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Conjugated Polymers Containing Arylamine Pendants for Light-Emitting Diodes

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ABSTRACT: New conjugated light-emitting polymers containing arylamine pendants have been designed, synthesized, and characterized. The resulting polymers are thermally stable, have rigid backbones, show high T_g and T_d values, and are readily soluble in organic solvents. The single-layer LED devices fabricated from these polymers emit light ranging from bright yellow to bright red. The color of the emitting light can be tuned by incorporating various aromatic units. The devices show very low turn-on voltages.

Introduction

Since the discovery of conjugated poly(*p*-phenylenevinylene) (PPV) as electroluminescent material for organic light-emitting diodes (LED), intensive research has been focused in this area.[1] Tremendous progress has been made since then in the discovery of new polymers and in the performance of the related LED devices.[2] It is known that in LED devices, electrons and holes are injected separately from two electrodes and move under a bias voltage into the emitting layer, where electrons and holes recombine to form excitons.[1,3] The light emission arises from the radiative decay of the excitons. An efficient LED device requires balanced injection and transport of both electrons and holes. Imbalanced charge injection and transport can lead to low device efficiency because the charge recombination in thin films often occurs close to the metal electrode where luminescence can be easily quenched.

One approach to an efficient LED device is to incorporate a hole- and/or electron-transport layer into a multilayer device to balance the charge injection and transport. This approach was first demonstrated by Tang and VanSlyke to fabricate efficient LED devices using an arylamine hole-transport layer for facile hole injection and transport.[4] Triarylamines have proved to be excellent hole-transport materials[5] and have been incorporated into polymers.[6,7] However, most of the studies are limited to incorporating arylamines into polymer main chains and using the polymers as hole-transport layers, but not emissive layers. Until now, no reports describe PPVs and their derivatives having arylamine moiety as pendant side chains. PPVs and their derivatives are among the most studied of conjugated polymers as EL materials and have shown a wide range of potential applications such as solid-state laser materials, organic transistors, and electroactive materials.[8] It has been demonstrated that PPVs substituted with electron donors such as alkoxy and amino groups show higher efficiency than unsubstituted PPVs for LED application.[2b,9] Alkoxy-substituted PPVs have been most intensively studied; however amino-substituted analogues are rarely investigated. In this paper, we report on the design, synthesis, and characterization of PPV polymers with arylamine pendants (Figure 1). Various aromatic groups, Ar, including substituted phenyl (**P1**), fluorene (**P2**), thiophene (**P3**), and naphthalene (**P4**), were incorporated into polymers to fine-tune the opto-electro properties. The Ar group in **P1** is the dialkoxy-substituted phenyl group, and **P1** can serve as direct comparison of the electron-donating nature between the amino group and alkoxy group such as poly(2-methoxy-5-(2-ethylhexyloxy))-1,4-phenylene vinylene (MEH PPV). Strong electron withdrawing groups such as CN on the vinyl double bond in **P2** increase the electron affinity of PPV polymers and facilitate electron injection.[10] The use of thiophene groups in **P3** can modify the band gap of the polymer. In **P4**, the electron-rich and more bulky naphthalene units modifies the band structure and molecular conformation of the polymer.[11] The long side chains in the polymers are introduced to increase the solubility.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300 MHz with TMS as an internal standard. Molecular weights for the polymers were determined via size exclusion chromatography (SEC) in THF using polystyrene standards. TGA analysis was performed on TA instruments, TGA 2950, and DSC on DSC 2920. Both TGA and DSC data were obtained at a heating rate of 10 °C/min under nitrogen. Melting points were measured with an Electrothermal 9200 melting point apparatus and are uncorrected. Common reagents were purchased from Aldrich, Acros, or Eastman Kodak Co. and used as received unless otherwise specified. PEDOT was purchased from Bayer Corp. as a 1.3% aqueous solution under the trade name Baytron P and used as received.

The indium tin oxide (ITO) glass substrate was obtained from Donnelly Applied Films and the ITO thickness is about 300 Å with a sheet resistance of about 68 ohms/square. Prior to the spin-coating of the polymer solution, the glass substrate was thoroughly cleaned by scrubbing, ultrasonication in a detergent, vapor degreasing, and irradiation in an UV-ozone chamber. The thickness of the polymer coating was measured by a TENCOR P-10 surface profiler. The thickness of PEDOT on ITO is about 700 Å. The cathode metals Mg:Ag (10:1 in volume ratio) was deposited by coevaporation with a deposition rate of 10 Å/s. The thickness of the cathode is 2000 Å. The luminance output and chromaticity values were measured using a Photo Research PR650 spectrophotometer. A DC voltage or current source was used to trace the current−voltage characteristics. UV−vis and photoluminescence spectra were recorded on a FluoroMax-2.

