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# Synthesis and Properties of Poly(fluorene-*alt*-cyanophenylenevinylene)-Based Alternating Copolymers for Light-Emitting Diodes

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The novel statistical alternating EL copolymers poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-1,4-phenylene vinylene] (polymer I), poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (polymer II), and poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-1,4-biphenylenevinylene] (polymer III) were synthesized using modified Heck coupling reactions, and their EL characteristics were investigated. These fluorene- and cyanophenylenevinylene-based alternating copolymers, which have strong electron-withdrawing CN groups on their vinylene units, were found to be completely soluble in common organic solvents and easily spin-coated onto indium−tin oxide (ITO) coated glass substrates. The HOMO and LUMO energy levels and the electrooptical properties of these copolymers can be tuned by varying the main-chain structures and the side-chain groups. These well-defined conjugated copolymers can be synthesized with or without dialkyloxy substituents on the phenylenevinylene or biphenylenevinylene units instead of the phenylenevinylene unit; these variations in composition give rise to different emission maxima, ranging from bright yellow to a yellowish-orange color. A double-layer polymer light-emitting diode (PLED) with an ITO/PEDOT/polymer II/Al configuration exhibited a maximum brightness and luminescence efficiency of 7500 cd/m$^2$ at 20 V and 0.21 lm/W at 6.7 V, respectively.

## Introduction

Since the advent of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV),[1] many research groups have investigated the properties of the electroluminescent (EL) polymers, PPV[2−4] and poly(9,9-dialkylfluorene) (PF)[5−8] and their derivatives, which are the most promising materials for LED applications. To realize a full-color PLED, EL polymers that emit the three basic colors red, green, and blue with a high luminescence efficiency are required. PPVs and PFs typically emit light in the blue to greenish-yellow region of the visible spectrum.[9] Most red-emitting polymers are composed of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), polythiophenes (PThs), 4-(dicyanomethylene)-2-methyl-6-[*p*-(dimethylamino)styryl]-4H-pyran (DCM), and their derivatives or of newly synthesized chromophores with electron-withdrawing substituents along the polymer backbone.[10−13] The advantage of EL polymers is that

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their solubility properties and HOMO and LUMO energy levels can be adjusted by varying the molecular structure of the polymer. Many methods have been developed for tuning emission colors, such as confining the conjugation length by changing the main-chain molecular structure, blending an EL polymer with a second active polymer or with low-molecular-weight fluorescence dyes, doping, or using multilayer device structures and copolymer systems.[14−18] The copolymerization method has been widely used in the preparation of EL polymers with the aim of producing easy tuning of emission colors through modification of the polymers' intramolecular energy transfer and physical properties. A number of PF derivatives are suitable wide-band-gap materials because of the ease of substitution at the carbon 9 position of the fluorene unit, which produces improvements in their processability and their photoluminescence (PL) and EL efficiencies. It is also possible to vary the emission colors of these derivatives via modifications of structure that affect the intramolecular energy transfer processes. A variety of fluorene-based alternating and random copolymers have been synthesized using fluorenes and other aromatic compounds, which now fully cover the red, green, and blue emission colors of the visible spectrum.[19−21]

A balance of the injection of electrons and holes into LEDs is crucial to their performance. Most $\pi$-conjugated polymers have a greater tendency to transport holes than electrons, which results in a charge imbalance and lower device performance. To solve these problems, many research groups have tried to introduce an electron-withdrawing 1,3,4-oxadiazole group into the main or side chain, or a cyano group into the vinylene unit, to increase the electron affinity of the polymers and to improve their electron injection.[22,23]

In our continuing attempts to improve the device performance of PLEDs, we have reported novel EL polymers such as alkylsilylphenyl- and alkyloxyphenoxy-substituted PPVs, the blending of systems with oxadiazole-containing electron transfer polymers, and the synthesis of alternating copolymers composed of PPV segments and aromatic amine blocks.[24−30]

In this article, we report the synthesis of a novel chromophore containing the bis(phenylenevinylene)-fluorene moiety and an electron-withdrawing cyano substituent on the vinylene unit and of a series of statistical light-emitting alternating copolymers composed of bis(cyanophenylenevinylene)fluorenyl and phenylenevinylene or biphenylenevinylene repeating units, as well as the results of measurements of their electrooptical properties.

## Experimental Section

**2,7-Bis(bromomethyl)-9,9-dihexylfluorene (1).** 9,9-Dihexylfluorene was synthesized according to the procedure from the literature.[31] A three-necked flask containing 10.5 g (31.4 mmol) of 9,9-dihexylfluorene, 9.43 g (314 mmol) of paraformaldehyde, 9.7 g (94.2 mmol) of sodium bromide, and acetic acid (50 mL) was placed in an ice bath. To this flask was carefully added 10 mL of 50% sulfuric acid solution in acetic acid, and the mixture was stirred for 24 h at 60−70 °C. The resulting mixture was extracted with methylene chloride, and the organic portion was concentrated. Finally, a viscous liquid was obtained by column chromatography with a yield of 37% (6.05 g). $^{1}$H NMR (CDCl$_3$, ppm): 7.65 (d, $J = 8.4$ Hz, 2H, ArH), 7.37 (d, $J = 6.2$ Hz, 4H, ArH), 1.92 (m, 4H, $\alpha$-CH$_2$ of the hexyl group at the 9 position of fluorene), 1.06 (12H, $\beta$-$\delta$-CH$_2$), 0.76−0.75 (10H, $\epsilon$-CH$_2$ and CH$_3$). Mass spectrum (EI) *m/z*: 522, 520, 518 (M$^+$, 40), 476 (7), 440 (M$^+$ − Br, 100), 395 (55), 377 (17), 360 (M$^+$ − 2Br, 97), 311 (7), 283 (91), 239 (27), 215 (39), 205 (100), 191 (92), 178 (20), 165 (13), 152 (6), 85 (8), 71 (24), 55 (35), 41 (84). Exact mass calcd for C$_{27}$H$_{36}$Br$_2$ 518.12, found 518.

**[7-(Acetyloxymethyl)-9,9-dihexylfluorene-2-yl]methyl Acetate (2).** A mixture of 6.0 g (11.5 mmol) of compound **1**, anhydrous sodium acetate (4.73 g, 57.6 mmol), acetic anhydride (3.29 mL, 34.6 mmol), and acetic acid (50 mL) was stirred at 90 °C for 18 h. The reaction mixture was cooled and extracted with methylene chloride. After evaporation of the solvent under reduced pressure, a yellow liquid was obtained (4.5 g, 82%). $^{1}$H NMR (CDCl$_3$, ppm): 7.69 (d, $J = 7.3$ Hz, 2H, ArH), 7.34 (d, $J = 8.1$ Hz, 4H, ArH), 5.15 (s, 4H, $-$CH$_2$O$-$), 2.12 (s, 6H, $-$OCOCH$_3$), 1.93 (m, 4H, $\alpha$-CH$_2$$-$ of the hexyl group at the 9 position of fluorene), 1.02 (12H, $\beta$-$\delta$-CH$_2$$-$), 0.76−0.70 (10H, $\epsilon$-CH$_2$$-$ and CH$_3$). Anal. Calcd for C$_{31}$H$_{42}$O$_4$: C, 77.79; H, 8.84. Found: C, 78.48; H, 8.99. Mass spectrum (EI) *m/z*: 479, 478 (M$^+$, 51), 419 (M$^+$ − OAc, 39), 393 (87), 347 (14), 333 (M$^+$ − 2CH$_2$OAc, 100), 322 (8), 309 (86), 291 (13), 273 (28), 263 (97), 250 (26), 231 (12), 219 (23), 204 (80), 191 (64), 179 (36), 165 (7), 69 (4), 55 (18), 43 (51). Exact mass calcd for C$_{31}$H$_{42}$O$_4$ 478.31, found 478.

