# Articles

# Design, Synthesis, and Electroluminescent Property of CN–Poly(dihexylfluorenevinylene) for LEDs

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ABSTRACT: A new green electroluminescence polymer, CN–poly(dihexylfluorenevinylene) (CN–PDHFV), which denotes poly[(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(1-cyanoethene-1,2-diyl)(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(2-cyaoethene-1,2-diyl)], was synthesized by condensation polymerization utilizing the Knoevenagel reaction. The resulting polymer exhibits good solubility in common organic solvents such as chloroform, THF, and ODCB. The polymer is also easily cast on a glass plate to green film. The UV–vis spectrum of the polymer exhibits characteristically a broad absorption band at 440 nm. This polymer shows photoluminescence around  $\lambda_{max} = 535$  nm (exciting wavelength 410 nm) and green electroluminescence around  $\lambda_{max} = 530$  nm. The current–voltage–luminance (*I*–*V*–*L*) characteristics of the polymer show a turn-on voltage of 4.8 V and a brightness of 600 cd/m<sup>2</sup> at 5.8 V in the Al/polymer/PEDOT/ITO device. The highest efficiency was observed to be 0.85 lm/W at 5.6 V.

# Introduction

Because of the academic interest and potential applications as large-area light-emitting displays, much attention have been focused at electroluminescence (EL) devices based on organic thin layers.<sup>1–5</sup> Since the polymeric light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV) were reported by Burroughes et al.,<sup>6</sup> various kinds of conjugated polymers have been developed for EL.<sup>7–11</sup>

In conjugated polymers, EL is well-known to be generated by the injection of electrons from one electrode and holes from the other, recombination, and radiative decay of the excited state.

Since the poly(fluorene) was applied in this field, electrochemical properties of fluorene-containing polymers including poly(dihexylfluorenevinylene) (PDHFV) have attracted much attention. Fluorene-based polymers are usually highly fluorescent, which is a required aspect for electroluminescence applications.<sup>12–14</sup> Balancing the rates of injection of electrons and holes from opposite contacts into the device is required to achieve high electroluminescence efficiency.

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Since it was revealed that the electron injection is more difficult than hole injection for the conjugated polymers investigated so far, it has been necessary to use polymers with increased electron affinity to reduce the barrier to electron injection.<sup>15</sup>

In this paper, we report the synthesis and characterization of a new EL polymer, CN-poly(dihexylfluorenevinylene) (CN-PDHFV), which denotes poly[(9,9dihexyl-9*H*-fluorene-2,7-diyl)(1-cyanoethene-1,2-diyl)(9,9dihexyl-9*H*-fluorene-2,7-diyl)(2-cyaoethene-1,2-diyl)]. To reduce the barrier to electron injection, a CN functional group was incorporated into the known poly(dihexylfluorenevinylene) (PDHFV). PDHFV was also synthesized to be compared with CN-PDHFV. PDHFV was synthesized via the Gilch reaction, which modified the recently reported method.<sup>16</sup>

#### **Experimental Section**

**General.** All used reagents were purchased from Aldrich and used without further purification. Solvents were purified by normal procedures and handled under a moisture-free atmosphere. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Gemini-200 (200 MHz) and Varian Gemini-500 (500 MHz) spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. UV spectra were recorded with a Varian Cary-5E UV/vis spectrophotometer. Molecular weights and polydispersities of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. An Oriel InstaSpec CCD detection systems of Busan Branch of Korea Basic Science Institute was used for photoluminescence spectroscopy.

For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the holeinjection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. Isopropyl solution of the PEDOT/PSS was spincoated on the surface-treated ITO substrate. On top of the PEDOT layer, the emissive polymer film was obtained by spincasting an ODCB (*o*-dichlorobenzene) solution of the polymer. The emissive polymer thin film prepared had a uniform surface with a thickness of around 110 nm. The emissive film was dried in a vacuum, and aluminum electrodes were deposited on the top of the polymer films through a mask by vacuum evaporation at pressures below  $10^{-7}$  Torr, yielding active areas of 4 mm<sup>2</sup>. For the determination of device characteristics, current–voltage (*I*–*V*) characteristics were measured using a Keithley 236 source measure unit. All processing steps and measurements mentioned above were carried out under air and at room temperature.