Dimethyl 2,5-Bis(dipheylamino)-3,6-dihydroterephthalate (Compound 1). Dimethyl succinylosuccinate (DMSS, 50 g, 0.22 mol) was placed into a round-bottomed flask. Aniline (100 mL) was used in excess as a solvent and the reaction

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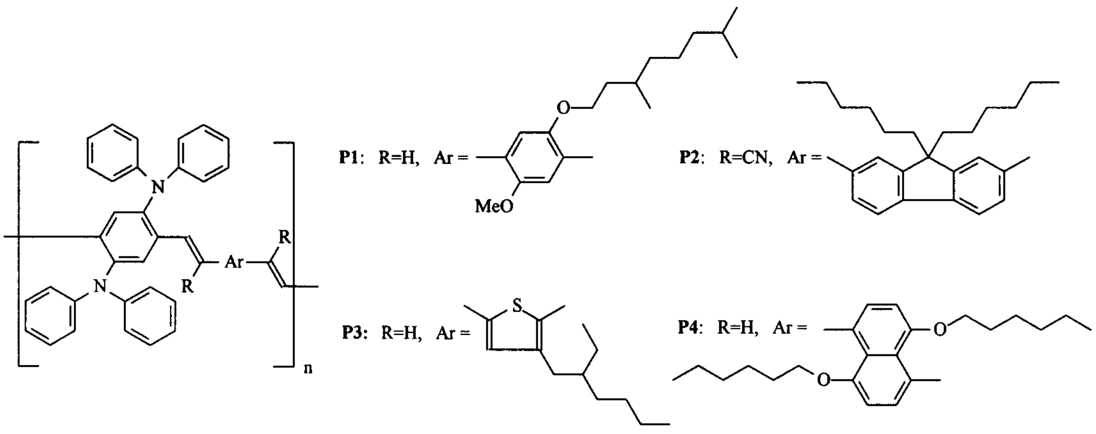


Figure 1. Chemical structures of the polymers.

mixture was heated to 100 °C for 2 h during which a solid precipitated out of solution. TLC analysis (CH_2Cl_2:hexane 1:1) showed the presence of DMSS so the reaction temperature was increased to 120 °C and stirred for additional 4 h. The reaction was cooled, and EtOH was added. The product was collected by vacuum filtration. The crude product was washed with additional EtOH until the washings were almost colorless. The product was oven dried to give an orange crystalline solid 82 g (quantitative yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.39 (s, 4 H), 3.65 (s, 6 H, $COOCH_3$), 7.09−7.38 (m, 10H, aromatics), 10.62 (s, 2 H, NH). ^{13}C NMR ($CDCl_3$): 27.65, 50.84, 88.71, 124.63, 124.75, 129.12, 139.35, 156.74, 169.31. Mp: 236−238 °C. FD−MS: *m*/*z* 378 (M^+).

Dimethyl 2,5-Bis(diphenylamino)terephthalate (Compound 2). Compound **1** (80 g, 0.21 mol) was dissolved in CH_2Cl_2 and heated gently in the air, during which the solution turned into dark red color. TLC (CH_2Cl_2:hexane 1:1) was used to monitor the reaction. Once all the starting material disappeared, CH_2Cl_2 was partially removed by rotary evaporation and replaced with EtOH. After all the CH_2Cl_2 was removed, the red solid was collected by vacuum filtration while hot and washed with EtOH until the washings were almost colorless. The product was collected and oven dried to give 73 g of a red solid (92% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.83 (s, 6 H, $COOCH_3$), 7.00−7.34 (m, 10 H, aromatics), 8.00 (s, 2H, aromatics), 8.56 (s, br, 2 H, NH). ^{13}C NMR ($CDCl_3$): 52.20, 118.58, 118.96, 119.71, 122.06, 129.38, 137.71, 141.88, 167.78. Mp: 164−166 °C. FD−MS: *m*/*z* 376 (M^+).

Dimethyl 2,5-Bis(diphenylamino)terephthalate (Compound 3). Compound **2** (40 g, 0.11 mol), iodobenzene (200 mL, 1.79 mol), K_2CO_3 (20 g, 0.14 mol), and copper (1.4 g, 0.022mol) were placed in a round-bottomed flask under N_2. The mixture was heated at 185 °C for 24 h. TLC (CH_2Cl_2:hexane 1:1) indicated the completion of the reaction. The reaction was cooled, and CH_2Cl_2 was added. After the reaction mixture was filtered and washed with CH_2Cl_2, the filtrate was concentrated to give a suspension. EtOH was added, and the resulting precipitate was collected by filtration and washed with EtOH. The product was oven dried to give a bright yellow solid 45 g (80% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 3.35 (s, 6 H, $COOCH_3$), 6.96−7.28 (m, 20 H, aromatics), 8.44 (s, 2 H, aromatics). ^{13}C NMR ($CDCl_3$): 51.94, 122.69, 123.00,129.18, 131.00, 132.47, 142.17, 147.32, 166.76. Mp: 249−251 °C. FD−MS: *m*/*z* 528 (M^+).