**[9,9-Dihexyl-7-(hydroxymethyl)fluorene-2-yl]methan-1-ol (3).** A mixture of compound **2** (4.5 g, 9.5 mmol) and sodium hydroxide (1.9 g, 47 mmol) in 70 mL of ethanol was stirred at 40 °C for 1 h. After being cooled, the mixture was poured into 100 mL of distilled water. Concentrated hydrochloric acid was added dropwise to the above solution until the pH of the suspension changed to 7. This solution was extracted with methylene chloride, and the organic portion was concentrated. Finally, a viscous liquid was obtained by column chromatography with a yield of 65% (2.5 g). $^{1}$H NMR (CDCl$_3$, ppm): 7.69 (d, $J = 8.4$ Hz, 2H, ArH), 7.32 (d, $J = 7.0$ Hz, 4H, ArH), 4.8 (s, 4H, $-$CH$_2$OH), 1.93 (m, 4H, $\alpha$-CH$_2$$-$ of the hexyl group at the 9 position of fluorene), 1.10 (12H, $\beta$-$\delta$-CH$_2$$-$), 0.80−0.70 (10H, $\epsilon$-CH$_2$$-$ and CH$_3$). Anal. Calcd for C$_{271}$H$_{38}$O$_2$: C, 82.18; H, 8.11. Found: C, 82.33; H, 8.35. Mass spectrum (EI) *m/z*: 395, 394.5 (M$^+$, 52), 378 (M$^+$ − OH, 6), 363 (M$^+$ − 2OH, 11), 309 (100), 291 (27), 279 (7), 261 (62), 249 (38), 238 (30), 225 (94), 203 (20), 191 (82), 179 (98), 165 (45), 152 (9), 71 (21), 58 (81), 41 (69). Exact mass calcd for C$_{27}$H$_{38}$O$_2$ 394.29, found 394.5.

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**9,9-Dihexylfluorene-2,7-dicarbaldehyde (4).** A solution of diol compound **3** (2.45 g, 6.2 mmol) in 100 mL of anhydrous methylene chloride was stirred and cooled with an ice bath while pyridinium chlorochromate (4.02 g, 18.6 mmol) was added in portionwise over a period of 20 min. The oxidation reaction was monitored by TLC, and the reaction mixture was stirred for 2 h at room temperature. After a dark brown suspension had formed, the mixture was diluted with 150 mL of diethyl ether and stirred for further 30 min. The mixture was then filtered through silica gel to remove inorganic salt. The solution was washed with 100 mL of 1 N HCl and then with water and dried over $MgSO_4$. The ether solution was filtered and concentrated, and the remaining yellow viscous liquid was purified by column chromatography (eluent *n*-hexane/ethyl acetate = 10:1). The pure white solid was obtained with a yield of 63% (1.53 g). mp 47.9−48.6 °C. $^1H$ NMR ($CDCl_3$, ppm): 10.20 (s, 2H, −CHO), 7.8 (s, 6H, ArH), 2.05 (m, 4H, $\alpha$-$CH_2$− of the hexyl group at the 9 position of fluorene), 1.05 (12H, $\beta$-$\delta$-$CH_2$−), 0.75−0.60 (10H, $\epsilon$-$CH_2$− and $CH_3$). Anal. Calcd for $C_{27}H_{34}O_2$: C, 83.03; H, 8.77. Found: C, 82.44; H, 8.22. Mass spectrum (EI) *m*/*z*: 390 ($M^+$, 100), 362 ($M^+$ − CHO, 75), 334 ($M^+$ − 2CHO, 8), 319 (10), 306 (100), 291 (10), 277 (47), 263 (6), 247 (33), 236 (80), 222 (100), 205 (93), 193 (97), 176 (96), 165 (95), 151 (41), 114 (21), 85 (16), 71 (69), 55 (86), 43 (52). Exact mass calcd for $C_{27}H_{34}O_2$ 390.26, found 390.

**2,7-Bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (5).** A mixture of compound **4** (3.0 g, 5.12 mmol) and 4-bromophenylacetonitrile (2.0 g, 10.24 mmol) was dissolved in 50 mL of dry ethanol under a nitrogen atmosphere in a 250 mL three-necked round-bottomed flask. A mixture of sodium hydroxide (51.2 mg, 1.28 mmol) and 30 mL of dry ethanol was added slowly, and then the crude product was precipitated in the reaction mixture. The reaction mixture was stirred for 10 h at room temperature, and the precipitate was filtered and washed with water. A yellow powder was obtained (yield 5.0 g, 86%). mp 139.5−141.0 °C. $^1H$ NMR ($CDCl_3$, ppm): 7.9−7.4 (16H, vinylic proton and ArH), 2.05 (m, 4H, $\alpha$-$CH_2$− of the hexyl group at the 9 position of fluorene), 1.10 (12H, $\beta$-$\delta$-$CH_2$−), 0.80−0.70 (10H, $\epsilon$-$CH_2$− and $CH_3$). $^{13}C$ NMR ($CDCl_3$, ppm): 14.0, 22.5, 24.1, 30.2, 32.1, 40.3, 58.0, 110.2, 118.3, 121.2, 123.8, 124.1, 128.0, 129.2, 132.2, 133.8, 134.1, 143.3, 152.4. Anal. Calcd for $C_{43}H_{42}Br_2N_2$: C, 69.17; H, 5.67, N, 3.75. Found: C, 69.84; H, 6.48, N 3.56. Mass spectrum (EI) *m*/*z*: 746 ($M^+$, 14), 591 ($M^+$ − 2Br, 8), 569 (50), 484 (10), 414 (29), 398 (60), 318 (6), 304 (33), 290 (49), 196 (7), 116 (68), 89 (31), 75 (17), 57 (100). Exact mass calcd for $C_{43}H_{42}Br_2N_2$ 744.17, found 746.