To examine electrochemical properties of the resulting polymer, the polymer film was cast from THF solution onto a platinum plate as a working electrode with an area of 1 cm<sup>2</sup>. Film thickness was controlled in the range of about 3  $\mu$ m by the amount of solution. After coating, the film adhering to the electrode was dried in a vacuum oven for 10 h. The electrochemical measurements were performed on 0.1 M tetrabuty-lammonium tetrafluoroborate (TBAF, freshly distilled, Aldrich) solution in acetonitrile. Platinum wire and a Ag/AgNO<sub>3</sub> electrode were used as a counter electrode and a reference electrode, respectively. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat at a constant scan rate of 100 mV/s.

Synthesis of 2,7-Dibromo-9,9'-dihexyl-9H-fluorene (1).17 To a stirred solution of 5 g (15.43 mmol) of 2,7-dibromo-9Hfluorene in 40 mL of DMSO under argon was added catalytic amounts of triethylbenzylammonium chloride. After 1 h at 60 C, 6.37 g (38.60 mmol) of n-bromohexane was added to the reaction mixture. After an additional 1 h at 60 C, the mixture was treated with 25 mL of 50% aqueous NaOH, stirred for 5 h at room temperature, and diluted with 500 mL of ethyl acetate. The organic layer was washed with 100 mL of a 1.0 M hydrochloric acid solution and 150 mL of water. The organic layer was dried (MgSO<sub>4</sub>) and concentrated under reduced pressure. The oily residue was purified by flash column chromatography ( $30 \times 150$  mm column, SiO<sub>2</sub>, 100% of hexane) to give 7.22 g (95.0%) of 2,7-dibromo-9,9'-dihexyl-9H-fluorene (c), white crystals; mp 61 °C,  $R_f 0.57$  (SiO<sub>2</sub>, hexane 100%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.45–0.68 (m, 4H), 0.77 (t, 6H J = 6.6 Hz), 0.90-1.20 (m, 12H), 1.86-1.95 (m, 4H), 7.43-7.54 (m, 6H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ (ppm) 13.98, 22.57, 23.63, 29.56, 31.45, 40.18, 55.66, 121.11, 121.45, 126.15, 130.13, 139.04, 152.53.

Synthesis of Diethyl 9,9'-Dihexyl-9H-fluorene-2,7-dicarboxylate (2). To a solution of 7.80 g (25 mmol) of 2,7-dibromo-9,9'-dihexyl-9H-fluorene (1) in 20 mL of EtOH at room temperature, 6.06 g (60 mmol) of triethlamine (Et<sub>3</sub>N), 44.3 mg (0.25 mmol) of PdCl<sub>2</sub>, and 131.7 mg (0.50 mmol) of Ph<sub>3</sub>P were added. The reaction mixture was placed in a 100 mL SUS-316 stainless steel autoclave under 5.1 MPa of carbon monoxide. Afterheating at 150 °C for 5 h the reaction mixture was washed with 100 mL of a 1.0 M hydrochloric acid solution. After removal of the solvent under reduced pressure, the oily residue was purified by flash column chromatography (60  $\times$ 150 mm column, SiO<sub>2</sub>, ethyl acetate:hexane = 1:10) to give 11.85 g (99.0%) of diethyl 9,9'-dihexyl-9H-fluorene-2,7,-dicarboxylate (2), yellow oils;  $R_f 0.20$  (SiO<sub>2</sub>, ethyl acetate:hexane = 1:10). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.42–0.63 (m, 4H), 0.74 (t, 6H J = 6.6 Hz), 0.90-1.20 (m, 12H), 1.99-2.08 (m, 4H), 7.78 (d, 2H, J = 7.6 Hz), 8.06 (d, 4H, J = 11.4 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>): δ (ppm) 13.94, 14.39, 22.50, 23.67, 29.53, 31.44, 40.04, 55.50, 61.07, 120.23, 124.10, 128.79, 129.97, 144.39, 151.78, 166.88.

