# New Polyquinoline Copolymers: Synthesis, Optical, Luminescent, and Hole-Blocking/Electron-Transporting Properties

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ABSTRACT: A series of polyquinolines containing the 9,9-di-*n*-hexylfluorene unit in the main chain were synthesized via Friedländer quinoline synthesis in good yields. The thermal, optical, luminescent, electrochemical, and hole-blocking/electron-transporting properties of these polyquinolines were examined. The glass transition temperatures ($T_g$) were in the range 195−243 °C, and these polyquinolines had initial decomposition temperatures of >388 °C. Their optical and luminescent properties varied with the chain rigidity and conjugation length. Cyclic voltammetry studies reveal that these polyquinolines undergo irreversible oxidation onset around −6.0 eV, and their LUMO level ranged from −2.78 to −3.21 eV. The application of two of these polyquinolines as a hole-blocking/electron-transporting layer in polymeric LEDs was demonstrated.

## Introduction

Polyquinolines,[1] which were developed during the 1970s by Stille and co-workers, are characterized by high thermal and oxidative stability, outstanding mechanical property, and optically clear film forming property. The initial research objective of polyquinoline synthesis was the preparation of thermally and oxidatively stable polymers with high use temperatures.[2] Recently, optical and electronic properties of polyquinolines such as electroluminescent,[3] third-order nonlinear optical,[4] and photoconductive properties[5] have been studied extensively for their potential use in photonics and electronic applications.

Since the first report on electroluminescence from poly(*p*-phenylenevinylene), PPV,[6] significant progress in polymeric light-emitting diodes (LEDs) has been made concerning the color tuning,[7] device efficiency,[8] and stability.[9] Due to the difficulties of achieving blue emission with inorganic materials, extensive efforts have been focused on the preparation of polymeric blue-emitting LEDs. Among others, poly(9,9-dihexylfluorene),[10] first prepared by Yoshino et al. using oxidative coupling, showed blue emission with maximum emission around 470 nm. Solid-state light-emitting electrochemical cells based on the polyfluorene derivative and a dissolved lithium salt emitted bright blue light at low operating voltages.[11] Recently, optimization of molecular structure for blue emission with high quantum efficiency in fluorene-based statistical copolymers synthesized by employing the Heck reaction was reported.[12]

In this paper, we report the synthesis of polyquinolines having a 9,9-di-*n*-hexylfluorene unit in the main chain and their thermal, optical, luminescent, electrochemical, and electron-transporting properties. Generally high molecular weight polyquinolines can be obtained from the bis(*o*-aminoketone) (AA type) monomers and bis(ketomethylene) (BB type) monomers by Friedländer quinoline synthesis. Four types of AA type monomers were used to control chain rigidity and conjugation length and hence to tune the emission color of resultant polymers. For BB type monomer 2,7-diacetyl-9,9-di-*n*-hexylfluorene was used to impart light-emitting properties of polyfluorene to the resultant polyquinolines. In addition, noticing the electron-deficient nature of polyquinolines, use of our polyquinolines for the electron-transporting layer in multilayer light-emitting diodes was attempted.

## Experimental Section

**Materials.** Palladium on activated carbon (5%) was purchased from Fluka, and diphenyl phosphate was purchased from Acros. Poly(vinylcarbazole) (PVK, $M_w$ ca. 1 000 000) was purchased from Aldrich and purified by precipitation from THF with methanol. Tetrahydrofuran (THF) was purified by distillation from sodium, and *m*-cresol was purified by distillation under reduced pressure.

**Monomer Synthesis.** 4,4′-Diamino-3,3′-dibenzoyl diphenyl ether,[13] 3,3′-dibenzoylbenzidine,[14] 4,4′-diamino-3,3′-dibenzoylstilbene,[15] and 2,7-diacetyl-9,9-di-*n*-hexylfluorene were synthesized according to the literature.[16] 4-Amino-3-benzoylphenyl sulfide was prepared by modifying a method reported.[17]

