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Synthesis and Luminescent Studies of Poly(phenylenevinylene)s Containing a Biphenyl Moiety

Ananda M. Sarker,[†] Liming Ding,[†] Paul M. Lahti,*[,‡] and Frank E. Karasz*[,†]

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

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ABSTRACT: The polymers discussed in this contribution consist of phenylenevinylene chromophores linked together across flexible biphenyl "hinges" to shorten the effective conjugation length and to give sufficiently twisted structures that interchain aggregation is limited or prevented. They are poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(4,4′-dihexyloxy-3,3′-biphenylenevinylene)] (**1**)**,** poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(2,2′-dihexyloxy-3,3′-biphenylenevinylene)] (**2**), and poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(2,2′-biphenylenevinylene)] (**3**). Absorption spectra in dilute solution and solid states are very similar for **1**−**3**, consistent with the absence of aggregation effects in their ground electronic states. Photoluminescence emission spectra showed substantial red shifts in the solid state relative to dilute solution phase spectra. Solution emission quantum yields ranged from 0.26 to 0.42. LEDs based on **1**−**3** gave blue-green emission with maxima in the 480−510 nm range. The similarity of the photoluminescence and electroluminescence spectra for the polymers is consistent with emission from the same or very similar excited-state species. For LEDs based upon the highest quantum efficiency photoluminescent emitter, **1**, better luminance was achieved using PEDOT-PSS hole injection layers in double-layer LEDs than using PPV.

Introduction

Light-emitting diode (LED) technologies that use organic π-conjugated polymers have substantial promise for electrooptical applications. Significant improvements have been made in recent years on the performance and color availability of organic LEDs.[1] However, device lifetimes and luminescent stability remain important issues for commercialization. Therefore, synthesis of new conjugated polymers as potential emissive layers continues to be an area of many endeavors. One of the main requirements in designing such polymers is a high luminescence quantum yield in the solid state. Many conjugated polymers have low quantum yield solid-state emission or sizable solid-state emission wavelength shifts relative to solution phase emission spectra, due to the presence of interchain interactions such as aggregation, excimer formation, and polaron pair formation.[2] One effective approach to minimize these undesirable effects is to introduce structural asymmetry into the polymer chain and limit its ability to pack effectively in the solid state. For example, the introduction of a meta-linkage in the main conjugated chain of the polymer can limit interchain interaction as well as constrain exciton migration to quenching sites.[3] The meta-linkage simultaneously interrupts the conjugation length of a π-conjugated polymer and allows the polymer to bend and twist more effectively than a para-linkage. Another approach is to use bulky substituents to limit close approach between aromatic chromophores.[4] A third is to design a polymer that is structurally required to twist in a manner that limits or precludes effective π-stacking, while still having sufficiently long conjugation length chromophores to allow fine-tuning of the emission wavelength, intensity, and lifetime.

In this paper, we describe a series of new light-emitting poly(phenylenevinylene)s containing alkoxy-substituted biphenyl moieties in the main chain (Scheme 1, **1**−**3**). Biphenyl units were incorporated here as conjugation interrupting units and to provide a strong twist of the polymer π-orbitals along the biphenyl central bond. In effect, the biphenyl unit is a structural hinge about which the planar phenylenevinylene units may pivot on the 2,2′-transannular bond. Attachment of long alkoxy substituents onto the biphenyl rings was intended to limit even further the ability of the chromophores to undergo π-stacking and formation of undesirable interchain polaron pairs.[5] By varying the positions of alkoxy substitution as in **1** compared to **2**, we also hoped to fine-tune the band gap and quantum yield of radiative emission in a manner analogous to other work.[6,7] In polymer **3**, the biphenyl moiety was connected to a vinylene unit in an ortho instead of a meta position, presumably yielding an even more twisted structure for the overall polymer.

Electronic spectral properties of polymers **1**−**3** were measured in both solution and solid film. The polymers were also used as emissive layers in the fabrication of test single and double-layer LEDs.

Experimental Section

General Methods. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analysis was carried out at the University of Massachusetts Microanalytical Laboratory. NMR spectra were obtained using a Bruker DPX300 NMR spectrometer at 300 MHz. Gel permeation chromatography (GPC) was used to determine molecular weights of polymers with THF as an eluent and polystyrene as standard on a Waters GPC system equipped with a U6K injector and a model 410 differential refractometer. Absorption spectra were measured on an IBM 9420 spectrophotometer. Emission and excitation spectra were taken on a Perkin-Elmer LS 50B spectrometer with xenon lamp light source. Emission quantum yields in chloroform solvent were determined at an excitation wavelength of 350 nm using external standard 9,10-diphenylanthracene in cyclohexane ($\phi_f = 0.90$) by a literature[8] procedure. The necessary

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[†] Department of Polymer Science & Engineering.

[‡] Department of Chemistry.

