Oxadiazole Containing Conjugated−Nonconjugated Blue and Blue-Green Light Emitting Copolymers

Min Zheng,[†] Liming Ding,[†] E. Elif Gürel,[†] Paul M. Lahti,[‡] and Frank E. Karasz*,[†]

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

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ABSTRACT: A series of segmented copolymers containing oxadiazole groups in the conjugated main chain have been synthesized with the objective of raising the electron transport ability. The present copolymers consist of alternating blocks of rigid chromophores containing oxadiazole units together with flexible spacer segments. The effects of chromophore substituents on the optical properties of the copolymers were investigated. Strong solvatochromic effects were observed, indicating intramolecular charge transfer in the excited states. The copolymers not only were used as blue-green electroluminescent materials but also were effective as electron transport/hole blocking layers in polymer light emitting diode architectures as a result of the introduction of electron transporting unit oxadiazole. The quantum efficiency of a single-layer device using PPV was greatly enhanced with the use of a thin film of the oxadiazole copolymer serving as an ETL layer. At 6.8 V, a brightness of 2400 cd/m^2 was achieved with an external quantum efficiency of 0.094%.

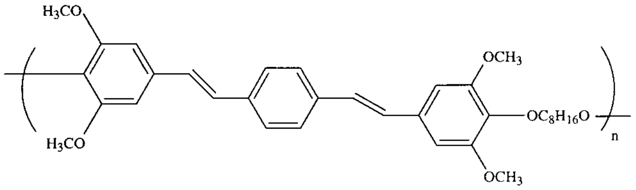
Introduction

Polymer LEDs have been widely studied, and the most efficient devices with a layered architecture reported are multilayer devices which comprise a sequence of a hole-transporting layer, an emitting layer, and an electron-transporting layer.[1−3] However, the assembly of multilayer devices is tedious and requires careful selection of solvents to avoid compromise of previously deposited films. To solve this problem, blended materials that contain mixtures of hole transporters, electron transporters, and emitters can be used to form efficient single-layer devices.[4] The advantage of the latter approach is that phase separation of the different components can be achieved providing the necessary exciton confinement. However, metastable phase separation may also reduce lifetimes for these devices. Alternatively, it is possible to covalently incorporate the electron-transport monomer in the conjugated polymer main chain to improve device performance.

It has been shown previously that PPV-related copolymers containing aromatic conjugated and aliphatic nonconjugated blocks are soluble, have good film-forming capability and mechanical properties, and are suitable for fabrication of light emitting devices.[5−8] These alternating block copolymers have been shown to be efficient light emitting electroluminescent materials in several LED architectures.[5−8] The monomeric oxadiazole moiety, a thermally and photolytically stable material, has been incorporated into these and other systems.[9−15]

In this contribution, to raise the electron transport ability relative to that of the reference alternating block copolymer "Blue" (Scheme 1),[5,6] a series of oxadiazole-containing conjugated and aliphatic nonconjugated blocks have been synthesized (Scheme 2). The effect of the substituents in the chromophore unit on the optical properties was also studied. The properties of these polymers and their electroluminescent characteristics for single- and double-layer LEDs were investigated.

Scheme 1. Structure of the Reference Copolymer "Blue"[5,6]



Experimental Section

General. Commercially available materials were used as received unless noted otherwise. Compounds **1** and **2** were synthesized according to published procedures.[16] Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. NMR spectra were collected on a Bruker DPX300 spectrometer in chloroform-*d* solution with tetramethylsilane (TMS) as internal standard. Elemental analyses was carried out in the University of Massachusetts Microanalytical Laboratory. Differential scanning calorimetry (DSC) was run on a Perkin-Elmer DSC-7 using Pyris software. The glass transition temperatures reported were taken as the onset temperature of the heat capacity discontinuity. The molecular weights of polymers were determined by gel permeation chromatography with THF as eluent and polystyrene as standard. UV−vis spectra were recorded on an IBM 9420 spectrometer. Emission spectra were obtained on a Perkin-Elmer LS 50B spectrometer with a xenon lamp as light source. The relative emission quantum yields were determined using 9,10-diphenylanthracene in cyclohexane as standard ($\Phi_f = 0.90$).[17]

