

New Conjugated Polymer Based on Dihydroindoloindole for LEDs

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New electroluminescence polymer, poly(5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole-2,7-diyl) (PININO) was synthesized by Yamamoto conditions with Ni(0) catalyst. The full characterization of structures and properties as well as the performances of the electroluminescence devices of the new polymer are presented. The resulting polymer, which exhibits good solubility in common organic solvents, was used as the electroluminescence layer for the light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al). PININO shows turn-on voltage of 2.5 V, and electroluminescence (EL) with maximum peak at 490 nm, maximum brightness of 40 cd/m² at 8 V, and efficiency of 0.002 cd/A at 350 mA/cm².

Key Words : Electroluminescence, Polymer, PLED, Light-emitting diodes (LEDs)

Introduction

Since the polymeric light-emitting diodes based on poly(*p*-phenylenevinylene) (PPV)¹ was reported, various kinds of conjugated polymers, as shown in Figure 1, have been developed for electroluminescence (EL) because of the potential application as large-area light emitting diodes (LEDs).² Among these conjugated polymers, the polyfluorenes (PFs) and polycyclopenta[def]phenanthrene (PCPP) for blue³ and PPVs for green⁴ or red⁵ color have acquired much attention because of their thermal and chemical stability, and exceptionally high solution and solid-state fluorescence quantum yield. Since there are rooms to improve the properties of PFs and PPVs,⁶ many researches have been performed.

In case of PPVs, oxidation of the polymer can introduce species such as carbonyl groups that have been shown to be efficient electron traps. Excited-state singlet oxygen appears to be at least partially responsible for this photo-oxidation by attacking the vinyl double bond in the PPV backbone of the polymer.⁷ P3OT, which does not contain this double bond, resists oxidation under identical circumstances.⁸ The extended conjugation length of PPVs may increase the electron density at the double bond, thereby making it more reactive to the singlet oxygen electrophile than in the case of stilbene monomer compound.⁹ It was also reported that the presence of electron-rich groups on the phenyl rings, such as alkoxy groups in PPV derivatives increases the likelihood of singlet oxygen 1,2-cycloaddition at the vinyl double bond.¹⁰

In this paper, we report the synthesis and properties of a new EL polymer utilizing new back-bone, poly(5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole-2,7-diyl) (PININO). In order to reduce oxidation of the vinylene group,¹¹ the vinylic group was cyclized using nitrogen containing 5-membered rings. The polymer, PININO, contains stilbene chromophore, but the vinyl group is located in the bicyclic

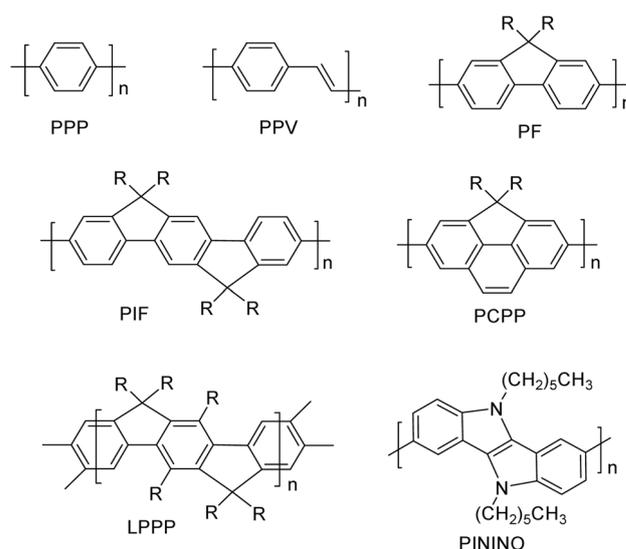
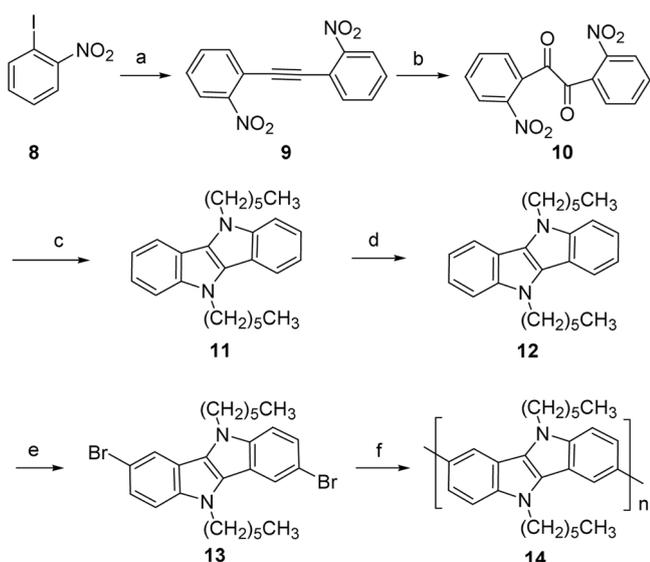


Figure 1. LED polymers.