**[4-(Acetyloxymethyl)-2-(2-ethylhexyoxy)-5-methoxyphenyl]methyl Acetate (6).** 1,4-Bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene was prepared as described earlier.[32] A mixture of 5.0 g (15 mmol) of 1,4-bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene, anhydrous sodium acetate (6.15 g, 75 mmol), acetic anhydride (4.26 mL, 45 mmol), and acetic acid (50 mL) was stirred at 90 °C for 3 h. After being cooled, the mixture was poured into 200 mL of water. The precipitate was washed throughly with distilled water and dried over $P_2O_5$ in a vacuum to give the product as a white solid (yield 5.1 g, 89%). mp 43.2−44.0 °C. $^1H$ NMR ($CDCl_3$, ppm): 6.9 (s, 2H, ArH), 5.1 (s, 4H, −$CH_2$Ac), 3.85 (d, *J* = 6.2 Hz, 2H, −$OCH_2$−), 3.77 (s, 3H, −$OCH_3$), 2.06 (s, 3H), 1.6−1.3 (m, 9H), 0.9 (m, 6H). Anal. Calcd for $C_{21}H_{32}O_6$: C, 66.29; H, 8.48. Found: C, 66.64; H, 8.99. Mass spectrum (EI) *m*/*z*: 380 ($M^+$, 100), 321 ($M^+$ − OAc, 45), 268 (15), 256 (19), 209 (93), 182 (37), 167 (75), 151 (35), 137 (80), 121 (40), 107 (44), 91 (48), 79 (31), 71 (76), 57 (92), 41 (94). Exact mass calcd for $C_{21}H_{36}O_6$ 380.22, found 380.

**[2-(2-Ethylhexyoxy)-4-(hydroxymethyl)-5-methoxyphenyl]methan-1-ol (7).** A mixture of compound **6** (1.9 g, 5.0 mmol) and sodium hydroxide (0.92 g, 25 mmol) in 60 mL of ethanol was stirred at 50 °C for 3 h. After being cooled, the reaction mixture was poured into 200 mL of distilled water. Diluted aqueous HCl solution was added dropwise until the pH of the suspension changed to 7. This solution was extracted with methylene chloride, and evaporation of the organic layer under reduced pressure afforded crystal-like solid (1.9 g, 91%). mp 47.8−48.5 °C. $^1H$ NMR ($CDCl_3$, ppm): 6.85 (s, 2H, ArH), 4.65 (s, 4H, −$CH_2$OH), 3.9 (d, *J* = 6.2 Hz, 2H, −$OCH_2$−), 3.8 (s, 3H, −$OCH_3$), 1.6−1.3 (m, 9H), 0.9 (m, 6H). Anal. Calcd for $C_{17}H_{28}O_4$: C, 68.89; H, 9.52. Found: C, 68.78; H, 8.84.

**2-(2-Ethylhexyoxy)-5-methoxybenzene-1,4-dicarbaldehyde (8).** A solution of compound **7** (2.0 g, 7.0 mmol) in 80 mL of anhydrous methylene chloride was stirred and cooled with an ice bath while pyridinum chlorochromate (PCC) (4.53 g, 21 mmol) was added in portionwise over a period of 20 min. The reaction mixture was then stirred for 8 h at room temperature until the oxidation was completed. After a dark brown suspension had formed, the mixture was diluted with 150 mL of diethyl ether and stirred for a further 30 min. The mixture was then filtered through silica gel to remove inorganic salt. The solution was washed with 100 mL of 1 N HCl and then with water and dried over $MgSO_4$. The ether solution was filtered concentrated, and the remaining green solid was purified by column chromatography (eluent hexane/ethyl acetate = 10:1). The pure green solid was obtained with a yield of 85% (1.8 g). mp 54.1−55.1 °C. $^1H$ NMR ($CDCl_3$, ppm): 10.51 (d, *J* = 5.9 Hz, 2H, −CHO), 7.46 (s, 2H, ArH), 3.9 (d, *J* = 5.9 Hz, 2H, −$OCH_2$−), 3.7 (s, 3H, −$OCH_3$), 1.6−1.3 (m, 9H), 0.9 (m, 6H). Anal. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27. Found: C, 69.57; H, 7.85. Mass spectrum (EI) *m*/*z*: 292 ($M^+$, 90), 193 (20), 179 (87), 162 (83), 134 (78), 120 (29), 112 (29), 92 (33), 83 (44), 71 (86), 55 (96), 41 (100). Exact mass calcd for $C_{17}H_{24}O_4$ 292.17, found 292.

**1-(2-Ethylhexyoxy)-4-methoxy-2,5-divinylbenzene (9).** A three-necked flask containing a solution of methyltriphenylphosphonium bromide (21.5 g, 60 mmol) in 200 mL of THF was stirred and cooled with an ice bath while *n*-butyllithium (1.6 M solution in hexane, 59 mmol) was added carefully under nitrogen atmosphere, and the mixture was stirred for 10 min at room temperature. To this reaction mixture, was added compound **8** (4.0 g, 14 mmol) in 50 mL of THF in a portionwise manner over a period of 30 min, and the mixture was stirred for 24 h at room temperature. After being cooled, the mixture was filtered and poured into 300 mL of water. This solution was extracted with methylene chloride, and the organic portion was concentrated. The remaining yellow viscous liquid was purified by column chromatography (eluent *n*-hexane/ethyl acetate = 9:1). The pure yellow liquid was obtained with a yield of 57% (2.24 g). $^1H$ NMR ($CDCl_3$, ppm): 7.2−7.0 (m, 4H, −CH=, ArH), 5.75 (d, *J* = 17.9 Hz, 2H, =$CH_2$), 5.3 (d, *J* = 11.0 Hz, 2H, =$CH_2$), 3.9 (d, *J* = 5.5 Hz, 2H, −$OCH_2$−), 3.8 (s, 3H, −$OCH_3$), 1.6−1.3 (m, 9H), 0.9 (m, 6H). $^{13}C$ NMR ($CDCl_3$, ppm): 10.6, 13.5, 22.2, 23.8, 28.7, 30.1, 39.4, 56.0, 71.2, 108.0, 109.8, 113.5, 126.9, 131.3, 150.3. Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 78.92; H, 9.32. Mass spectrum (EI) *m*/*z*: 288 ($M^+$, 15), 277 (43), 215 (8), 201 (18), 192 (8), 176 (73), 163 (13), 152 (12), 133 (16), 121 (8), 115 (16), 91 (24), 77 (63), 71 (20), 57 (56), 41 (100). Exact mass calcd for $C_{19}H_{28}O_2$ 288.21, found 288.

**Poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9*H*-fluorene-2,7-yl-*alt*-1,4-phenylenevinylene] (Polymer I).** The polymer was prepared using the Heck coupling reaction between 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9*H*-fluorene (**5**) and 1,4-divinylbenzene. A mixture of compound **5** (1.0 g, 1.34 mmol), 1,4-divinylbenzene (0.172 mg, 1.34 mmol), $Pd(OAc)_2$ (1.5 mg, 0.068 mmol), tri-*o*-tolyphosphine (0.164 mg, 0.54 mmol), and tributylamine (2 mL) in 8 mL of DMF was stirred at 80 °C in a 50 mL Schlenk flask. To this flask was added 4 mL of NMP, and the mixture was stirred for 3 days at 120 °C. The hot reaction mixture was poured into 500 mL of hexane to precipitate the polymer. The collected polymer was redissolved in 100 mL of chloroform and then washed with 400 mL of deionized water. The water layer was decanted. The catalyst particles in the polymer solution were removed by filtration followed by evaporation of the solvent using a rotary evaporator. The polymer was dissolved in a small amount of chloroform and then poured into hexane. The polymer was collected by

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(32) Wudl, F.; Srdanov, G. U.S. Patent 5,189,136, 1993.

filtration and dried under vacuum (0.5 g, 52%). $^1$H NMR ($CDCl_3$, ppm): 8.0−7.3 (br, 20H, vinylic proton and ArH), 7.2−7.0 (br, 4H, vinylic proton), 2.1−1.8 (br, 4H, $\alpha$-$CH_2$ of the hexyl group at the 9 position of fluorene), 1.2−0.9 (br, 12H, $\beta$-$\delta$-$CH_2$−), 0.8−0.6 (10H, $\epsilon$-$CH_2$− and $CH_3$). Anal. Calcd for $(C_{53}H_{50}N_2)_n$: C, 89.03; H, 7.05. Found: C, 88.75; H, 6.93.

Poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (polymer II) and poly[bis{2-(4-phenylenevinylene)-2-cyanoethenyl}-9,9-dihexyl-9H-fluorene-2,7-yl-*alt*-1,4-biphenylenevinylene] (polymer III) were synthesized using the procedure described for polymer I. $^1$H NMR (polymer II): 8.0−7.3 (br, 20H, vinylic proton and ArH), 7.2−7.0 (br, 4H, vinylic proton), 4.1−3.8 (br, 5H, $-OCH_3$, $-OCH_2-$), 2.1−1.8 (br, 5H), 1.2−0.9 (br, 18H), 0.8−0.6 (br, 16H) Anal. Calcd for $(C_{62}H_{68}N_2O_2)_n$: C, 85.28; H, 7.85. Found: C, 85.01; H, 7.63. $^1$H NMR (polymer III): 8.0−7.3 (br, 24H, vinylic proton and ArH), 7.2−7.0 (br, 4H, vinylic proton), 2.1−1.8 (br, 4H, $\alpha$-$CH_2$ of the hexyl group at the 9 position of fluorene), 1.2−0.9 (br, 12H, $\beta$-$\delta$-$CH_2$−), 0.8−0.6 (10H, $\epsilon$-$CH_2$− and $CH_3$) Anal. Calcd for $(C_{59}H_{54}N_2)_n$: C, 89.58; H, 6.88. Found: C, 88.58; H, 6.21.

**Characterization.** $^1$H and $^{13}$C NMR spectra were recorded using a Bruker AM-300 spectrophotometer. Each material was dissolved in chlorobenzene at a concentration of 1.0 wt % and spin-coated onto precleaned fused silica with a thickness of around 80 nm. The absorption spectra of the thin films were recorded using a Varian 5E UV−vis−NIR spectrometer. Thermogravimetric analysis (TGA) was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 800 °C. The molecular weight and polydispersity of each polymer were determined using Waters gel permeation chromatography (GPC) analysis and a model 590 pump. Cyclic voltammogram of the polymers was obtained using an AUTOLAB/PG-STAT12 instrument at room temperature in a three-electrode cell under a nitrogen atmosphere at a scan rate of 100 mV/s, with Pt as the counter electrode, an Ag/AgCl reference electrode, and 0.1 M tetraethylammonium tetrafluoroborate in acetonitrile as the electrolyte. For the preparation of the LEDs, glass substrates coated with an ITO layer with a conductivity of about 10 Ω/square (from Samsung Corning) served as the anodes. The wet cleaning of the ITO substrates consisted of successive rinsing with acetone; wiping with tissues to remove adhering glass particles (from the cutting process); and ultrasonic treatment with distilled water, acetone, ethanol, and finally distilled water, followed by drying of the ITO substrates with nitrogen gas. For the double-layer devices, poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT/PSS) (Baytron P, Al 4083, Starck GmbH, Leverkusen, Germany) as a hole-injection layer and smoothening was spin-coated from an aqueous solution with 10 wt % of isopropyl alcohol onto the ITO surface. A solution of each EL polymer (1.0 wt % in chlorobenzene) was filtered with a 0.45 $\mu$m syringe filter and deposited by spin-coating onto the PEDOT/PSS layer in uniform and pinhole free films with a thickness of around 100 nm. The Al electrode was deposited by vacuum evaporation at a pressure below $10^{-6}$ Torr at rates in the range of 0.5−1.0 nm/s. The active areas of the devices were approximately 4 mm$^2$. The current density−voltage−luminance ($J-V-L$) characteristics were measured using a current−voltage source (Keithley 238) and an optical power meter (Newport 818-SL). All measurements were carried out in air at room temperature.

## Results and Discussion

The synthetic routes for the new monomers, 2,7-bis-[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene and 2-[(2-ethylhexyl)oxy]-5-methoxy-1,4-divinylbenzene, are outlined in Scheme 1. Bromomethylation of the fluorene unit was achieved using formaldehyde and sodium bromide in the presence of sulfuric acid and acetic acid. Acetate groups were easily introduced into the 2 and 7 positions of the fluorene unit, and this procedure was followed by hydrolysis to give compound **3** containing the hydroxymethyl substituent. The intermediate molecule 9,9-di-hexylfluorene-2,7-dicarbaldehyde was prepared by oxidation of compound **3** using PCC in anhydrous methylene chloride. A Knoevenagel-type condensation of 4-bromophenylacetonitrile with compound **4** produced the fluorene-based monomer **5** containing the electron-withdrawing bis(cyanophenylenevinylene) unit in a yield of 75%.

To tune the emission colors by varying the molecular structure of the main-chain backbone, we synthesized the dialkyloxy-substituted divinylbenzene and 4,4′-divinyl-1,1′-biphenyl as comonomers according to a literature procedure.[33] The divinylbenzene-based monomers were synthesized using the Wittig formylation between terephthalaldehyde or its derivatives and methyltriphenylphosphonium bromide in THF solvent. Statistical alternating EL copolymers were synthesized using 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (**5**) and the 1,4-divinylbenzene derivatives or 4,4′-divinyl-1,1′-biphenyl as comonomers through the modified Heck coupling reaction shown in Scheme 2. The modifications of the Heck polymerization conditions, namely, the use of DMF and NMP as cosolvents and of tributylamine instead of triethylamine, increase the molecular weight of the EL polymers over that achieved with DMF as the solvent in conventional Heck coupling reactions. The resulting EL polymers were purified by successive Soxhlet extraction with different solvents including methanol and hexane, dissolved in $CHCl_3$, and then reprecipitated into methanol. The molecular structures and purities of the monomers and the corresponding EL polymers were confirmed using $^1$H NMR spectroscopy and elemental analysis.

