Novel Efficient Blue Fluorescent Polymers Comprising Alternating Phenylene Pyridine Repeat Units: Their Syntheses, Characterization, and Optical Properties

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ABSTRACT: A novel series of poly(2,5-dialkoxy-1,4-phenylene-*alt*-2,5-pyridine)s functionalized with alternating donor/acceptor repeat units was synthesized using a Suzuki coupling approach and characterized by FT-IR, NMR (^{13}C and ^{1}H), UV−vis, fluorescence spectroscopy, gel permeation chromatography, and thermal analyses. The derived polymers were soluble in common organic solvents and trifloroacetic acid and exhibited good thermal stability. In all cases, the electronic and optical properties of these novel copolymers were consistent with the rigid-rod conjugated structure. They emitted intense blue light under UV irradiation in both the film and solution phases with high quantum yields. Single-layer blue light-emitting diodes were successfully fabricated using these materials as emitting layers. The electrochemical behavior of these new polymers depicted facile n-doping and good electron transporting properties attributable to the presence of the electron-withdrawing pyridinyl unit. These polymers displayed bathochromic shift when protonated with trifluoroacetic acid in chloroform solutions. The surface morphologies of the polymer films cast from chloroform and chloroform/trifloroacetic acid mixtures were investigated by scanning electron micrographs.

Introduction

Light-emitting diodes (LEDs) and lasers (LDs) are currently dominated by inorganic-based semiconductors. However, their application is still limited by their fabrication approaches which are not amenable to large-panel displays, in particular for blue electroluminescent (EL) devices. Consequently, over the past decade blue-emitting conjugated polymers are highly sought after for potential applications in flat color displays. Polyalkylfluorene (PDAF) was the first reported blue-emitting polymer[1] followed by poly(*p*-phenylene) (PPP).[2] Unfortunately, these polymers are insoluble. Subsequently, soluble functionalized PPPs were synthesized and studied.[3] Thereafter, the search for materials with improved processibility, mechanical properties, and stability represents a continuing research challenge. Recently, novel blue electroluminescent materials which were afforded through controlling the effective conjugation were reported. Among these approaches, blue EL polymers have been synthesized by capping the polymer backbone by nonconjugated units, separating the light-emitting units by nonconjugated spacers as conjugated−nonconjugated block copolymers,[4−7] inserting meta linkages in the main chain,[8] or imposing steric distortions in the main chain.[9] Although there has been rapid progress, the fabrication of stable, highly efficient, bright blue electroluminescent devices remains a major challenge.

It is well-known that electroluminescence in conjugated polymers is afforded by the recombination of electrons injected at the cathode and holes injected at the anode in polymer thin films.[10,11] The charge balance for injection and transport of electrons and holes is a critical parameter in controlling quantum efficiencies. Ideally, electron and hole mobilities should be of comparable magnitude. For most conjugated polymers, several efficient approaches for improving charge balance have been reported, such as application of low work function metal as the cathodic materials,[12] multilayer devices incorporating charge-transporting layers,[13] and single-layer devices from blended materials comprising mixtures of holes, electron-transporters, and emitters.[14] However, these are not without shortcomings. Consequently, it is necessary to design and synthesize conjugated polymers with high electron-donating and electron-accepting properties, which would help to balance the rates of injection of electrons and holes naturally. This represents a current burgeoning area of research actively pursued by numerous researchers.[8a,15−18]

Meanwhile, one of our research group has been actively pursuing the structure−properties correlation studies and applications of conjugated polymers with electron-donating moieties in the polymer backbone.[19−21] Recently, we reported the studies on green-emitting LEDs based on AB type copolymers of thiophene and phenylene rings.[20] As an extension of this work, we modified the backbone of this AB type conjugated polymer to incorporate alternating donor/acceptor moieties with the aim of deriving efficient blue single-layer polymer LEDs. The phenylene moiety was retained since the analogous PPPs have high blue photoluminescent (PL) efficiency.[3c] The presence of the dialkoxy pendants would increase the polymer's electron-donating property and also serve to improve the material's solubility and consequent processibility. The application of pyridine as the π-deficient moiety is driven by the consideration that its homopolymer (PPy) has been used in blue-emitting devices[22,23] and that other pyridine-containing copolymers have been demonstrated to be

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highly luminescent.[18] In addition, introduction of the pyridinyl moiety in the polymer backbone not only increases the electron affinity of the polymer, which makes the polymer more resistant to oxidation and also gives the polymer better electron-transporting properties, but also avoids fluorescence quenching due to the intersystem crossing (ISC) effect of heavy atom S.[24] Further, the presence of nitrogen with its lone pair of sp^2 electrons allows for the study of the influence of protonation on polymer properties. On the basis of these considerations, we have successfully synthesized novel blue fluorescent alternating donor/acceptor copolymers with high photo- and electroluminescence. The PL and EL properties of poly(2,5-dioctyloxy-1,4-phenylene-*alt*-1,4-pyridine) (PHPY08) have been briefly communicated earlier.[25]

Experimental Section

Materials. The reagents, hydroquinone (Fisher), trimethyl borate (Fluka), 2,5-dibromopyridine (Fluka), bromine (AnalaR), 1-bromoalkane (Fluka), *n*-butyllithium (Merck), and palladium (II) chloride (Acros), were purchased from commercial sources and used without further purification except tetrabutylammonium perchlorate (Merck) which was dried under high vacuum before use. The solvents, chloroform (J.T. Baker), acetonitrile (J.T. Baker), tetrahydrofuran (J.T. Baker), and diethyl ether (J.T. Baker), were reagent grade and were dried prior to use. 1,4-Alkoxybenzenes,[26] 1,4-dibromo-2,5-dialkoxybenzenes,[26] and tetrakis(triphenylphosphino)palladium (0) catalyst[27] were synthesized according to the literature.

Instrumentation. Elemental analyses of all monomer and polymer samples were performed at the NUS Microanalytical Laboratory on a Perkin-Elmer 240C elemental analyzer for C, H, and N determination. Halogen determinations were done either by ion chromatography or the oxygen flask method. Mass spectra (MS) were obtained using a micromass VG 7035E mass spectrometer at an ionizing voltage of 70 eV. FT-IR spectra were recorded on a Bio-Red TFS 156 spectrometer by dispersing samples in KBr disks. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker ACF 300 FT-NMR spectrometer operating at 300 MHz. Deuterated chloroform was used as the solvent, and tetramethylsilane (TMS) was used as the international standard. Solution-phase absorption and fluorescence spectrum measurements were conducted on a Perkin-Elmer Lambda 900 spectrophotometer and Shimadzu RF5000 fluorescence spectrophotometer, respectively. Dilute polymer solution dissolved in spectro-grade chloroform (10^{-6} M) was used for analysis, and quinine sulfate (10^{-5} M in 0.1 M H_2SO_4) was used as the standard. Optical absorption and PL measurements from thin polymer films deposited onto indium−tin oxide (ITO) coated glass plates were obtained on a Hitachi 330 spectrophotometer and Hitachi F-2000 fluorescence spectrophotometer, respectively. Film state fluorescence quantum efficiency measurements were conducted by excitation of the polymer film using a Spectra-Physics BeamLok 2060 continuous wave argon laser, whose beam intensity is modulated by passing it through a HMS light-beam chopper 220 operated at 200 rpm. Emitted light intensity was measured using an Oriel 70491 integrating sphere attached to a Stanford Research System model SR830 DSP lock in amplifier. Thermogravimetric analysis (TGA) of polymer powders was conducted on a DuPont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of 20 °C min^{-1} with an air or nitrogen flow of 70 mL min^{-1} was used. The temperature regime was room temperature to 1000 °C. Gel permeation chromatography analysis (GPC) was carried out using a Perkin-Elmer model 200 HPLC system equipped with Phenogel MXL and MXM columns using polystyrene as the standard and chloroform as the eluant. Cyclic voltammetry (CV) of polymer films was conducted in a three-electrode compartment cell with a total electrolyte (0.1 M $Bu_4N^+ClO_4^-$ in acetonitrile) volume of about 2 mL, using a $Ag/AgNO_3$ electrode as reference, a platinum wire as counter electrode, and a platinum disk (effective area 0.5 cm^2) as working electrode. The thin polymer films were obtained by evaporation of a chloroform solution on the working electrode. Scanning electron micrographs (SEM) spectra were obtained on a JEOL JSM-35CF scanning microscope by spin-coating polymer solution on ITO glass.