**4-Amino-3-benzoylphenyl Sulfide.** Palladium on activated charcoal (5%, 0.51 g) was added to a suspension of 4 g (9.5 mmol) of 5,5′-thiobis(3-phenyl-2,1-benzisoxazole) in 70 mL of dry THF and 1.7 mL of triethylamine. The vigorously stirred suspension was flushed with hydrogen gas and was stirred 48 h at room temperature. The catalyst was removed by filtration through a bed of Celite 545, and the solvent was removed under reduced pressure. The resulting oil was solidified by trituration with *n*-hexane, and the yellow solid was recrystallized from ethanol (25 mL/g) to give 2.7 g (67%) of yellow crystals; mp 118−120 °C. IR (KBr window): 3474, 3360 ($NH_2$), 1615 (C=O, benzophenone), 1105 (Ar−S−Ar) cm$^{-1}$. $^1$H NMR ($CDCl_3$, 200 MHz): $\delta$ 7.37−7.48 (m, 12H), 7.24−7.28 (dd, 2H), 6.66 (d, 2H), 6.15 (bs, 4H). Anal. Calcd for $C_{26}H_{20}N_2O_2S$: C, 73.56; H, 4.75; N, 6.66; S, 7.55. Found: C, 73.15; H, 4.88; N, 6.88; S, 7.74.

**Polymerization.** The syntheses of polyquinolines were carried out via Friedländer quinoline synthesis between the appropriate AA type monomer (bis(*o*-aminoketone)) monomer and 2,7-diacetyl-9,9-di-*n*-hexylfluorene (BB type monomer) in good yields. Syntheses of POF66 and P1F66 are described in

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our previous communication.[18] P-3, used as emitting layer in multilayer EL devices, was synthesized via Heck reaction according to the literature.[12]

**(1) PSF66.** A solution containing 0.6383 g (1.5 mmol) of 4-amino-3-benzoylphenyl sulfide, 0.6279 g (1.5 mmol) of 2,7-diacetyl-9,9-di-*n*-hexylfluorene, 5 mL of *m*-cresol, and 7.5 g of diphenyl phosphate[19] was prepared. The mixture was heated to 140−142 °C for 2−3 h under nitrogen gas flow. After 60 h, the polymer was precipitated by pouring the reaction mixture into 500 mL of ethanol containing 50 mL of triethylamine. The polymer was continuously extracted in a Soxhlet apparatus with ethanol. After drying, 1.06 g (84%) of PSF66 was obtained. Anal. Calcd for $(C_{55}H_{50}N_2S)_n$: C, 85.67; H, 6.54; N, 3.63; S, 4.16. Found: C, 85.66; H, 6.59; N, 3.63; S, 3.89.

**(2) P2F66.** P2F66 was synthesized in the same manner of PSF66, using 0.4185 g (1 mmol) of 4,4′-diamino-3,3′-dibenzoylstilbene and 0.4186 g (1 mmol) of 2,7-diacetyl-9,9-di-*n*-hexylfluorene, to give 0.76 g (90.7%) of P2F66. Anal. Calcd for $(C_{57}H_{52}N_2)_n$: C, 89.49; H, 6.85; N, 3.66. Found: C, 86.13; H, 7.09; N, 3.30.

**Characterization.** IR spectra recorded from a NaCl window on a Midac FT-IR spectrophotometer and a Varian 200 (200 MHz) were used for NMR measurements. $CDCl_3$-*d* or DMSO-$d_6$ was used as solvent, and all chemical shifts were listed in ppm downfield from tetramethylsilane. Melting points were determined on a micro melting point apparatus (Yanaco) and are uncorrected. GPC analysis of the polymer was performed on a Waters HPLC component system equipped with five Ultra-$\mu$-styragel columns ($10^5$, $10^4$, $10^3$, and 500 Å) using THF as solvent. DSC analysis was performed on a Perkin-Elmer DSC7 at a heating rate of 10 °C /min, and TGA analysis was conducted with a Du Pont 2950 at a heating rate of 10 °C /min under a nitrogen gas flow. The UV−vis spectrum was recorded with a HP 8452A diode array spectrophotometer. Photoluminescence (PL) spectra and electroluminescence (EL) spectra were obtained using an ISS PL1 fluorimeter equipped with a 300 W xenon arc lamp. The *I*−*V*−*L* characteristics were recorded on a Keithely 236 source/measure unit for the voltage−current relationship and by a Newport powermeter (model 1830-C) for voltage−electroluminescence intensity. The film thickness was measured by a TENCOR P-10 surface profiler. Cyclic voltametry measurements were carried out at an ITO electrode in a 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile at a constant scan rate of 20 mV/s using a three-elecreode cell and potentiostat assembly (model 362, EG&G Princeton Applied Research). The potentials were measured versus Ag/AgCl (4 M KCl and saturated AgCl) reference electrode with ferrocene as internal standard, and a Pt plate was used as a counter electrode.