LED Fabrication and Characterization. Solutions of the polymers (20 mg/mL in chloroform) were filtered through 0.2 μm Millex-FGS filters (Millipore Co.) and were then spin-coated onto commercially available indium tin oxide (ITO)-coated glass substrates (OFC Co.) under nitrogen. The polymer films were typically ~80 nm thick. Calcium (400 nm) was evaporated onto the polymer at about 10^{-7} Torr, followed by a protective coating of aluminum. Double-layer devices were fabricated by spin-casting onto the ITO surface with a methanol solution of the PPV precursor.[18] The precursor layer was eliminated at 250 °C for 2 h under an argon atmosphere. The

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[†] Department of Polymer Science & Engineering.

[‡] Department of Chemistry.

* To whom correspondence should be addressed. E-mail: fekarasz@polysci.umass.edu.

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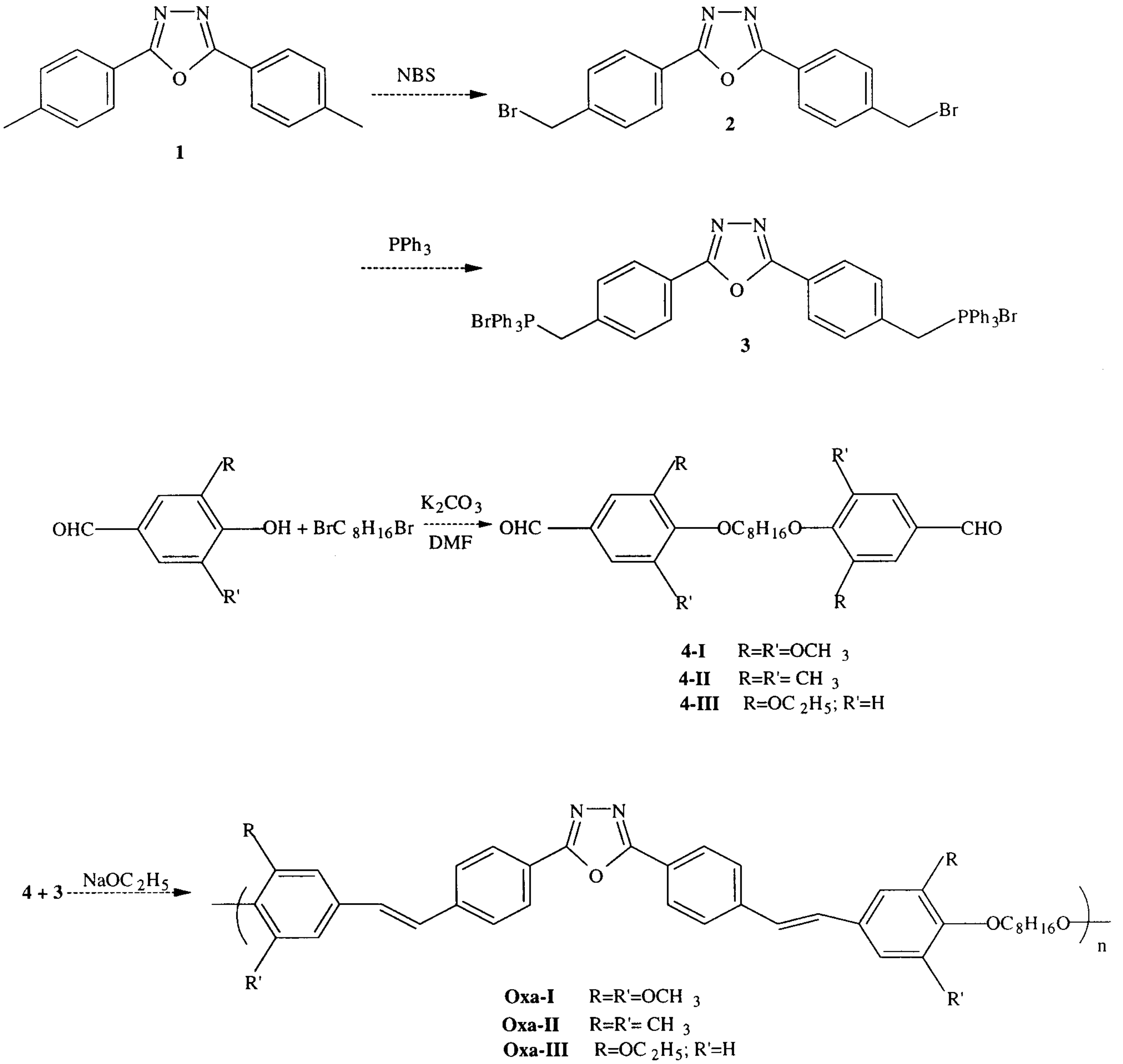
Scheme 2. Synthetic Route to "Oxa" Copolymers



devices were characterized using a system constructed in our laboratory, which has been described elsewhere.[4]