**Synthesis of (9,9'-Dihexyl-7-hydroxymethyl-9H-fluorene-2-yl)-methanol (3).** To a stirred solution of 2.57 g (5.38 mmol) of diethyl 9,9'-dihexyl-9H-fluorene-2,7-dicarboxylate **(2)** in 10 mL of tetrahydrofuran at -78 C under argon was added 26.9 mL (26.9 mmol) of a 1 M solution of diisobutylaluminum hydride in THF. After 3 h at -78 C, the reaction mixture was cautiously treated with 3 mL of methanol, warmed to room temperature, and diluted with 200 mL of diethyl ether. The solution was washed with 10 mL of a saturated aqueous sodium chloride solution. The aqueous layer was extracted with 2 × 50 mL of diethyl ether. The combined organic extract was dried (MgSO<sub>4</sub>) and concentrated. The oily residue was purified by flash chromatography (30 × 100 mm column, SiO<sub>2</sub>, ethyl acetate:hexane = 1:6) to give 1.89 g (89%) of diol **3**, a yellow oil:  $R_f$  0.35 (SiO<sub>2</sub>, ethyl acetate:hexane = 1:4). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.45–0.68 (m, 4H), 0.78 (t, 6H J = 6.6 Hz), 0.90–1.20 (m, 12H), 1.69 (s, 2H), 1.90–1.98 (m, 4H), 4.77 (s, 4H), 7.31 (d, 4H, J = 7.6 Hz), 7.66 (d, 2H, J = 8.4 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.91, 22.51, 23.68, 29.63, 31.42, 40.28, 54.93, 65.53, 119.56, 121.44, 125.69, 139.71, 140.28, 151.22.

Synthesis of 2,7-Bis(chloromethyl)-9,9'-dihexyl-9Hfluorene (4). To a stirred solution of 1.026 g (2.60 mmol) of diol 3 in 10 mL of benzene at room temperature under argon was added 1.89 mL of SOCl<sub>2</sub> and heated at 40 °C for 3 h. The reaction mixture was cooled and diluted with 2 mL of 50% HCl. The organic layer was washed with 10 mL of a saturated aqueous sodium chloride solution. The total aqueous extracts were washed with 2  $\times$  10 mL of ethyl acetate, and the combined organic extract was dried (MgSO<sub>4</sub>) and concentrated. The oily residue was purified by flash chromatography (30 imes100 mm column, SiO<sub>2</sub>, ethyl acetate:hexane = 1:10) to give 1.04 g (92%) of dichloride 4, a yellow solid:  $R_f 0.34$  (SiO<sub>2</sub>, hexane 100%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.50-0.70 (m, 4H), 0.78 (t, 6H J = 7.3 Hz), 1.03–1.20 (m, 12H), 1.94-1.97 (m, 4H), 4.68 (s, 4H), 7.45 (d, 4H, J = 9 Hz), 7.66 (d, 2H, J = 7.5 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.86, 22.37, 23.57, 29.45, 31.24, 40.02, 46.63, 55.04, 119.88, 123.06, 127.44, 136.53, 140.63, 151.45.

Synthesis of Poly(9,9'-dihexylfluorenevinylene) (5) Using the Gilch Reaction. To a stirred solution of 1.369 g (3.24 mmol) of 2,7-bis(chloromethyl)-9,9'-dihexyl-9H-fluorene (4) in 20 mL of THF at 40 °C under argon was added, drop by drop, 97.06 mL (19.41 mmol) of a 0.25 M solution of potassium tert-butoxide in THF using the dropping funnel over a period of 1 h. During this addition, the reaction mixture had color change from colorless via greenish to yellow, and the viscosity increased significantly. After the addition was complete, the reaction mixture was stirred for 10 h at room temperature. The reaction mixture was slowly poured into 200 mL of intensively stirred methanol. The precipitated polymer was filtered off, washed with water, and dried under reduced pressure at room temperature to generate 660 mg of the crude polymer as yellow power. The resulting polymer was redissolved in 1.1 L of THF (60 °C), cooled to 40 °C, and reprecipitated by dropwise addition of 1.2 L of methanol. The precipitated polymer was dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol to generate 415 mg (56.5%) of poly-(9,9'-dihexylfluorenevinylene) (5) as a light yellow polymer fiber. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.50–0.74 (m, 4H), 0.74-0.90 (m, 6H), 0.94-1.24 (m, 12H), 1.90-2.20 (m, 4H), 7.12 (d, 1H, J = 33 Hz), 7.30 (d, 2H, J = 10.5 Hz), 7.50-7.62 (m, 4H), 7.68 (d, 1H, J = 33 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.93, 22.59, 23.74, 29. 7 6, 31.54, 40.58, 55.04, 119.59, 120.66, 122.94, 125.86, 128.67, 130.55, 140.66, 151.58,

