

Synthesis and Characterization of a Blue Light Emitting Polymer Containing Both Hole and Electron Transporting Units

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A luminescent bipolar polymer **7**, consisting of a Ar₃N–stilbene moiety and an oxadiazole moiety, has been synthesized. A smooth and dense thin film of polymer **7** is easily obtained by spin-coating from its chloroform solution. This film exhibits a strong fluorescence in the blue. More importantly, polymer **7** possesses an extremely high thermal stability with a 5% weight loss temperature of 480 °C under nitrogen, and a relatively high glass transition temperature (T_g) of 239 °C. Single-layer EL devices fabricated with this polymer emitted low intensity blue light after a turn-on voltage of 5 V. The brightness, luminance, and apparent quantum efficiency of these devices are drastically improved by adding, between polymer **7** and the Al cathode, another spin-coated polymer layer containing an oxadiazole derivative.

Introduction

The first report in 1990¹ on the electroluminescence (EL) of poly(*p*-phenylenevinylene) triggered a large amount of interest in polymer emitting layers. The advantages of the emitting polymeric materials over their molecular counterparts, first reported in 1987 by Tang and VanSlyke,² are an easy process for formation of films by spin-coating and a drastic decrease in the potential for crystallization of the film which is quite common among small organic molecules. Since their initial appearance, many improvements have been made in polymer-based devices, including emission across the entire visible spectrum, low drive voltage, and good efficiency and brightness.³ Organic light emitting diodes (OLEDs) are readily available in all three primary colors. However, blue emission in organic materials remains an area of intense research activity to compete with the newly developed GaN-based inorganic LEDs.⁴ Efficient, organic stable blue light emitting materials are also needed to serve for energy transfer when used in conjunction with added fluorophores.

The polymer approach to blue electroluminescent devices can be divided into two classes: fully conjugated and partially conjugated polymers. Representatives of fully conjugated polymers are, for instance, polymers based on derivatives of fluorene,^{5,6} *p*-phenylene,^{7–9} *p*-phenylenevinylene,^{10,11} triazole-distyrylbenzene,¹² acetylene,¹³ *p*-phenylenediylvinylene,¹⁴ and thiophene-oxadiazolyl phenylene.¹⁵ In partially conjugated polymers, the chromophore can either be attached as side groups to the nonconjugated backbone,^{16–18} or be integrated in the backbone itself.^{19–29} Representatives of chromophores in these polymers are, for instance, the following subunits: phenylenevinylene,^{17,20,21,26,28} oligophenylene,²³

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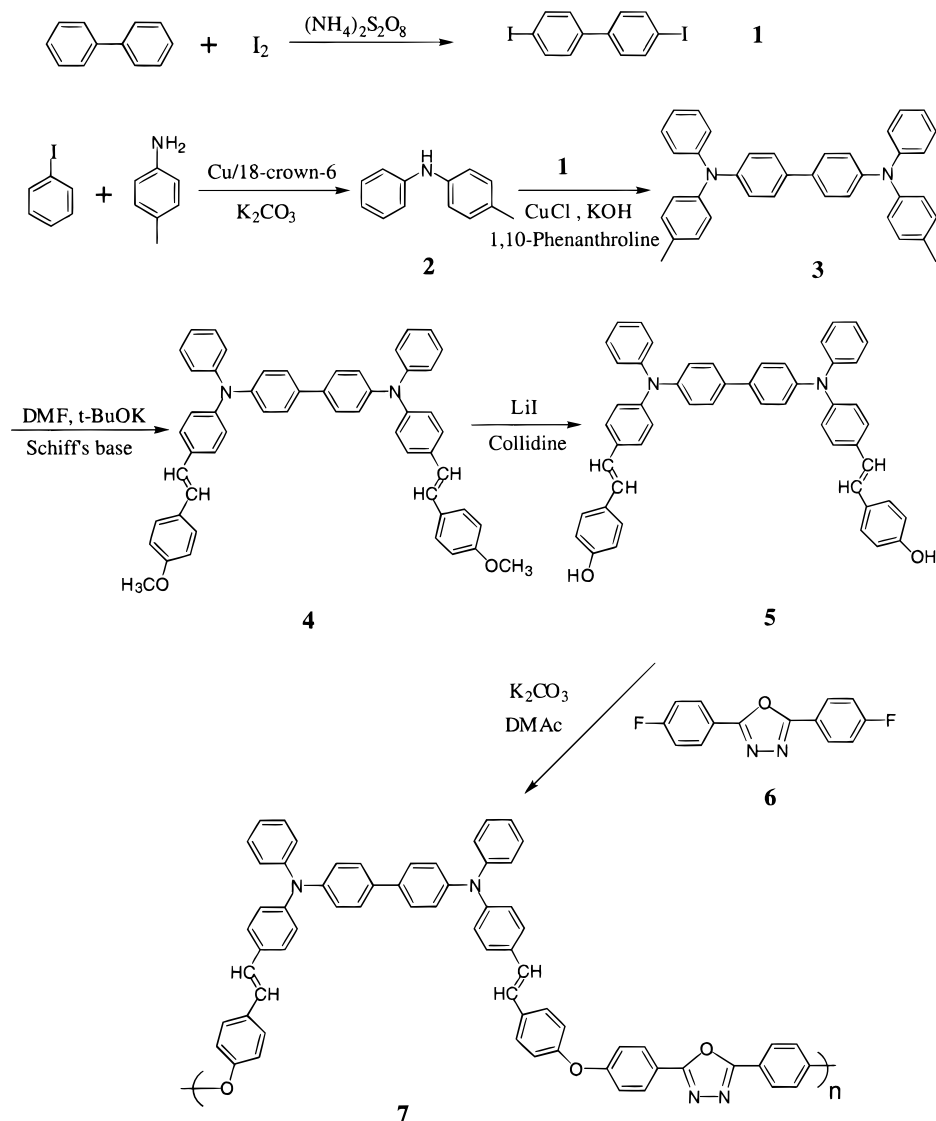
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Scheme 1. Synthetic Route to Polymer 7