1,4-Dihydroxymethyl-2,5-bis(diphenylamino)benzene (Compound 4). To a round-bottomed flask equipped with a reflux condenser, a stirring bar, and a nitrogen inlet was added anhydrous THF (400 mL), and the flask was cooled to 0 °C. $LiAlH_4$ (6.4 g, 0.17 mol) was added in portions under nitrogen to form a suspension. Compound **3** (40 g, 0.076 mol) was added in portions over 60 min. The mixture was warmed to room temperature for 15 min and then refluxed for 45 min. TLC indicated (CH_2Cl_2:hexane 1:1) the completion of the reaction. The reaction was cooled to 0 °C and quenched carefully with water. After stirring for 30 min, ether was added. The aqueous layer was extracted four times with ether. The combined organic phase was dried over Na_2SO_4 and concentrated to give a brown solid. The solid was recrystallized from toluene to give a yellow solid in 34 g yield (95%). ^{1}H NMR ($CDCl_3$) δ (ppm): 4.36 (s, 4 H, benzylic), 7.00−7.50 (m, 22 H, aromatics). ^{13}C NMR (DMSO): 59.16, 121.27, 121.88, 127.77, 129.54, 139.78, 140.56, 147.03. Mp: 208−210 °C. FD−MS: *m*/*z* 472 (M^+).

2,5-Bis(diphenylamino)terephthaldicarboxyaldehyde (Monomer 1). Pyridinium chlorochromate (30 g, 0.064 mol) and anhydrous CH_2Cl_2 (350 mL) were placed in a flask under N_2. Compound **4** was added in portions during which time the mixture turned black. TLC (CH_2Cl_2:hexane 1:1) indicated the disappearance of the starting material after 90 min while a new red spot appeared. The entire reaction mixture was filtered through a pad of Celite on a fritted funnel and was washed thoroughly with CH_2Cl_2 until the washings were almost colorless. The filtrate was concentrated and purified by column chromatography (CH_2Cl_2:hexane 1:1) to give pure product as a dark red crystalline solid in 21.5 g yield (72%). ^{1}H NMR ($CDCl_3$) δ (ppm): 7.01−7.06 (m, 12 H), 7.24−7.29 (m, 8 H), 7.61 (s, 2 H), 10.13 (s, 2 H). ^{13}C NMR ($CDCl_3$): 123.13, 123.53, 129.10, 129.80, 136.49, 146.49, 148.34, 189.51. Mp: 260−262 °C. FD−MS: *m*/*z* 468 (M^+).

1-(3,7-Dimethyloctyloxy)-4-methoxybenzene (Compound 5). 1-Bromo-3,7-dimethyloctane was prepared by the reaction between 3,7-dimethyloctanol and PBr_3 at room-temperature overnight and purified by vacuum distillation at 67% yield. 4-Methoxyphenol (100 g, 0.81 mol) was dissolved in 600 mL of methanol. To this solution was added sodium methoxide (44 g, 0.82 mol) in 600 mL of methanol at room temperature. 1-Bromo-3,7-dimethyloctane (200 g, 0.90 mol) was then added dropwise to the above mixture. The reaction was heated at reflux for 3 days until completion. The reaction was quenched with water and the solvent was removed. The reaction was extracted with ether, and the organic phase was washed with brine and dried over $MgSO_4$. Solvent was removed and the product was purified by vacuum distillation to give 375 g of an oil (88% yield), bp 155−160 °C/1 mmHg. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.86 (t, J = 6.6 Hz, 6 H, terminal CH_3), 0.95 (d, J = 6.6 Hz, 3 H, CH_3), 1.10−1.88 (m, 10H), 3.76 (s, 3 H, OCH_3), 3.88−3.98 (m, 2 H, OCH_2), 6.84 (d, J = 0.8 Hz, 4 H).

1-(3,7-Dimethyloctyloxy)-2,5-dibromomethyl-4-methoxybenzene (Compound 6). Compound **5** (37.5 g, 0.14 mol) and paraformaldehyde (13.0 g, 0.43 mol) were mixed with 400 mL of acetic acid. To this mixture was added HBr (30 wt % in acetic acid, 120 g, 0.44 mol). The orange reaction mixture was stirred at room-temperature overnight. The reaction was poured into water, and the light yellow precipitate was filtered, washed with a large amount of water and CH_3CN, and dried to give 38.4 g pure product as off-white solid (60% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.86 (d, J = 6.6 Hz, 6 H, terminal CH_3), 0.95 (d, J = 6.5 Hz, 3 H, CH_3), 1.14−1.91 (m,10 H, alkyl), 3.86 (s, 3 H, OCH_3), 3.99−4.05 (m, 2 H, OCH_2), 4.52 (s, 4 H, benzylic), 6.86 (s, 2 H, aromatic). ^{13}C NMR ($CDCl_3$): 19.75, 22.62, 22.72, 24.71, 28.00, 28.58, 29.86, 36.35, 37.30, 39.26, 56.27, 67.43, 113.84, 114.79, 127.40, 127.65, 150.86, 151.17. Mp: 54−56 °C. FD−MS: *m/z* 448 (M^+).