[2.2.0] system. The resulting polymer, PININO, which exhibits good solubility in common organic solvents, was used as the electroluminescence layer for the light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al).

Experimental Section

General. Used all reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. ¹H and ¹³C NMR spectra were recorded with a Unityplus-300 (300 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride



Scheme 1. Synthetic routes for monomer and polymer of poly(dihydroindoloindole) (PININO). (a) C_2H_2 , $Pd(OAc)_2$, CuI , $(Ph_3P)_3$, Et_3N , CH_3CN/H_2O ; (b) $KMnO_4$, ADOGEN 464, $AcOH$, $ClCH_2CH_2Cl/H_2O$; (c) $SnCl_2 \cdot 2H_2O$, $AcOH$, $HCl(35\%)$; (d) $C_6H_{13}Br$, NaH , THF ; (e) Br_2 , $Pyridine$, CCl_4 ; (f) $Ni(COD)_2$, 2,2'-dipyridyl, cyclooctadiene, $DMF / Toluene$

gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F pre-coated aluminium plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. The PL of the thin film and EL spectra of the device were measured using an Oriel InstaSpec IV CCD detection systems. For PL spectrum measurements, xenon lamp was used as the excitation source, and incident beam took the maximum absorption peak of the polymer. Molecular weights and polydispersities of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration.

Synthesis of 2,2'-Dinitrotolane (2). To a stirred mixture of 225 mg (1.00 mmol) of $Pd(OAc)_2$ and 263 mg (1.00 mmol) of triphenylphosphine at room temperature under argon was added 191 mg (1.00 mmol) of cuprous iodide in 30 mL of acetonitrile and 10 mL of distilled water over 20 min. The reaction mixture was treated with a solution of 5 g (20.08 mmol) of 1-iodo-2-nitrobenzene (**1**) and 15 mL of triethylamine in 50 mL of acetonitrile. After purging with about 1500 cm^3 of acetylene gas, the reaction mixture was stirred at room temperature for 10 min, and extracted with 500 mL of methylene chloride. The organic phase was washed with 50 mL of water and 50 mL of brine, dried with $MgSO_4$, concentrated under reduced pressure, and purified by flash chromatography (30 \times 50 mm column, SiO_2 , ethyl acetate : hexane = 1 : 10) to give 4.6 g (85%) of 2,2'-dinitrotolane **2** as a dark brown solid: R_f 0.28 (SiO_2 , ethyl acetate : hexane = 1 : 4); 1H -NMR (300 MHz, $CDCl_3$) δ (ppm) 7.58 (t, 2H, $J = 7.8$ Hz), 7.70 (t, 2H, $J = 7.8$ Hz), 7.86 (d, 2H, $J = 8.0$ Hz), 8.17 (d, 2H, $J = 8.0$ Hz); ^{13}C -NMR (75

MHz, $CDCl_3$) δ (ppm) 14.22, 62.18, 93.89, 121.27, 125.85, 132.16, 133.48, 135.44, 149.48, 163.81.

Synthesis of 2,2'-Dinitrobenzyl (3). To a stirred solution of 4.6 g (17.15 mmol) of 2,2'-dinitrotolane (**2**) in 110 mL of ethylene dichloride at room temperature under argon was added 13.55 g (85.75 mmol) potassium permanganate dissolved in 90 mL of water, 6 mL of ADOGEN 464, and 7 mL of acetic acid. The stirred reaction mixture was refluxed for 3 h, cooled to room temperature and treated with 6 g of sodium bisulfate. The resulting organic phase was separated, dried with $MgSO_4$, and concentrated under reduced pressure. The oily layer was filtered by flash chromatography (60 \times 150 mm column, SiO_2 , 100% methylene chloride) to give 1.85 g (48.0%) of compound **3** as a yellow solid: R_f 0.30 (SiO_2 , ethyl acetate : hexane = 1 : 4); 1H -NMR (300 MHz, $CDCl_3$) δ (ppm) 7.73 (t, 2H, $J = 7.8$ Hz), 7.81 (d, 2H, $J = 8.0$ Hz), 7.94 (t, 2H, $J = 7.8$ Hz), 8.31 (d, 2H, $J = 8.0$ Hz). ^{13}C -NMR (125 MHz, $CDCl_3$) δ (ppm) 124.14, 129.39, 132.15, 132.68, 135.38, 147.50, 187.53.