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Scheme 1

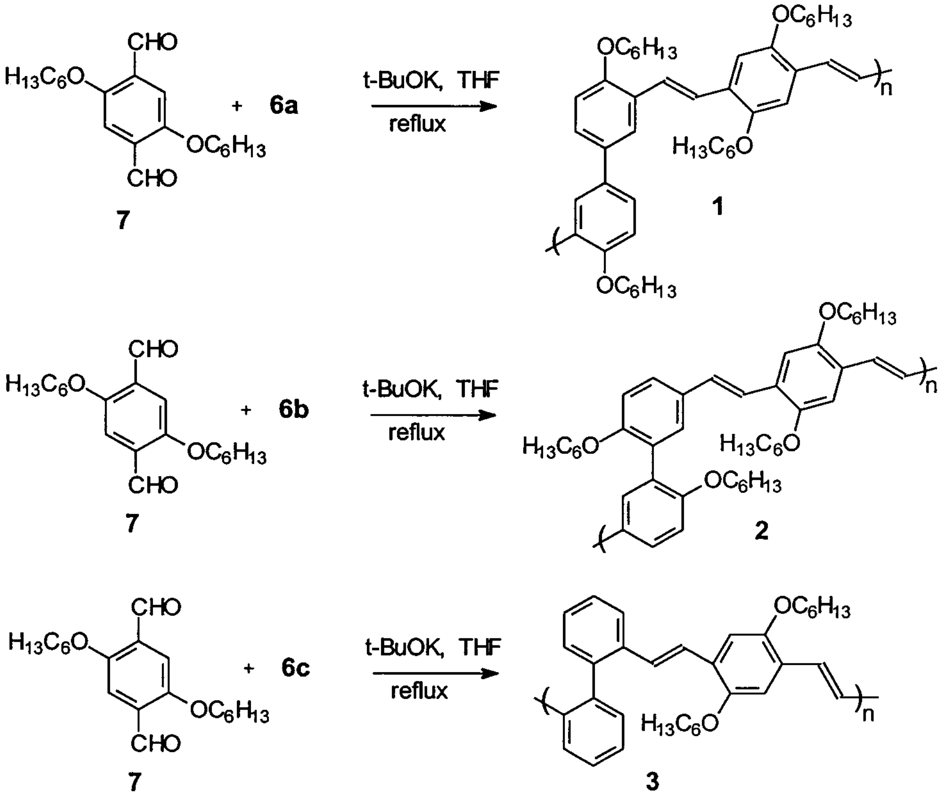


Table 1. Electronic Spectroscopy of 1−3 in Chloroform and Film

properties	1	2	3
absorption λ_{max}(chloroform),[a] nm	399	395	387
absorption λ_{max}(film),[a,b] nm	405	396	387
emission λ_{max}(chloroform),[c,d] nm	460	452	455
	480 (sh)	477 (sh)	478 (sh)
emission λ_{max}(film),[c,d] nm	513	500	484
Stokes shift,[d] nm	108	104	98
Φ_f[e]	0.42	0.38	0.26

[a] Solution spectrum at room temperature. [b] Spin-cast from chloroform solvent and dried under vacuum for 24 h. [c] Excited at 380 nm. [d] Difference between absorption and emission maxima in films. Estimated errors are ~5%. [e] Quantum yields in chloroform solution, using the method of ref 8.

solvent refractive index and the instrumental spectral response corrections were made for quantum yields determination. The reported quantum yields (Table 1) are the average of three independent measurements. The maximum absorbance of polymer solution was less than 0.1 in order to minimize errors due to inner filter effects.

4,4′-Dihexyloxy-1,1′-biphenyl (4a).[9] To a solution of 4,4′-dihydroxy-1,1′-biphenyl (8.0 g, 42.96 mmol) in 100 mL of dry acetone was added anhydrous potassium carbonate (36 g, 260.53 mmol), 1-bromohexane (18.24 g, 103.10 mmol), and a catalytic amount of sodium iodide. The mixture was refluxed for 48 h. It was poured into ice water. The product was filtered, washed with water, and dried. After recrystallization from acetone, product **4a** was obtained as white crystalline plates (80%) with mp 126−127 °C. ^1H NMR ($CDCl_3$, δ): 7.46 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.6 Hz, 4H), 3.98 (t, J = 6.6 Hz, 4H), 1.80 (m, 4H), 1.47 (m, 4H), 1.34 (m, 8H), 0.91 (t, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 158.66, 133.72, 128.06, 115.15, 68.48, 32.06, 29.74, 26.20, 23.07, 14.50. Anal. Calcd for $C_{24}H_{34}O_2$: C, 81.37; H, 9.60. Found: C, 81.31; H, 9.58.

2,2′-Dihexyloxy-1,1′-biphenyl (4b). To a solution of 2,2′-dihydroxy-1,1′-biphenyl (11.0 g, 59.1 mmol) in 200 mL of dry acetonitrile was added anhydrous potassium carbonate (48 g, 0.35 mol), 1-bromohexane (20 g, 121.15 mmol), and a catalytic amount of sodium iodide. The mixture was refluxed for 72 h. The reaction was cooled to room temperature and filtered. The solvent was evaporated under vacuum. The liquid product was purified by silica gel column chromatography eluent with hexane/dichloromethane (7:3). Compound **4b** was obtained as light yellow oil (82%). ^1H NMR ($CDCl_3$, δ): 7.26 (m, 4H), 6.94 (m, 4H), 3.88 (t, J = 6.6 Hz, 4H), 1.59 (m, 4H), 1.22 (m, 12H), 0.84 (t, J = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 157.07, 132.01, 128.79, 128.68, 120.40, 112.54, 68.80, 34.45, 31.99, 26.11, 23.08, 14.46.

3,3′-Bis(bromomethyl)-4,4′-dihexyloxy-1,1′-biphenyl (5a). This bromomethylation reaction was carried out according to a previously published procedure.[9] To a suspension of 4,4′-dihexyloxy-1,1′-biphenyl (10 g, 28.23 mmol) and paraformaldehyde (4.0 g, 133.0 mmol) in 90 mL of acetic acid was added 25 mL of 31% HBr in one portion at 80 °C. The reaction mixture became clear immediately. The reaction was stirred for 3 h at this temperature. It was then cooled to room temperature. The product crystallized after 24 h at 8 °C. The solid product was filtered and washed with water. The organic layer was dissolved in methylene chloride, neutralized with aqueous sodium bicarbonate solution, and dried. The solvent was evaporated and recrystallized from acetone/hexanes. The product was obtained as white crystals (5.32 g, 35%) with mp 93−94 °C. ^1H NMR ($CDCl_3$, δ): 7.49 (d, J = 2.40 Hz, 2H), 7.43 (dd, J = 2.40 Hz, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 4.62 (s, 4H), 4.06 (t, J = 6.4 Hz, 4H), 1.86 (m, 4H), 1.55 (m, 4H), 1.36 (m, 8H), 0.92 (t, J = 6.4 Hz, 6H). ^{13}C NMR ($CDCl_3$, δ): 156.61, 133.10, 129.50, 128.63, 126.88, 112.47, 68.81, 31.96, 29.63, 29.60, 26.20, 23.06, 14.49. Anal. Calcd for $C_{26}H_{36}Br_2O_2$: C, 57.82; H, 6.67; Br, 29.59. Found: C, 57.66; H, 6.61; Br, 29.67.