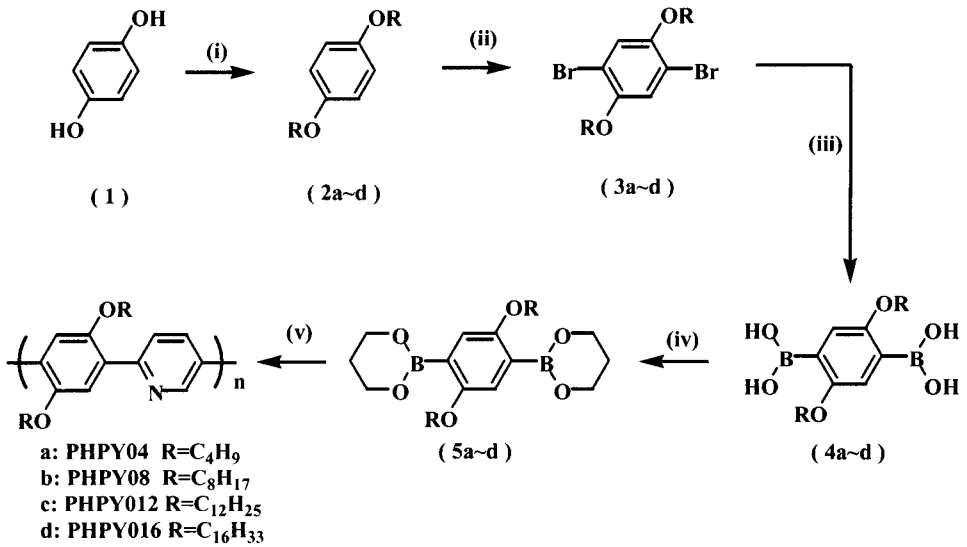
Device Fabrication. The single-layer LED was prepared by the following procedure. A thin polymer film was formed on an ITO quartz plate that has a sheet resistance of 10 Ω by spin-coating a chloroform solution of the polymer (ca. 10 mg mL^{-1}), and then magnesium−indium alloy was deposited on top of the polymer layer. The Mg−In alloy was evaporated in a bell jar under vacuum (<10^{-6} Torr). The EL device therefore has a sandwich structure of ITO/polymer/Mg−In. The active area of this EL device was approximately 4 mm^2. The emission spectrum was measured by a Nikon P-250 spectrometer with a photomultiplier (R928 Hamamatsu Photonics Co.) and a silicon photodiode. All measurements were carried out under dc biased conditions.

2,5-Dibutyloxybenzene-1,4-bis(trimethyleneboronate) (5a).[28] Butyllithium (141 mL, 1.6 M in hexane, 0.225 mol) was slowly added to a solution of 1,4-dibromo-2,5-dibutyloxybenzene (38 g, 0.1 mol) in absolute diethyl ether (800 mL) under nitrogen at −78 °C. After being stirred for half an hour at −78 °C, the solution was allowed to warm to room temperature gradually and stirred continuously for 2 more hours. The reaction solution was then cooled to −78 °C, while a solution of trimethyl borate (1 mol, 111 mL) dissolved in diethyl ether (300 mL) was added. This mixture was allowed to warm slowly to room temperature and then stirred for 20 h. After that, the mixture was hydrolyzed by hydrochloric acid (2 M, 550 mL) for 20 more hours. The precipitate was filtered and washed with copious deionized water. Further purification was done by dissolving the crude product in hot acetone and reprecipitating with hydrochloric acid (2 M, 500 mL). After drying in a vacuum at ambient temperature, the diboronic acid was esterified with 1,3-propanediol (2.02 mol-equiv) in dichloromethylene (100 mL). Recrystallization from hexane afforded the derive compound as white needles. Yield: 33.1%. Melting point: 75.0−76.5 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.10 (s, 2H, ArH), 4.15 (t, 8H, $-BOCH_2-$), 3.93 (t, 4H, $Ar-OCH_2-$), 2.04 (p, 4H, $-BOCH_2CH_2-$), 1.74 (m, 4H, $ArOCH_2CH_2-$), 1.51 [m, 4H, $ArO(CH_2)_2CH_2-$], 0.96 (t, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 13.8−31.8 (aliphatic −C), 61.8 ($B-O-CH_2-$), 68.2 ($Ph-O-CH_2-$), 119.8, 157.3. FT-IR (KBr disk, cm^{-1}): 2943, 2869, 1495, 1464, 1391, 1297, 1203, 1123, 1049, 978, 920, 886, 845, 769, 721. Anal. Calcd for $C_{20}H_{32}B_2O_6$: C, 61.85; H, 8.27. Found: C, 61.43; H, 8.40. HR-MS Anal. Calcd: 390.2385. Found: 390.2396.

2,5-Dioctyloxybenzene-1,4-bis(trimethyleneboronate) (5b). Compound **5b** was prepared according to the procedure described for **5a** except that 1,4-dibromo-2,5-dioctyloxybenzene was used instead of 1,4-dibromo-2,5-dibutyloxybenzene. Yield: 35.2%. Melting point: 78.0−80.5 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.10 (s, 2H, ArH), 4.15 (t, 8H, $-BOCH_2-$), 3.93 (t, 4H, $Ar-OCH_2-$), 2.04 (p, 4H, $-BOCH_2-CH_2-$), 1.75 (m, 4H, $ArOCH_2CH_2-$), 1.47−1.28 (m, 20H, $ArO-(CH_2)_2(CH_2)_5-$), 0.88 (t, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 14−31.7 (aliphatic −C), 61.8 ($B-O-CH_2-$), 69.7 ($Ph-O-CH_2$), 119.8, 157.3. FT-IR (KBr, cm^{-1}): 2921, 2851, 1496, 1467, 1420, 1390, 1295, 1249, 1205, 1155, 1124, 1050, 882, 812, 721. Anal. Calcd for $C_{28}H_{48}B_2O_6$: C, 66.95; H, 9.63. Found: C, 66.39; H, 9.37. HR-MS Calcd: 502.3637. Found: 502.3622.

2,5-Didodecyloxybenzene-1,4-bis(trimethyleneboronate) (5c). Compound **5c** was prepared according to the procedure described for **5a** except that 1,4-dibromo-2,5-didodecyloxybenzene was used instead of 1,4-dibromo-2,5-dibutyloxybenzene. Yield: 40.1%. Melting point: 80.5−81.5 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.10 (s, 2H, ArH), 4.15 (t, 8H, $-BOCH_2-$), 3.92 (t, 4H, $Ar-OCH_2-$), 2.05 (p, 4H, $-B-OCH_2-CH_2-$), 1.72 (m, 4H, $ArOCH_2CH_2-$), 1.47−1.26 (m, 36H, $ArO-(CH_2)_2(CH_2)_9-$), 0.88 (t, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 14−31.7 (aliphatic −C), 61.8 ($B-O-CH_2-$), 69.7 ($Ph-O-CH_2-$), 119.8, 157.3. FT-IR: 2920, 2848, 1497, 1466, 1425, 1401, 1374, 1294, 1269, 1249, 1204, 1155, 1130, 1076, 1046,

Scheme 1. Synthesis of the Polymers[a]



[a] Reagents and conditions: (i) KOH, RBr, EtOH. (ii) Br_2, CCl_4. (iii) *n*-BuLi, EtOEt, −78 °C; then $B(OMe)_3$, room temperature for 24 h; 2N HCl, 24 h. (iv) $HOCH_2CH_2CH_2OH$, CH_2Cl_2, Δ. (v) 2,5-Dibromopyridine, $Pd(PPh_3)_4$, $NaHCO_3$, THF/H_2O, Δ.