2,5-Bis{[(*p*-triphenylphosphonio)methyl]phenyl}-1,3,4-oxadiazole Dibromide (3). This synthesis was carried out by heating a mixture of triphenylphosphine (9 g, 33.6 mmol) and 2,5-bis(*p*-bromomethylphenyl)-1,3,4-oxadiazole (6.0 g, 14.4 mmol)[16] in dimethylformamide (100 mL) at 105−110 °C under nitrogen overnight. The product was obtained as a precipitate, leaving unreacted starting materials and monosubstituted phosphonium salt in solution. The product was filtered followed by washing with diethyl ether (100 mL) to give the phosphonium salts (75% yield); mp >200 °C. ^{1}H NMR ($CDCl_3$, ppm, δ): 7.9−7.5 (m, 30H), 7.3 (d, 4H), 7.2 (d, 4H), 6.05 (d, 4H). ^{13}C NMR (DMSO, ppm, δ): 163.89, 163.86, 135.59, 134.53, 134.40, 132.84, 132.72, 132.25, 132.18, 130.64, 130.47, 127.28, 123.32, 123.26, 118.47, 117.33. ^{31}P NMR (DMSO, ppm, δ): 24.34. Elemental calcd for $C_{52}H_{42}Br_2ON_2P_2$: C, 66.97; H, 4.54; Br, 17.13; P, 6.64; N, 3.00. Found: C, 65.85; H, 4.80; Br, 16.77; P, 6.5; N, 3.03.

1,8-Bis(4-formyl-2,6-dimethoxylphenoxy)octane (4-I). This compound was synthesized according to literature procedures.[19] All physical and spectra properties were in accord with previously published values.

1,8-Bis(4-formyl-2,6-dimethylphenoxy)octane (4-II). This compound was synthesized according to the literature for **4-I** from 1.55 g (10.32 mmol) of 3,5-dimethyl-4-hydroxy benzaldehyde, 1.41 g (5.16 mmol) of 1,8-dibromooctane, and 1.93 g of potassium carbonate. The crude product was recrystallized twice from ethanol to yield 53% with mp 87−88 °C. ^{1}H NMR ($CDCl_3$, δ): 9.8 (s, 2H), 7.6 (s, 4H), 4.0 (t, 4H), 2.4 (s, 12H), 1.8 (m, 4H), 1.4 (m, 8H). Elemental calcd for $C_{26}H_{34}O_4$: C, 76.11; H, 8.29. Found: C, 75.84; H, 8.34.

1,8-Bis(4-formyl-2-ethoxyphenoxy)octane (4-III). This compound was synthesized analogously to the above from 1.25 g (7.52 mmol) of 3-ethoxy-4-hydroxybenzaldehyde and 1.03 g (3.77 mmol) of 1,8-dibromooctane. The crude product was recrystallized from ethanol twice to obtain compound **4-III** as white crystals. Mp 101−102 °C. ^{1}H NMR ($CDCl_3$, δ): 9.8 (s, 2H), 7.3 (m, 4H), 7.1 (d, 2H), 4.0 (m, 8H), 1.9 (m, 4H), 1.4 (m, 14H). Elemental calcd for $C_{26}H_{34}O_6$: C, 70.60; H, 7.69. Found: C, 70.40; H, 7.74.