1-(3,7-Dimethyloctyloxy)-2,5-bis(methylenediethyl phosphate)-4-methoxybenzene (Monomer 2). Triethyl phosphite (46 mL, 0.27 mol) and compound **6** (30 g, 0.067 mol) and was heated at 100 °C for 4 h. Excess of triethyl phosphite was distilled off and the crude product was recrystallized from hexane at low temperature to give 30 g of white waxy crystalline product (85% yield). ^{1}H NMR ($CDCl_3$) δ 0.86 (d, $J = 6.5$ Hz, 6 H, terminal CH_3), 0.93 (d, $J = 6.5$ Hz, 3 H, CH_3), 1.13−1.85 (m, 21 H, alkyl), 3.12 (dd, $J_1 = 20.5$ Hz, $J_2 = 4.8$ Hz, 4 H, benzylic), 3.80 (s, 3 H, OCH_3), 3.94−4.01 (m, 10 H, CH_3 of $PO(CH_2CH_3)_2$ and OCH_2 of alkyloxy), 6.91 (s, 1 H, aromatic), 6.94 (s, 1 H, aromatic). ^{13}C NMR ($CDCl_3$): 16.33, 16.41, 19.72, 22.61, 22.71, 24.73, 28.00, 29.95, 36.54, 37.39, 39.29, 56.17, 61.86, 61.94, 67.41, 114.05, 114.06, 115.09, 115.11, 119.35, 119.39, 119.46, 119.50, 119.57, 119.61, 119.68, 119.72, 150.55, 150.58, 150.64, 150.67, 150.95, 150.98, 151.03, 151.07. Mp: 32−34 °C. FD−MS *m/z* 532 (M^+).

3-(2-Ethylhexyl)thiophene (Compound 7). Dry magnesium turnings (10.2 g, 0.42 mol) and 40 mL of anhydrous THF were placed in a three-necked round-bottomed flask. A crystal of iodine was added to initiate the Grignard reaction. 2-Ethylhexyl bromide (79.0 g, 0.41 mol) in 100 mL of anhydrous THF was then added dropwise to magnesium turnings. After the addition, the reaction was heated to reflux for 1 h, cooled to room temperature, and diluted with 100 mL of THF. To another flask were added 3-bromothiophene (50.0 g, 0.31 mol), [1,3-bis(diphenylphosphino)propane]dichloronickel (1.7 g, 0.003 mol), and 100 mL of anhydrous THF, and the flask was cooled in an ice-bath. The Grignard reagent was added slowly to the above solution via a cannula. After being stirred at room-temperature overnight, the reaction was quenched with 2 N HCl, extracted with ethyl ether. The combined organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by column chromatography on silica gel using hexane as an eluent to give 27.5 g pure product as light yellow liquid (46% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.84−0.89 (m, 6 H), 1.19−1.33 (m, 8 H), 1.53−1.57 (m, 1 H), 2.56 (d, $J = 6.8$ Hz, 2 H), 6.87−6.90 (m, 2 H), 7.19−7.23 (m, 2 H). ^{13}C NMR ($CDCl_3$): 10.86, 14.12, 23.05, 25.70, 28.95, 32.58, 0.34, 40.46, 120.64, 124.79, 128.80, 141.93. FD−MS: *m/z* 196 (M^+).

2,5-Bis(bromomethyl)-3-(2-ethylhexyl)thiophene (Compound 8). Compound **7** (7.0 g, 0.036 mol) and paraformaldehyde (2.57 g, 0.086 mol) were dissolved in 3 mL of acetic acid and HBr solution (30% in acetic acid, 0.088 mol, 18 mL). The reaction was stirred at room temperature under nitrogen overnight. The reaction was diluted with 200 mL of ethyl ether washed with water, saturated $NaHCO_3$ solution (caution: bubbling) and brine. After the solvent was removed, 9.6 g of light brown oil was obtained (70% yield), which was sufficiently pure for next step reaction. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.84−0.91 (m, 6 H), 1.19−1.33 (m, 8 H), 1.53−1.61 (m, 1 H), 2.45 (d, $J = 7.2$ Hz, 2 H), 4.63 (s, 4 H), 6.81 (s, 1 H). ^{13}C NMR ($CDCl_3$): 10.89, 14.09, 23.01, 25.33, 25.89, 26.66, 28.90, 32.73, 40.25, 130.49, 135.51, 140.00, 141.96. FD−MS: *m/z* 380 (M^+).

3-(2-Ethylhexyl)-2,5-bis(methylenediethylphophate)-thiophene (Monomer 4). Compound **8** (9.6 g, 0.025 mol) reacted with triethyl phosphite (10.8 mL, 0.063 mol) at 100 °C for 4 h. The crude product was purified by column chromatography on silica gel using acetone−hexane (25:75) as an eluent to give 9.0 g of light yellow oil (72% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.82−0.89 (m, 6 H), 1.25−1.31 (m, 20 H), 1.47−1.55 (m, 1 H), 2.42 (d, $J = 7.1$ Hz, 2 H), 3.19−3.29 (m, 4 H), 4.01−4.11 (m, 8 H), 6.70 (s, 1 H). ^{13}C NMR ($CDCl_3$): 10.90, 14.10, 16.38, 16.45, 16.46, 23.08, 25.70, 28.98, 32.66, 32.69, 32.70, 40.48, 40.48, 125.63, 129.37, 129.47, 139.91. FD−MS: *m/z* 496 (M^+).