995, 952, 925, 871, 818, 785. Anal. Calcd for $C_{36}H_{64}B_2O_6$: C, 70.36; H, 10.49. Found: C, 70.38; H, 10.37. HR-MS Calcd: 614.4889. Found: 614.4904.

2,5-Dihexadecyloxy-1,4-bis(trimethyleneboronate) (5d). Compound **5d** was prepared according to the procedure described for **5a** except that 1,4-dibromo-2,5-dihexadecyloxybenzene was used instead of 1,4-dibromo-2,5-dibutyloxybenzene. Yield: 45.0%. Melting point: 84.5−85.5 °C. ^{1}H NMR ($CDCl_3$, ppm): δ 7.09 (s, 2H, ArH), 4.14 (t, 8H, $-BOCH_2-$), 3.91 (t, 4H, $Ar-OCH_2-$), 2.04 (p, 4H, $-BOCH_2CH_2-$), 1.74 (m, 4H, $ArOCH_2CH_2-$), 1.46−1.24 (m, 52H, $ArO(CH_2)_2(CH_2)_{13}-$), 0.86 (t, 6H, $-CH_3$). ^{13}C NMR ($CDCl_3$, ppm): δ 14−31.7 (aliphatic −C), 61.8 (B−O−CH_2-), 69.7 (Ph−O−CH_2-), 119.8, 157.3. FT-IR: 2919, 2848, 1497, 1466, 1426, 1401, 1374, 1294, 1269, 1249, 1205, 1155, 1130, 1073, 1034, 952, 925, 871, 855, 812, 715. Anal. Calcd for $C_{44}H_{80}B_2O_6$: C, 72.72; H, 11.09. Found: C, 72.69; H, 10.93. HR-MS Calcd: 726.6141. Found: 726.6128.

General Procedure for Polymerization. In a typical experimental procedure, 2,5-dibutyloxybenzene-1,4-bis(trimethyleneboronate) **(5a)** (585 mg, 1.5 mmol), 2,5-dibromopyridine (354 mg, 1.5 mmol), tetrakis (triphenylphosphino)-palladium(0) (23.0 mg, 0.02 mmol), and sodium bicarbonate (1700 mg, 20.2 mmol) were placed in a 100 mL two-neck round-bottom flask and deaerated with nitrogen. Thereafter, equivalent volumes of degassed water (20 mL) and tetrahydrofuran (20 mL) were syringed into the reaction flask. This reaction mixture was stirred and refluxed for 3 days and then precipitated into methanol. The polymer was filtered and washed with copious amounts of water, methanol, and acetone. The crude product was purified by dissolving it in chloroform and reprecipitating upon addition of methanol.

Poly(2,5-dibutyloxy-1,4-phenylene-*alt*-2,5-pyridine) (PHPY04). Yield: 95.0%. ^{1}H NMR (extracted by chloroform; $CDCl_3$, ppm, main peaks): δ 8.96 (s, H at Py-ring), 8.13 (br, m, H at Py-ring), 8.01 (br, m, H at Py-ring), 7.72 (m, H at Ph-ring), 7.11 (s, H at Ph-ring), 4.11 (br, m, $PhOCH_2-$), 1.78−0.96 (br, m). FT-IR (KBr disk, cm^{-1}): 3051, 2959, 2932, 2868, 1590, 1544, 1506, 1460, 1421, 1357, 1308, 1270, 1230, 1199, 1140, 1066, 1022, 974, 877, 843, 769, 737. Anal. Calcd for $(C_{19}H_{23}O_2N)_n$: C, 76.73; H, 7.79; N, 4.71. Found: C, 74.94; H, 7.86; N, 4.63; Br, 0.69.

Poly(2,5-dioctyloxy-1,4-phenylene-*alt*-2,5-pyridine) (PHPY08). Yield: >98%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.97 (s, 1H, H at Py-ring), 8.14 (br, 1H, H at Py-ring), 8.01 (br, 1H, H at Py-ring), 7.71 (br, 1H, H at Ph-ring), 7.10 (br, 1H, H at Ph-ring), 4.10 (br, m, 4H, $PhOCH_2-$), 1.81−0.87 (br, m, 30H). FT-IR (KBr disk, cm^{-1}): 3052, 2923, 2852, 1590, 1544, 1507, 1460, 1421, 1357, 1307, 1264, 1227, 1201, 1140, 1026, 968, 882, 842, 775, 715. Anal. Calcd for $(C_{27}H_{39}O_2N)_n$: C, 79.17; H, 9.59; N, 3.42. Found: C, 77.24; H, 9.37; N, 3.52; Br, 0.72.

Poly(2,5-didodecyloxy-1,4-phenylene-*alt*-2,5-pyridine) (PHPY012). Yield: >98%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.98 (s, 1H, H at Py-ring), 8.15 (br, 1H, H at Py-ring), 8.03 (br, 1H, H at Py-ring), 7.72 (br, 1H, H at Ph-ring), 7.11 (br, 1H, H at Ph-ring), 4.11 (br, m, 4H, $PhOCH_2-$), 1.78−0.86 (br, m, 46H). FT-IR (KBr disk, cm^{-1}): 3056, 2923, 2853, 1590, 1544, 1507, 1460, 1421, 1357, 1307, 1270, 1230, 1201, 1140, 1027, 968, 842, 775, 721. Anal. Calcd for $(C_{35}H_{55}O_2N)_n$: C, 80.56; H, 10.62; N, 2.68. Found: C, 79.45; H, 10.56; N, 2.76; Br, 0.64.

Poly(2,5-dihexadecyloxy-1,4-phenylene-*alt*-2,5-pyridine) (PHPY016). Yield: 96%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.96 (s, 1H, H at Py-ring), 8.15 (br, 1H, H at Py-ring), 8.03 (br, 1H, H at Py-ring), 7.72 (br, 1H, H at Ph-ring), 7.10 (br, 1H, H at Ph-ring), 4.11 (br, 4H, $PhOCH_2-$), 1.78−0.86 (br, m, 62H). FT-IR (KBr disk, cm^{-1}): 3051, 2920, 2850, 1590, 1544, 1508, 1467, 1420, 1395, 1357, 1307, 1264, 1229, 1202, 1140, 1049, 1027, 1001, 964, 882, 844, 821, 775, 718. Anal. Calcd for $(C_{43}H_{71}O_2N)_n$: C, 81.45; H, 11.28; N, 2.21. Found: C, 79.69; H, 11.29; N, 2.27; Br, 1.00.

Results and Discussion

Synthesis and Characterization of the Polymers. Syntheses of the new polymers were effected using the Suzuki coupling approach.[29] Scheme 1 depicts the synthetic route to these polymers. 1,4-Dibromo-2,5-dialkyloxybenzene (**3**) was synthesized using the approach of Ruiz et al.[26] Thereafter, **3** was reacted with *n*-butyllithium and subsequently quenched with trimethyl borate and then hydrolyzed with hydrochloric acid to afford 2,5-dialkyloxybenzene-1,4-bis(boronic acid) (**4**). Since boronic acids generally are easy to condense spontaneously to boroxines to varying degrees,[30] the diboronic acid (**4**) was esterified with 1,3-propanediol to afford 2,5-dialkyloxybenzene-1,4-bis(trimethyleneboronate) (**5**). Polymerization was effected in THF/H_2O mixtures in the presence of $NaHCO_3$ with catalytic amounts (2 mol %) of $Pd(PPh_3)_4$ under nitrogen atmosphere. After the reaction was completed, the polymer was precipitated by pouring into methanol. Purification was carried out by dissolving the polymer in $CHCl_3$ and reprecipitating in methanol.