5,5′-Bis(bromomethyl)-2,2′-dihexyloxy-1,1′-biphenyl (5b). To a mixture of 4,4′-dihexyloxy-1,1′-biphenyl (13.5 g, 38.11 mmol) and paraformaldehyde (2.45 g, 81.67 mmol) in 150 mL of acetic acid was added 32 mL of 31% hydrobromic acid at 65 °C all at once. It was heated to this temperature for 4 h. As the reaction proceeded, the suspension changed to clear solution first and then became a white suspension again. It was then cooled to room temperature, and 150 mL of cold water was added with constant stirring. The precipitate was filtered and washed with copious water. The solid was dissolved in methylene chloride, neutralized with aqueous sodium bicarbonate solution, and finally washed with brine. After drying over magnesium sulfate, solvent was evaporated from the organic layer. After recrystallization from methylene chloride, the product was obtained as a white solid (12.0 g, 58%) with mp 91−92 °C. ^{1}H NMR (CDCl$_3$, δ): 7.32 (m, 4H), 6.87 (d, J = 9.2 Hz, 2H), 4.52 (s, 4H), 3.90 (t, J = 6.4 Hz, 4H), 1.62 (m, 4H), 1.23 (m, 12H), 0.84 (t, J = 6.4 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ): 157.00, 133.00, 129.80, 129.42, 127.95, 112.44, 68.87, 34.68, 31.90, 29.50, 26.08, 23.00, 14.43. Anal. Calcd for $C_{26}H_{36}Br_2O_2$: C, 57.82; H, 6.67; Br, 29.59. Found: C, 57.60; H, 6.64; Br, 29.71.

3,3′-Bis(diethylphosphonatomethyl)-4,4′-dihexyloxy-1,1′-biphenyl (6a). A mixture of 3,3′-bis(bromomethyl)-4,4′-dihexyloxy-1,1′-biphenyl (4.31 g, 7.98 mmol) and triethyl phosphite (10.25 g, 61.68 mmol) was heated to 85−90 °C for 16 h. Excess triethyl phosphite was separated by vacuum distillation. Hexanes (25 mL) were added, and the reaction was stirred at 50 °C for 30 min. Again solvent was removed by vacuum distillation. The product **6a** was obtained as thick oil (58% yield). ^{1}H NMR (CDCl$_3$, δ): 7.52 (s, 2H), 7.38 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.07 (m, 8H), 3.31 (d, J = 22.0 Hz, 4H), 1.82 (m, 4H), 1.50 (m, 4H), 1.34 (m, 8H), 1.24 (t, J = 6.8 Hz, 6H), 0.92 (t, J = 6.8 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ): 156.24, 133.13, 129.86, 126.79, 120.81, 111.97, 68.77, 62.38, 31.96, 29.69, 27.90, 26.17, 22.97, 16.77, 14.40.

5,5′-Bis(diethylphosphonate)-2,2′-dihexyloxy-1,1′-biphenyl (6b). Synthesized as described above for compound **5b** (62% yield). ^{1}H NMR (CDCl$_3$, δ): 7.25 (d, J = 8.2 Hz, 2H), 7.09 (s, 2H), 6.84 (d, J = 8.2 Hz, 2H), 4.0 (m, 4H), 3.86 (t, J = 6.4 Hz, 4H), 3.09 (d, J = 21 Hz, 4H), 1.58 (m, 4H), 1.23 (m, 18H), 0.84 (t, J = 6.4 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ): 156.08, 133.06, 129.93, 128.53, 122.94, 112.28. 68.70, 62.46, 33.12 (d), 31.93, 29.60, 26.00, 22.96, 16.83, 14.37.

2,2′-Bis(diethylphosphonate)-1,1′-biphenyl (6c). By following the procedure of **6a** and using 2,2′-bis(bromomethyl)-1,1′-biphenyl (Aldrich) as starting material, we obtained compound **6c** as thick oil. ^{1}H NMR (CDCl$_3$, δ): 7.59 (d, J = 7.2 Hz, 2H), 7.30 (m, 6H), 3.95 (m, 4H), 2.97 (d, J = 22 Hz, 2H), 2.91 (d, J = 22 Hz, 2H), 1.22 (t, J = 7.2 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H). ^{13}C NMR (CDCl$_3$, δ): 141.15, 131.10, 130.48, 130.42, 128.10, 126.97, 62.32, 30.50 (d), 16.71.

2,5-Dihexyloxy-1,4-dicarboxylaldehyde (7). To a solution of 2,5-dihexyloxy-1,4-dibromobenzene[10] (3.50 g, 8.02 mmol) in diethyl ether (90 mL) was added 2.5 M butyllithium solution (8.05 mL) in hexane at 0 °C under nitrogen. It was stirred for 30 min and allowed to come to room temperature. Then it was refluxed for an hour while white precipitate was formed. *N*,*N*-Dimethylformamide (1.75 mL) was added at 0 °C and stirred for overnight at room temperature. Aqueous ammonium chloride (20%, 20 mL) was added and the organic layer separated. After washing several times with water and brine, it was dried over magnesium sulfate. The solvent was evaporated and the solid product was recrystallized from 2-propanol (52% yield); mp 73−74 °C. ^{1}H NMR (CDCl$_3$, δ): 10.52 (s, 2H), 7.43 (s, 2H), 4.09 (t, J = 6.4 Hz, 4H), 1.84 (m, 4H), 1.48 (m, 4H), 1.34 (m, 8H), 0.91 (t, J = 6.6 Hz, 6H). ^{13}C NMR (CDCl$_3$, δ): 189.77, 155.58, 129.61, 111.94, 69.59, 31.85, 29.55, 29.38, 26.06, 22.94, 14.37. Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.87; H, 8.98. Found: C, 71. 80; H, 9.02.

