in 300 mL of dry acetone. After vacuum drying, white powder **8** (2.50 g, 75%) was obtained with mp 135–136 °C (dec). Anal. Calcd for $C_{22}H_{35}S_2Br_3O$: C, 42.68; H, 5.65; S, 10.36; Br, 38.72. Found: C, 42.49; H, 5.53; S, 10.15; Br, 38.98. ^{1}H NMR (80 MHz, CD_3OD): δ 7.99 (s, 1 H), 7.69 (s, 1 H), 4.83 (s, 2 H), 4.63 (s, 2 H), 4.25 (t, 2 H, $J = 7$ Hz), 3.64 (m, 8 H), 2.47 (m, 8 H), 1.47 (m, 8 H), 0.98 (asym t, 3 H, $J = 7$ Hz).

Polyelectrolyte 9. Bis-sulfonium salt **7** (2.35 g, 4.78 mmol) was dissolved in 30 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 *n*-pentane was added to the flask, and the resulting two-phase system was cooled to 0 °C under argon. Similarly, a solution of tetramethylammonium hydroxide was also cooled to 0 °C under argon/pentane. Both solutions were thoroughly purged with bubbled argon. Then, the base (2.00 mL, 5.35 mmol) was added swiftly by syringe to the stirred solution of monomer **7**. The polymerization was allowed to proceed for 1 h at 0 °C. After completion, the excess base was neutralized with 6 M aqueous HCl solution to a phenolphthalein end point. The precursor polymer **9** precipitated from the reaction solution at this point, and was scraped out of the reaction flask. This material may be dissolved in a minimum amount of methanol and used as is for conversion to polyether **11**. Solutions may be stored for months under argon at <10 °C. Free-standing greenish-yellow flexible films were cast on dichlorodimethylsilane-treated glass dishes at room temperature. These films could be redissolved in methanol or water–methanol mixtures but are insoluble in THF, $CHCl_3$, and CH_2Cl_2.

Polyelectrolyte 10. Polymerization of 3.90 g (6.30 mmol) of monomeric salt **8** in 84 mL of 4:1 v/v methanol:water solvent (0.075 M) by the procedure described for **9** gave a greenish solution of polyelectrolyte **10**. The solution of **10** was then dialyzed against methanol:water (1:1) (Spectropore 1 filters, M_w cutoff 6000–8000) for 4 days to give a greenish solution. This solution was used to cast films or to synthesize polyether **12**. The film-casting behavior and solubility of **10** are similar to those of **9**. This reaction may also be carried out with an equivolume amount of degassed pentane as a cosolvent, under which conditions the product **10** is found by a derivative-based thiophenoxide GPC assay[11] to have $M_w = 55\,000$ and $M_n = 24\,000$.

Polyether 11. The sulfonium polyelectrolyte **9** was dissolved in a minimal amount of methanol. The solution was stirred for 3 weeks under argon, during which time **11** precipitated from the solution. The gummy orangish material was completely soluble in $CHCl_3$ or THF and slightly soluble in MeOH and was highly extendable. It was dissolved in THF