Yamamoto et al. had reported that some π-conjugated donor/acceptor copolymers were prepared using a zero-

Table 1. Properties of the Polymers

polymer	yield (%)	color	$M_n \times 10^{-3}$	PDI	P_n[b]
PHPY04	95	green	2.3[a]	1.19	7
PHPY08	>98	yellow	22.0	1.44	54
PHPY012	>98	yellow	23.7	1.19	46
PHPY016	95	yellow	19.5	1.21	31

[a] Extracted by $CHCl_3$. [b] Number of repeat units per polymer.

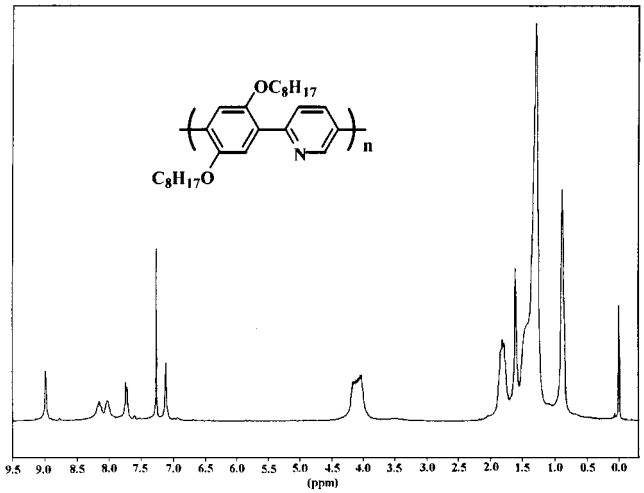


Figure 1. ^1H NMR spectrum of the polymer PHPY08.

valent nickel complex,[31] including the poly(1,4-phenylene-*alt*-2,5-pyridine) (PHPY) in high yields. Here, we found that all polymerizations were conducted smoothly under the stipulated reaction conditions reported herein with high yields. The polymerization results are summarized in Table 1. The solubility of the polymers varied with the length of the pendant moiety. All polymers were soluble in trifloroactic acid. PHPY04 was partially soluble in chloroform, while the other polymers can be dissolved in chloroform, tetrahydrofuran, and methylene chloride. In comparison with the homopolymers poly(2,5-diheptyloxyphenylene) (HO-PPP)[3b] and poly(2,5-pyridine) (PPY)[23] as well as PHPY, which dissolved only in common organic solvent or acid media, the new polymers' solubility was extended.

All polymers were characterized by FT-IR, NMR, and elemental analyses. A representative ^1H NMR spectrum of the polymer PHPY08 is depicted in Figure 1. The chemical shifts of the pyridinyl protons were manifested at δ 8.97, 8.14, and 8.01 ppm while phenylene protons appeared at 7.71 and 7.10 ppm. The remaining resonance at δ 4.09 and 0.87−1.81 ppm corresponded to the *n*-octyloxy pendant chains. Due to the presence of both the head-to-head (HH) and head-to-tail (HT) units, the resonance peaks depicted broad signals. Similar behavior has been reported in other copolymers containing pyridinyl moieties.[31] The FT-IR spectra of the polymers depicted two different aromatic ring stretchings.

Other polymers depicted similar FT-IR and NMR spectra. The elemental analysis data of the polymers showed good agreement with the expected structures except for the presence of bromine ascribable to those at the polymer chain termini.

The molecular weights of polymers were determined by GPC using $CHCl_3$ as the eluent and polystyrene as the standard. The results are summarized in Table 1. Except for PHPY04, which had poor solubility in $CHCl_3$, other polymers had a mean molecular weight range (M_n) from 19.5 to 23.7 KDa with the polydispersity of 1.19−1.44, corresponding to the presence of 31−54 repeat

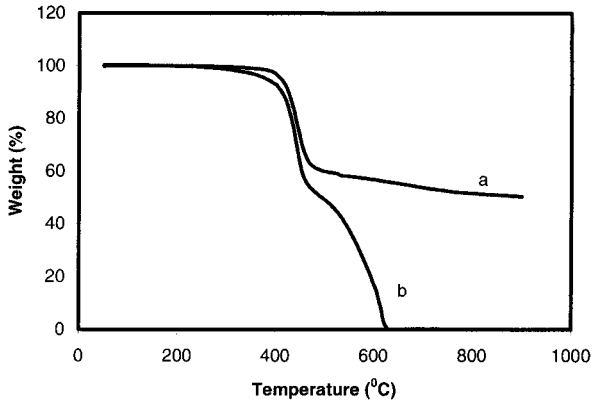


Figure 2. TGA scans for polymer PHPY08 carried out in (a) nitrogen atmosphere and (b) air atmosphere.

units. The molecular weights of the polymers were closely related to the length of the pendant. When the pendant was long, for example, hexadecyloxy, the sterically hindered side chain decreased the solubility of monomer (**5d**) and the produced polymer, preventing the obtainment of high molecular weight during polymerization.

Thermal Properties. The polymer thermal stability was determined using TGA under either nitrogen or air atmosphere. The copolymers depicted very good thermal stability with all of them exhibiting an onset of degradation greater than 300 °C in both air and nitrogen atmospheres. In nitrogen atmosphere, an apparently one-step degradation attributable to the cleavage of the pendant group was observed. It began at temperatures ranging from 340 to 380 °C and was completed at 430−480 °C. The percentages of residues decrease with increasing alkyloxy chain length which is relevant with degradation of pendant chains of increasing content in the polymers. However, the char yields of polymers in nitrogen atmosphere were very high even at 1000 °C, due to the stability of conjugated backbone. On the other hand, the polymer in air had a lower onset of degradation at 300−340 °C, which is consistent with a two-step decomposition. The first step occurring in the temperature range of 300−430 °C corresponded to the cleavage of the alkoxy chain. The next weight loss step which took place in the temperature range of 430−620 °C was attributed to the degradation of the polymer chain. In all cases, a small residue content of less than ca. 2% was left behind, indicating the efficient removal of catalyst after workup. A representative TGA curve of PHPY08 in air and nitrogen atmospheres is depicted in Figure 2.

Electrochemical Properties. The n-doping characteristics of these conjugated polymers were investigated using cyclic voltammetry. The derived polymers were electroactive in the cathodic region. The onset of the n-doping process (reduction) occurred at a potential of ca. −1.7 V. The cathodic current increased quickly with a cathodic peak appearing at ca. −2.2 V, and the corresponding reoxidation (n-dedoping) peak occurred at ca. −2.05 V, in contrast to that of PHPY (n-doping peak, −2.49 V; n-dedoping peak, −2.21 V).[31] This indicated that the new polymers were more easily reduced or n-dopable than PHPY. At the same time, the n-doping of polymers was accompanied by an obvious color change (electrochromism) from yellow in the neutral films to dark brown in the n-doped polymer films. Figure 3 depicts the cyclic voltammograms of