Poly[1,8-octanedioxy-2,6-dimethoxyl-1,4-phenylene-1,2-ethenylene-1,4-phenylene-(1,3,4-oxadiazole-2,5-diyl)-1,4-phenylene-1,2-ethenylene-3,5-dimethoxyl-1,4-phenylene] (Oxa-I). A solution of sodium (0.28 g, 12 mmol) in 16 mL of anhydrous ethanol was added dropwise at ambient temperature under nitrogen to a mixture of 1,8-bis(2,6-dimethoxy-4-formylphenoxy)octane (1.88 g, 4 mmol) and phosphonium salt **5** (3.7 g, 4 mmol) in 64 mL of anhydrous ethanol/dry chloroform (5/3, v/v). The mixture was stirred at room temperature overnight. The polymerization was quenched by adding dilute hydrochloric acid (2% in water) and stirring for a few minutes. The pastelike product was collected and thoroughly washed with 90:10 ethanol/water to remove byproducts. The resulting material was dissolved in a minimum amount of chloroform and was added dropwise to ethanol while being stirred to precipitate the polymer. The dried polymer was subsequently isomerized into all-trans configuration by refluxing overnight in toluene in the presence of a catalytic amount of iodine under a nitrogen atmosphere. After removal of the toluene, the product was dissolved in 30 mL of chloroform to reprecipitate in 90% ethanol. Reprecipitation was performed four times on the isomerized polymeric product, which was subsequently dried under vacuum at 40 °C to give 1.4 g (52% yield) of Oxa-I as a yellowish fibrous polymer. ^{1}H NMR ($CDCl_3$, δ): 8.1 (d, 4H), 7.6 (d, 4H), 7.15 (d, 2H), 7.05 (d, 2H), 6.75 (s, 4H), 4.05 (t, 4H), 3.9 (s, 12H), 1.8−1.2(m, 12H). ^{13}C NMR ($CDCl_3$, δ): 152.63, 137.41, 131.04, 130.27, 129.62, 128.23, 126.16, 125.72, 125.01, 103.72, 71.40, 55.13, 29.09, 28.41, 24.81. Elemental calcd for $(C_{42}H_{44}N_2O_7)_n$: C, 73.23; H, 6.44; N, 4.07. Found: C, 72.36; H, 6.63; N, 3.94.

Poly[1,8-octanedioxy-2,6-dimethyl-1,4-phenylene-1,2-ethenylene-1,4-phenylene-(1,3,4-oxadiazole-2,5-diyl)-1,4-phenylene-1,2-ethenylene-3,5-dimethyl-1,4-phenylene] (Oxa-II). The synthesis was analogous to that for Oxa-I (60% yield). ^{1}H NMR ($CDCl_3$, δ): 8.0 (d, 4H), 7.5 (d, 4H), 7.1 (s, 4H), 6.8−7.0 (m, 4H), 3.7 (t, 4H), 2.15 (s, 12H), 1.8−1.2 (m, 12H). ^{13}C NMR ($CDCl_3$, δ): 156.86, 132.45, 131.72, 131.32, 131.11, 129.92, 129.67, 127.72, 127.61, 127.17, 127.07, 72.83; 30.83, 29.95, 26.53, 16.83, 16.67. Elemental calcd for $(C_{42}H_{44}N_2O_3)_n$: C, 80.73; H, 7.09; N, 4.48. Found: C, 79.69; H, 7.35; N, 4.29.

Poly[1,8-octanedioxy-2-ethoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene-(1,3,4-oxadiazole-2,5-diyl)-1,4-phenylene-1,2-ethenylene-5-ethoxy-1,4-phenylene] (Oxa-III). The synthesis was analogous to that described above for Oxa-I (48% yield). ^{1}H NMR ($CDCl_3$, δ): 8.0 (d, 4H), 7.5 (d, 4H), 7.2−6.7 (m, 10H), 3.8−4.0 (m, 8H), 1.85 (m, 4H), 1.5−1.3 (m, 14H). ^{13}C NMR ($CDCl_3$, δ): 148.46, 148.05, 147.90, 139.86, 129.75, 128.73, 126.12, 125.62, 124.16, 119.54, 112.30, 110.43, 68.07, 63.69, 28.68, 28.23, 27.87, 24.82, 13.92. Elemental calcd for $(C_{42}H_{44}N_2O_5)_n$: C, 76.80; H, 6.75; N, 4.26. Found: C, 76.00; H, 6.86; N, 4.12.