1,5-Dihexyloxynaphthalene (Compound 9). To a 500 mL round-bottomed flask were added potassium carbonate (27.2 g, 0.2 mol), 1,5-dihydroxynaphthalene (15.0 g, 0.094 mol), *n*-hexylbromide (32.5 g, 0.2 mol), and 200 mL of DMF. The reaction was heated to 90 °C overnight, cooled to room temperature, and poured into 700 mL of water. The dark brown precipitate was filtered and washed with hot methanol to give a light green solid 25.2 g (80% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.92 (t, $J = 6.5$ Hz, 6 H), 1.35−1.41 (m, 8 H), 1.52−1.57 (m, 4 H), 1.85−1.92 (m, 4 H), 4.10 (t, $J = 6.4$ Hz, 4 H), 6.81 (d, $J = 7.6$ Hz, 2 H), 7.30−7.36 (m, 2 H), 7.84 (d, $J = 8.3$ Hz, 2 H). Mp: 92−93 °C.

1,5-Bis(bromomethyl)-4,8-Dihexyloxynaphthalene (Compound 10). Compound **9** (10.0 g, 0.030 mol) and paraformaldehyde (1.92 g, 0.064 mol) were dissolved in 10 mL of acetic acid and HBr in acetic acid solution (33% in acetic acid,12.3 mL, 0.064 mol). The reaction was heated at 50 °C for 5 h and cooled to room temperature. The greenish precipitate was filtered, washed with water and methanol, and dried. The crude product was recrystallized from hexane to yield off-white needlelike crystals in 14.7 g yield (94%). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.92 (t, $J = 6.5$ Hz, 6 H), 1.36−1.41 (m, 8 H), 1.51−1.57 (m, 4 H), 1.99−2.09 (m, 4 H), 4.13 (t, $J = 6.4$ Hz, 4 H), 5.31 (s, 4 H), 6.84 (d, $J = 8.2$ Hz, 2 H), 7.37 (d, $J = 8.2$ Hz, 2 H). Mp: 105−107 °C.

1,5-Dihexyloxy-4,8-bis(methylenediethyl phosphate)-naphthalene (Monomer 5). Compound **10** (9.0 g, 0.017 mol) reacted with triethyl phosphite (7.5 mL, 0.044 mol) at 100 °C for 4 h. The crude product was purified by column chromatography on silica gel using acetone:methylene chloride (10:90) as an eluent to give a light brown solid which was recrystallized from hexane to give 6.5 g of pure product as off-white needlelike crystals (59% yield). ^{1}H NMR ($CDCl_3$) δ (ppm): 0.92 (t, $J = 6.8$ Hz, 6 H), 1.08 (t, $J = 7.1$ Hz, 6 H), 1.36−1.41 (m, 8 H), 1.47−1.54 (m, 4 H), 1.95−2.05 (m, 4 H), 3.75−3.91 (m, 8 H), 4.06−4.14(d and t overlap, 8 H, benzylic and OCH_2), 4.14 (s, 4 H), 6.80 (d, $J = 8.2$ Hz, 2 H), 7.23−7.27 (m, 2 H). ^{13}C NMR ($CDCl_3$): 13.94, 16.23, 16.31, 22.52, 25.94, 28.84, 31.60, 33.92, 35.76, 61.34, 61.43, 68.84, 106.28, 106.29, 119.77, 119.92, 130.14, 130.24, 156.04. Mp: 80−82 °C. FD−MS: *m/z* 628 (M^+).