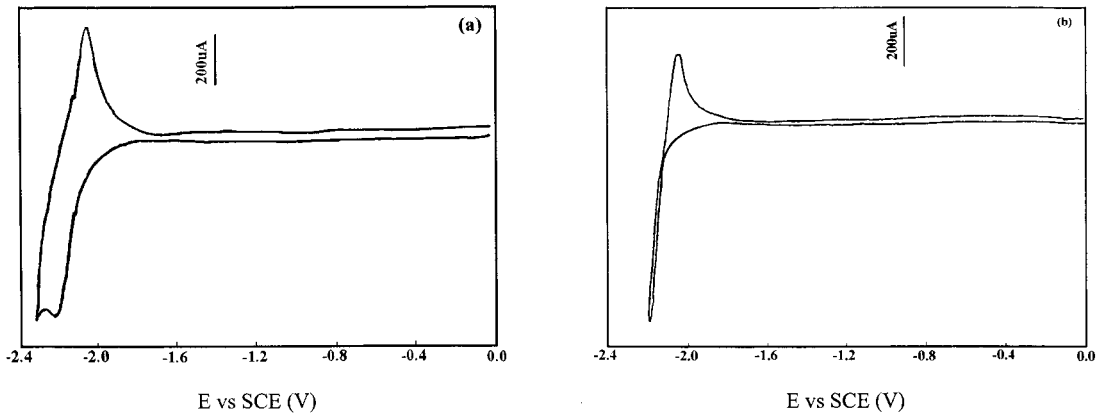


Figure 3. Cyclic voltammograms of the polymers (a) PHPY04 and (b) PHPY08, measured in 0.1 M Bu_4NClO_4 solution of acetonitrile with a scan rate of 100 mV s^{-1}.

Table 2. Optical Properties of the Polymers

	solution λ (nm)[a]			film λ (nm)[c]			
polymer	UV	emission	quantum yield[b]	UV	PL[d]	EL[d]	band gap (eV)
PHPY04	375	434	1.12	383	440	444	3.0
PHPY08	378	434	1.09	387	442	444	3.0
PHPY012	378	434	1.17	388	442	444	3.0
PHPY016	378	434	1.18	389	500	445	3.0

[a] 10^{-6} M in $CHCl_3$ solution. [b] Relative to quinine sulfate (10^{-5} M in 0.1 M H_2SO_4). [c] Spin-coating from $CHCl_3$ solution. [d] The main emission peak, operated at 300 K.

polymers PHPY04 and PHPY08. From Figure 3, the dedoping current was substantially smaller than the doping current. This suggested that nonelectrochemical dedoping reactions take place to some extent during the cathodic scan.[32]

Optical Properties in Solution. The optical properties of copolymers were of primary importance in our experiment. The solution-phase UV−vis absorption and fluorescence emission spectra were recorded at room temperature in dilute chloroform solutions. To avoid the possibility of concentration quenching or reabsorption and reemission, the solvent was purged with N_2 prior to measurement and the concentration was about 10^{-6} M. All spectral data for measurements are summarized in Table 2.

All polymers showed almost identical electronic properties in solution. The absorption spectra exhibited an absorption maximum (λ_{max}) at ca. 378 nm with a minor peak at ca. 304 nm. The PL spectra, which are attributed to fluorescence on account of the short lifetime of the excited states,[33] were obtained by irradiative excitation at the wavelength of the absorption maxima. Very strong blue fluorescence resulted with emission maxima at ca. 434 nm, which correlate approximately with the onset of the absorption band. This is indicative that photoluminescence took place by migration of electrons in a conduction band (π^* level) to a valence band (π level). Figure 4 depicts the UV−vis absorption and fluorescence spectra of the polymer PHPY012 in chloroform solution.

The quantum yield for emission in solution was determined according to the method described by Davey et al.[34] relative to quinine sulfate in 0.1 M H_2SO_4. The absorption of polymers and the standard was between 0.13 and 0.16. Due to strong self-absorption and excimer formation of the polymers, the determined quantum yields were highly dependent on the concentration and excitation wavelength upon irradiation. The results are

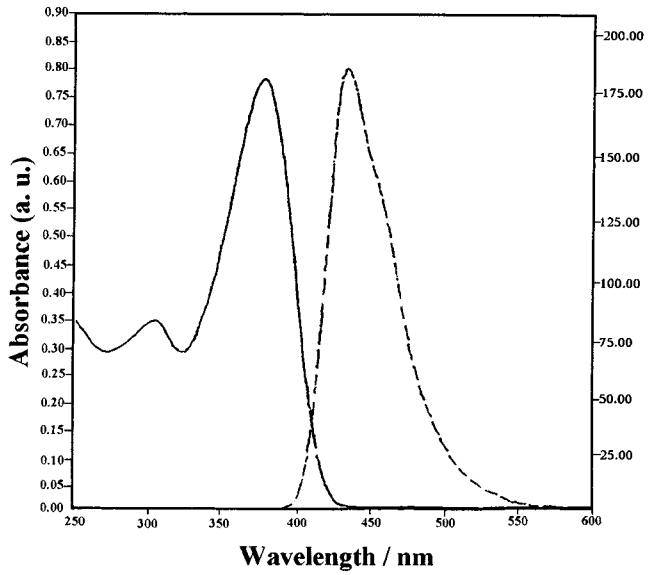


Figure 4. UV−vis absorption and fluorescence spectra of PHPY012 in $CHCl_3$ solution.

summarized in Table 2. The data given here were averaged over three measurements. All novel polymers were found to be strongly emissive with high quantum yields. This could be attributable to the rigid structure of the copolymer with the effect that relaxation from the excited state through nonradiative (e.g., thermal) processes will be reduced with consequently higher fluorescence quantum yield.[35]

The optical properties of the derived polymers in solution were investigated in $CHCl_3$−CH_3OH mixtures. In $CHCl_3$−CH_3OH mixtures, unlike some substituted polythiophenes which showed strong solvatochromism,[36,37] the position of UV maximum absorption slightly shifted to a longer wavelength (ca. 12 nm) with different volume fractions of $CHCl_3$ and CH_3OH (Figure 5a). The emission spectrum was nearly independent of addition of CH_3OH, with marginal differences at higher emission energies (Figure 5b).

With the aim of investigating the effect of protonation on the polymers, we measured UV and fluorescence spectra of the polymers in $CHCl_3$−CF_3COOH mixtures. Figure 6 depicts the changes in the absorption spectra and fluorescence spectra of PHPY08 with increasing concentration of CF_3COOH. From Figure 6a, addition of CF_3COOH (0−26.4×10^{-5} M) to a $CHCl_3$ solution of PHPY08 (2.5×10^{-5} M) led to a quick decrease in the

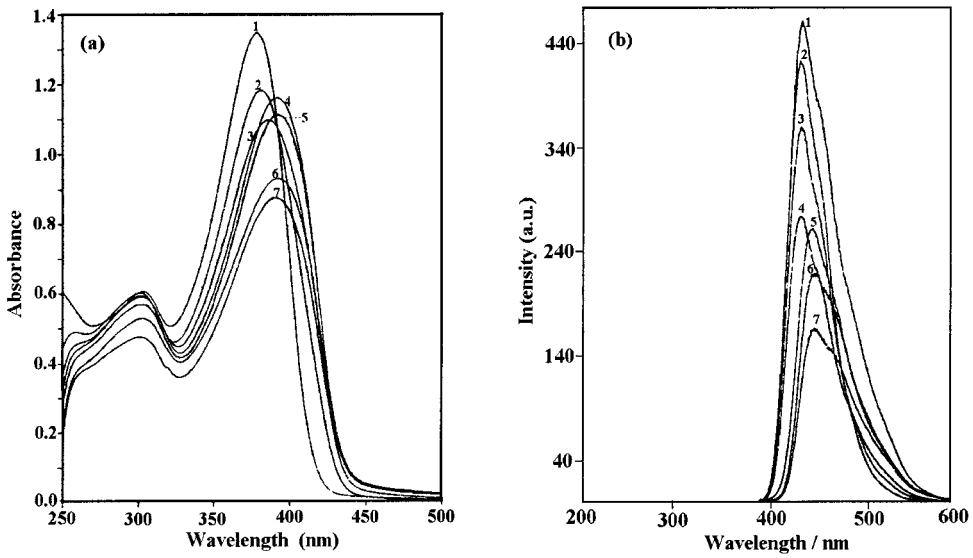


Figure 5. Changes in the absorption and emission spectra of PHPY08 (6.6×10^{-5} M) in $CHCl_3$−CH_3OH mixtures (10 mL) at different volume fractions of methanol: (1) 0, (2) 2, (3) 3, (3) 4, (4) 5, (5) 6, (6) 7, and (7) 7.5. (a) UV spectrum; (b) emission spectrum (excitation at absorption maxima).