Synthesis of Polymers: General Procedure. A solution of dialdehyde (0.76 mmol) in 5 mL of anhydrous THF was added to a solution of the corresponding phosphonate derivative (0.76 mmol) in 5 mL of THF under a nitrogen atmosphere. Then solid *tert*-BuOK (2.5 equiv) was added at room temperature portion by portion under nitrogen. After stirring for 2 h at room temperature, the mixture was heated to reflux for 36 h. The reaction was quenched with 2% hydrochloric acid at room temperature. The polymer was precipitated from methanol and filtered. It was purified by dissolving in chloroform and reprecipitated from methanol. After drying under vacuum for 24 h polymer was obtained as yellowish solid.

Poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(4,4′-dihexyloxy-3,3′-biphenylenevinylene)] (1). By following the general procedure and using monomers **6a** and **7** as starting materials, polymer **1** was obtained as yellow solid (47% yield). ^{1}H NMR (CDCl$_3$, δ): 7.82 (br s, 2H), 7.56 (s, 4H), 7.41 (m, 2H), 7.18 (s, 2H), 6.96 (m, 2H), 4.05 (br s, 8H), 1.85 (br s, 8H), 1.51 (br s, 8H), 1.33 (br s, 24H), 0.85 (br m, 12H). Anal. Calcd for $C_{46}H_{64}O_4$: C, 81.19; H, 9.41. Found: C, 80.72; H, 9.32.

Poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(2,2′-dihexyloxy-3,3′-biphenylenevinylene)] (2). By following the general procedure and using monomers **6b** and **7** as starting materials, polymer **2** was obtained as yellow solid (41% yield). ^{1}H (CDCl$_3$, δ): 7.47 (br s, 6H), 7.34 (d, J = 16 Hz, 2H), 7.11 (d, J = 16 Hz, 2H), 6.95 (m, 2H), 4.02 (m, 4H), 3.93 (m, 4H), 1.83 (m, 4H), 1.61 (m, 4H), 1.48 9 (m, 4H), 1.32−1.21 (m, 20H), 0.84 (m, 12H). Anal. Calcd for $C_{46}H_{64}O_4$: C, 81.19; H, 9.41. Found: C, 80.63; H, 9.44.

Poly[(2,5-dihexyloxy-*p*-phenylenevinylene)-*alt*-(2,2′-biphenylenevinylene)] (3). By following the general procedure and using monomers **6c** and **7** as starting materials, polymer **3** was synthesized according to the general procedure described above in 54% yield. ^{1}H NMR (CDCl$_3$, δ): 7.77 (br s, 2H), 7.32−7.20 (br m, 8H), 6.84 (m, 2H), 6.63 (br s, 2H), 3.67 (br s, 4H), 1.56 (m, 4H), 1.29 (m, 12H), 0.89 (br s, 6H). Anal. Calcd for $C_{34}H_{40}O_2$: C, 85.01; H, 9.80. Found: C, 84.43, H, 9.69.

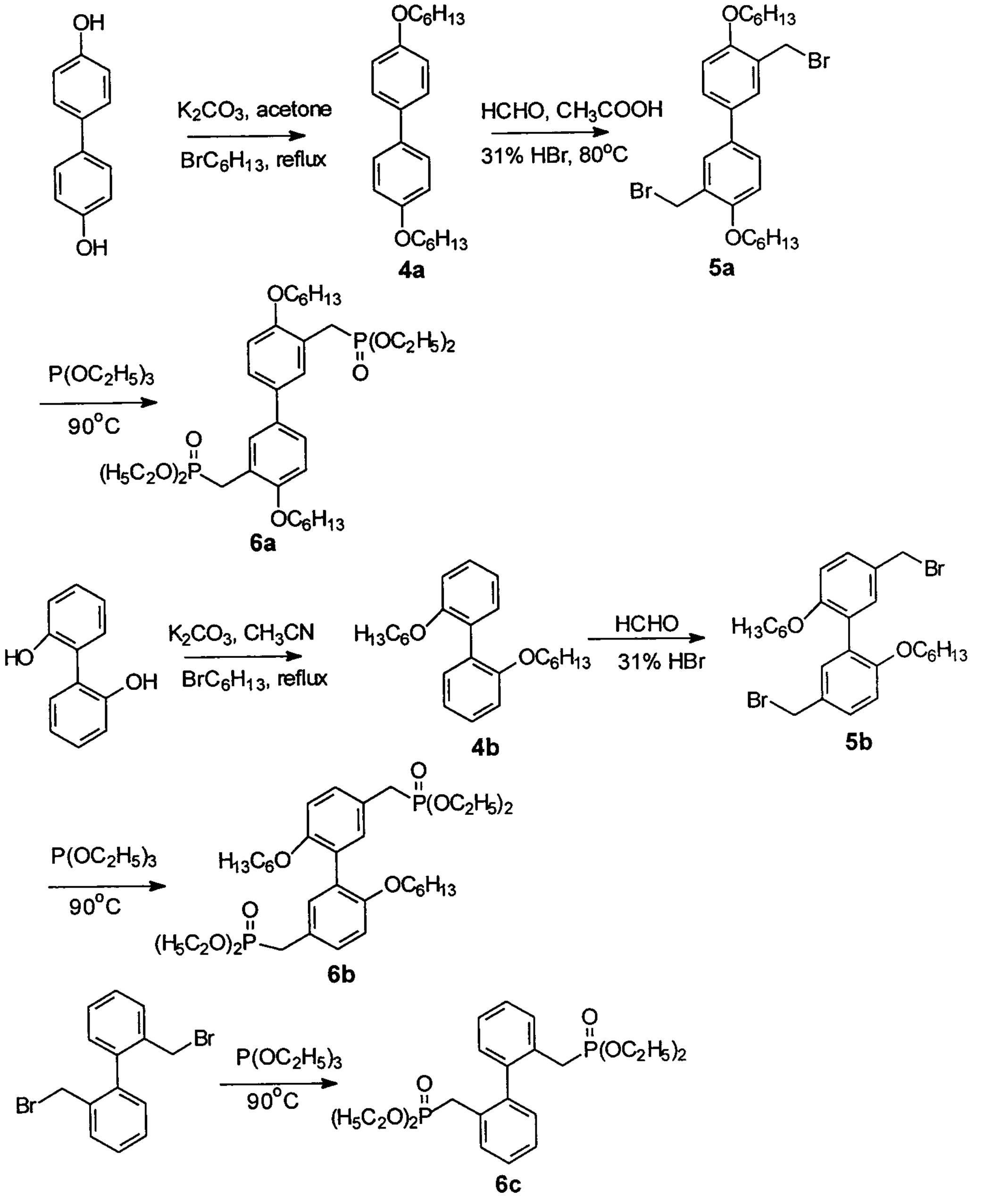
Device Fabrication and Measurements. Polymer solutions (20 mg/mL in chloroform) were filtered through 0.2 μm Millex-FGS filters (Millipore) and spin-cast onto ITO glass, PPV/ITO substrates, or PEDOT/ITO substrates under a nitrogen atmosphere in a glovebox. PPV/ITO substrates were obtained by spin-casting sulfonium polyelectrolyte precursor polymer[11] as a methanol solution onto ITO glass (OFC Co.) and then doing thermal conversion to PPV under flowing argon at 250 °C for 2.5 h). For double-layer LEDs, PEDOT−PSS (Bayer) layers were spin-cast onto ITO glass and then dried in vacuo at 60 °C for 2 days. The polymer films were typically 75 nm thick as measured by ellipsometry under usual conditions. Calcium electrodes of 400 nm thickness were evaporated onto the polymer films at about 0.1 μTorr pressure through a mask, followed by deposition of a protective coating of aluminum. The devices were characterized using a spectral measurement system constructed in our laboratory that is described elsewhere.[12] The devices were operated using pulsed voltage for spectral measurements and dc voltage for current density determinations.