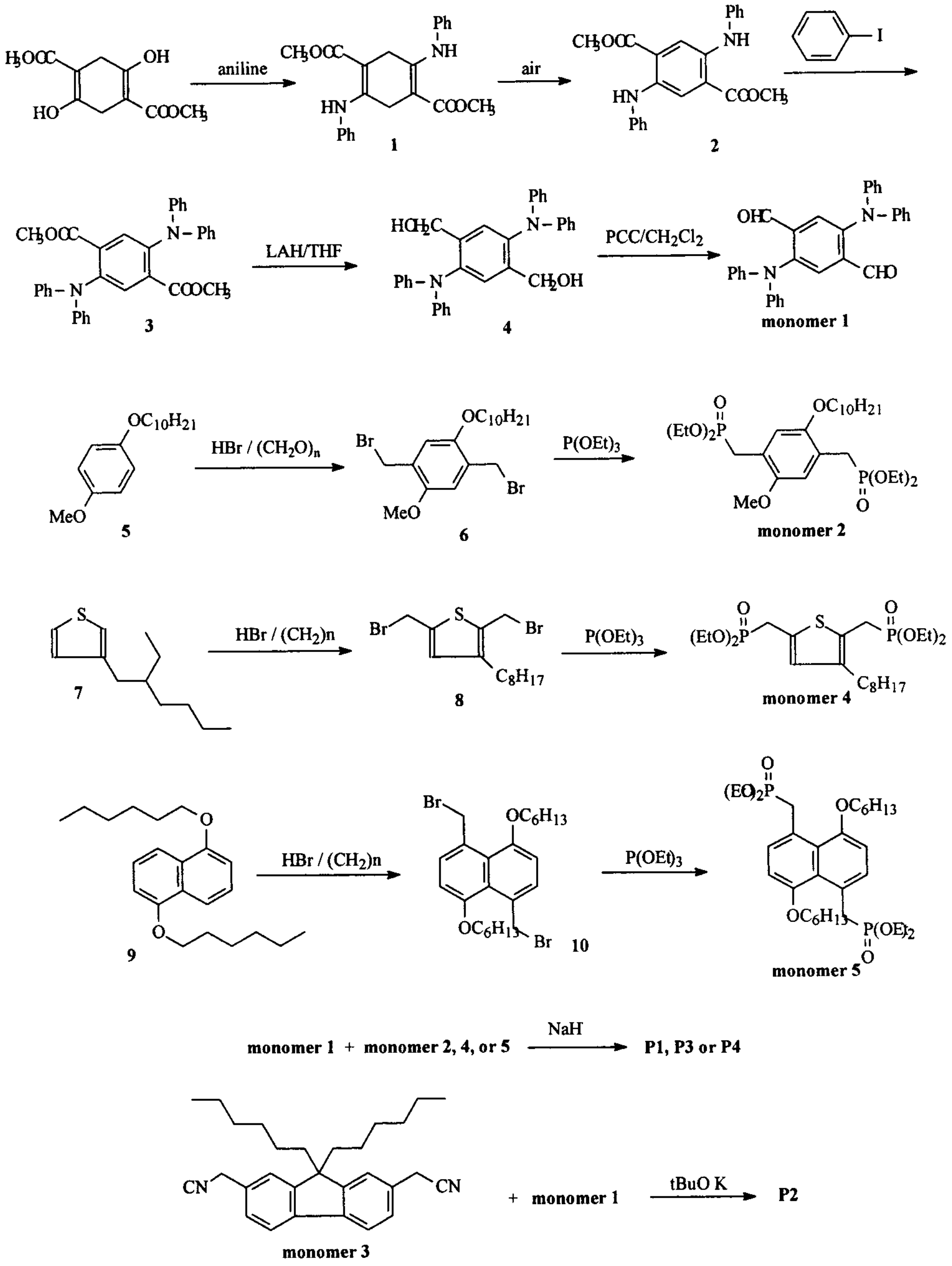
General Procedure for a Horner—Emmons Reaction (P1, P3, and P4). Equimolar dicarboxyaldehyde and diphosphate monomers were dissolved in anhydrous THF under nitrogen. To this solution was added 2.5 equiv of NaH. The reaction was stirred at room-temperature overnight under nitrogen. A small amount of benzaldehyde was added to endcap the phosphate endgroup and the aldehyde endgroup was capped by diethylbenzyl phosphate. The polymer was precipitated into methanol, filtered, redissolved in chloroform, and precipitated twice from methanol. The resulting polymer was dried under vacuum at 45 °C overnight. **P1** was obtained as a bright orange solid, **P3** as a red solid, and **P4** as a yellow-orange solid. Anal. Calcd for $C_{51}H_{52}N_2O_2$ (**P1**): C, 84.49; H, 7.23; N, 3.86. Found: C, 83.22; H, 7.03; N, 3.97. Calcd for $C_{46}H_{44}N_2S$ (**P3**): C, 84.10; H, 6.75; N, 4.26; S, 4.88. Found :C, 80.58; H, 6.43; N, 4.06; S, 4.51. Calcd for $C_{56}H_{56}N_2O_2$(**P4**): C, 85.24; H, 7.15; N, 3.55. Found: C, 81.64; H, 6.84; N, 3.65.

Synthesis of P2 via the Knoevenagel Reaction. Equimolar dicarboxyaldehyde and dicyano monomers were dissolved in a mixed solvent of 1:1 anhydrous THF and *tert*-butyl alcohol under nitrogen. To this solution was added catalytic amount of potassium *tert*-butoxide. The reaction was stirred at room-temperature overnight under nitrogen. The endgroups were capped by benzaldehyde and benzyl nitrile. The polymer was precipitated into methanol, filtered, redissolved in chloroform, and precipitated twice from methanol. The resulting red polymer was dried under vacuum. Anal. Calcd for $C_{61}H_{56}N_4$: C, 86.69; H, 6.68; N, 6.63. Found: C, 86.24; H, 6.65; N, 6.65.

Results and Discussion

The synthesis of the monomers and polymers is shown in Scheme 1. The key monomer to the synthesis of all the polymers is the arylamine containing monomer **1**. Monomer **1** can be synthesized easily on a 100 g scale via five steps at 50% overall yield. Compounds **1**−**3** were synthesized in high yields, purified by simple filtration, and rinsed with appropriate solvents. Compound **3** was

Scheme 1. Synthesis of Monomers and Polymers



reduced to give dialcohol compound **4** at 95% yield, which was purified by a simple recrystallization process. Monomer **1** was then obtained by the oxidation of the dialcohol to dialdehyde and purified by passing through silica gel. Monomer **1** is a very useful monomer, which can be used to synthesize conjugated polymers via Wittig, Horner–Emmons, or Knoevenagel reaction. The synthesis of the di-phosphate monomers **2**, **4**, and **5** involved two steps: bromomethylation of the aromatic rings and the reaction with triethyl phosphite. Monomer **3** was synthesized according to literature procedures.[12]

Table 1. Characterization Results of the Polymers

polymer	M_w[a]	PDI	T_d (°C)	T_g (°C)	UV[b] (nm)	PL[b] (nm)	PL[c] (nm)	EL (nm)
P1	32000	2.39	412	121	485	555	557	556
P2	36000	1.91	395	149	404	658	664	668
P3	6920	1.68	388	120	508	591	596	620
P4	3440	1.54	350	105	413	506	559	572

[a] Molecular weight determined by SEC in THF using polymer styrene standards. [b] Absorption and emission spectra obtained from dilute toluene solutions. [c] PL in solid-state thin film.