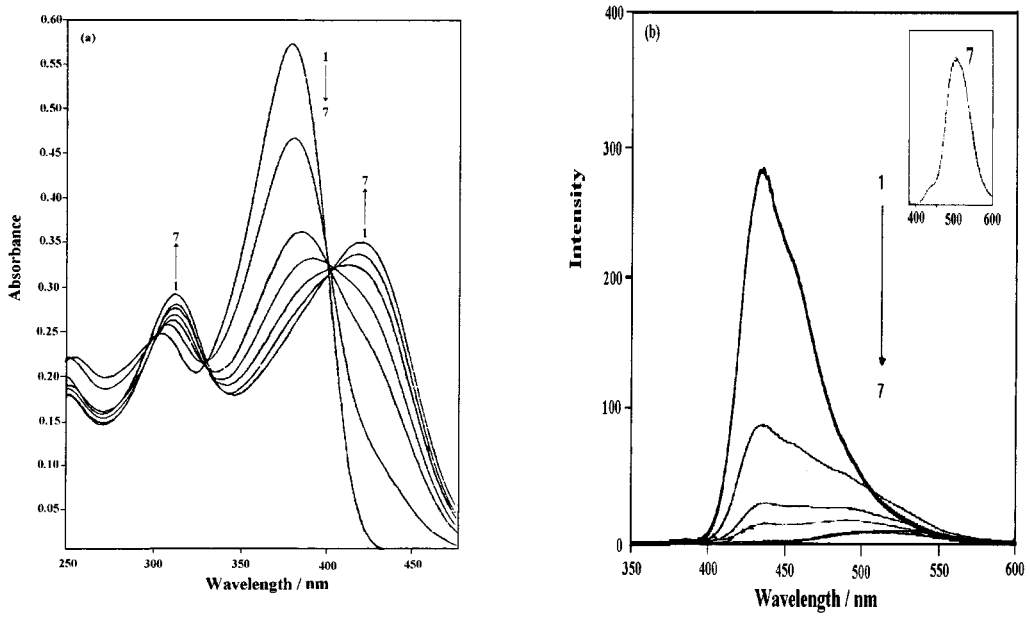


Figure 6. Changes in the absorption and emission spectra of PHPY08 (2.6×10^{-5} M) in $CHCl_3$−CF_3COOH mixtures (10 mL) at different concentrations of CF_3COOH: (1) 0 M, (2) 4.4×10^{-5} M, (3) 8.8×10^{-5} M, (4) 13.2×10^{-5} M, (5) 17.6×10^{-5} M, (6) 22×10^{-5} M, and (7) 26.4×10^{-5} M. (a) UV spectra; (b) emission spectra.

intensity of the absorption at 378 nm and, at the same time, an appearance of a new band at 420 nm with three isosbestic points at about 301, 331, and 402 nm. In contrast, the absorption at 304 nm showed only a minor change from added CF_3COOH, revealing that the absorption at 378 nm is more sensitive to the protonation. These results suggested that absorption at a longer wavelength mainly originates from a $\pi-\pi^*$ transition along the main polymer chain. Moreover, this $\pi-\pi^*$ transition is strongly affected by the protonation of nitrogen in PHPY08, which causes distortion of the inter-ring bonds ascribable to an increase in steric repulsion.[38] The emission spectra appeared to be more strongly affected by the addition of CF_3COOH than did the UV spectra. The emission maxima were red-shifted from 434 nm (blue) to 505 nm (green) when the CF_3COOH concentration was increased from 0 to 26.4×10^{-5} M. Meanwhile, the emission intensity diminished rapidly. Other polymers also displayed similar changes in the absorption and emission spectra in $CHCl_3$−CF_3COOH mixtures. Detailed studies on the relationship between polymer structures and their optical properties in acid media are currently in progress in our laboratory.

Optical Properties in the Film Phase. *(a) Electronic Properties in the Film Phase.* In contrast to other alternating donor/acceptor polymers such as poly(thiophene-*co*-pyridine),[31] poly(furan-*co*-pyridine),[31] and poly(thiophene-*co*-pyrido[3,4-*b*]pyrazine),[39] which showed UV−vis absorption maxima at a longer wavelength than their homopolymers due to the donor/acceptor structure, the copolymers reported herein have absorption maxima at about 386 nm, which is close to that of poly(2,5-pyridine) at $\lambda_{max} = 390$ nm.[31] In comparison with the absorption in solution, a red shift of only 8−10 nm was observed in film states, which is indicative of minimal

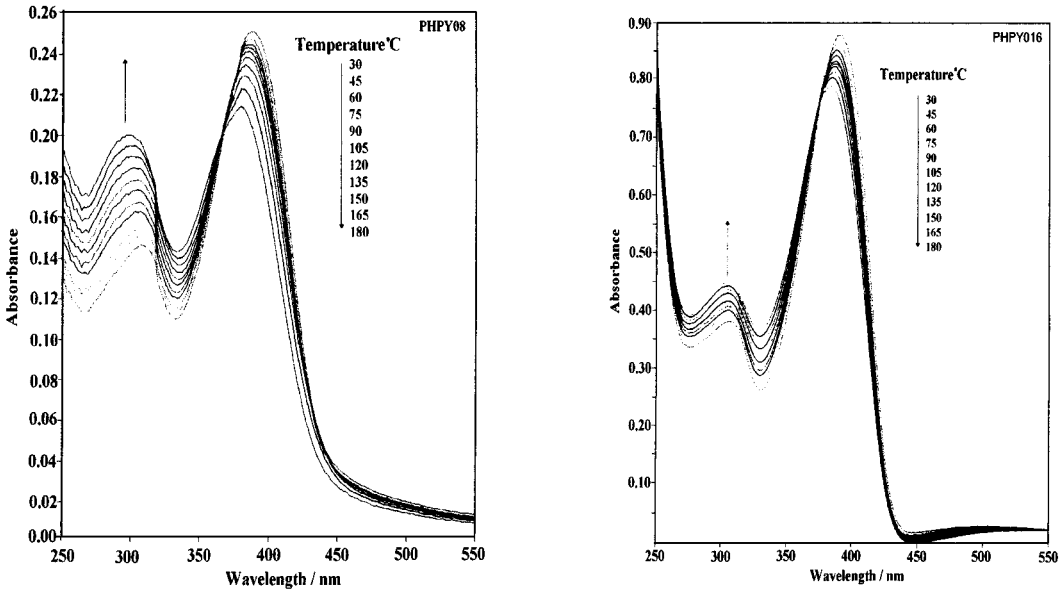


Figure 7. Temperature-dependent UV−vis absorption spectra of PHPY08 and PHPY016 in the solid state.

conformational changes in both the solution and film states presumably due to the rigid polymer backbones. The band gap energy of the polymers determined from extrapolation of the low energy absorption edge of film samples in UV−vis absorption spectra was about 3.0 eV, which is between that of poly(2,5-diheptoxy-phenylene) (HO-PPP) (3.4 eV)[3b] and PPY (2.88 eV).[31]

The temperature-dependent UV−vis absorption spectra of the polymers is depicted in Figure 7. During heating, the absorption maxima are blue-shifted by only ca. 5 nm with a marginal decrease in intensity. Meanwhile, the intensity of the minor band increases with observation of an isosbestic point. These effects are ascribable to minimal changes in the polymer chain conformation upon heating due to their rigid-rod backbone structure. The copolymer absorption is nearly independent of temperature implying that the devices fabricated with these polymers would likely be stable during long operation time.