Synthesis of 9,9'-Dihexyl-9H-fluorene-2,7-dicarbaldehyde (6). To a stirred solution of 2.28 g (5.80 mmol) of the diol 3 in 15 mL of DMF at 0 °C under a argon atmosphere was added 5.22 g (13.87 mmol) of pyridinium dichromate. After 4 h at 0 °C, the reaction mixture was treated with 1 mL of water, diluted with 100 mL of diethyl ether, washed with 2 imes10 mL of water, and dried (MgSO<sub>4</sub>). After removal of the solvent under reduced pressure, the oily residue was purified by flash chromatography ( $30 \times 100$  mm column, SiO<sub>2</sub>, ethyl acetate:hexane = 1:5) to give 1.88 g (83%) of aldehyde 6, a yellow solid:  $R_f 0.35$  (SiO<sub>2</sub>, ethyl acetate:hexane = 1:10). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) 0.40-0.64 (m, 4H), 0.74 (t, 6H J = 6.6 Hz), 0.80–1.20 (m, 12H), 2.03–2.12 (m, 4H), 7.92 (s, 6H), 10.11 (s, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.91, 22.47, 23.74, 29.47, 31.40, 40.02, 55.56, 121.30, 123.34, 130.31, 136.39, 145.59, 152.84, 192.19.







Scheme 2. Synthetic Routes for Monomer and Polymer of CN-PDHFV



Synthesis of 2,7-Bis(bromomethyl)-9,9'-dihexyl-9Hfluorene (7). To a stirred solution of 2.18 g (5.52 mmol) of diol 3 in 20 mL of benzene at 0 °C under argon was added, drop by drop, 1.57 mL (16.57 mmol) of PBr<sub>3.</sub> After stirring at 45 °C for 6 h, the reaction mixture was cooled and diluted with 5 mL of water. The aqueous layer was separated and extracted with  $2 \times 10$  mL of CHCl<sub>3</sub>. The combined organic extract was dried (MgSO<sub>4</sub>) and concentrated. The oily residue was purified by flash chromatography ( $40 \times 150$  mm column, SiO<sub>2</sub>, 100% hexane) to give 2.79 g (97%) of dibromide 7, colorless oil:  $R_f$ 0.35 (SiO<sub>2</sub>, ethyl acetate:hexane = 1:8). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.45–0.68 (m, 4H), 0.78 (t, 6H J = 6.6 Hz), 0.90-1.20 (m, 12H), 1.89-1.98 (m, 4H), 4.60 (s, 4H), 7.34 (d, 4H, J = 2.2 Hz), 7.64 (d, 2H, J = 8.0 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.99, 22.48, 23.62, 29.53, 31.35, 34.47, 40.07, 55.12, 120.04, 123.64, 127.99, 136.86, 140.72, 151.63.

Synthesis of (7-Cyanomethyl-9,9'-dihexyl-9H-fluorene-2-yl)acetonitrile (8). To a stirring solution of 0.39 g (0.89 mmol) of 2,7-bis(bromomethyl)-9,9'-dihexyl-9H-fluorene (7) in 10 mL of acetonitrile at room temperature under argon were added 0.36 mL (2.67 mmol) of trimethylsilyl cyanide and 2.67 mL (2.67 mmol) of tetrabutylammonium fluoride (TBAF). The light yellow reaction mixture was concentrated under reduced pressure. The oily residue was purified by flash chromatography ( $30 \times 70$  mm column, SiO<sub>2</sub>, methylene chloride:hexane = 1:9) to give 0.33 g (90%) of acetonitrile 8, a yellow solid:  $R_f$ 0.35 (SiO<sub>2</sub>, ethyl acetate:hexane = 1:10). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.40–0.64 (m, 4H), 0.74 (t, 6H J = 6.6 Hz), 0.90-1.20 (m, 12H), 1.90-1.99 (m, 4H), 3.84 (s, 4H), 7.28 (d, 4H, J = 7.4 Hz), 7.67 (d, 2H, J = 8.4 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.57, 22.08, 23.28, 23.34, 29.12, 30.96, 39.72, 54.94, 117.76, 119.95, 122.04, 126.39, 128.72, 139.77, 151.39.