Results and Discussion

Synthesis and Characterization. The chemical structures and synthetic routes are depicted in Scheme 2. Dialdehydes **4-I**, **4-II**, and **4-III** were obtained by a Williamson reaction between alkoxy- or alkyl-substituted 4-hydroxybenzaldehyde and the dibromide in DMF. The polymers were synthesized using Wittig polycondensation and then were isomerized and purified as described above. In the ^{1}H NMR and ^{13}C NMR spectra, resonances for aldehyde group were absent, showing that no monomeric residues remains in the polymers. The ^{1}H NMR spectrum around 6.5 ppm also confirmed the absence of the cis-vinylic group.

All the polymers are highly soluble in chloroform, methylene chloride, and tetrahydrofuran. Uniform, pinhole-free thin films could readily be obtained by spin-coating. GPC analysis showed that the weight-average molecular weights and the molecular weight distributions of the polymers (Table 1) are in the range of (3.7−9.2) × 10^4 and 1.9−3.1, respectively. Glass transition temperatures of the polymers were determined by DSC in a nitrogen atmosphere at a heating rate of 20 °C/min with results listed in Table 1. All T_g's were obtained from a second heating cycle. Neither a melting point nor any other first-order transition attributed to liquid crystal behavior could be observed in the heating or cooling cycles in the range of 30−200 °C. It is noted that the introduction of oxadiazole moiety provides a substantial increase in T_g. For example, the T_g of Oxa-I is 40 °C higher than the parent reference polymer.[6] This indicates that the incorporation of the oxadiazole stiffens the main chain.

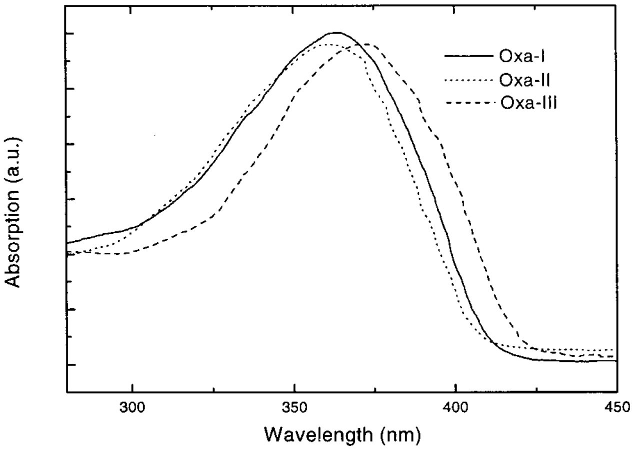


Figure 1. Absorption spectra of Oxa-I, Oxa-II, and Oxa-III in chloroform (10^{-5} M); room temperature.

Table 1. Molecular Weight and Thermal Properties of Copolymers

polymer	$M_w \times 10^4$	M_w/M_n	T_g (°C)
Oxa-I	9.2	3.1	118
Oxa-II	5.4	2.4	100
Oxa-III	3.7	1.9	93
Blue	3.5	2.9	81

Table 2. Optical Properties of Copolymers in Chloroform (10^{-5} M)

polymer	λ_{max} (nm) absorption	λ_{max} (nm) emission	φ_f
Oxa-I	365	450	0.32
Oxa-II	362	432	0.26
Oxa-III	372	443	0.35
Blue	365	439	0.40

Optical Properties. The UV-absorption spectra of Oxa-I, Oxa-II, and Oxa-III in chloroform (1 × 10^{-5} M) are shown in Figure 1, and the related data are listed in Table 2. The spectra of these copolymers are almost similar in shape, though because of the electron donating effect of the alkoxy groups in Oxa-I and Oxa-III, the absorption maxima shift slightly to lower energies relative to Oxa-II.

All copolymers show strong blue fluorescence under UV irradiation in dilute chloroform solution. Figure 2 shows the respective photoluminescence spectra. The fluorescence quantum yields were obtained from three independent experiments, and the results are listed in Table 2. The copolymers Oxa-I and Oxa-III show emission maxima at approximately 445 nm with similar spectra shapes. In comparison with the reference copolymer Blue (λ_{max}^{em} = 439 nm),[20] λ_{max}^{em} is slightly redshifted, indicating an increase of aromatic content in the emissive chromophore unit. On the other hand, the emission of copolymer Oxa-II is blue-shifted by approximately 15 nm, and the fluorescence quantum yield is lower than that of the other polymers. The methyl group in Oxa-II induces a torsional twist in the chain, resulting in reduced planarity, less π-delocalization of the conjugated system and a decrease in emission ef-