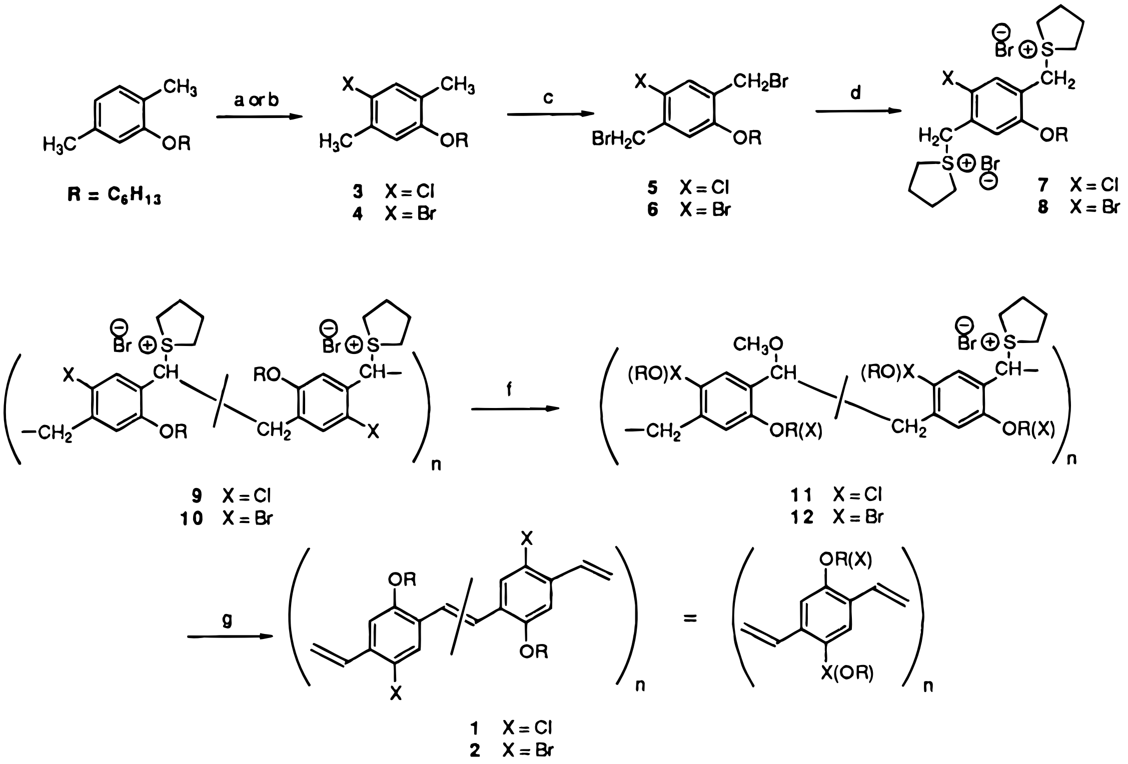


Figure 1. Syntheses of **1** and **2**: (a) *N*-chlorosuccinimide/cat. HCl/CCl$_4$ for **3**, *N*-bromosuccinimide/CCl$_4$ for **4**; (b) *N*-bromosuccinimide/CCl$_4$/cat. AIBN/*hν*; (c) tetrahydrothiophene/methanol/Δ; (d) Me$_4$NOH/H$_2$O/0 °C; (e) MeOH/room temperature/3 weeks; (f) 210−240 °C/10 h.

and passed through a 0.2 *μ*m filter for gel permeation chromatography. The filtered solution was used for film casting and device fabrication. Films cast in this manner can be redissolved in CHCl$_3$ or THF. The IR spectrum for **11** is available in the supporting information for this article. Gel permeation chromatography in tetrahydrofuran gave M_w = 19 500 and M_n = 7000. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 0.91 (broadened t, terminal CH$_3$, *J* ≈ 6 Hz), 1.36 (CH$_2$ chain), 1.5 *δ* (CH$_2$), 1.82 (penultimate CH$_2$), 3.29 and 3.44 (br s, OCH$_3$), 3.92−4.06 (br m, OCH$_2$), 4.72 (br s, OH?), 5.75 (br s, arylene C*H*(OMe)), 7.0−7.3 (broadened multiplet, arylene CH).

Polyether 12. The same procedure used for converting polyelectrolyte **9** to polyether **11** was also used to convert polyelectrolyte **10** to polymer **12**. The only change was that after the initially formed **12** precipitated from methanol, this product was isolated, redissolved in THF, and then reprecipitated from methanol again. The final product was gummy, orangish curds that appeared to be indefinitely stable in the refrigerator. This material was dissolved in CHCl$_3$ and passed through a 0.2 *μ*m filter for use in gel permeation chromatography, film casting, and device fabrication. Films cast in this manner could be redissolved in CHCl$_3$ or THF. The IR spectrum for **12** is available in the supporting information for this article. Gel permeation chromatography in tetrahydrofuran gave M_w = 14 900 and M_n = 3800. ^{1}H NMR (500 MHz, CDCl$_3$): *δ* 0.91 (broadened t, terminal CH$_3$, *J* ≈ 6 Hz), 1.37 (CH$_2$ chain), 1.49 (CH$_2$), 1.83 (penultimate CH$_2$), 3.2 and 3.4 (br s, OCH$_3$), 3.92−4.06 (br m, OCH$_2$), 5.76 (broadened t, *J* ≈ 6 Hz, arylene C*H*(OMe)), 7.09−7.29 (four peaks, arylene CH).