Synthesis of Poly[(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(1cyanoethene-1,2-diyl)(9,9-dihexyl-9*H*-fluorene-2,7-diyl)-(2-cyaoethene-1,2-diyl)] (CN-PDHFV) (9). To a stirred solution of 0.32 g (0.81 mmol) of **8** and 0.33 g (0.81 mmol) of **6** in 23.3 mL of THF and 11.7 mL of MeOH at reflux (65–66 °C) under argon was added 0.41 mL of Bu<sub>4</sub>NOH in methanol (1 M). After refluxing for 12 h, the reaction mixture was treated with 30 mL of MeOH and cooled to 0 °C over 5 min. The resulting solid (0.50 g) obtained was then filtered off and purified by Soxhlet extraction with methanol to generate 0.58 g (80.6%) of poly[(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(1-cyanoethene-1,2-diyl)(9,9-dihexyl-9*H*-fluorene-2,7-diyl)(2-cyaoethene-1,2-diyl)] (CN-PDHFV) **(9)**, yellow powders. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 0.50–0.90 (m, 10H), 0.90–1.30 (m, 12H), 1.90–2.20 (m, 4H), 7.60–8.10 (m, 7H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 13.98, 22.58, 23.80, 29.69, 31.47, 40.29, 55.57, 111.43, 118.53, 120.24, 120.63, 125.21, 133.54, 134.11, 142.55, 152.25.

#### **Results and Discussion**

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1 and Scheme 2. The PDHFV monomer, 2,7-bis(chloromethyl)-9,9'-dihexyl-9H-fluorene (4), was synthesized using commercially available 2,7-dibromo-9*H*-fluorene as the starting material, which was converted to 2,7-dibromo-9,9'-dihexyl-9H-fluorene (1) by catalytic amounts of triethylbenzylammonium chloride, 50% aqueous NaOH, and 1-bromohexane. Diethyl-9,9'-dihexyl-9H-fluorene-2,7-dicarboxylate (2) was prepared by using ethanol, triethylamine, and palladium complex catalyst under high pressures. Reduction with diisobutylaluminum hydride (DIBAL) and subsequent reaction with thionyl chloride afforded 2,7bis(chloromethyl)-9,9'-dihexyl-9H-fluorene (4). The PDH-FV monomer 4 was polymerized by the Gilch polymerization with potassium *tert*-butoxide in THF to generate the polymer PDHFV (5). The monomer CN-PDHFV was synthesized using (9,9'-dihexyl-7-hydroxy-methyl-9H-fluorene-2-yl)methanol (3), which was oxidized to 9,9'-dihexyl-9H-fluorene-2,7-dicarbaldehyde (6) by pyridinium dichromate (PDC). And the diol 6 was bromi-



**Figure 1.** UV-vis absorption spectra of PDHFV and CN-PDHFV.

Table 1. Polymerization Results of PDHFV and CN-PDHFV

polymers	yield (%)	$ar{M}_{ m n}{}^a$	$ar{M}_{\! m w}{}^a$	PDI <sup>a</sup>
PDHFV	56.5	39 300	69 600	2.28
CN–PDHFV	80.6	7 800	12 100	1.54

 ${}^{a}\bar{M}_{n}$ ,  $\bar{M}_{w}$ , and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

nated with PBr<sub>3</sub> in benzene to generate 2,7-bis-(bromomethyl)-9,9'-dihexyl-9*H*-fluorene **(7)**. The resulting dibromide was cyanized with trimethylsilylcyanide by the nucleophilic substitution reaction. The new conjugate polymer, CN–PDHFV, was synthesized using the Knoevenagel condensation reaction, which were carried out in THF/MeOH mixtures ( $^{2}/_{3}$ ,  $^{1}/_{3}$  in volume) with tetrabutylammonium hydoxide as catalyzer at 65 °C, in a similar way as was reported by the Cambridge group<sup>15</sup> for the preparation of cyano-substituted poly-(phenylenevinylene) (CN–PPV).