styrylamine,¹⁹ carbazole,¹⁶ quinoline,²² oxadiazole,²⁴ naphthylethene,²⁵ diphenylanthracene,²⁷ and fluorene.²⁹ In all these devices, the blue light emitting polymer is either used alone, sandwiched between the indium tin oxide (ITO) anode and a low work function metal cathode, or it is blended with another polymer which is able to transport holes (usually poly(vinyl carbazole)³⁰), and/or with an electron transporting molecule or a

polymer containing an oxadiazole derivative, usually PBD³¹ (PBD is 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole). Bilayer devices are also used. In that case, the blue light emitting polymer is in one layer and an electron transport molecule (usually PBD) is in the other layer.

Since oxadiazoles are often associated with blue luminescent polymers, either in the same layer or in a bilayer, a polymer comprising a blue luminescent Ar₃N–stilbene moiety and an oxadiazole moiety has been synthesized. This polymer has been labeled polymer **7** (see Scheme 1). Light emitting triarylamine derivatives with a molecular structure similar to that of the blue emitting Ar₃N–stilbene moiety in polymer **7** are also reputed to be a hole transport material.^{32–35} This paper

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reports details of the synthesis of polymer **7**, its photoluminescence, and its use in single layer and bilayer OLED devices. It will be shown that interesting EL levels are only obtained with polymer **7** in a bilayer configuration with PBD.

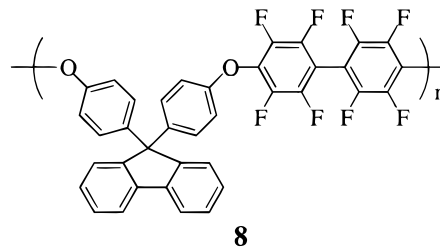
Experimental Section

Materials. Reagent-grade solvents and chemicals were used without further purification unless otherwise noted. Biphenyl, ammonium persulfate, potassium *tert*-butoxide, lithium iodide, iodobenzene, *p*-toluidine, *p*-anisaldehyde, aniline, and *N*-cyclohexyl-2-pyrrolidinone (CHP) were purchased from Aldrich. *N,N*-Dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) were purchased from Fisher Scientific, while 2,4,6-collidine was obtained from Lancaster. 2,5-Bis(4-fluorophenyl)-1,3,4-oxadiazole **6** was synthesized according to the procedure reported by Hedrick.³⁶ 4-Methoxybenzaldehyde was prepared from the reaction of *p*-anisaldehyde with aniline (distilled twice before use) by a modification of the literature procedure.³⁷