Table 1 summarizes the polymerization results, molecular weights, and thermal properties of the statistical alternating copolymers. The polymerization yields, weight-average molecular weights ($M_w$), and polydispersities of the polymers were found to be in the ranges 52−85%, $(4.5-13.4) \times 10^3$, and 1.95−2.9, respectively. The thermal stabilities of polymers I−III were investigated using TGA under a nitrogen atmosphere. Polymers I and III have higher thermal stabilities than polymer II, with 5% losses of weight at 367, 450, and 332 °C, respectively. These differences in thermal stability are attributed to the introduction of ethylhexyloxy substituents as pendant groups into the phenylenevinylene units of polymer II and the rigid biphenyl units of polymer III. The ethylhexyloxy groups decrease the strengths of the intermolecular interactions between the polymer chains and thus increase the solubilities of the polymers in common organic solvents.

Figure 1 shows the $^1$H NMR spectra of 2-[(2-ethylhexyl)oxy]-5-methoxy-1,4-divinylbenzene (a), 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene (b), and polymer II (c) in $CDCl_3$. The $^1$H NMR spectrum of polymer II contains vinylic proton peaks at 7.0−7.2 ppm; all of the other peaks of the polymer correspond to those of the monomers. High-quality optical thin films without any defects could be spun-cast onto ITO-coated glass substrates.

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[33] Chen, C. *Synlett* **2000**, *10*, 1491.

**Scheme 1. Synthetic Routes to the Monomers**

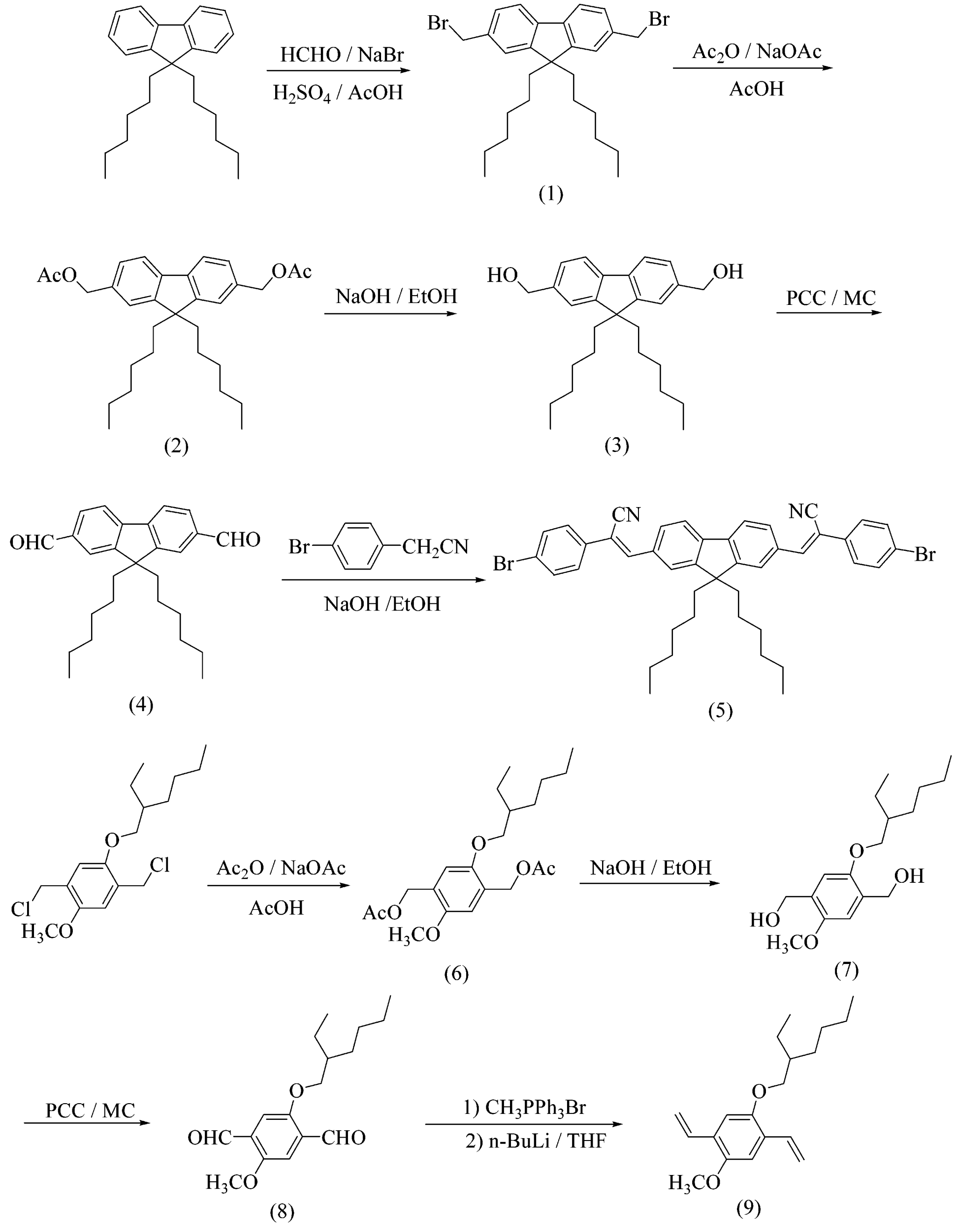

Figure 2 displays the absorption and emission spectra of thin films of polymers I−III. The absorption spectra of polymers I−III have sharp maximum absorption peaks at 419, 439, and 417 nm, respectively, with corresponding onsets of absorption at 514, 550, and 496 nm. From the onsets of the absorption spectra, the band gaps of polymers I−III were calculated to be 2.41, 2.25, and 2.50 eV, respectively. The larger band gap of polymer III is due to the noncoplanar nature of its rigid biphenyl backbone.

The red-shift of the absorption maximum for polymer II is due to the introduction of dialkyloxy substituents on the phenylenevinylene repeating unit, which extends the $\pi$-electron delocalization along the conjugated polymer backbone. The PL spectra of thin films of polymers I−III were recorded using excitation wavelengths corresponding to the absorption maximum wavelengths. As expected, the incorporation of dialkyloxy substituents on the phenylenevinylene units in polymer II red shifts its emission maximum to 602 nm. However, the PL emission of polymer III was blue-shifted by 40 nm relative to that of polymer I, which is caused by the interruption of the effective conjugation length at the out-of-plane rigid biphenyl main-chain structure. The emission spectra of polymers I and III are broader than that of polymer II, which is probably due to an increase in the intermolecular $\pi-\pi$ interactions between the polymer backbones.