Poly(2[5]-Chloro-5[2]-(hexyloxy)-1,4-phenylenevinylene) (1). A film (0.104 g) of **11** was clamped between Teflon plates and thermally eliminated for 10 h (<0.01 mmHg) at 240 °C. A red polymer film of **1** (0.065 g) was obtained which was insoluble in CHCl$_3$, THF, and MeOH. Anal. Calcd for C$_{14}$H$_{17}$OCl: C, 71.03; H, 7.24; Cl, 14.97; S, 0.0. Found: C, 68.80; H, 7.09; Cl, 15.34; S, 0.55. IR (neat, cm^{-1}): 960 (*trans* HC═CH). UV−vis (neat film on quartz, λ_{max}): 450 nm. PL (neat film on quartz, λ_{max}, λ_{excit} = 390 nm): 626 nm. The IR spectrum for this material is available in the supporting information for this article.

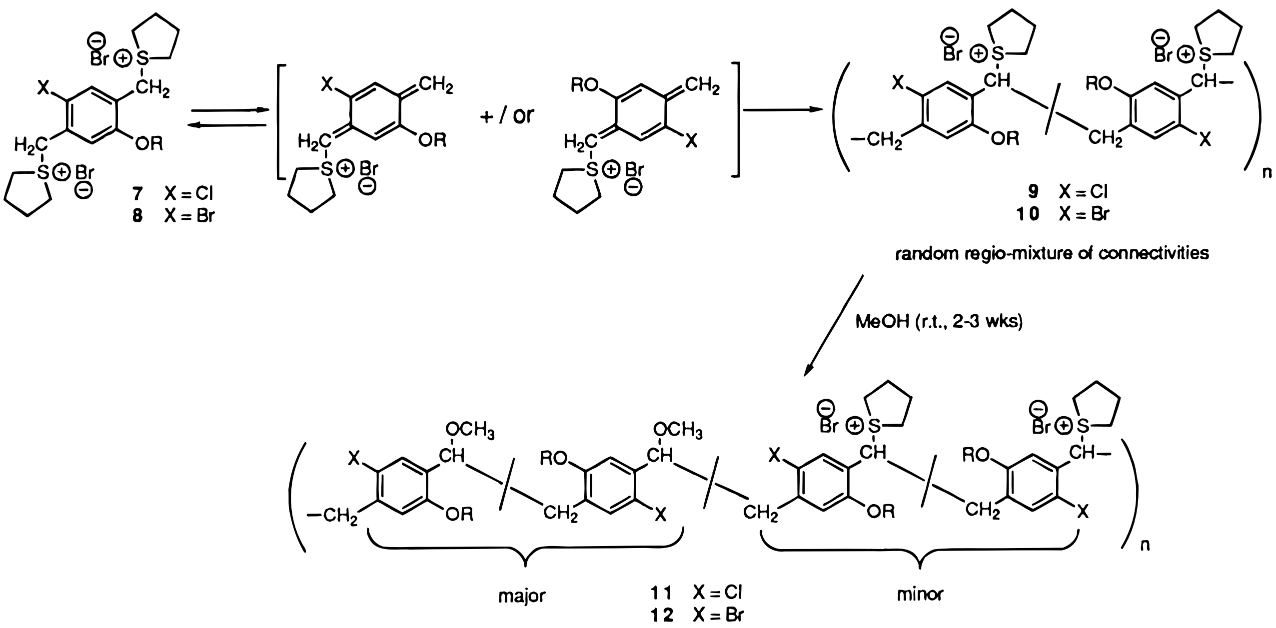
Poly(2[5]-bromo-5[2]-(hexyloxy)-1,4-phenylenevinylene) (2). A film of **12** was clamped between two 0.125-in.-thick Teflon sheets, and then heated at 210 °C for 10 h under a vacuum of 0.001 mmHg to give a red film of **2**. TGA showed no further appreciable loss of weight under these conditions upon further heating. The final polymer films were insoluble in CHCl$_3$, THF, and MeOH. Anal. Calcd for C$_{14}$H$_{17}$OBr: C, 59.83; H, 6.05; Br, 28.43; S, 0.0. Found: C, 57.98; H, 5.99; Br, 28.69; S, 0.80. FTIR (neat film, cm^{-1}): 957 (*trans* HC═CH). UV−vis (neat film on quartz, λ_{max}): 435 nm. PL (neat film on quartz, λ_{max}, λ_{excit} = 390 nm): 618 nm. The IR spectrum for this material is available in the supporting information for this article.