Characterization. ¹H NMR spectra were recorded on a JEOL 270 NMR spectrometer. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Kratos Kompact MALDI-III TOF mass spectrometer with the instrument set in the positive reflection mode to obtain higher resolution. Inherent viscosity of polymer **7** was measured in CHCl₃ (0.5 g/dL) at 25.0 ± 0.1 °C by using an Ubbelohde viscometer. The molecular weight of polymer **7** was determined by gel permeation chromatography (Waters 510) with CHCl₃ as an eluent and polystyrene as the standard. Thermal analyses were conducted on Seiko 220 DSC and 220 TGA/DTA instruments at a heating rate of 20 °C/min under nitrogen atmosphere. UV-vis absorption spectra were recorded on a Hitachi double beam spectrophotometer, model 100-60. Solid-state UV-vis spectra of polymer **7** were obtained by spin-coating thin films from its chloroform solution onto precleaned glass slides. A bare glass slide was used in the reference beam. UV-vis spectra of solid films of chromophore **4** and oxadiazole monomer **6** were obtained by the same method. A UV lamp was used to induce the photoluminescence that was detected edgewise by an ISA monochromator, a photomultiplier and a Pacific Precision Instruments 126 photometer. A 400-nm filter was placed between the slide edge and the entrance of the photon counter. For these experiments, the films were coated on glass slides.

Fabrication and Characterization of EL Devices. Two types of EL devices were fabricated. The first type was a single-layer device with an [ITO/polymer **7**/Al] structure. Polymer **7** was spin-coated (500 rpm) on ITO (30 Ω/square) from a solution of 6 mg of polymer **7** in 1 mL of chloroform to obtain a film of about 50 to 60 nm thick (measured by AFM). The second type of device was a bilayer device with an [ITO/polymer **7**/PBD in **8**/Al] structure. Polymer **7** was spin-coated first under the same conditions as above. A second layer containing PBD and a host polymer (**8**) was spin-coated (800 rpm) from a solution of 24 mg of PBD + 12 mg of **8** in 4 mL of ethyl acetate to obtain a film of about 40 nm thick. PBD is a commercial electron transport material available from Aldrich. It forms a solid solution in the host polymer **8**

which has a *T_g* of 262 °C. This polymer whose chemical structure is as follows



is a poly(arylene ether) synthesized from decafluorobiphenyl that was previously prepared by Mercer.³⁸ PBD has good solubility in **8**, higher than 70 wt %. Since polymer **7** does not dissolve in ethyl acetate, this procedure therefore allows the spin-coating of both layers of the bilayer device. For the two types of devices, five OLEDs were fabricated at the same time on the same ITO covered glass plate. The dimensions of each OLED are 2 × 15 mm.

Current-voltage curves and luminance-voltage curves were recorded simultaneously on two *x-y* recorders (EG&G: model RE0089). The voltage source was an EG&G model 175 Universal Programmer. Luminance was measured with a model J18 Tektronik Lumacolor II photometer. Electroluminescence spectra were recorded using a monochromator (ISA Instruments), a photomultiplier, and a photometer (Pacific Precision Instruments, model 126).

Synthesis of 4,4'-Diiodobiphenyl 1. A 250-mL three-neck round-bottom flask equipped with a magnetic stirrer and a condenser was charged with biphenyl (10.41 g, 67.5 mmol), iodine (19.65 g, 77.4 mmol), ammonium persulfate (23.69 g, 103.6 mmol), water (18 mL), concentrated sulfuric acid (5 mL), and glacial acetic acid (90 mL). The reaction mixture was heated to reflux temperature, and then vigorously stirred at this temperature until HPLC analyses showed that almost all biphenyl was converted to 4,4'-diiodobiphenyl. The reaction was substantially complete after about 8 h. After cooling, the product was isolated by filtering the reaction mixture, and then washed consecutively with 100 mL of methanol, 1 L of water, and 20 mL of methanol. Recrystallization from benzene yielded 22.20 g of the desired 4,4'-diiodobiphenyl as colorless flaky crystals in 81% yield. Mp: 202–203 °C (lit.³⁹ 202–203 °C).

Synthesis of 4-Methyldiphenylamine 2. To a 250-mL three-neck round-bottom flask fitted with a mechanic stirrer, a reflux condenser, and a nitrogen inlet were added *p*-toluidine (28.0 g, 0.262 mol), iodobenzene (20.0 mL, 0.179 mol), K₂CO₃ (20.0 g), electrolytic copper powder (17.4 g), 18-crown-6 (4.7 g), and xylene (25 mL). The reaction mixture was stirred at about 155 °C for 20 h under nitrogen. After cooling, ethanol (100 mL) was added. The resulting mixture was filtered to remove the inorganic solids, and the filtrate was then concentrated under diminished pressure. Excess *p*-toluidine and the product were separated from the solid residue, respectively, with a Kugelrohr distillation apparatus by virtue of the significant difference in boiling points of these two compounds. The product was collected by gathering the fraction coming out at 80–120 °C/5 μmHg. After recrystallization from hexane, 13.54 g of the product **2** was obtained as white needles. Yield: 41%. Mp: 88–89 °C (lit.⁴⁰ 89 °C).