Synthesis of 5,10-Dihydroindolo[3,2-b]indole (4). To a stirred solution of 1.6 g (5.33 mmol) of 2,2'-dinitrobenzyl (**3**) was added 60 mL of warm acetic acid, 12 g (53.29 mmol) of stannous chloride dihydrate, and 7 mL of 1N HCl. After stirring the reaction mixture for 5 h at 80 $^\circ C$, the resulting fine yellow precipitate was filtered, and washed with 30 mL of acetic acid, 30 mL of 1.0 N HCl, 30 mL of water, and 30 mL of ethanol. The resulting solid was dried under reduced pressure for 12 h to give 340 mg (31%) of indoloindole **4** as a pale yellow solid: R_f 0.45 (SiO_2 , ethyl acetate : hexane = 1 : 5); 1H -NMR (300 MHz, acetone- d_6) δ (ppm) 7.71 (t, 2H, $J = 7.8$ Hz), 7.72 (t, 2H, $J = 8.0$ Hz), 7.54 (d, 2H, $J = 8.0$ Hz), 7.79 (d, 2H, $J = 8.0$ Hz); ^{13}C -NMR (75 MHz, $CDCl_3$) δ (ppm) 113.00, 118.43, 119.22, 122.54, 141.83, 205.88, 206.29. Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.89; N, 13.58. Found: C, 81.74; H, 4.95; N, 13.13.

Synthesis of 5,10-Dihexyl-5,10-dihydroindolo[3,2-b]indole (5). To a stirred solution of 340 mg (1.65 mmol) of indoloindole **4** in 15 mL of THF at room temperature under argon was added 158 mg (6.59 mmol) of NaH in 10 mL of THF. After 10 min at room temperature, 816 mg (4.95 mmol) of n-bromohexane was added to the reaction mixture. After being stirred at reflux overnight, the reaction mixture was treated with 20 mL of water. The aqueous layer was separated, and extracted with 3 \times 10 mL of methylene chloride. The combined organic extract was dried with $MgSO_4$, concentrated under reduced pressure, and purified by flash chromatography (30 \times 150 mm column, SiO_2 , 100% hexane) to give 590 mg (95%) of compound **5** as a white solid: R_f 0.14 (SiO_2 , 100% hexane); 1H -NMR (300 MHz, acetone- d_6) δ (ppm) 0.84 (t, 6H, $J = 7.0$ Hz), 1.41 (m, 12H), 1.92 (m, 4H), 4.61 (t, 4H, $J = 7.0$ Hz), 7.15 (t, 2H, $J = 8.0$ Hz), 7.29 (t, 2H, $J = 8.0$ Hz), 7.60 (d, 2H, $J = 8.4$ Hz), 7.92 (d, 2H, $J = 7.6$ Hz).

Synthesis of 2,7-Dibromo-5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole (6). To a stirred solution of 590 mg (1.58 mmol) of 5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole (**5**) in 6 mL of pyridine at room temperature under

argon was slowly added 3.47 mL (3.47 mmol) of bromine in 34.7 mL of carbon tetrachloride. After stirring for 1 h at room temperature, the reaction mixture was treated with 3 mL of 1 N HCl, extracted with 20 mL of methylene chloride, dried with MgSO₄, concentrated under reduced pressure, and purified by flash chromatography (30 × 150 mm column, SiO₂, hexane 100%) to give 410 mg (48%) of dibromide **6**, a white solid: R_f 0.21 (SiO₂, 100% hexane); ¹H-NMR (300 MHz, CD₂Cl₂) δ (ppm) 0.88 (t, 6H, *J* = 6.8 Hz), 1.374 (m, 12H), 1.93 (m, 4H), 4.46 (t, 4H, *J* = 7.0 Hz), 7.30 (dd, 2H, *J*₁ = 8.4 Hz, *J*₂ = 1.8 Hz), 7.64 (s, 2H), 7.72 (d, 2H, *J* = 8.8 Hz); ¹³C-NMR (75 MHz, CDCl₃) δ (ppm) 10.96, 19.73, 23.89, 27.30, 28.74, 42.62, 109.96, 110.31, 112.39, 115.97, 118.42, 123.00, 138.31. Anal. Calcd for C₂₆H₃₂Br₂N₂: C, 58.66; H, 6.06; N, 5.26. Found: C, 58.53; H, 6.15; N, 5.10.