Results and Discussion

One standard method of making poly(arylenevinylenes) is by conventional Wittig reaction between phosphonium salts and aldehydes. However, this condensation reaction gives mixtures of trans and cis olefinic bonds in the main polymer chain and often exhibits inferior luminescent properties in LEDs.[13] An attractive alternative to make predominately trans vinylene units in the polymer chain is the Horner−Emmons condensation polymerization used to make polymers **1**−**3**, as shown in Scheme 1. Starting from the appropriate dihydroxybiphenyl, aromatic bis-esters **4a**,**b** were synthesized and bromomethylated to compounds **5a**,**b** according to literature procedures (Scheme 2).[9] Subsequent Arbuzov reaction with triethyl phosphite yielded phosphonate esters **6a**,**b** as thick oils. The simpler monomer **6c** was made by reaction between 2,2′-bis(bromomethyl)biphenyl and triethyl phosphite.

The polymerization of **6a**−**c** with 2,5-dihexyloxy-1,4-benzenedicarboxaldehyde **7** to give polymers **1**−**3** was carried out in refluxing THF solution under a nitrogen atmosphere using potassium *tert*-butoxide as base. The crude product was worked up as described in the Experimental Section and purified by multiple precipitation into methanol. No detectable amounts of cis

Scheme 2



olefinic bond formation were found by ^{1}H NMR in the polymers after purification. The lack of aldehyde spectral signatures in the ^{1}H NMR spectrum shows that no significant amount of monomeric residues remained and that the molecular weight was high enough to preclude spectral end group analysis. It is possible—even likely—that lower weight fractions of the material were lost during the purification process. The isolated polymeric materials readily dissolved in THF, chloroform, and other halogenated solvents and were subjected to gel permeation chromatographic (GPC) analysis using polystyrene standards to yield number-average molecular weights of 21 000, 16 000, and 26 000, respectively. The degrees of polymerization are therefore roughly DP = 31, 23, and 54, with the caveat that polystyrene may not be a totally ideal GPC molecular weight standard for **1**–**3**.

Electronic Spectroscopy. The UV–vis absorption spectra of **1**–**3** in chloroform at micromolar concentrations and as solid films are shown in Figures 1 and 2, respectively. All of the polymers have similar $\pi-\pi^*$ transitions with $\lambda_{\max}$ ranging from 387 to 405 nm (Table 1) in solution and solid. A small red shift in the absorption maximum was observed for **1** compared to **2**, presumably due to the difference in positional substitution of the hexyloxy groups. The average conformational structure in the ground state 4,4′-linked **1** is expected to be more planar that of **2**, which has steric strain inducing substitution at the 2,2′-positions.[14] If this is the effect that gives rise to the slightly longer wavelength of the absorption maximum in **1**, it is not significant. By comparison, the $\pi-\pi^*$ transition for **3** is significantly blue-shifted compared to **1** and **2**. Either the biphenyl moiety in **3** is more twisted due to steric repulsions between vinylic and ortho C–H bonds[14] or possibly the lack of alkoxy groups in **3** leads[15] to a blue shift. It is probable that the two effects reinforce one another.

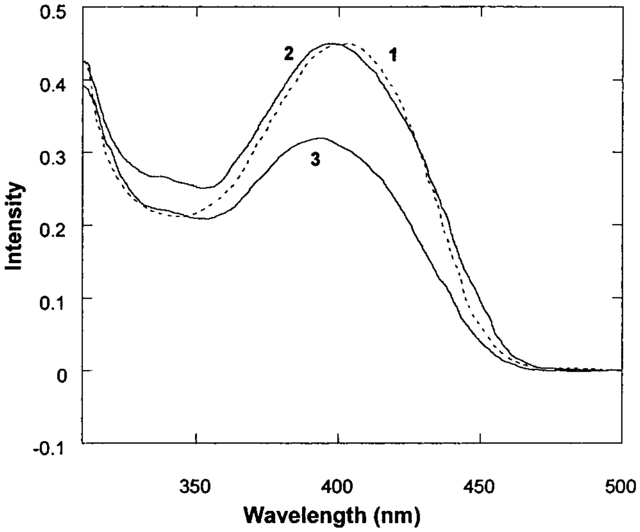


Figure 1. Absorption spectra of **1**−**3** in chloroform (10^{-6} M).