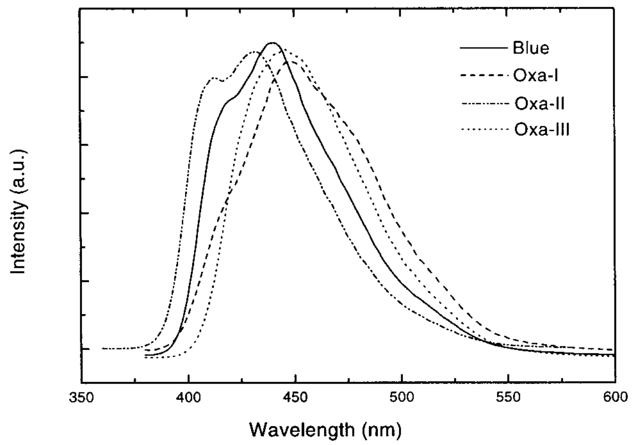


Figure 2. Emission spectra of Oxa-I, Oxa-II, Oxa-III, and the reference copolymer “Blue” (Scheme 1) in chloroform (10^{-5} M); room temperature.

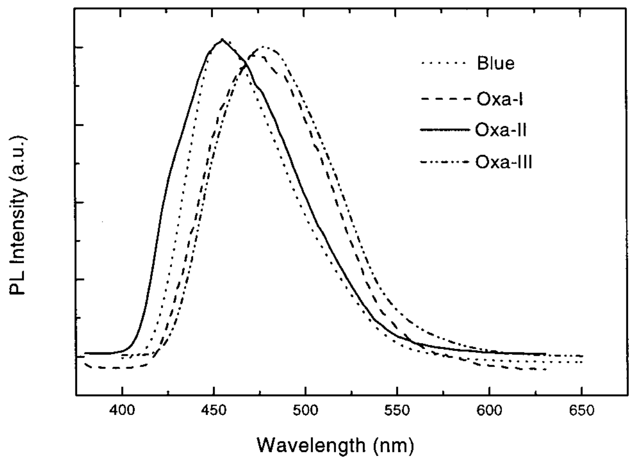


Figure 3. Photoluminescence spectra of Oxa-I, Oxa-II, Oxa-III, and the reference copolymer “Blue” (Scheme 1) thin films; room temperature.

Table 3. Optical Properties of Polymer Films

polymer	$\lambda_{\max}^{\mathrm{ab}}$ (nm)	$\lambda_{\max}^{\mathrm{PL}}$ (nm)	$\lambda_{\max}^{\mathrm{el}}$ (nm)
Oxa-I	368	475	494
Oxa-II	356	455	509
Oxa-III	370	478	480
Blue	370	458	477

ficiency.[21,22] Additionally, it could be that the electron donating power of the methyl group in Oxa-II is less than that of the alkoxy group in Oxa-I and III, leading to a lower increase in the HOMO level of the former and consequently a blue shift in emission.

The absorption spectra of films and corresponding solutions are almost identical, while the emission from films is somewhat red-shifted (Table 3 and Figure 3) compared to dilute solutions, which is due to the ordered structure of the solid state resulting from both intra- and intermolecular $\pi-\pi$ interactions of the chromophores.[23] Oxa-I and Oxa-III excited by 370 nm both yield emissions with maxima at 475 nm. As in solution, Oxa-II showed a 20 nm blue shift relative to the two other polymers in solid states. Possible explanations are discussed in the preceding paragraph.

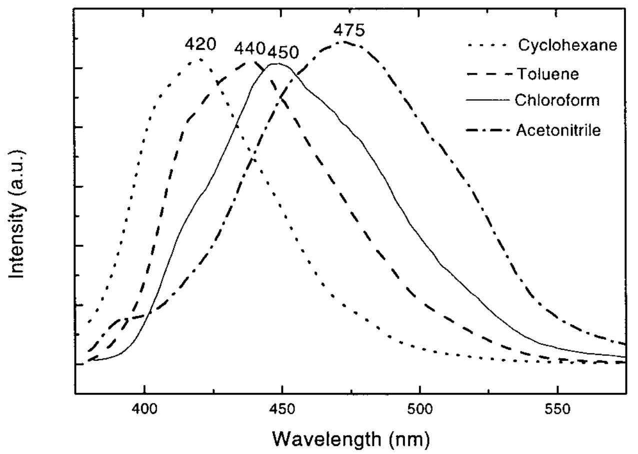


Figure 4. Emission spectra of Oxa-I in different solvents; maxima indicated.