Synthesis of Poly(5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole-2,7-diyl) (7). In a three neck flask was placed 466 mg (1.69 mmol) of Ni(COD)₂, 265 mg (1.69 mmol) of 2,2'-dipyridyl, 0.21 mL (1.69 mmol) of cyclooctadiene, and 5 mL of DMF. After three freezing-thaw cycles, the catalyst was heated to 80 °C for 30 min to form the purple complex. The reaction mixture was treated with 410 mg (0.77 mmol) of 2,7-dibromo-5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole (**6**) in toluene (7 mL), and heated at 80 °C for 4 days. After being cooled to room temperature, the reaction mixture was poured into the mixture of 100 mL of HCl, 100 mL of acetone and 100 mL of methanol, and stirred for 2 h. The precipitation was filtered, re-dissolved in chloroform and precipitated again with large amount methanol. The pale yellow solid was dried in vacuum at 60 °C for 48 h to give 0.14 g (48.8%) of poly(5,10-dihexyl-5,10-dihydroindoloindole) (**7**) as a dark green solid. Anal. Calcd for C₂₆H₃₂N₂: C, 83.82; H, 8.66; N, 7.52. Found: C, 83.35; H, 8.78; N, 7.29.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymer, PININO **7**, are outlined in Scheme 1. In the first step, iodo-2-nitrobenzene (**1**) was treated with acetylene gas, palladium diacetate, triphenylphosphine, and cuprous iodide in acetonitrile and water to generate dinitrotolane (**2**).¹² Oxidation of dinitrotolane (**2**) with KMnO₄ in water and methylene chloride provided 2,2'-dinitrobenzyl (**3**).¹³ Reduction of compound **3** was accomplished using stannous chloride dihydrate in a mixture of acetic acid and hydrochloric acid¹⁴ to generate compound **4**. Alkylation of indolo[3,2-*b*]indole (**4**) with *n*-bromohexane and NaH in THF afforded 5,10-dihexyl-5,10-

dihydroindolo[3,2-*b*]indole (**5**). Dihexylindoloindole **5** was brominated by bromine in pyridine to generated monomer 2,7-dibromo-5,10-dihexyl-5,10-dihydroindolo[3,2-*b*]indole (**6**). The polymerization of this monomer was affected under Yamamoto conditions with Ni(0) catalyst to yield the desired polymer, PININO **7**.

As shown in Table 1, the number-average molecular weights (*M_n*) and the weight-average molecular weights (*M_w*) of the resulting polymer, determined by GPC using polystyrene standard, were 7,800 and 12,100, respectively, with polydispersity index of 1.54. The resulting polymer, was soluble in organic solvents such as chloroform, chlorobenzene, THF, CH₂Cl₂, ODCB, etc., and easily cast on glass plate to give bright green thin film for PININO. Thermal property of the synthesized polymer was evaluated by the means of TGA under nitrogen atmosphere. The weight loss of the polymer was less than 5% in heating to about 340 and 370 °C. The polymer 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

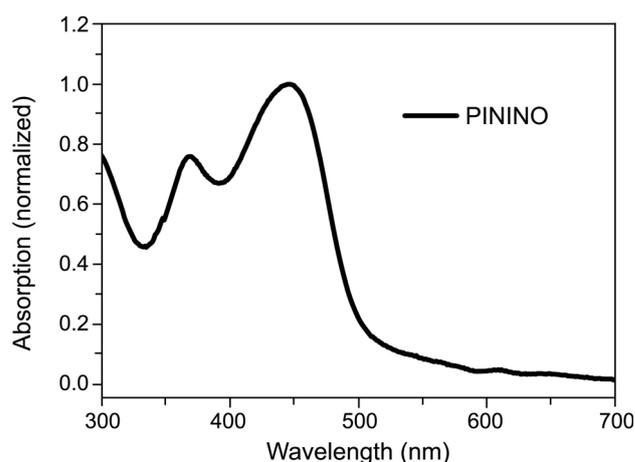


Figure 2. UV-visible absorption spectrum of PININO in the solid state.