The external PL quantum efficiency ($\Phi$) is an important factor in the design of the molecular structure of emitting materials and in the efficiency of the PLED. The $\Phi$ values of polymers I−III and MEH-PPV for comparison were measured using an integrating sphere method.[34] Spin-coated thin films of polymers I−III and MEH-PPV produced $\Phi$ values of 5.7, 14.7, 3.5, and 10%,

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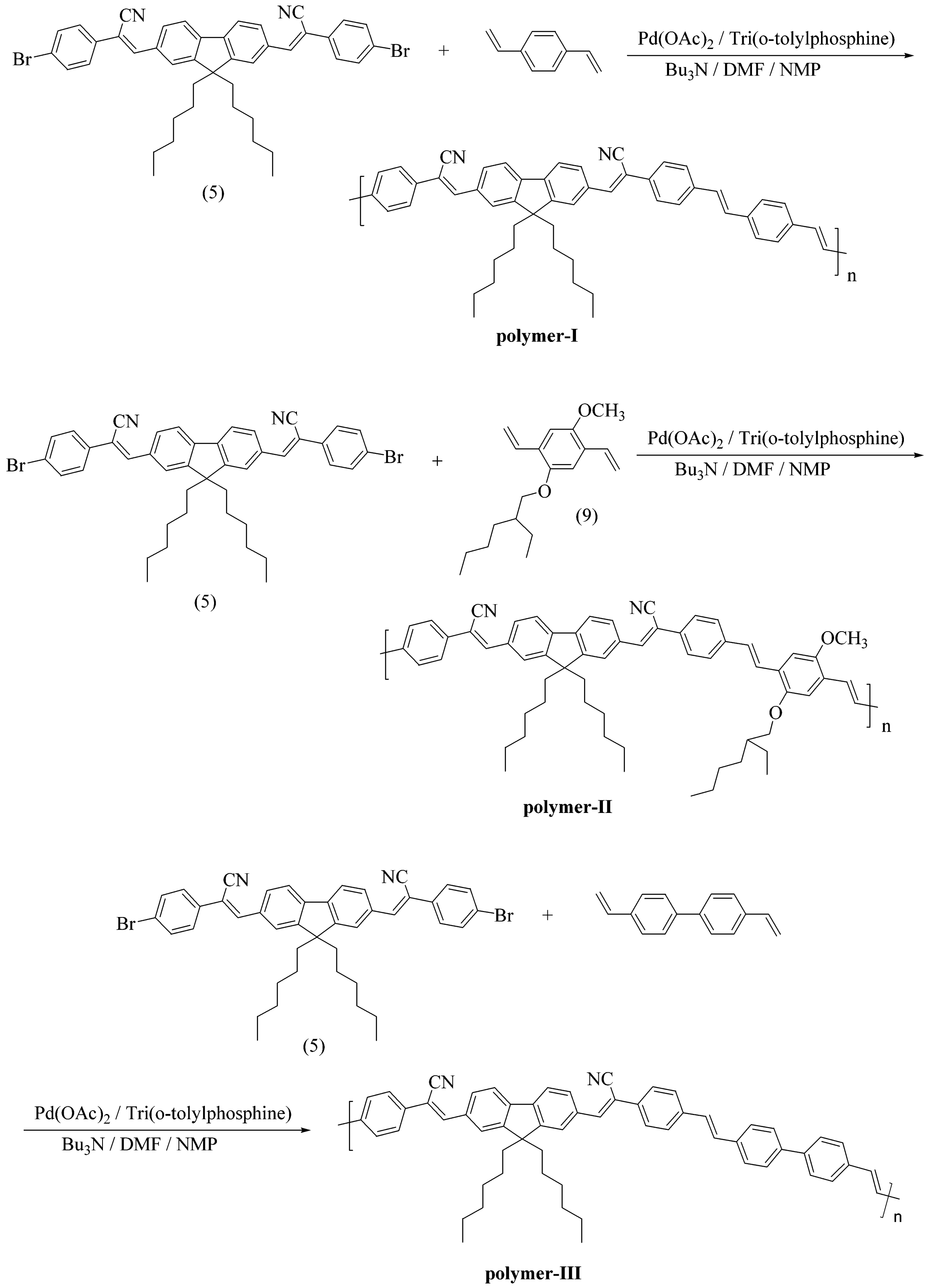
(34) John, C.; Mello, C.; Winmann, F.; Friend, R. H. *Adv. Mater.* **1997**, *9* (3), 230.

**Scheme 2. Synthetic Routes to the Polymers**



respectively. The Stokes shifts were found to be 7.22 eV for polymer I, 7.62 eV for polymer II, and 6.82 eV for polymer III. Polymer II has a smaller Stokes shift and a higher external PL quantum efficiency than polymers I and III in the thin-film state, and this is assumed to be due to the lesser extents in polymer II of formation of excimer-like adducts between photoexcited polymers and/or of internal charge transfer along the polymer backbone.[35] The strength of the intermolecular interactions between polymer II backbones is decreased by the introduction of the dialkyloxy substituents into the phenylenevinylene units.

To evaluate the charge injection and device performance, the energy band diagram can be calculated from electrochemical measurements, in particular by using

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[35] Ojha, U. P.; Krishnamoorthy, K.; Kumar, A. *Synth. Met.* **2003**, *132*, 279.

**Table 1. Polymerization Results, Molecular Weights, and Thermal Data for Polymers I−III**

| sample | yield (%) | $M_w$ ($\times 10^{-3}$)[a] | PDI | TGA (5%)[b] |
|---|---|---|---|---|
| polymer I | 65 | 9.3 | 2.1 | 367 |
| polymer II | 85 | 13.4 | 2.9 | 332 |
| polymer III | 60 | 4.5 | 2.0 | 450 |

[a] Determined by GPC in THF based on polystyrene standards. [b] Temperature at 5% weight loss under nitrogen.

cyclic voltammetry (CV) for the HOMO binding energy with respect to a ferrocene standard, and by determining the band gap from the optical absorption spectrum. All measurements were calibrated using a ferrocene/ferrocenium reference (−4.8 eV). From the CV measurements, the HOMO energy levels of polymers I−III were found to be 5.59, 5.38, and 5.68 eV, respectively. The LUMO level was calculated approximately by subtracting the optical band gap from the HOMO binding energy. The cyanovinylene units of polymers I−III lower their LUMO levels (3.13−3.18 eV), although these values are higher than those of MEH-PPV (3.0 eV) and PPV (2.6 eV). This implies that the polymers have improved electron-injection and transport properties. It is clear from these results that the presence of substituents on the EL polymers strongly affects their HOMO and LUMO energy levels. The electrooptical properties of the EL devices are summarized in Table 2.