Synthesis of *N,N*-Diphenyl-*N,N*-bis(4-methylphenyl)-benzidine 3. A 250-mL three-neck round-bottom flask equipped with a magnetic stirrer, condenser, and a nitrogen inlet was charged with 4-methyldiphenylamine (18.0 g, 98.4 mmol), 4,4'-diiodobiphenyl (10.0 g, 24.6 mmol), 1,10-phenanthroline (0.84 g), cuprous chloride (0.52 g), and xylene (50 mL). The resulting mixture was heated to reflux with stirring under nitrogen. When all the solids were dissolved in the xylene to form a homogeneous brown solution, 5.5 g of KOH was added. After

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4 h, an additional 4.0 g of KOH was added, and the reaction mixture was further stirred at about 155 °C for another 4 h. After cooling, 100 mL of toluene was added to dilute the solution. The crude product was isolated by filtering off the inorganic solids, distilling out solvents under reduced pressure, and removing excess 4-methyldiphenylamine in a Kugelrohr distillation apparatus. After recrystallization twice from heptane/toluene, 10.71 g of white crystalline powder was obtained in 84.3% yield. Mp: 169–170 °C (lit.⁴¹ 166 °C).

Synthesis of *N,N*-Diphenyl-*N,N*-bis(4'-methoxystilben-4-yl) benzidine 4. Into a 250-mL three-neck round-bottom flask fitted with a magnetic stirrer, a condenser, and a nitrogen inlet were placed **3** (4.00 g, 7.75 mmol), 4-methoxybenzaldehyde (6.56 g, 31.3 mmol), *t*-BuOK (5.24 g, 46.8 mmol), and DMF (80 mL). The mixture was brought up to 105 °C and stirred at this temperature for 8 h under a slow stream of nitrogen. Then, an additional 3.00 g of 4-methoxybenzaldehyde and 2.50 g of *t*-BuOK were added, and the reaction mixture was further stirred for another 8 h. The product was isolated by pouring the reaction mixture into 200 mL of methanol and filtering the precipitate. The crude product was purified by recrystallization from DMF to afford 5.32 g (91%) of pale yellow solids. Mp: 273–274 °C. ¹H NMR (CDCl₃): δ (ppm) 7.48 (d, 4H, *J* = 8.6 Hz), 7.44 (d, 4H, *J* = 8.6 Hz), 7.39 (d, 4H, *J* = 9.0 Hz), 7.29 (t, 4H, *J* = 7.4 Hz), 7.19–7.07 (m, 12H), 7.04 (t, 2H, *J* = 7.4 Hz), 6.96 (s, 4H), 6.90 (d, 4H, *J* = 8.6 Hz), 3.82 (s, 6H, -CH₃). MALDI-MS: 752 (calcd: 752).

Synthesis of *N,N*-Diphenyl-*N,N*-bis(4'-hydroxystilben-4-yl)benzidine 5. A 250-mL three-neck round-bottom flask equipped with a magnetic stirrer, a condenser, and a nitrogen inlet was charged with **4** (3.00 g, 3.98 mmol), lithium iodide (24.0 g, 0.179 mol), and 2,4,6-collidine (80 mL). Upon heating, **4** and lithium iodide dissolved in 2,4,6-collidine to form a yellow homogeneous solution. The resulting solution was stirred continuously at about 175 °C under nitrogen until HPLC analysis showed that almost all the methyl groups of **4** were cleaved. The demethylation reaction was complete after ~4 days. After cooling, 5 mL of acetic acid, 50 mL of DMF, and 50 mL of ethanol were added. The product was isolated by pouring the solution into 600 mL of 1.5 M acetic acid aqueous solution and then filtering the precipitate. After recrystallization from toluene/heptane, 2.26 g of bisphenol **5** was obtained as yellow powder in 78% yield. Mp: 236–237 °C. ¹H NMR (DMSO): δ (ppm) 9.57 (s, 2H), 7.59 (d, 4H, *J* = 8.8 Hz), 7.49 (d, 4H, *J* = 8.6 Hz), 7.41 (d, 4H, *J* = 8.4 Hz), 7.35 (t, 4H, *J* = 8.0 Hz), 7.14–6.96 (m, 18H), 6.78 (d, 4H, *J* = 8.4 Hz). MALDI-MS: 724 (calcd: 724).