(b) PL and EL Properties in the Solid Phase. In the film state, the emission maxima (upon irradiative excitation at absorption maxima) occur at 440−442 nm for polymers PHPY04, PHPY08, and PHPY012 and at 500 nm for PHPY016. The film-phase quantum yield (under excitation by an argon laser at 363.7 nm) as determined using an integrating sphere was evaluated to be about 20%, which is comparable with the efficient blue-emitting polydialkylfluorene.[40]

Single-layer devices fabricated by using these novel polymers as active layers gave strong blue light emission. Figure 8 depicts the photoluminescence and electroluminescence spectra of polymer PHPY012 operated at 77 and 300 K. At 300 K, polymers gave the main emission peak at ca. 444 nm with a shoulder at ca. 468 nm. Similar fine structure was reported in pyridine-based copolymers by Epstein et al.[41] However, at 77 K, obvious vibronic structure appeared in PL and EL spectra. The electroluminescence spectra of the polymers PHPY04, PHPY08, and PHPY012 are almost identical to those for photoluminescence, indicating that the same excited state is involved in the two processes.

As evaluated from cyclic voltammetry and the UV−vis absorption spectra, the electron affinity (EA) of these polymers is ca. 2.6 eV. This value is comparable to that

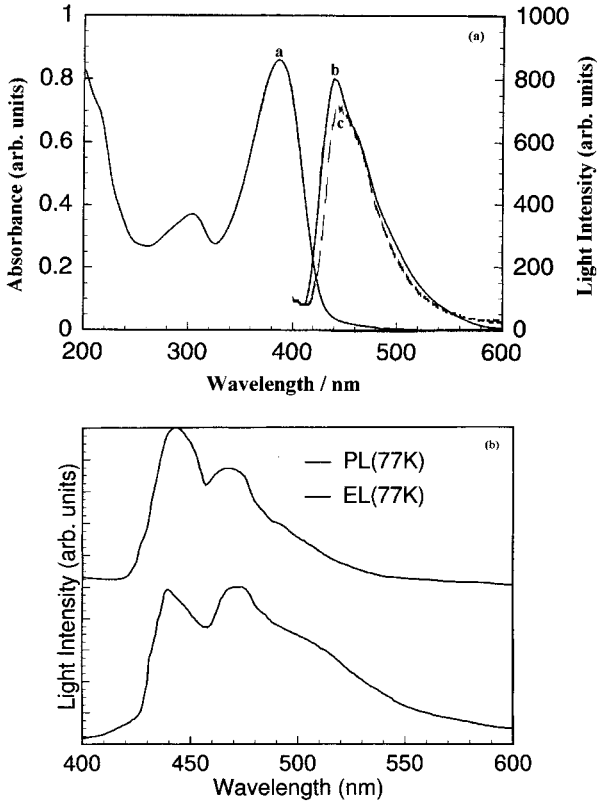


Figure 8. UV−vis absorption, photoluminescence, and electroluminescence spectra of the polymer PHPY012 film on ITO glass: (a) UV−vis absorption, PL, and EL spectra at 300 K and (b) PL and EL spectra at 77 K.

of copolymers containing oxadiazole moieties,[42] which are widely used as electron-transporting materials in LEDs. This can be attributed directly to the presence of electron-withdrawing pyridinyl moieties in the polymer backbone which decreases the lowest unoccupied molecular orbital (LUMO) energy. Consequently, these polymers may have similar electron-injection properties as those typical oxadiazole-containing electron-transporting polymers when they are used as active materials in PLEDs. It implies that electron injection from the cathode will be facile due to the lower LUMO energy,

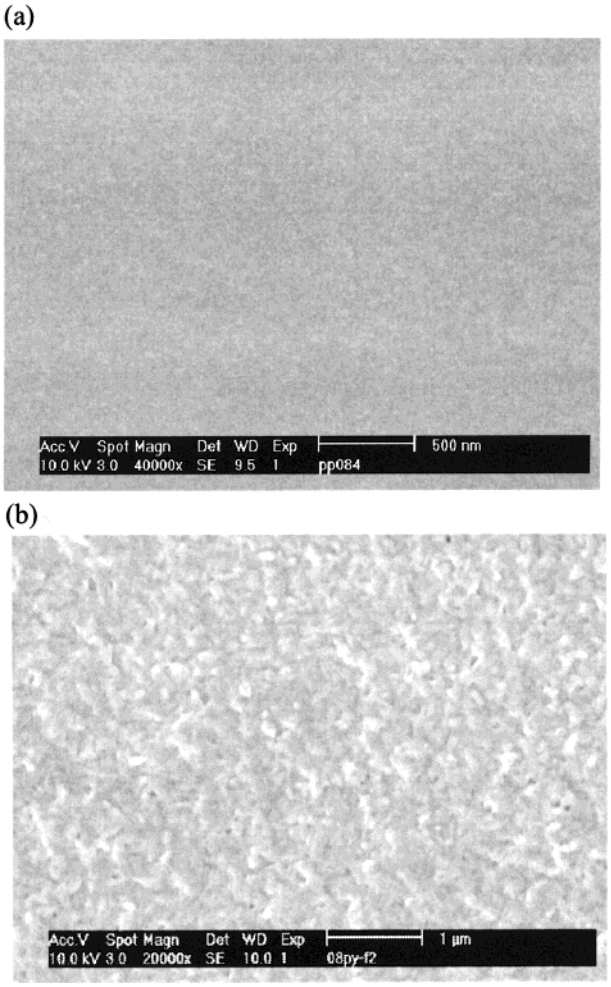


Figure 9. SEM of polymer PHPY08 film on ITO glass: (a) $CHCl_3$ as solvent and (b) $CF_3COOH/CHCl_3$ as solvent.

making possible the use of a lower work function and consequently more stable metals as the cathode. This has previously been demonstrated by experimental results of devices fabricated with these polymers.[43]

Surface Morphology of Polymers. Scanning electron micrographs of polymer films were measured at room temperature. Thin films were obtained by spin-coating on an ITO glass from $CHCl_3$ or THF solution. SEM micrographs of the polymer films from THF or $CHCl_3$ are the same and reveal that the surface of polymer films is very homogeneous with small spherical granules that are neatly packed close to each other (Figure 9a). For comparison purposes, we also prepared polymer film by spin-coating on an ITO glass from a $CHCl_3/CF_3COOH$ mixture, as shown in Figure 9b, which clearly depicted a very different morphology. This may be ascribable to the interaction of polymer and CF_3COOH which resulted in aggregation of the polymer backbones. Further investigation is in progress in our group.

Conclusion

In summary, novel conjugated polymers comprising alternating electron-donating phenylene and electron-accepting pyridinyl units were synthesized by Suzuki coupling reactions. The derived polymers depicted good solubility in common organic solvents, such as chloroform and THF, and trifloroacetic acid. Our investigation showed that the polymers' electronic and optical properties were consistent with a rigid-rod conjugated backbone structure. They showed strong blue emission in their solution and film states with high photoluminescence quantum yields. Single-layer devices prepared using these novel polymers gave bright blue light emission. These polymers in $CHCl_3-CF_3COOH$ mixtures depicted bathochromic shift. The electrochemical behavior of the polymers depicted facile n-doping and good electron-transporting properties. The polymers were easily cast into film, and the morphology of film surfaces was closely related to the properties of the solvents used.