Energy band diagrams for the double-layer ITO/PEDOT/polymer/Al devices are shown in Figure 3. The dialkyloxy substituents on the phenylenevinylene ring raise the HOMO energy level in polymer II, and the introduction of the electron-withdrawing cyano group into the phenylenevinylene unit increases the energy of the LUMO state. The barrier heights for hole injection were found to be 0.89, 0.68, and 0.98 eV at the interface of ITO/HOMO state, and those for electron injection were found to be 1.12, 1.17, and 1.12 eV at the interface of Al/LUMO state for the devices containing polymers I−III, respectively. Judging from these energy levels, it is expected that the major carriers in these devices are holes rather than electrons. Because of the smaller band offset between ITO and HOMO interfaces, holes can be more easily injected into polymer II than into polymers I and III. To evaluate the devices' performance, we fabricated double-layer PLEDs with the configuration of ITO/PEDOT/polymer/Al. The effect of using PEDOT as the hole-injection-transport layer has been studied by many research groups.[36−38] The PE-

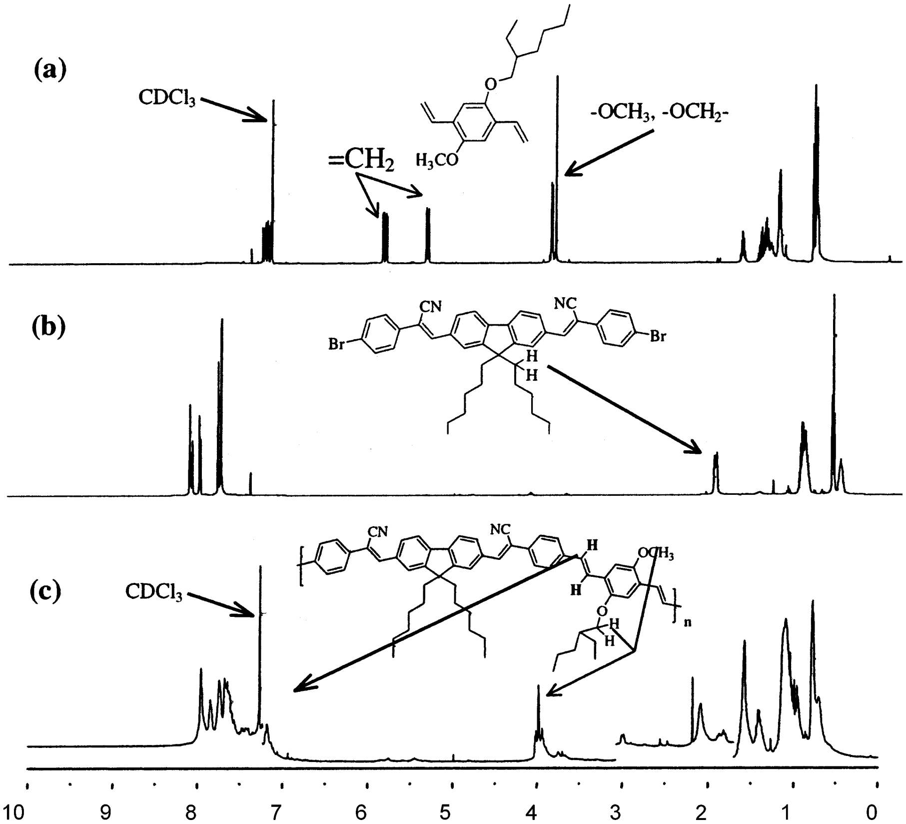


**Figure 1.** $^1$H NMR spectra of (a) 1-(2-ethylhexyoxy)-4-methoxy-2,5-divinylbenzene, (b) 2,7-bis[2-(4-bromophenyl)-2-cyanoethenyl]-9,9-dihexyl-9H-fluorene, and (c) polymer II in $CDCl_3$.

**Table 2. Electrooptical Data and EL Characteristics of ITO/PEDOT/Polymer/Al Devices**

| | $\lambda_{max}$ (nm)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| sample | UV | PL | EL | Φ (%)[b] | turn-on voltage (V) | $L_{max}$ (cd/m$^2$)[c] | $\eta_{max}$ (lm/W)[d] | CIE ($x$, $y$)[e] |
| polymer I | 419 | 591 | 599, 557 (s)[f] | 5.7 | 15.0 | 3000 (30 V) | 0.07 (20.9 V) | (0.48, 0.48) |
| polymer II | 439 | 602 | 596 | 14.7 | 5.0 | 7500 (20 V) | 0.21 (6.7 V) | (0.53, 0.44) |
| polymer III | 417 | 551, 580 (s) | 557, 585 | 3.5 | 5.0 | 1600 (16 V) | 0.02 (10.5 V) | (0.43, 0.45) |

[a] Measured in the film state on fused silica substrate. [b] Absolute quantum efficiency of the photoluminescence. [c] Maximum luminescence. [d] Maximum luminance efficiency. [e] Calculated from the EL spectrum. [f] Shoulder.

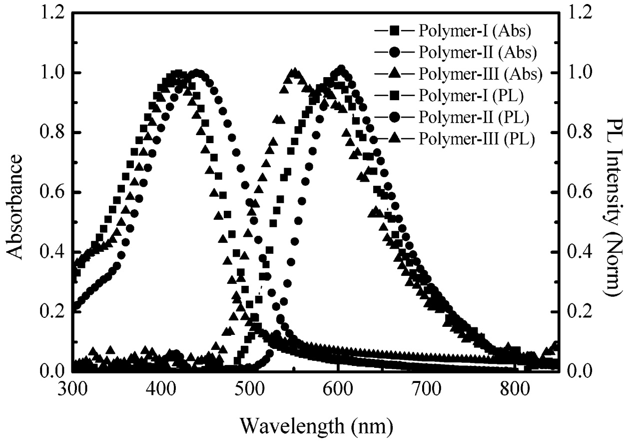


**Figure 2.** UV−visible absorption and PL spectra of polymers I−III in the solid state.

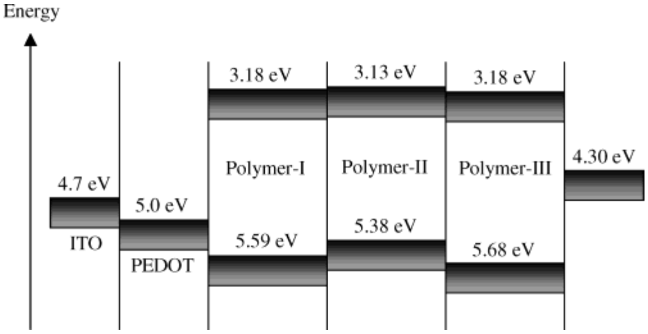
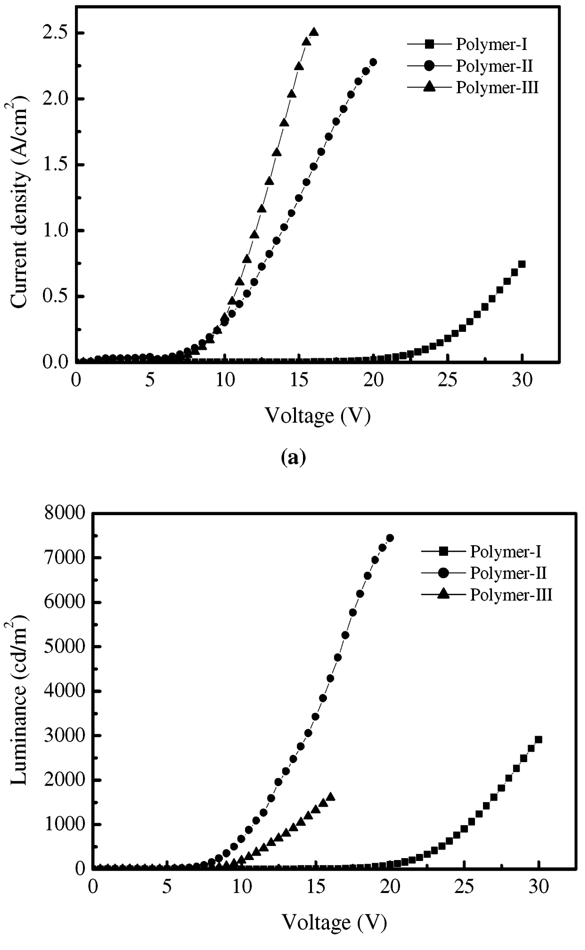


**Figure 3.** Hypothesized energy diagram of ITO/PEDOT/polymer/Al devices.

DOT/PSS layer was coated onto the ITO coated glass substrate, and the emitting polymers were spin-coated onto the PEDOT/PSS layer. After soft baking of these layers at 100 °C under a vacuum for 1 h, the Al electrodes were deposited by thermal evaporation at a pressure of $10^{-6}$ Torr.