Preparation of Poly(arylene ether oxadiazole) 7. A typical synthesis of poly(arylene ether oxadiazole) **7** was conducted in a 25-mL three-neck flask equipped with an argon inlet, magnetic stirrer, a Dean–Stark trap, and condenser. The flask was flushed with argon, and then charged with bisphenol monomer **5** (0.5004 g, 0.690 mmol), K₂CO₃ (0.21 g), DMAc (5 mL), and toluene (5 mL). The reaction mixture was heated to reflux under argon, and kept at reflux for 1.5 h to azeotrope off the resulting water with toluene. The toluene was then removed, and the reaction mixture was cooled. After cooling, 0.1843 g (0.714 mmol) of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole **6** was added. The mixture was heated to 165 °C. After 1 h, the solution became very viscous, and an additional 5 mL of CHP was added to dilute the solution. The reaction temperature was brought up to 185 °C and kept at this temperature for another 2 h to finish the polymerization reaction. The resulting polymer solution was cooled and then poured into 150 mL of methanol to precipitate out the polymer that was collected by filtration. The polymer was redissolved in CHCl₃, filtered through a thin layer of Celite to remove inorganic salts, and reprecipitated out by dropwise adding the filtrate into methanol. Pale yellow fibrous polymer was collected, which was further purified by reverse precipitation and a final reprecipitation, and then dried at 80 °C in vacuo for 12

h. Finally, 0.57 g (86% yield) of the desired polymer **7** was obtained. GPC analysis showed that the number-average and the weight-average molecular weight of polymer **7** were 20 800 and 84 600, respectively.

Results and Discussion

Direct Iodination of Biphenyl. 4,4'-Diiodobiphenyl was prepared by a modification of the method³⁹ patented by Xerox Corporation in 1980. The recommended reaction temperature in the patent was 80 °C. However, we found that the reaction temperature was an important factor. The reaction should be conducted at a temperature higher than the melting point (113–114 °C) of 4-iodobiphenyl. Otherwise, the crude product will contain much 4-iodobiphenyl which is not easy to remove by recrystallization. We also found that 4,4'-diiodobiphenyl was difficult to be further iodinated even over prolonged reaction times and in the presence of excess ammonium persulfate since 4,4'-diiodobiphenyl precipitates out from the reaction mixture due to its poor solubility. As a result, 4,4'-diiodobiphenyl as prepared was quite pure.

Synthesis of 4-Methyldiphenylamine and *N,N*-Diphenyl-*N,N*-bis(4-methylphenyl)benzidine. Both 4-methyldiphenylamine **2** and *N,N*-diphenyl-*N,N*-bis(4-methylphenyl)benzidine **3** were synthesized by employing an Ullmann condensation reaction of aryl halides with primary or secondary arylamines. Many modified methods for the Ullmann reaction have been reported in the literature. By using phase-transfer catalyzed catalysts, such as 18-crown-6,⁴² or 1,10-phenanthroline-ligated copper(I) catalysts⁴³ instead of copper metal, the Ullmann reaction can be conducted at a relatively low temperature and provide desired products in high yield and purity. These methods become particularly important when products with electronic grade purity are required, such as for use as charge transporting materials in LEDs. Through several experiments, we found that the combination of electrolytic copper powder with 18-crown-6 was an effective catalyst for the preparation of **2**. To minimize the formation of unwanted 4-methyltriphenylamine, a large excess (nearly 50%) of *p*-toluidine was used. Compound **3** was synthesized from **2** by a modification of the process⁴³ reported for the preparation of TPD by Xerox Corporation in 1997. By using xylene as the reaction solvent instead of toluene,⁴³ the reaction can be conducted at a higher temperature to increase the reaction yield. We found that the product **3** can be easily isolated by removing the excess **2** with a Kugelrohr distillation apparatus, while in ref 43 the product, TPD, was isolated by replacing toluene with a special solvent (ISOPAR M) and then filtering the precipitate.

Synthesis of Chromophore 4. Triarylamines containing stilbene derivatives (Ar₃N–stilbene) have been successfully used as hole transporting blue light emitting materials in organic LEDs.³² By using PBD as an electron transporting material, a bright electroluminescence of 400 cd/m² at a current density of 100 mA/cm² was obtained from a vacuum sublimed bilayer device with the structure of [ITO/Ar₃N–stilbene (E15)/PBD/MgAg]. Therefore, we chose chromophore **4** as one of

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the repeating units of polymer **7** that would be expected to exhibit the desired properties and also provide synthetic versatility. Chromophore **4** was prepared by the so-called "Anil Synthesis", which involves the condensation of Schiff's bases with methyl groups.^{44–46} The Anil Synthesis proceeds rapidly with molecules that have an electron-withdrawing group in the para position to the methyl group, however the reaction proceeds even without activating groups. We found that under modified reaction conditions, using longer reaction times, higher reaction temperatures, and an excess of Schiff's bases and *t*-BuOK, methyl groups even with electron-donating substituents in their para positions can be completely converted into styryl groups by the Anil Synthesis. This is exemplified by the successful preparation of chromophore **4** in very high yield. This opens a new route for the synthesis of Ar₃N–stilbene type compounds. For the preparation of chromophore **4**, the reaction temperature is a very critical factor. If the reaction is run at 75 °C, not all the methyl groups of *N,N*-diphenyl-*N,N*-bis(4-methylphenyl)benzidine **3** react, which results in a mixture of monostilbene-substituted and distilbene-substituted products. However, too high a reaction temperature can lead to the decomposition of the Schiff's base, which also decreases the reaction yield. Through several experiments, we found that the optimum reaction temperature was in the range of from 100 °C to 110 °C.