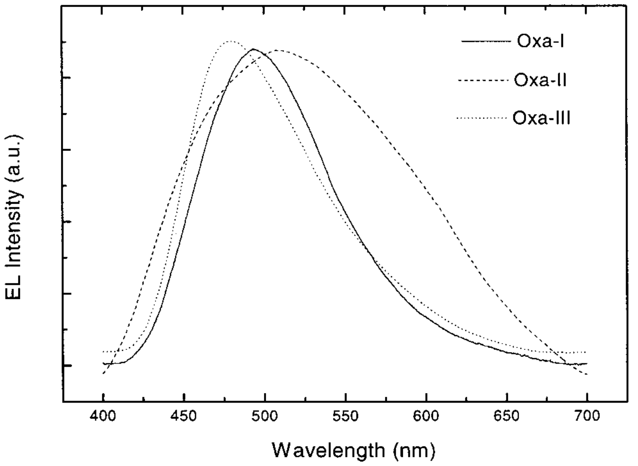


Figure 5. Electroluminescence spectra of single-layer devices based on Oxa-I, Oxa-II, and Oxa-III.

It is known that solvent polarity affects the energy levels of the excited states in the polymers containing both electron-donating and -withdrawing groups.[24,25] Therefore, both the peak position and the fluorescence spectral shape of the polymers can be expected to be affected. Figure 4 shows the normalized PL spectra for Oxa-I dissolved in solvents of different polarities. The copolymer Oxa-I contains both donor and acceptor groups, and its PL spectrum is sensitive to the polarity of the environment. At equal concentrations (~10^{-7} M), as the solvent polarity increases, e.g., from cyclohexane to acetonitrile, the emission spectra are red-shifted. Concurrently, the full width at half-maximum (fwhm) of the emission increases from 55 to 95 nm. A similar result was found for Oxa-III. This indicates an intramolecular charge transfer within the excited state (ICT),[21,26] which is believed to be populated through relaxation of the initially formed locally excited state.[21,27] The emission spectrum of Oxa-II is less sensitive to solvent polarity, because this copolymer is methyl-substituted. Similar results have been observed for other methyl-substituted PPV polymers.[21,25]

Electroluminescence. Figure 5 shows the EL spectra for single-layer devices; the EL maxima are given in Table 3. Devices based on Oxa-I, Oxa-II, and Oxa-III emit light at 494, 509, and 480 nm, respectively. The EL spectra for Oxa-I and Oxa-III are similar to their PL spectra, indicating that EL and PL originate from the same excited state.[18] However, electroluminescence of Oxa-II is found to be significantly red-shifted compared with the photoluminescence. Similar phenomena have been reported in conjugated polymers, most recently in refs 28 and 29. In these cases excimer emissions were held responsible for the unusual emissive

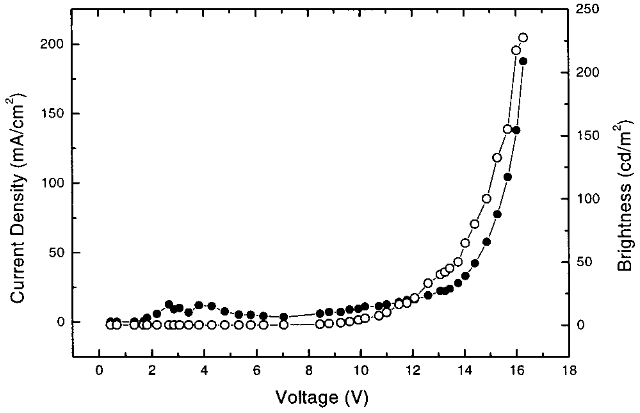


Figure 6. Current density (●) and EL intensity (○) as a function of voltage for ITO/Oxa-III(80 nm)/Ca/Al LED.