Results

Polymer Synthesis and Characterization. Figure 1 details the syntheses of polymers **1** and **2**. Straightforward alkylation of 2,5-dimethylphenol could give any of a number of alkoxy-substituted arene synthetic intermediates, of which we chose the hexyloxy material. *N*-Chloro- and *N*-bromosuccinimide in the presence of the appropriate HX acid gave ring halogenation of the hexyloxy ether to give intermediates **3** and **4**. Ziegler bromination at the benzylic positions for **3** or **4** gave **5** or **6**, respectively. Treatment of **5** and **6** with tetrahydrothiophene leads to ready isolation of the bis(tetrahydrothiopheniomethyl) salts **7**−**8**. Precursor salts **7** and **8** appear to be indefinitely stable when stored dry in a refrigator.

We have previously described a UV−vis methodology to optimize the choice of reaction solvent for Wessling-type polymerization of salts such as **7** and **8**.[10] This technique was useful in allowing us to observe the formation of xylylene intermediates from both **7** and **8**, which showed transient UV−vis absorptions at 350 and 327 nm, respectively. Overall, **7** and **8** polymerized well in water or methanol/water to give aqueous solutions of polyelectrolyte precursors **9** and **10**. The pendant sulfonium side chains in **9** and **10** are mostly converted to methoxy groups by prolonged stirring at room temperature in methanol of the appropriate polyelectrolyte, yielding precursors **11** and **12**, which were soluble in

Scheme 1



organic solvents such as methanol and chloroform. We show **11** and **12** as having some number of remaining sulfonium groups for reasons that will be discussed below—however, for ease in nomenclature, we shall refer to **11** and **12** as polyethers due to the predominance of conversion to this form.

The organic solubility of polyethers **11** and **12** is particularly convenient both for analysis by gel permeation chromatography (GPC) and for film casting of these polymers by spin-coating. GPC versus polystyrene standards gave M_n (M_w) of 7000 (19 500) for **11** and 3800 (14 900) for **12**, corresponding to degrees of polymerization (DPs) of about 26 and 12, respectively, assuming complete conversions of polyelectrolyte to polyether. While it is not clear that the use of polystyrene standards will give a completely accurate determination of the DPs for **11** and **12**, previous molecular weight determinations of functionalized PPV precursor polymers have been in reasonable agreement[11] with the molecular weights determined by independent light scattering studies. The polydispersities of **11** and **12** are in the 2.0–3.5 range, which is not atypical by comparison to previous investigations of Wessling PPV precursors.[11] The observed DPs are not particularly high by comparison to previous reports, but considerable improvement in DPs can be achieved by rigorous purification of starting materials and fine-tuning of polymerization conditions, albeit at a considerable cost in money and effort.[12] For example, optimization of molecular weight for **12** using a mixed solvent system and rigorous purification of salt **8**[12f] gave M_n/M_w up to 140 000/250 000 using the thiophenoxide-functionalization method[11] for determining molecular weight. For the purposes of the initial LED and optical behavior tests in this study, the lower molecular weight, unoptimized material suffices.