Deprotection of Chromophore 4. The methyl group is a very stable protecting group which is difficult to remove. Typical reagents for cleaving methyl ethers include trimethylsilyl iodide (TMSI) in CH₂Cl₂,⁴⁷ BBr₃ in CH₂Cl₂,⁴⁸ AlCl₃ in CH₂Cl₂,⁴⁹ EtSNa in DMF,⁵⁰ and AlCl₃/pyridine in CHCl₃.⁵¹ However, none of these is effective in the demethylation of chromophore **4**. BBr₃ has been reported to be especially effective in the cleavage of phenol methyl ethers. We found that the treatment of chromophore **4** with BBr₃ led to the formation of an insoluble unknown product probably due to the interaction between Ar₃N–stilbene moieties of chromophore **4** and Lewis acid BBr₃. Fortunately, we finally found that with LiI,⁵² over a very long reaction period of 4 days, almost all the O–Me bonds of chromophore **4** were cleaved. To prevent the product from being oxidized, the demethylation reaction was run under O₂-free nitrogen and shielded from light.

Preparation of Polymer 7. J. L. Hedrick has demonstrated the utility of the oxadiazole-activated halo displacement reaction to prepare high molecular weight poly(aryl ether oxadiazoles) by the polymerization reaction of 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole with bisphenol A.³⁶ However, due to the poor solubility of BPA potassium salts in the reaction solvent (NMP/

CHP), it needed a relatively long time (about 8 h) to obtain high molecular weight polymer. On the contrary, the potassium salts of our bisphenol monomer **5** are quite soluble in DMAc even at room temperature, and as a result the polymerization reaction between 2,5-bis(4-fluorophenyl)-1,3,4-oxadiazole and bisphenol monomer **5** proceeds very rapidly. In fact, the polymerization solution became very viscous within 1 h, and required dilution with additional CHP and higher polymerization temperature (185 °C) to maintain solubility. After 3 h, the polymerization reaction was complete, and polymer **7** with a high molecular weight was obtained, demonstrated by its inherent viscosity of 0.54 dL/g in CHCl₃. To control the molecular weight of polymer **7**, a slight excess (3.4%) of oxadiazole monomer **6** was used. Thus, polymer **7** would be end-capped by oxadiazole groups and possess high oxidation resistance. Although most poly(aryl ether oxadiazoles) have limited solubility in common organic solvents at ambient temperatures,³⁶ polymer **7** can be easily dissolved in chloroform or 1,1,2,2-tetrachloroethane. A smooth and pinhole-free thin film of polymer **7** can be obtained by spin-coating from its chloroform solution.

Thermal Properties. The thermal properties of polymer **7** were investigated using Seiko 220 DSC and 220 TGA/DTA instruments under nitrogen. The *T*_g of polymer **7** is 239 °C. Thermogravimetric analysis of polymer **7** shows that it is thermally stable. Indeed, an initial weight loss occurred at 459 °C and 95% of its original weight was still present at 480 °C. For the sake of comparison, the *T*_g of poly[2-(2'-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH–PPV) is 65 °C and MEH–PPV begins to show weight loss at 295 °C and has lost 46% of its original weight by 480 °C. However, *T*_g of MEH–PPV has been drastically improved to *T*_g = 146 °C by designing a novel copolymer consisting of tetraphenyldiaminobiphenyl (TPD) and MEH–PPV moieties. This polymer transports holes and shows yellow electroluminescence.³⁵ The use of materials with high *T*_gs and high thermal stability is of interest in OLEDs since it has been reported that they improve the thermal stability of the devices.⁵³

Absorbance and Photoluminescence Properties. The UV–vis absorption spectrum of a spin-coated film of polymer **7** is shown in Figure 1A. Figure 1B displays [1] the absorbance of the oxadiazole moiety (molecule **6** in Scheme 1) and [2] that of the Ar₃N–stilbene moiety (chromophore **4** in Scheme 1). The two absorption peaks at 320 and 377 nm of polymer **7** can therefore be attributed to the oxadiazole and the Ar₃N–stilbene moieties, respectively. The photoluminescence (PL) emission of a spin-coated film of polymer **7** is shown in Figure 2A (full line). The PL emission of the Ar₃N–stilbene moiety is also given in Figure 2A (dotted line). The same normalized emission is obtained from a mixture of Ar₃N–stilbene and oxadiazole moieties, which implies that the contribution of oxadiazole to the luminance is negligible, as it was also checked experimentally. The strong blue emission with a peak at 465 nm of polymer **7** arises therefore exclusively from the Ar₃N–stilbene moiety of the molecule.