The resulting polymers are highly soluble in common organic solvents including THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, ODCB, etc., and easily cast on a glass plate to give bright greenish-blue and green thin films for PDHFV and CN-PDHFV, respectively. The number-average molecular weights  $(M_n)$  and the weight-average molecular weights  $(M_{\rm w})$  of the resulting polymers, determined by GPC using polystyrene standard, were in the range of 7800-39 300 and 12 100-69 600 with a polydispersity index of 1.54-2.28. The polymerization results of PDHFV and CN-PDHFV polymers are summarized in Table 1. Thermal properties of the synthesized polymers were evaluated by the means of TGA under a nitrogen atmosphere. The weight losses of the polymer were less than 5% in heating to about 450 °C. The polymers did not show either an endo or exo curve in DSC thermograms due to side chain scission or thermal cross-linking until the temperature of initial decomposition.

**Optical and Photoluminescence Properties.** The UV–vis absorption spectra and photoluminescence spectra of PDHFV and CN–PDHFV as thin films are shown in Figure 1 and Figure 2.

The thin films were prepared by spin-coating on quartz plates from the polymer solutions in o-dichlorobenzene (ODCB). The PDHFV exhibit absorption spectra with a maximum peak of 420 nm attributed to the  $\pi$ - $\pi$ \* transition of the conjugated backbones and a shoulder at 370 nm due to the  $\pi$ - $\pi$ \* transition of fluorene units. CN-PDHFV has a strong absorption band at around 440 nm which is attributed to the  $\pi$ - $\pi$ \* transition of the conjugated segments. The absorption



Figure 2. Photoluminescence spectra of PDHFV and CN-PDHFV.

onset wavelengths of polymers were 486 and 521 nm, which correspond to band gaps of 2.55 and 2.38 eV. The PL spectra of polymers all consist of a typical vibronically structured band comprising a maximum, a shoulder, and a tail. The PL spectrum of the PDHFV thin film exhibits a maximum at 505 nm and two shoulder at 480 and 550 nm, and the PL spectrum of the CN–PDHFV thin film exhibits a maximum at 535 nm and a shoulder at 500 nm, which are red-shifted about 30 nm relative to the corresponding features measured from PDHFV (exciting wavelength 410 nm).

**Electrochemical Properties of the Polymers.** The cyclic voltammetry was used to investigate the electrochemical behavior of the polymers. The CV was performed in a solution of tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under the protection of argon. A platinum electrode (~0.05 cm<sup>2</sup>) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO<sub>3</sub> electrode were used as the counter electrode and reference electrode, respectively. All measurements were calibrated against an internal standard, ferrocene (F<sub>c</sub>), which has the IP value (-4.8 eV) of the F<sub>c</sub>/F<sub>c</sub><sup>+</sup> redox system.<sup>18</sup>

All of the polymers exhibit irreversible processes in an oxidation scan. The oxidation onsets of the polymers were estimated to be 0.6 and 0.7 V for PDHFV and CN-PDHFV, respectively, which correspond to HOMO energy levels of 5.4 and 5.5 eV.<sup>19,20</sup> The LUMO energy levels of polymers can be calculated with the HOMO and optical band gap. The LUMO energy levels of PDHFV and CN-PDHFV were thus determined to be 2.85 and 3.12 eV, respectively. The HOMO and LUMO energy levels of CN-PDHFV are lower than that of PDHFV, which can be attributed to the introduction of the electron-withdrawing cyano group. The barrier height were found to be 1.35 and 1.08 eV at the interface of the Al (4.2 eV)/LUMO state for the electron. The red shift in the spectroscopic features of CN-PDHFV was caused by the greater increase of the work function of the LUMO (from 2.85 to 3.12 eV) as compared to that of the HOMO (from 5.40 to 5.50 eV). The Cambridge group have reported that the cyano-substituted PPV lowered the HOMO and LUMO levels by 0.6 and 0.9 eV, respectively, compared with those of PPV. When indium tin oxide coated with a PPV layer, which helps to localize charge at the interface between the PPV and the cyano-substituted PPV, was used, they were able to achieve high internal efficiencies (photons emitted per electrons injected) of up to 4%.<sup>15</sup>



Figure 3. Energy band diagram of PDHFV and CN-PDHFV.