Preparation of PPVs. It is possible to cast films of polyelectrolytes **9** and **10** or polyethers **11** and **12** onto glass or quartz surfaces, from either of which the final conjugated polymers **1** and **2** may be generated by thermolysis at >200 °C. TGA is useful to decide the best compromise for speedy elimination of the precursors without the onset of weight loss due to decomposition. UV–vis spectra of solid thin films of **1** and **2** are the same whether the sulfonium or polyether precursor is thermolyzed. Both **1** and **2** are red polymers, having major absorption at 430–450 nm. Thick films of **1** and **2** are strong, free-standing, flexible, and somewhat iridescent. It is quite convenient to use polyethers **11** and **12** for spin-coating of very thin films from volatile organic solvents, so the electronic spectral studies reported herein are based on samples made by this method. However, it is also possible to use aqueous solvent systems to cast films of polyelectrolytes **9** and **10**. This would allow the possibility of using either an aqueous or organic soluble precursor for casting precursor films to **1** and **2**, a useful bifunctionality for device manufacture by casting of different films from different, immiscible solvents, as has been shown[3] for making flexible LEDs.

IR spectral analysis clearly shows the production of conjugated units upon precursor thermolysis, especially by the growth of the olefinic out-of-plane bending mode at ca. 960 cm^{-1}. Chemical analysis of **1** and **2** obtained by thermolysis of **11** and **12** typically shows a modest deficit of carbon as well as the presence of 0.3–0.5% of sulfur. Apparently, a few of the sulfonium pendant groups in **9** and **10** not only resist displacement by methanol but also are very slow to be eliminated by thermolysis. Repeated heating of the same sample at 250 °C shows no further change in elemental composition. Other PPVs have shown evidence of site resistance to elimination.[9a]

Preparation of Spectroscopic Samples and 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 an inert atmosphere at room temperature. The ITO electrodes are 160 nm thick films coated on glass squares (about 1.2 cm × 1.2 cm); the device has a resistance of 100 Ω. The plates were cleaned using chloroform and dried under vacuum for 5 h before use. Precursor **11** or **12** was then spin cast under a nitrogen atmosphere as 20 mg/mL solutions in chloroform at 4000 rpm onto the ITO plates, to give polymer films of about 1000 Å thickness. The precursor films on the plates were then subjected to thermal elimination under vacuum to **1** or **2** at 250 °C, followed by heat-vapor deposition of an aluminum or calcium cathode through a mask (about 2 mm × 2

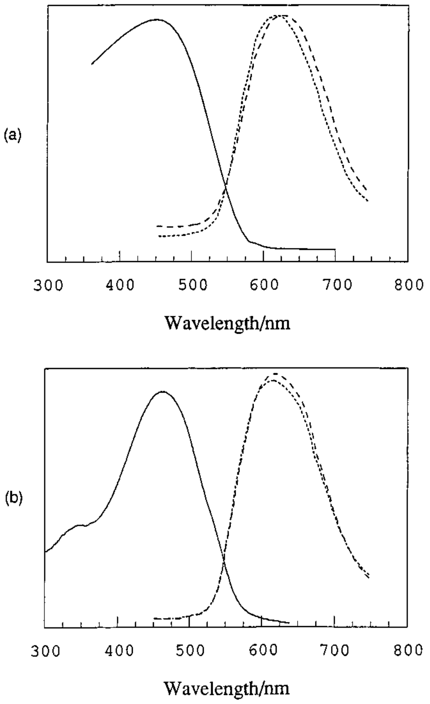


Figure 2. UV–vis (solid), photoluminescence (dashed), and electroluminescence spectra (dotted) for **1** and **2** are shown in (a) and (b), respectively. Intensities of absorption and emission are arbitrarily scaled to the same ordinate scale to allow comparison of wavelength maxima and lineshapes. All spectra were obtained using thin films at room temperature.

mm) at $< 2\ \mu$mHg. The overall pixel areas are 6 mm^2. The approximate thickness of each layer in the final devices is about 20 μm (200 nm). The final LED devices are stored in a glovebox at room temperature under nitrogen or argon.