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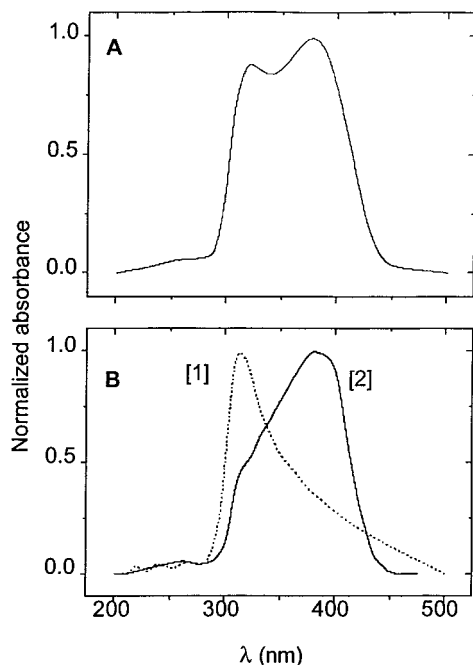


Figure 1. (A) UV-vis absorption spectrum of a spin-coated film of polymer **7** and (B) UV-vis absorption spectra of solid films of [1] the oxadiazole moiety (molecule **6** in Scheme 1) and [2] the Ar₃N-stilbene moiety (chromophore **4** in Scheme 1).

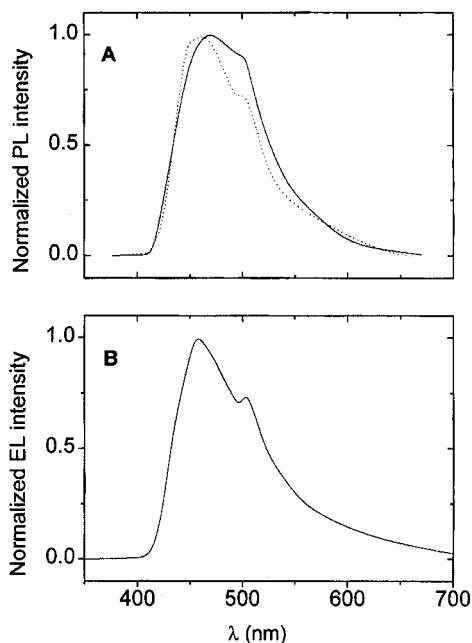


Figure 2. (A) Photoluminescence spectra of a spin-coated film of polymer **7** (full line) and of the Ar₃N-stilbene moiety (dotted line) and (B) electroluminescence spectrum from a spin-coated film of polymer **7** in an [ITO/polymer **7**/Al] structure.

Electroluminescent Device Experiments. As anticipated, single-layer devices with polymer **7** emitted blue light at a turn on voltage of about 5 V ($\sim 1 \times 10^6$ V/cm). Their luminance was rather low and only reached 5 cd/m² at 29 V and 130 mA/cm². At this current density, the apparent quantum efficiency is about 0.003%. The EL spectrum of the device is presented in Figure 2B. This spectrum is essentially similar to the PL spectrum. The photoluminescence and electroluminescence spectra

both show distinct emission peaks at about 465 and 503 nm associated with the Ar₃N-stilbene moiety. This is consistent with the radiative decay of a singlet exciton which can be generated by photoexcitation across the HOMO-LUMO gap of the polymer. The onset of absorption occurs rapidly above the HOMO-LUMO gap of the polymer and the EL spectrum occurs on the low-energy side (high wavelength) of the absorption. The broadened features of the absorption and emission spectra in emitting polymers and small molecules are generally attributed to vibronic coupling characteristic of optical transitions in molecular materials with singlet excitons as excited states. The EL spectrum has a more pronounced long wavelength tail. Experimentally, the static electric field necessary to inject charges can affect the conformation of the molecules as well as lead to a Drude-like conductivity associated with the flow of free carriers. The frequency dependence of the conductivity gives rise to a "Drude-tail" extending to long wavelengths.