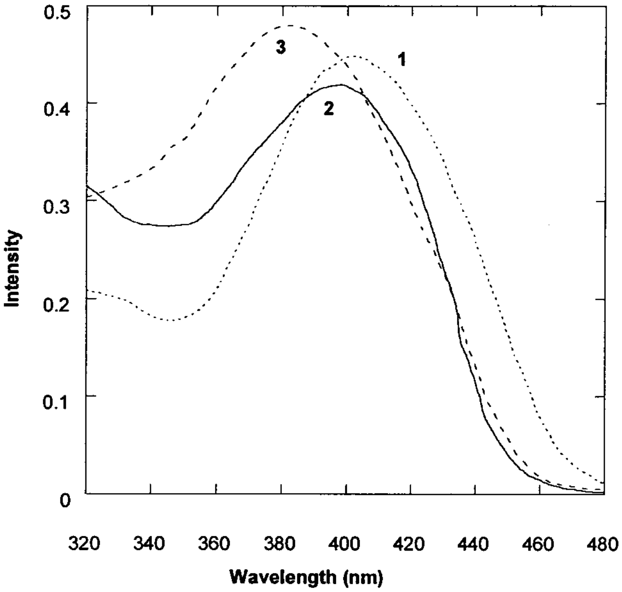


Figure 2. Absorption spectra of **1**−**3** in spin-cast films.

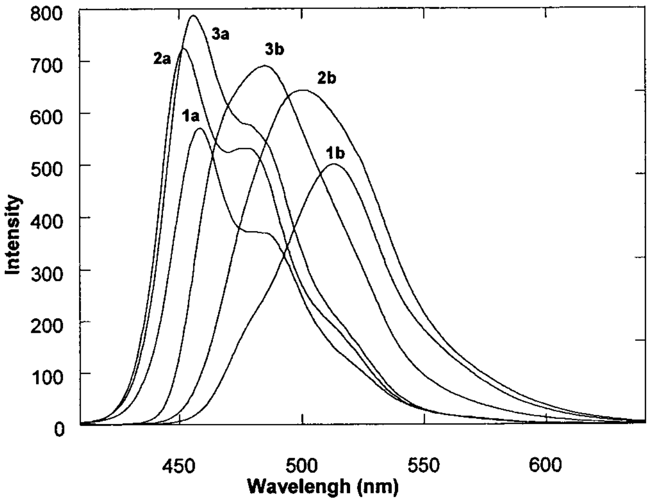


Figure 3. Photoluminescence spectra (excited at 380 nm) of **1**−**3** in (a) chloroform and (b) spin-cast films.

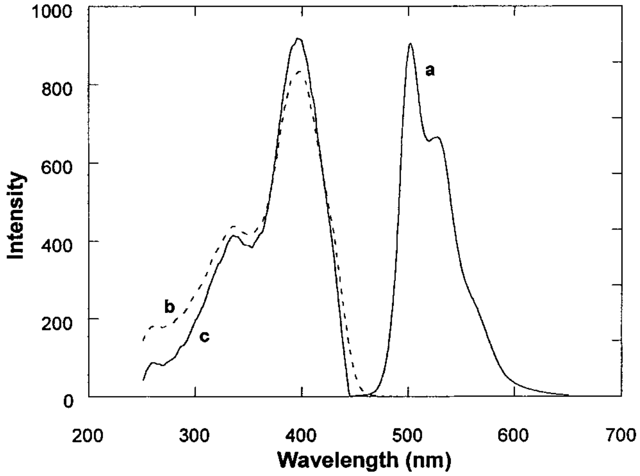


Figure 4. Photoluminescence spectra of **2** in chloroform (a). Excitation spectra of **2** at 478 nm (b) and 455 nm (c).

The absorption maxima of PPV type conjugated polymers, in general, show a red shift in the solid film as compared to the dilute solution, which has been explained as an effect of interchain π-stacking.[16] Ground-state interactions between chains in polymers **1**−**3** apparently do not influence their absorption spectroscopy, given that the solid film absorption are very similar to the solution spectra.[17]

Photoluminescence Spectra. The photoluminescence (PL) spectra of **1**−**3** were taken in chloroform at micromolar concentrations and in spin-cast films (Figure 3). The results are summarized in Table 1. The emission spectra of all of the polymers in solution are qualitatively similar. They are also insensitive to excitation wavelength, such that the same spectral features are observed upon excitation at either 360 or 380 nm, save for emission intensity. The splitting of the emission spectra into two well-resolved bands is a common feature in PPV-type chromophores, which are characterized by a vibronic structure which is attributed to a coupling of the phenylene ring stretching modes of the main chain to the electronic transitions between π and π^* states.[18] Since the PL spectra of a dilute solution of a conjugated polymer represent emission from isolated single polymer chains,[19] the shoulder-like emission band at lower energy region of the PL spectra (Figure 3) is not likely to be due to interchain interactions. To support this proposition further, excitation spectra were obtained for **2** at 455 and 478 nm, respectively (Figure 4). Very little difference was observed in the intensities and positions of the emission bands but only a change in overall PL spectral intensity. This behavior strongly supports the assignment of the emission peaks at 455 and 478 nm to the same chromophore.