Polymers **P1**, **P3**, and **P4** were synthesized by the Horner–Emmons reaction, and **P2** was prepared by the Knoevenagel reaction. The characterization results are summarized in Table 1. All the polymers are highly fluorescent materials. Polymer **P1** is a bright orange solid, **P2** and **P3** are red solids, and **P4** is a yellow-orange solid. The polymers are readily soluble in organic solvents such as toluene, chloroform, THF, and 1,2-dichloroethane. A pinhole-free thin film was obtained easily by spin coating from a toluene solution. The molecular weights of the polymers were determined by size exclusion chromatography (SEC) using polystyrene standards in THF. **P1** and **P2** show higher molecular weights than 30 000, while **P3** and **P4** have lower molecular weights which can be attributed to the steric hindrance between the vinyl group and the long side

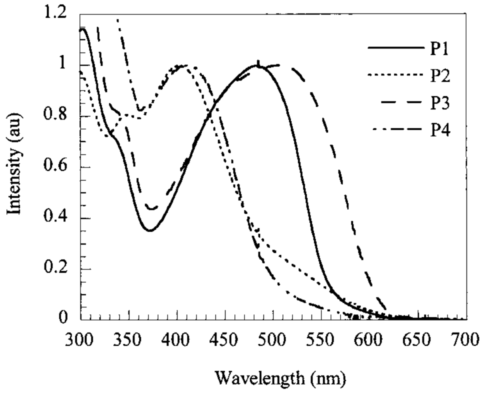


Figure 2. Absorption spectra of the polymers in solution.

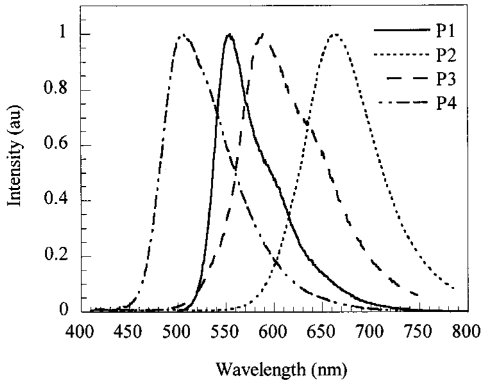


Figure 3. Emission spectra of the polymers in solution.

chain. Such a steric effect could slow the polymerization rate and lead to lower molecular weight. The thermal stability of the polymers was analyzed by DSC and TGA. The polymers show a high glass transition temperature, T_g, regardless of the flexible long side chains, which could be due to the rigidity of the polymer backbone. All the polymers are thermally stable. This is indicated by high onset thermal decomposition temperature, T_d.

The absorption spectra of the polymers are shown in Figure 2. Polymer **P1** shows a strong absorption peak at 485 nm which is the absorption of the PPV backbone. This absorption is about 30 nm red-shifted with respect to the alkoxy-substituted PPV, which is caused by the strong electron-donating nature of the diphenylamino groups. For polymers **P2** and **P4**, the absorption peaks from PPV backbone is blue-shifted close to 400 nm and 404 and 413 nm, respectively. This suggests a noncoplanar assembly of the vinyl double bond and the aromatic rings due to the steric hindrance. Polymer **P3** has a strong absorption at 508 nm, which corresponds to thienylene vinylene units. Based on the absorption edges, the band gap energies of polymers **P1**−**P4** are 2.22, 2.05, 2.04, and 2.44 eV, respectively. Compared to MEH PPV which has a band gap of 2.1 eV, **P1** has a slightly larger band gap. This might suggest that arylamino substituents have less stronger electron-donating characteristic than the alkoxy groups. The band gap data suggest that the cyano groups in **P2** and the thiophene groups in **P3** lower the band gap as expected, and the noncoplanar nature of the vinyl double bond and the aromatic rings in **P4** increases the band gap.

The emission spectra in toluene solutions were compared in Figure 3. **P1** shows an emission maximum at 555 nm, which is similar to that of alkoxy-substituted PPV. The emission is blue-shifted to 506 nm in **P4** due to the steric hindrance between the vinyl hydrogen and alkoxy side chain. Both **P2** and **P3** show red emission which can be attributed to the electron withdrawing cyano group in **P3** and the thiophene unit in **P4**. Polymer solutions show high quantum efficiencies, for example, **P1** has an efficiency of 88%, and **P2** shows 30%. In solid thin films, the emission spectra of the polymers are red-shifted slightly in **P1**−**P3**, but significantly in **P4**. **P1** has a quantum efficiency of 8% in solid state and **P2** has 10%. It is noteworthy that the photoluminescence of the thin films is sufficiently stable without much decay even after exposed to ambient atmosphere for a long time.