Figure 4 shows the current density−voltage−luminance ($J-V-L$) characteristics of the ITO/PEDOT/polymer/Al devices. The current density (Figure 4a) and luminance intensity (Figure 4b) increase exponentially with increasing forward bias voltage above the turn-on voltage, and all of the EL devices exhibit excellent diode characteristics. The turn-on voltages for the devices using polymers I−III were found to be 15.0, 5.0, and 5.0 V, respectively, for current and luminance. The maximum brightness of the devices using polymers I−III were found to be about 3000 cd/m$^2$ with a current density of 0.75 A/cm$^2$ at 30 V, 7500 cd/m$^2$ with a current density of 0.9 A/cm$^2$ at 20 V, and 1600 cd/m$^2$ with a current density of 2.5 A/cm$^2$ at 16 V, respectively.



(a)

(b)

**Figure 4.** (a) Current density−voltage and (b) luminance−voltage characteristics of ITO/PEDOT/polymer/Al devices.

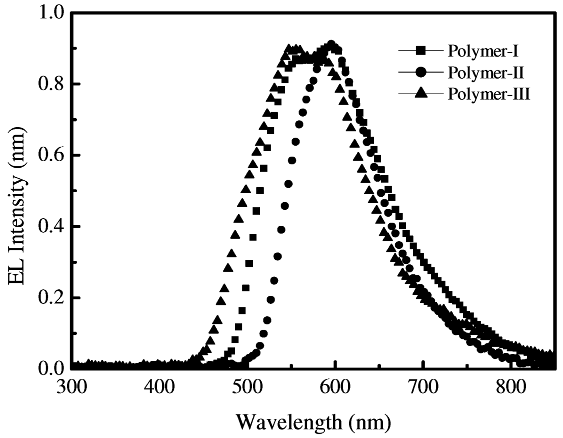


**Figure 5.** Electroluminescence spectra of ITO/PEDOT/polymer/Al devices.

Figure 5 shows the EL spectra of the ITO/PEDOT/polymer/Al devices. The EL spectra of polymers I−III are almost identical to their PL spectra, which indicates that their emission mechanisms are the same as their excitation processes. To investigate their color purities, chromaticity coordinates using the Commission International l'Eclairage (CIE) (1931) color-matching function were obtained from the EL spectra, and the results are listed in Table 2. The emission color of polymers I and III at the CIE coordinates of $x = 0.48$, $y = 0.48$ and $x = 0.43$, $y = 0.45$ is yellow. However, the emission color of polymer II was slightly red-shifted compared to that of polymers I and III, being a yellowish-orange color ($x = 0.53$, $y = 0.44$) with maximum emission peak at 596 nm. Because of the rigid biphenylenevinylene units along the polymer backbone, the EL maximum peak of poly-

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(36) Jönsson, S. K. M.; Birgerson, J.; Crispin, X.; Greczynski, G.; Osikowicz, W.; van der Gon, A. W. D.; Salaneck, W. R.; Fahlman, M. *Synth. Met.* **2003**, *139*, 1.

(37) Carter, S. A.; Angelopoulos, M.; Karg, S.; Brock, B. J.; Scott, J. C. *Appl. Phys. Lett.* **1997**, *70*, 20673

(38) Cao, Y.; Yu, G.; Zhang, C.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *81*, 171.

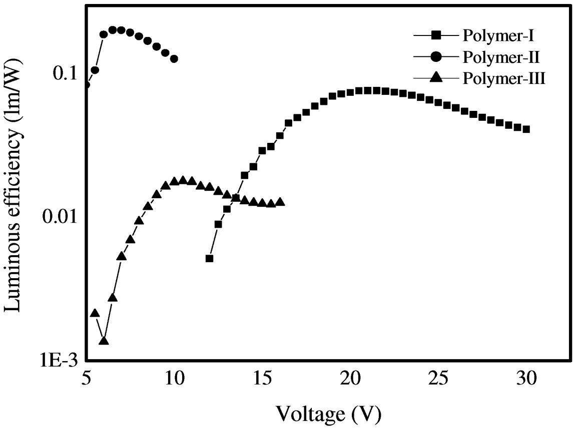

**Figure 6.** Current−luminance efficiency curves of the ITO/PEDOT/polymer/Al devices.

mer III is blue-shifted by 15 nm compared to those of polymers I and II.

Figure 6 displays plots of the luminance efficiency versus voltage for the ITO/PEDOT/polymer/Al devices. The maximum luminance efficiency of polymer II is 0.21 lm/W at 6.7 V, which is 3 and 10 times higher than those of polymers I and III, respectively. The better device performance of polymer II is consistent with its HOMO state, as shown in the energy diagram in Figure 3. The EL characteristics and device performances of these EL polymers are summarized in Table 2. Even though the configurations of these devices have not been optimized, EL polymers with cyanofluorenevinylene and phenylenevinylene repeating units are clearly promising EL materials because these devices exhibit high brightnesses and low turn-on voltages.

Further optimization of these EL devices, such as the introduction of an electron-transport layer (ETL) or a lower work function metal as a cathode electrode, is expected to produce even better EL performance.

## Conclusions

Cyanofluorenylvinylene-based statistical alternating copolymers composed of cyanophenylenevinylene and phenylenevinylene units with various substituents or biphenylenevinylene units were synthesized using modified palladium-catalyzed Heck coupling reactions. The resulting EL polymers exhibit good solubilities in common organic solvents, as well as good thermal stabilities. The electrooptical properties of these polymers depend on the main-chain structure as well as on the side-chain substituent on the phenylenevinylene unit. The turn-on voltages of the present polymers in ITO/PEDOT/polymer/Al devices were found to be 5−15 V. The emission colors of these statistical alternating copolymers can be tuned from yellow to yellowish-orange by fine-tuning of their molecular structure or copolymer compositions. The external quantum efficiency and device performance of a device using polymer II are higher than those of devices using polymers I and III and MEH-PPV. The maximum brightness and luminance efficiency of this device were found to be 7500 cd/m$^2$ at 20 V and 0.21 lm/W at 6.7 V, respectively.

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