**Figure 4.** Electroluminescence (EL) spectra of PDHFV and CN–PDHFV with a configuration of ITO/PEDOT:PSS/polymer/Al.

**Electroluminescent Properties and Current-**Voltage-Luminance. The double-layered polymer light-emitting diodes (PLEDs) with the configuration ITO/PEDOT/polymer/Al were fabricated to investigate the electroluminescent properties and the currentvoltage-luminance characteristics of PDHFV and CN-PDHFV. Polymer films of thickness approximately 110 nm were spin-cast onto a PEDOT layer which had been precast on the ITO substrate. The forward bias current was obtained when the ITO electrode was positively biased and the aluminum electrode was negative. The electroluminescence from the polymer in the device was greenish-blue for PDHFV and green for CN-PDHFV. As shown in Figure 4, the EL spectra of PDHFV and CN-PDHFV show maximum peaks at 505 and 535 nm, respectively. These features are similar to those observed in the PL spectra of the corresponding polymer films. The voltage-current density characteristics of the devices fabricated from PDHFV and CN-PDHFV are shown in Figure 5. In the forward bias, the turn-on voltages of PDHFV and CN-PDHFV are 5.0 and 4.8 V, respectively. The maximum brightness of CN-PDHFV is 600 cd/m<sup>2</sup> at 8 V. However, PDHFV reaches a brightness of 300 cd/m<sup>2</sup> at 8 V. As shown in Figure 3, the more negative energy of the LUMO of CN-PDHFV indicates the electron injection process is easier in CN-PDHFV than in PDHFV. From this result, a higher quantum efficiency of CN-PDHFV as compared to that of PDHFV can be expected due to its improved electron injection ability from the cathode. Figure 6 shows the EL efficiency of CN-PDHFV is higher than that of PDHFV. The highest efficiency of CN-PDHFV was observed to be 0.85 lm/W at 5.6 V, which was higher than 0.29 lm/W at 6.0 V of PDHFV.



**Figure 5.** Current–voltage–luminescence (I-V-L) characteristics of PLEDs of (a) PDHFV and (b) CN–PDHFV with a configuration of ITO/PEDOT:PSS/polymer/Al.



**Figure 6.** Efficiency of PLEDs of PDHFV and CN–PDHFV with a configuration of ITO/PEDOT:PSS/polymer/Al.

## Conclusion

A new electroluminescence polymer, CN-poly(dihexylfluorenevinylene) (CN-PDHFV), was synthesized by condensation polymerization utilizing the Knoevenagel reaction. The resulting polymer exhibits good solubility in common organic solvents such as chloroform, THF, and ODCB. This polymer shows photoluminescence around  $\lambda_{max} = 535$  nm (exciting wavelength 410 nm) and green electroluminescence around  $\lambda_{max} = 530$ nm. The current-voltage-luminance (I-V-L) characteristics of the polymer shows a turn-on voltage of 4.8 V and a brightness of 600 cd/m<sup>2</sup> at 5.8 V in the Al/polymer/PEDOT/ITO device. Poly(dihexylfluorenevinylene) (PDHFV) was also prepared to be compared with CN-PDHFV. PDHFV was synthesized by the Gilch reaction, which modified the recently reported method.<sup>16</sup> The monomer of PDHFV was synthesized by using 2,7-dibromo-9H-fluorene as the starting material for the purpose of synthesizing pure 2,7-bis(chloromethyl)-9,9'-dihexyl-9H-fluorene. The highest efficiency of CN-PDHFV was observed to be 0.85 lm/W at 5.6 V, which was higher than that of PDHFV due to the improved electron injection ability from the cathode caused by the cyano functionality.

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#### **References and Notes**

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