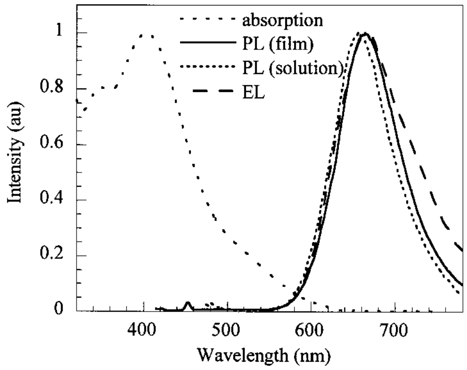


Figure 4. Absorption, emission, and EL spectra of polymer **P2**.

Single-layer devices ITO/polymer/Mg:Ag were fabricated to investigate the electroluminescent properties of the polymers. Polymer solutions were spin-coated from toluene solutions on ITO substrates and cathode Mg:Ag was deposited under high vacuum. The coating thickness was about 700 Å, and the active device area was 0.1 cm^2. The current and light output vs the voltage were measured in forward bias (a positive voltage was applied at the ITO electrode and a negative bias for the Mg/Ag electrode). All the devices exhibited typical diode behavior. The forward current was observed to increase superlinearly with the increase of applied voltage after exceeding the turn-on voltage. All devices emitted bright light and the emitting color ranging from bright yellow to saturated red. The device from **P1** emitted bright yellow light, **P2** saturated red light, **P3** red light, and **P4** orange light. The emitting color from the device can be fine-tuned by incorporating the desired comonomers. The absorption, emission, and EL spectra of **P2** are shown in Figure 4. The device emitted bright red light with a peak at 668 nm (chromaticity values $x = 0.682$, $y = 0.317$), almost identical to the solid-state PL emission, indicating that the same radiative excited states are involved in both EL and PL process.[13] The current−voltage ($I-V$) characteristic of a device fabricated from **P1** and **P2** is shown in Figure 5. The threshold voltages for sufficient light emission are lower than 3 V. This could indicate that the injection of both charge carriers into polymer is very easy. It is known that the contacts between the polymer and the electrodes are important parameters to improve device efficiency. One strategy is to modify the ITO surface with a thin layer of conducting polymer such as polyaniline[14] and poly(3,4-ethylene dioxythiophene) (PEDOT).[15] The device efficiency could be improved at least an order of magnitude in the presence of thin PEDOT interlayer. The luminous efficiency of the device from

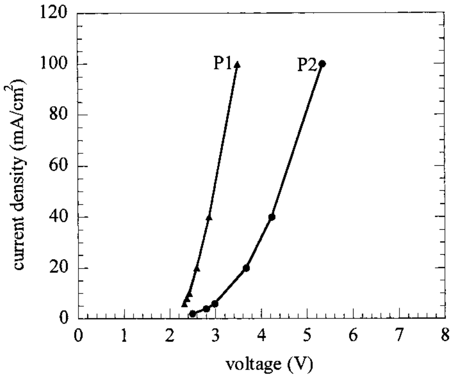


Figure 5. Current density–voltage characteristic for single-layer devices fabricated from **P1** and **P2**.

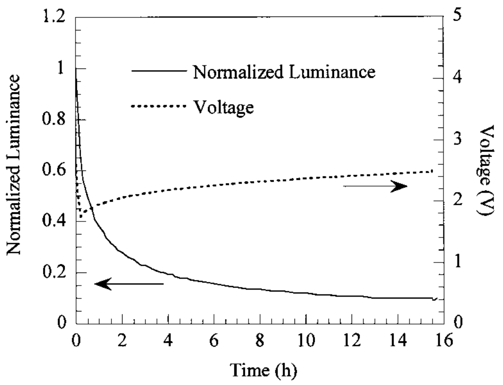


Figure 6. Lifetime plot of device ITO/PEDOT/**P2**/Mg:Ag.

P1 with PEDOT is 0.6 Cd/A at 20 mA/cm^2 with the luminance of 118 Cd/m^2 and driving voltage of 3.6 V. It is noteworthy that the devices are stable after kept at ambient atmosphere for 2 years under occasional dc operation. Under continuous dc operating conditions, the luminance decayed with time and the driving voltage increased slightly. This is common to all the devices reported in the literature.[16] Figure 6 shows the lifetime of the device made from **P2** under constant current density 20 mA/cm^2 with an initial luminance of 23 Cd/m^2. Considering the device was fabricated in the air under ambient light and the device configuration was not optimized, these preliminary device data are indeed very promising and encouraging. Future work will focus on improving device efficiency and lifetime by optimizing device structures.

Conclusions

New conjugated light-emitting polymers containing arylamine pendants have been designed, synthesized, and characterized. The resulting polymers have rigid backbones, show high T_g and T_d, and are readily soluble in organic solvents. Polymer thin films show very stable and efficient photoluminescence. The single-layer LED devices fabricated from these polymers emit light ranging from bright yellow to bright red. The devices show very low turn-on voltages. The color of the emitting light can be tuned by incorporating various comonomers.

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