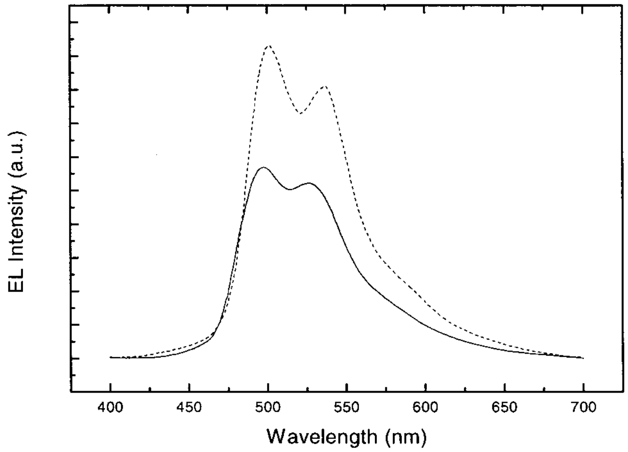


Figure 7. EL spectra for ITO/PPV(32 nm)/Ca/Al (solid line) and ITO/PPV(32 nm)/Oxa-III(19 nm)/Ca/Al (dashed line).

phenomenon.[30] Further investigation is required to understand the origin of the phenomenon in the present system.

The dependence of current density and EL intensity on voltage for the single-layer device, ITO/Oxa-III/Ca/Al, is shown in Figure 6. This device shows typical rectifying behavior with a readily balanced carrier injection. The turn-on voltage is 10 V.

As mentioned in refs 10, 11 and 15, the present copolymers containing oxadiazole unit to facilitate electron injection are also suitable for use as electron transporting materials in bilayer LEDs. The electroluminescence spectra for the double-layer device ITO/PPV-(32 nm)/Oxa-III(19 nm)/Ca/Al and the single-layer device ITO/PPV(32 nm)/Ca/Al are shown in Figure 7. For the double-layer device, no emission from Oxa-III can be observed, indicating that the PPV serves as the emitting layer and Oxa-III as the electron transport layer, respectively. The brightness and efficiency of a ITO/PPV/Ca/Al LED can be improved by more than a factor of 10^3 with the introduction of a thin Oxa-III layer (Figure 8). The double-layer device has a brightness of 2400 cd/m^2 at 6.8 V with an external quantum efficiency of 0.094%. For efficient electroluminescence, a balanced carrier injection and good hole/electron recombination to form sufficient singlet excitons are needed. The Oxa-III copolymer has better electron-transport capability and improves electron injection from the cathode while also blocking hole transport from the PPV layer. The Oxa-III layer moves the recombination zone away from the calcium interface and increases the probability of hole/electron recombination in the PPV emitting layer.[10]

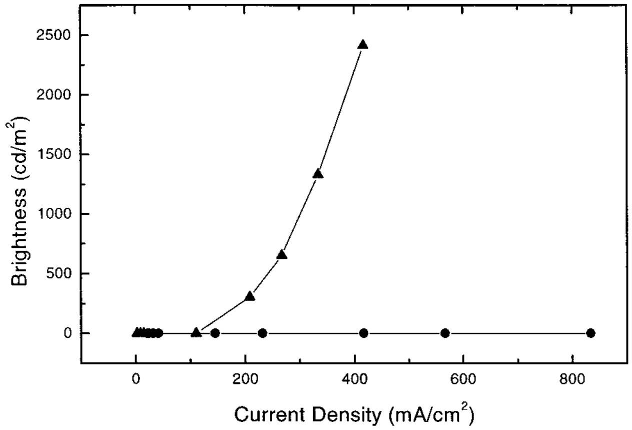


Figure 8. Current density vs EL intensity for ITO/PPV(32 nm)/Ca/Al (●) and ITO/PPV(32 nm)/Oxa-III(19 nm)/Ca/Al (▲) devices.

Conclusion

We have reported the synthesis and the optical properties of a series of PPV-related alternating block copolymers containing additionally oxadiazole units in the conjugated block, which can be used directly as blue-green light emitting polymers or in coordination with other chromophores as electron accepting/hole blocking materials in LEDs. The addition of a 19 nm thin layer of Oxa-III greatly enhances the device efficiency. Intramolecular charge transfer was observed through solvatochromic effects.

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