In each measurement, the same sample was tested for photoluminescence (PL) and electroluminescence (EL). Figure 2 shows the UV–vis, PL, and EL spectra for **1** and **2**, respectively. The spectra have been scaled to the same ordinate, to allow comparison of line shapes. Band-pass filters were used to select the 390 nm region for excitation to measure PL spectra. Pulsed voltage—rather than dc—was used to observe the EL spectra.

Discussion

The syntheses of **1** and **2** are remarkably easy to carry out on a large scale, since they involve a small number of reaction steps and the use of well-established techniques for thermal elimination of precursor polymers to the final conjugated polymers. It is notable that ring halogenation to give intermediates **3** and **4** is readily carried out without use of halogen gases. Once the necessary bis-sulfonium salt monomers **7** and **8** are made, they are readily converted in the presence of base by the Wessling method[12] into water- or methanol-soluble precursor polyelectrolytes **9** and **10**. These polyelectrolytes are conveniently dialyzed and stored in solution as precursors to PPVs **1** and **2**. Polyelectrolyte films can also be easily cast into thick, free-standing films that may be heated to give strong, flexible films of **1** and **2**. Functionalization of the polyelectrolytes **9** and **10** to polyethers **11** and **12** is similar to strategies previously[13] used to make organic soluble precursors to PPVs. Chloroform or methanol solutions of **11** and **12** are stable for many weeks at <10 °C and are very convenient for spectroscopic studies or for film-casting. Although films of **11** and **12** may be redissolved by washing with chloroform or tetrahydrofuran, the eliminated polymers **1** and **2** did not redissolve after 72 h in boiling tetrahydrofuran.

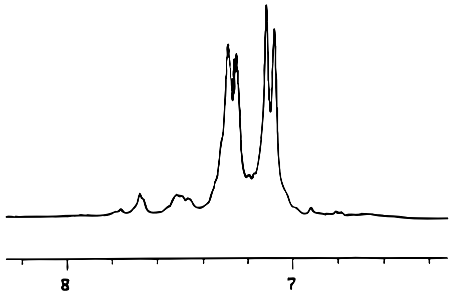


Figure 3. Aromatic region of the ^{1}H NMR spectrum for polyether **12**; spectrum obtained at 500 MHz in CDCl$_3$.

In Figure 1 we have represented all of the precursor polymers **9** and **12** and the conjugated products **1** and **2** as being regiorandom copolymers and hence complicated the nomenclature[14] of **1** and **2** by noting the interchangeability of the 2- and 5-positions in the final PPVs. We have previously suggested such scrambling of substituents to be likely for asymmetrically substituted PPVs that are made by the Wessling method,[9,12] especially given the apparent UV–vis spectral observation of more than one reactive xylylene intermediate[10,15] (Scheme 1) from asymmetrically substituted monomer bis-sulfonium salts such as **7** and **8**. The ^{1}H-NMR spectrum of polyether **12** supports the contention of regiochemical scrambling in the polymerization. In the region of best resolution, the 500 MHz aromatic region of **12** (Figure 3) shows four separate resonances for the two different aromatic protons, at δ 7.088, 7.123, 7.277, and 7.290, consistent with the two distinct environments of a regiochemically scrambled structure; the similar peak heights suggest nearly complete scrambling in **10**. Although this result is not too surprising given findings to date on the Wessling polymerization,[10,12,16] the NMR spectrum represents some of the clearest support to date for regiochemical scrambling in an asymmetrically substituted reaction. It is worth noting that poly(2-bromo-5-(dodecyloxy)-1,4-phenylenevinylene) made via base-induced xylylene generation under non-Wessling conditions from the appropriate bis(bromomethyl)benzene precursor appears to be regioregular,[9b] possibly due to the increased steric effect of the dodecyloxy group by comparison to the hexyloxy group used in polymers **1** and **2**. No LED properties were reported for poly(2-bromo-5-(dodecyloxy)-1,4-phenylenevinylene), but a comparison of electronics in the regioregular vs regiorandom connectivities would be instructive.