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References and Notes

(1) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991**, *30*, L1941.
(2) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.
(3) (a) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934. (b) Hamaguchi, M.; Yoshino, K. *Jpn. J. Appl. Phys.* **1995**, *34*, L587. (c) Stampfl, J.; Tasch, S.; Leising, G.; Scherf, U. *Synth. Met.* **1995**, *71*, 2125.
(4) Zyung, T.; Hwang, D. H.; Kang, I. N.; Shim, H. K.; Hwang, W. Y.; Kim, J. J. *Chem. Mater.* **1995**, *7*, 1499.
(5) Baigent, D. R.; Friend, R. H.; Lee, J. K.; Schrock, R. R. *Synth. Met.* **1995**, *71*, 2171.
(6) Kim, K. D.; Park, J. S.; Kim, H. K.; Lee, T. B.; No, K. T. *Macromolecules* **1998**, *31*, 7267.
(7) Konstandakopoulou, F. D.; Gravalos, K. G.; Kallitsis, J. K. *Macromolecules* **1998**, *31*, 5264.
(8) (a) Song, S. Y.; Jang, M. S.; Shim, H. K.; Hwang, D. H.; Zyung, T. *Macromolecules* **1999**, *32*, 1482. (b) Ahn, T.; Jang, M. S.; Shim, H. K.; Hwang, D. H.; Zyung, T. *Macromolecules* **1999**, *32*, 3279.
(9) Musfeldt, J. L.; Reynolds, J. R.; Taner, D. B.; Ruiz, J. P.; Wang, J. P.; Pomerantz, M. *J. Polym. Sci., Part B*: *Polym. Phys.* **1994**, *32*, 2395.
(10) Chandross, M.; Mazumdar, S.; Jeglinski, S.; Wei, X.; Vardeny, Z. V.; Kwock, E. W.; Miller, T. M. *Phys. Rev.* **1994**, *50*, 14702.
(11) Fesser, K.; Bishop, A. R.; Campbell, D. K. *Phys. Rev. B* **1983**, *27*, 4804.
(12) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.
(13) Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969. Tokito, S.; Tanaka, H.; Noda, K.; Okada, A.; Taga, Y. *Appl. Phys. Lett.* **1997**, *70*, 1929.
(14) Brown, A. R.; Bradley, D. D. C.; Burroughes, J. H.; Friend, R. H.; Greenham, N. C.; Burn, P. L.; Holmes, A. B.; Kraft, A. *Appl. Phys. Lett.* **1992**, *61*, 2793.
(15) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628. Oelkrug, D.; Tompert, A.; Gierschner, J.; Egelhaaf, H. J.; Hanack, M.; Hohloch, M.; Steinhuber, E. *J. Phys. Chem. B* **1998**, *102*, 1902.
(16) Bao, Z.; Peng, Z. H.; Calvin, M. E.; Chandross, E. A. *Chem. Mater.* **1998**, *10*, 1201.
(17) Strehmel, B.; Sarker, A. M.; Malpert, J. H.; Strehmel, V.; Seifert, H.; Neckers, D. C. *J. Am. Chem. Soc.* **1999**, *121*, 1226.
(18) Wang, Y. Z.; Gebler, D. D.; Fu, D. K.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1179.
(19) (a) Ng, S. C.; Yu, W. L.; Huan, A. C. H. *Adv. Mater.* **1997**, *9*, 887. (b) Ng, S. C.; Miao, P.; Chan, H. S. O. *Chem. Commun.* **1998**, 153. (c) Ng, S. C.; Zhou, X. C.; Miao, P.; Chan, H. S. O.; Li, S. F. Y.; Fu, P. *Langmuir* **1998**, *14*, 1748. (d) Ng, S. C.; Miao, P.; Chen, Z. K.; Chan, H. S. O. *Adv. Mater.* **1998**, *10*, 782. (e) Ng, S. C.; Xu, L. G.; Chan, H. S. O. *J. Mater. Sci. Lett.* **1997**, *16*, 1738. (f) Ng, S. C.; Xu, L. G. *Adv. Mater.* **1998**, *10*, 1525.
(20) Ng, S. C.; Xu, J. M.; Chan, H. S. O.; Fujii, A.; Yoshino, K. *J. Mater. Chem.* **1999**, *9*, 381.
(21) (a) Ng, S. C.; Miao, P. *Macromolecules* **1999**, *32*, 5313. (b) Ng, S. C.; Xu, J. M.; Chan, H. S. O. *Macromolecules* **2000**, *33*, 7349.

(22) Yamamoto, T.; Suganuma, H.; Saitoh, Y.; Maruyama, T.; Inoue, T. *Jpn. J. Appl. Phys.* **1996**, *35*, L1142.
(23) Kanbara, T.; Kushida, T.; Saito, N.; Kuwajima, I.; Kubota, K.; Yamamoto, T. *Chem. Lett.* **1992**, 583.
(24) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publ. Co.: New York, 1978; p 48.
(25) Ng, S. C.; Lu, H. F.; Chan, H. S. O.; Fujii, A.; Laga, T.; Yoshino, K. *Adv. Mater.* **2000**, *15*, 1122.
(26) Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules* **1992**, *25*, 849.
(27) Coulson, D. R. *Inorganic Synthesis*; Cotton, F. A., Ed.; McGraw-Hill: New York, 1972; Vol. XIII, p 121.
(28) Remmers, M.; Schulze, M.; Wegner, G. *Macromol. Rapid. Commun.* **1996**, *17*, 239.
(29) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314.
(30) Todd, M. H.; Balasubramanian, S.; Abell, C. *Tetrahedron Lett.* **1997**, *38*, 6781.
(31) Yamamoto, T.; Zhou, Z. H.; Kanbara, T.; Shimura, M.; Kizu, K.; Maruyama, T.; Nakamura, Y.; Fukuda, T.; Lee, B. L.; Ooba, N.; Tomaru, S.; Kurihara, T.; Kaino, T.; Kubota, K.; Sasaki, S. *J. Am. Chem. Soc.* **1996**, *118*, 10389.
(32) Hamaguchi, M.; Nambu, H.; Yoshino, K. *Jpn. J. Appl. Phys.* **1997**, *36*, L124.
(33) Swager, T. M.; Gil, C. G.; Wrighton, M. S. *J. Phys. Chem.* **1995**, *99*, 4886.
(34) Davey, A. P.; Elliott, S.; O'Connor, O.′; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433.
(35) Kang, T. J.; Kim, J. Y.; Kim, K. J.; Lee, C.; Rhee, S. B. *Synth. Met.* **1995**, *69*, 377.
(36) Lanzi, M.; Bizzarri, P. C.; DellaCasa, C. *Synth. Met.* **1997**, *89*, 181. Bertinelli, F.; DellaCasa, C. *Polymer* **1996**, *37*, 5469.
(37) Richter, M. M.; Fan, F.-R. F.; Klavetter, F.; Heeger, A. J.; Bard, A. *J. Chem. Phys. Lett.* **1994**, *226*, 115.
(38) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930.
(39) Lee, B. L.; Yamamoto, T. *Macromolecules* **1999**, *32*, 1357.
(40) Shkunov, M. N.; Österbacka, R.; Fujii, A.; Yoshino, K.; Vardeny, Z. V. *Appl. Phys. Lett.* **1999**, *74*, 1648.
(41) Wang, Y. Z.; Gebler, D. D.; Fu, D. K.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1179.
(42) Janietz, S.; Schulz, B. *Eur. Polym. J.* **1996**, *32*, 465. Janietz, S.; Schulz, B.; Törrönen, M.; Sundholm, G. *Eur. Polym. J.* **1993**, *29*, 545.
(43) Fujii, A.; Ootake, R.; Fujisawa, T.; Ozaki, M.; Ohmori, Y.; Laga, T.; Yoshino, K.; Lu, H. F.; Chan, H. S. O.; Ng, S. C. *Appl. Phys. Lett.* **2000**, *77*, 660.

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