The PL spectra of spin-cast films of **1**−**3** show featureless, broad, red-shifted emission compared to those of the solution. The peak maxima of the solid film PL spectra of **1**−**3** compared to the UV absorption spectra show shifts of about 100 nm (Table 1). The spectra width and featureless nature, combined with these large shifts, suggest that interchain interactions play a factor in the excited-state emission mechanisms of **1**−**3**, despite the nonplanar ground-state conformations expected for the polymers.

The strong red shift in the PL spectra of **1**−**3** relative to the UV spectra may be due to excimer formation rather than aggregation, judging by the lack of spectral shifts in the absorption spectra for the solution by comparison to the solid state. Aggregation is a ground-

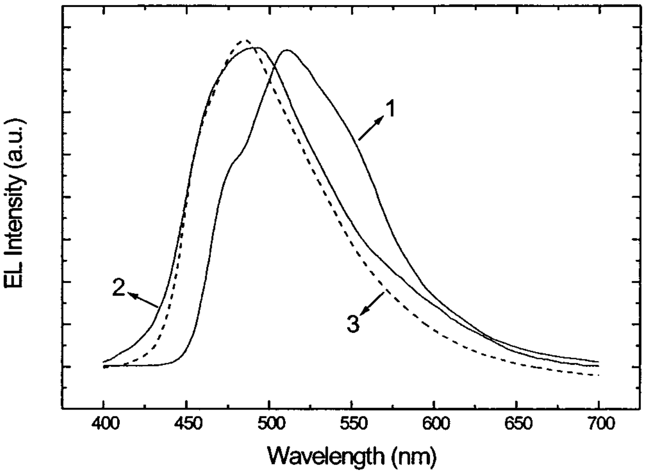


Figure 5. Electroluminescence spectra for double-layer devices ITO/PEDOT-PSS/polymer/Ca(Al).

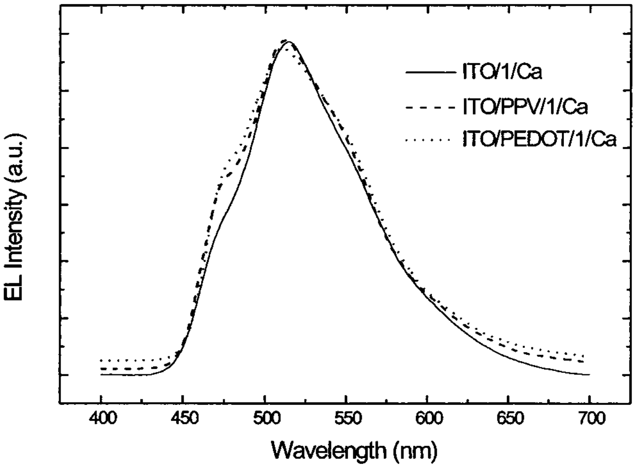


Figure 6. Electroluminescence spectra for devices ITO/**1**/Ca-(Al), ITO/PPV/**1**/Ca(Al), and ITO/PEDOT-PSS/**1**/Ca(Al).

state property, which should, in principle, be observed in the absorption spectra. Alternatively, the Stokes shift may be enhanced (at least in part) by energy migration to emissively important, but geometrically minor, conformations.[1] The large red shifts in the emission spectra are consistent with the flexible structures of polymers **1**−**3**. The polymer chain flexibility allows appreciable change in excited-state geometries as compared to ground-state geometries, a factor that increases the shift relative to that observed in more rigid π-systems. Overall, the absorption and emission spectra demonstrate both the flexibility of the polymers under excited-state conditions and the lack of substantial aggregation between polymer chains. The similarity of emission spectral peak maxima in the photoluminescence and electroluminescence spectra further supports a lack of substantial interchain electronic interactions in **1**−**3**.

Solution Emission Quantum Yields. The quantum yields of emission for **1**−**3** were determined in anhydrous chloroform at micromolar concentrations and are shown in Table 1. Compared to planar poly(*p*-phenylenevinylene)s and other, more rigid fluorophores **1**−**3** show lower quantum yields.[20] The twisted conformations of the polymer chains should favor nonradiative relaxation processes for **1**−**3** in solution. The lowest quantum yield in the series for **3** is attributable to its having the maximum nonplanarity, leading to increased nonradiative relaxation. This is consistent with the ortho connectivities in this polymer. Generally, internal conversion (IC) and intersystem crossing (ISC) are the main relaxation processes of excited states in solution aside from radiative decay, given that there is no interchain interaction at high dilution. However, the contribution of IC to nonradiative decay depends on the energy gap between S_1 and S_0.[21] The energy gaps for **1**−**3** are relatively small (around 65 kcal/mol),[22] which makes IC a contributing factor to nonradiative decay. The rate of ISC in biphenyls increases with the dihedral angle of the biaryl bonds.[23] Therefore, in the biphenyl-based polymers **1**−**3**, it is reasonable to observe lower quantum yields in emission due to higher rates of IC and ISC than occur in more planar, fully conjugated PPVs.

Electroluminescence. Double-layer LEDs of the configuration ITO/PEDOT-PSS/polymer/Ca(Al) were fabricated with **1**−**3** and found to emit blue-green light with EL peak wavelengths of 511, 492, and 485 nm, respectively. The EL spectra shown in Figure 5 are quite similar to the corresponding PL spectra in Figure 3, supporting the conclusion that both EL and PL originate from the same radiative decay process of the singlet exciton.[24] Through the series from **1** to **3**, the EL spectra show a modest blue shift, which we attribute to a band gap increase resulting from decreased net conjugation length due to polymer chain twisting.