Despite the fact that polymer **7** contains hole and electron transporting moieties, it is suspected that most of the holes injected at the anode in polymer **7** are able to neutralize at the Al cathode or to react in its vicinity with electrons injected at the cathode. No or very little luminescence is expected from these events. This presumption is based on the differences between electron and hole mobilities characterizing oxadiazole derivatives and tetraphenylbenzidine, respectively. Indeed, electron drift mobilities of oxadiazole derivatives, including PBD, doped in polycarbonate have been measured at room temperature.⁵⁴ These results indicate that the mobility of electrons increases with the PBD concentration. A value of about 10^{-7} cm²/V·sec is reported at an applied field of 7.5×10^5 V/cm for 25 wt % PBD in polycarbonate. This concentration is about the same as that (23.3 wt %) of the oxadiazole moiety in polymer **7**. On the other hand, polytetraphenylbenzidine, a hole transport polymer with a tetraphenylbenzidine content of 72 wt % exhibits a hole mobility of 5×10^{-5} cm²/V·sec at an applied field of 10^6 V/cm.⁵⁵ Since PBD and tetraphenylbenzidine have similar molecular structures, respectively, to those of the electron and the hole transport moieties in polymer **7**, a difference of at least 2 orders of magnitude is therefore expected between hole and electron mobilities in polymer **7**.

Drastically improved luminances were obtained by using bilayer devices with an [ITO/polymer **7**/PBD in **8**/Al] structure. In this case, holes injected in polymer **7** now accumulate at the interface with the layer containing PBD in **8** where they are able to neutralize part of the electrons injected in PBD at the cathode. Figure 3 presents typical current-voltage and luminance-voltage characteristics for these devices. Turn on voltages are of the order of 17 V ($\sim 1.7 \times 10^6$ V/cm) and maximum luminances at 29 V are of the order of 110 cd/m² at about 60 mA/cm². The apparent quantum efficiency is about 0.15%. The EL spectrum of these devices is same as that of single-layer devices already presented in Figure 2B. The maximum luminance

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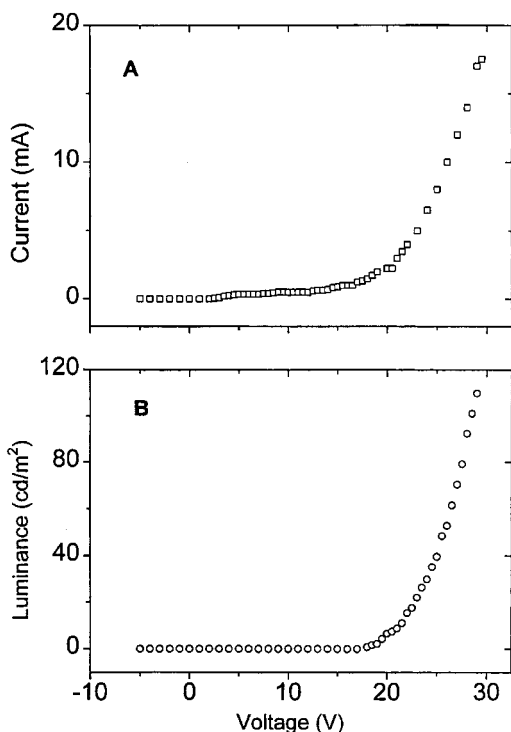


Figure 3. Typical current–voltage (A) and luminance–voltage (B) curves for a device having an [ITO/spin-coated polymer 7/spin-coated mixture of PBD in 8/Al] structure.

reported for the bilayer device in this work is in the range of luminance values (between 30 and 200 cd/m^2) reported in the literature for some blue emitting poly-

mer devices at similar current densities.^{12,19,21,22,24,27,29}

Conclusions

We have reported the synthesis of polymer 7, a blue light emitting soluble polymer containing both hole transporting and electron transporting units. This polymer has a high T_g and a high thermal stability (5% weight loss temperature as high as 480 °C). The key synthetic steps are the preparation of chromophore 4 via the “Anil Synthesis”, the demethylation of chromophore 4 with LiI, and the polymerization via the oxadiazole-activated fluoro displacement. Polymer 7 was obtained in high yield. Smooth and dense films of polymer 7 on ITO anodes are easily obtained by spin-coating from its chloroform solution. These films were used in single layer or in bilayer EL devices with Al as cathode. As anticipated, the single-layer EL devices fabricated with polymer 7 emitted blue light after the turn-on voltage of about 5 V but their luminances were low. Improved luminance (110 cd/m^2 at $\sim 60 \text{ mA/cm}^2$) was obtained with bilayer devices using PBD in a host polymer as electron transporting material.

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