The elemental compositions of **1** and **2** made via polyethers **11** and **12** show <1% of sulfur, consistent with minor amounts of uneliminated sites. The FT-IR spectra for **1** and **2** show strong bands for the *trans*-ethylenic out-of-plane bending mode consistent with the product having the expected long units of conjugation after elimination. Both **1** and **2** have red shifted UV–vis maxima relative to the UV–vis maximum of about 425 nm[12f] of parent PPV itself. The UV–vis maxima for **1** and **2**, 450 and 435 nm, respectively, are similar to the 434 nm UV–vis maximum reported for the related poly[2(5)-bromo-5(2)-methoxyphenylenevinylene).[17] Both **1** and **2** show PL maximum emission at 620–630 nm (1.97–2.00 eV), vs about 560 nm (2.21 eV) for PPV[5] itself. Such red or red-orange emitting organic polymers are not yet common. An alternating copolymer of a poly(2,5-dialkoxy-1,4-phenylenevinylene) with poly(2,5-dialkoxy-1,4-phenylene-α-cyanovinylene) can be made into an LED with maximum emission at 710 nm, apparently the most red-shifted EL among the PPVs.[8] This copolymer has not been made by a processible precursor method but is soluble and may be made into devices. However, the soluble precursor methodology has an advantage in that films may be cast from either hydroxylic or nonpolar solvent media, making the fabrication of multilayer devices easier by film casting with alternating solvents such that each new layer does not mix with the previous layer.

Although other ring-substituted PPVs made by soluble precursor methods have shown strong red shifts relative to parent PPV (e.g., MEH-PPV at 600 nm or 2.07 eV[18,19]), the systems **1** and **2** are among the most red-shifted PL emitters of the PPVs[20] and hence are very suitable for red light emission. When this characteristic is combined with their ease of synthesis and processibility, **1** and **2** become very promising targets for LED-related experiments. A synthetic advantage of this methodology is the ability to reach **1** and **2** either via precursors **9** and **10** soluble in hydroxylic media, or via precursors **11** and **12** soluble in water-immiscible organic solvents. Multilayer strategies such as that employed in manufacture of flexible LEDs[3,18] are facilitated when successive polymer layers may be laid down in solvents that will not dissolve the top existing layer on the growing LED. This may be easily accomplished under a variety of conditions with the presently described chemistry, given the choices offered by using either **9** and **10** or **11** and **12**.

The similarity of the qualitative line shape and emission maximum for the PL and EL spectra of both **1** and **2** suggests that for these systems—as for others[21,22]—the same excited state is responsible for luminescence by both photoexcitation and electric field excitation. The EL spectra are readily obtained even without fabrication of added hole injection or electron injection layers into the test LEDs, though the added transport layers should greatly enhance the luminescence efficiency. The red-tinted emission from **1** or **2** is easily seen in muted room light when calcium is used as the cathode. For a typical single-layer LED made using ITO/**1**/Ca, the output brightness was measured to be 20 cd/m^2 at 30 V pulsed input voltage using 1 mA of current. Calcium is preferred to aluminum for these LEDs due to a better match of its work function to that of the PPVs, despite the lower environmental stability of calcium; an aluminum outer coating of the calcium can be used for added stability. Considering that efforts to engineer the best emissive output from new LED substrates are still ongoing, we feel that these results are promising.

Summary

The qualitative efficacy of **1** and **2** as red light emitters in single-layer ITO/polymer/Ca LEDs is encouraging, especially given the ease of synthesizing considerable quantities of **1** and **2** and closely related analogues. A limited number of red light emitters is as yet available, and fewer still are so readily processed as **1** and **2**. Numerous options for fabrication of LEDs containing **1** and **2** remain to optimize their red light emissive output and lifetimes. An ultimate goal is fabrication of LEDs containing multiple layers of different but similarly substituted PPVs and PPV analogues that will give white light and polychromic emission capability.[23] We continue to work on controlling the emissive wavelengths and improving the emissive lifetimes of such devices and will report results in future work.

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Supporting Information Available: IR spectra for PPVs **1** and **2** and polyethers **11** and **12** (3 pages). Ordering information is given on any current masthead page.

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