To compare the effects of different hole injection materials, PPV and PEDOT-PSS were used to fabricate LEDs based on the most strongly photoluminescent polymer **1**.[10,25,26] A single-layer LED was also fabricated as a benchmark for an EL device without a hole injection layer. The three device configurations—ITO/**1**/Ca(Al), ITO/PPV/**1**/Ca(Al), and ITO/PEDOT-PSS/**1**/Ca-(Al)—all gave blue-green emission maxima at wavelengths of 514, 513, and 511 nm, respectively (Figure 6). These results show that the thin layer of PPV used in our device protocol—11 nm by ellipsometry—did not significantly contribute as an emissive chromophore, but instead acted only as a hole injection layer. Notably, in both the PPV and PEDOT-PSS containing double-layer devices, the shoulder emission at 479 nm became stronger. This band is similar to the 0−0 vibronic band in the PPV emission spectrum.[10] The 0−0 and 0−1 vibronic transitions in the PL and EL spectra of PPV films are associated with surface and bulk state formation, respectively. In the double-layer devices based on **1**, because of the good hole injection energy level match, the recombination center presumably will move from the bulk toward the polymer/Ca interface. As a result, there should be more emission from the excitons formed close to the interface, resulting in EL spectra that reflect an intensity increase of the 479 nm shoulder, as is in fact observed.

PPV and PEDOT-PSS were expected to reduce the hole-injection barrier at the anode interface and reduce the turn-on voltage[27] relative to the single-layer LEDs. The turn-on voltage is defined here as the voltage at which the luminance from the device increases abruptly. With PPV or PEDOT-PSS, the turn-on voltage for the LEDs based on **1** decreased from 7 to 6 V, respectively, as shown in Figures 7a−c. In a comparison of the hole injection effects at an operating pulsed voltage of 9 V, the three LEDs ITO/**1**/Ca(Al), ITO/PPV/**1**/Ca(Al), and ITO/PEDOT-PSS/**1**/Ca(Al) show luminances of 110, 450, and 595 cd/m^2, respectively, with corresponding external quantum efficiencies of 0.0082%, 0.068%, and 0.17%. The PEDOT-PSS layer improves the device performance

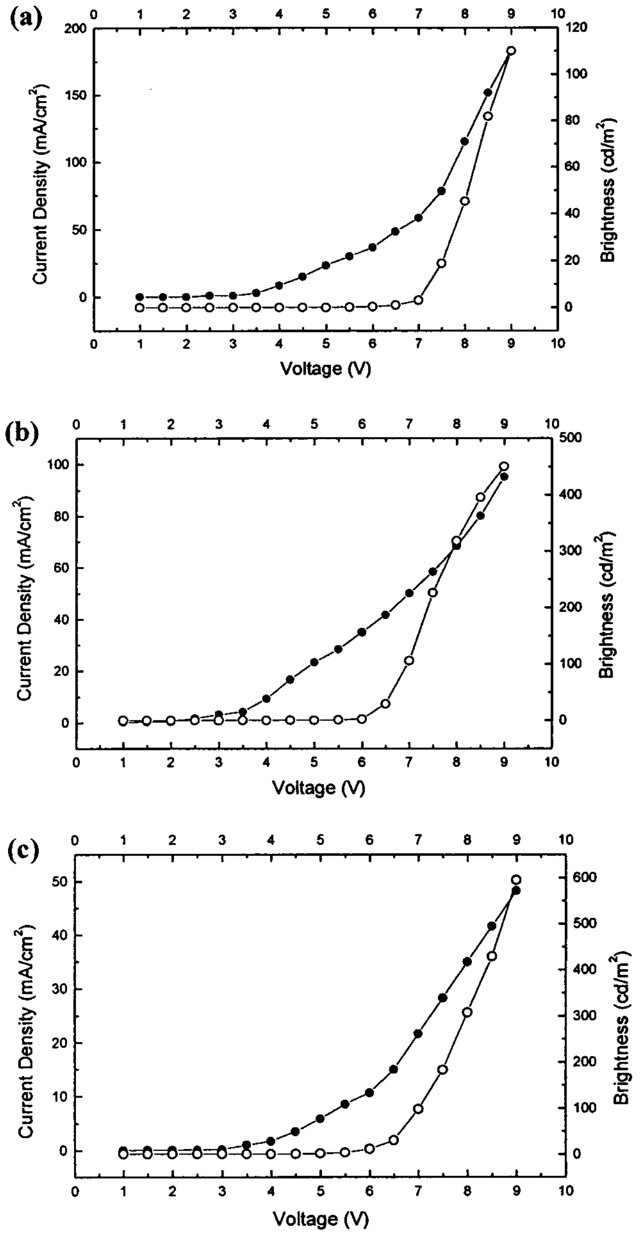


Figure 7. Current−voltage−brightness plots for LEDs based upon polymer **1**: (a) ITO/**1**/Ca(Al); (b) ITO/PPV/**1**/Ca(Al); (c) ITO/PEDOT-PSS/**1**/Ca(Al); current density (●); luminance (○).

greatly relative to the single-layer device, more so than the PPV hole injection layer. Presumably this is due to the fact that the HOMO of PEDOT-PSS (5.2/5.3 eV) lies lower than that of PPV (5.0 eV).[27,28] This causes a higher built-in field across the emissive polymer layer, which corresponds to the work function difference between the cathode and anode. The higher built-in field gives rise to a strong luminance in the devices with PEDOT-PSS hole injection layers.

Summary

Polymers **1**−**3** were readily synthesized in high purity with moderate degrees of polymerization. They do not exhibit aggregation-type shifts in their absorption spectra, presumably due the design strategy of making them twisted and flexible about the biphenyl central bond, rendering π-stacking much more difficult than in rigid, planar chromophores. The solution-phase photoluminescence Stokes shifts that are consistent with significant geometric relaxation of the flexible polymer in the excited state by comparison to the ground state or with energy migration to emissively important minor conformations in the polymer chain. The electroluminescence spectra are very similar to the solid-state photoluminescence spectra, consistent with the origination of emission from the same excitons in both measurements. Device luminance, as expected, is substantially improved by incorporation of hole injection layers into the LEDs, with PEDOT-PSS giving superior results to PPV in this respect. Overall, the use of biphenyl linkers to control net conjugation length in LED polymers should allow substantial fine-tuning of emissive behavior, depending upon the choice of polymer connectivity and substitution patterns.

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