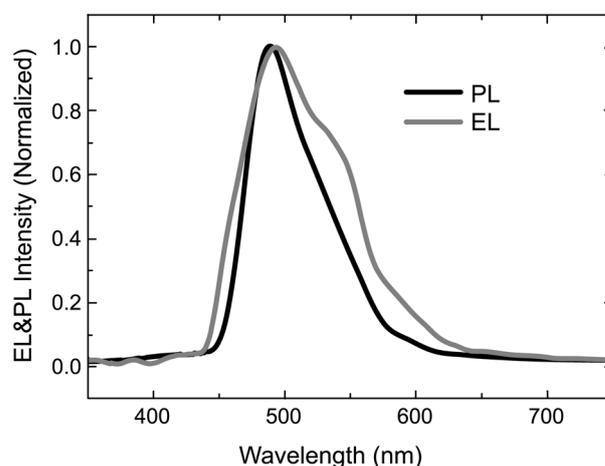


Figure 3. PL and EL spectra of PININO in the solid state.

Table 1. Polymerization Results of PININO

Polymer	Yield (%)	<i>M_n</i> ^a (× 10 ³)	<i>M_w</i> ^a (× 10 ³)	PDI ^a (<i>M_w</i> / <i>M_n</i>)	T _g ^b (°C)	T _d ^c (°C)
PININO 7	80.6	7,800	12,100	1.54	—	370

^a*M_n*, *M_w*, and PDI of the polymer were determined by gel permeation chromatography using polystyrene standards.

Table 2. Optical Properties and Device Performance Characteristics of PININO

Polymer	Abs (nm) ^a	PL λ_{\max} (nm) ^a	EL λ_{\max} (nm)	E _g (eV) ^b	Turn-on (V)	LE _{max} (cd/A) ^c	CIE (x,y) ^d
PININO	450	490	490	2.44	2.5	0.002	(0.205, 0.312)

^aDetermined from thin film on the quartz plate. ^bCalculated from the absorption spectrum edge. ^cMaximum luminescence efficiency. ^dCalculated from the EL spectrum.

absorption spectrum and photoluminescence spectrum of PININO as thin film is shown in Figure 2 and Figure 3. The thin film was prepared by spin-coating on quartz plate from the polymer solution with ODCB. The PININO exhibits absorption spectrum with a maximum peak at 450 nm attributed to π - π^* transition of the conjugated backbone. The absorption onset wavelength of PININO was 510 nm, which correspond to band gaps of 2.44 eV. The PL spectrum of polymer consists of a typical vibronic structured band comprising a maximum, and a shoulder. The PL spectrum (exciting wavelength, 410 nm) of the PININO thin film exhibits a maximum at 490 nm and a shoulder at 520 nm.

Electroluminescent Properties and Current Density-Voltage-Luminescence (*J-V-L*) Characteristics. For the EL experiment, poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS), as the hole-injection-transport layer, was introduced between emissive layer and ITO glass substrate cleaned by successive ultrasonic treatments. The solution of the PEDOT/PSS in aqueous isopropyl alcohol was spin-coated on the surface-treated ITO substrate and dried on a hot plate for 30 min at 110 °C. On top of the PEDOT layer, the emissive polymer film was obtained by spin casting *o*-dichlorobenzene (ODCB) 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 vacuum, and aluminum electrode was deposited on top of the polymer film through a mask by vacuum evaporation at pressures below 10⁻⁷ Torr, yielding active area of 4 mm². 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.

Figure 3 shows the EL spectrum of ITO/PEDOT/polymer/Al devices. The EL spectrum of PININO is similar to the PL spectrum. The EL spectrum of PININO shows maximum peak at 490 nm. The blue-shift in PL and EL spectra of PININO as compared to that of PPV indicates the decrease of the effective conjugation length. The blue shift was caused by the structure of PININO. In PININO, the vinylene group is located at the *meta* position from the phenylene group of the adjacent repeating unit, which should cause the decrease of the effective conjugation length. In the EL spectrum of PININO, a small peak was observed around 550 nm, which corresponds to the excimer formation. PININO has flat dihydroindoloindole group in the repeating unit. Also, it has un-branched normal hexyl groups. With this type of flat structure, the chain morphology of PININO can cause aggregate formation between neighboring chains. To over-

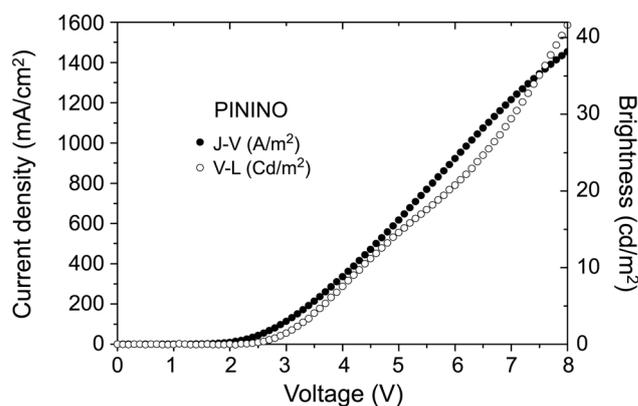


Figure 4. Current-voltage-luminescence (*J-V-L*) characteristics of PLEDs of PININO with a configuration of ITO/PEDOT:PSS/polymer/Al.

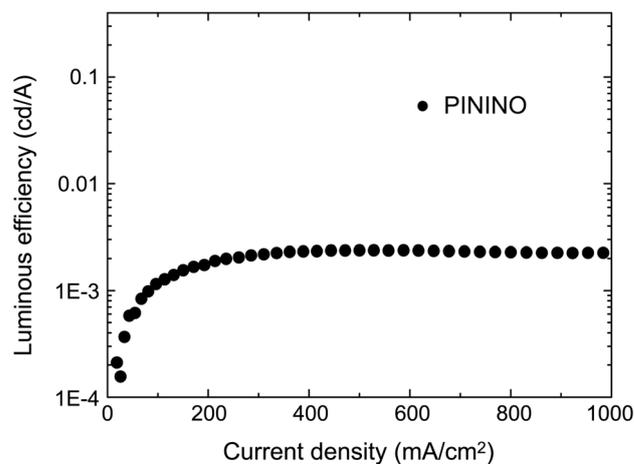


Figure 5. Current density-luminous efficiency of PLED of PININO with the configuration of ITO/PEDOT:PSS/polymer/Al.

come this excimer formation, bulky side chain could be introduced on the nitrogen to reduce the excimer formation. The current density-voltage-luminescence (*J-V-L*) characteristics of ITO/PEDOT/polymer/Al device are shown in Figure 4. In the forward bias, the turn-on voltage of PININO is 2.5 V. The luminescence intensity of the polymer was exponentially increased with an increase in voltage. However, PININO reaches a brightness of 40 cd/m² at 8 V. The lower brightness of PININO was possibly caused by the poor morphology of the polymer film, the low molecular weight, and the structure of the PININO. In PININO, the vinylene group is located at the *meta* position from the phenylene group of the adjacent repeating unit, which should inhibit the effective conjugation. To overcome this

structural problem, it is under investigation to synthesize the monomer with the bromo-groups at the *para* position from the vinylene group.

To investigate the color purity, chromaticity coordinates using the Commission Internationale de L'Eclairage (CIE) (1931) color matching function were converted from the EL spectrum, and the results are listed in Table 2. The emission color of PININO with the CIE coordinates of $x = 0.205$, $y = 0.312$ was green.

Figure 5 shows the EL efficiency of PININO. The highest efficiency of PININO was observed to be 0.002 cd/A at 350 mA/cm². Even though PININO shows low turn-on voltage, the efficiency was poor caused by the low molecular weight and poor morphology of the polymer film.

Conclusion

New electroluminescence polymer with new back-bone structure, PININO 7, was synthesized by Yamamoto conditions with Ni(0) catalyst. The resulting polymer, which exhibits good solubility in common organic solvents, was used as the electroluminescence layer for the light-emitting diodes (LEDs) (ITO/PEDOT/polymer/Al). PININO shows turn-on voltage of 2.5 V, and electroluminescence (EL) with maximum peak at 490 nm, maximum brightness of 40 cd/m² at 8 V, and efficiency of 0.002 cd/A at 350 mA/cm².

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