**LED Device Fabrication.** The single polyquinoline:PVK blend (20/80 by weight) layer device was fabricated by spin-coating the polymer thin film (∼100 nm) onto an ITO-covered glass substrate. For the fabrication of bilayer LEDs, the P-3:PVK blend (20/80 by weight) layer (∼100 nm) was spin-cast on top of ITO on glass, and spin-coating of polyquinolines in their formic acid solution (∼30 nm) followed. For the three-layer devices a hole injection poly(*N*-vinylcarbazole) (PVK) layer (∼60 nm) was first spin-cast onto the ITO glass, using chlorobenzene as the solvent, followed by the spin-coating of P-3 in tetrachloroethylene, which is known as a nonsolvent for PVK, and then the polyquinoline layer was further spin-cast on top of the P-3 layer to form an electron-transporting/hole-blocking layer (∼30 nm). The cathode Al electrode (∼150 nm) was deposited by thermal evaporation under vacuum below $10^{-6}$ Torr, yielding an active layer with an area of 0.18 $cm^2$.

## Results and Discussion

The polyquinolines POF66, PSF66, P1F66, and P2F66 were synthesized successfully according to Scheme 1 with good yields of >84%. Properties (molecular weights, thermal properties) of these polyquinolines are summarized in Table 1. These polyquinolines except for P2F66 were readily soluble in common organic solvents such as chloroform, THF, and chlorochlorobenzene. P2F66 is partially soluble in THF, which is thought to be due to its rigid-rod main-chain structure, so the actual molecular weight of P2F66 should be higher than the measured value. As shown in Table 1, the glass transition temperature increases as the chain rigidity increases, ranging from 195 to 243 °C. These $T_g$ values are much higher compared to those of typical polyfluorene[20] (∼55 °C) or MEHPPV (∼65 °C), indicating that the quinoline ring significantly enhanced the thermal stability of the polymers. These polyquinolines showed highly thermal stabilities with initial decomposition temperatures of >388 °C.

**Scheme 1. Synthesis of Polyquinolines**

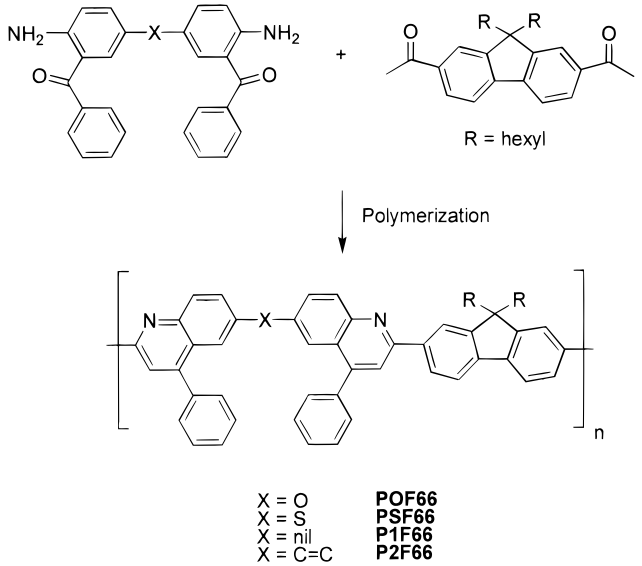


**Table 1. Molecular Weights and Thermal Properties of Polyquinolines**

| polymer | yield (%) | $M_n$ ($\times 10^{-3}$) | $M_w$ ($\times 10^{-3}$) | $M_w/M_n$ | $T_g$ (°C) | $T_d$[b] (°C) |
|---|---|---|---|---|---|---|
| POF66 | 89 | 27.3 | 60.1 | 2.20 | 204 | 425 |
| PSF66 | 84 | 11.6 | 43.5 | 3.75 | 195 | 388 |
| P1F66 | 84 | 14.1 | 25.7 | 1.82 | 214 | 420 |
| P2F66 | 91 | 6.87[a] | 18.1[a] | 2.63 | 243 | 410 |

[a] THF-soluble parts. [b] Onset of decomposition.

Figures 1 and 2 show the absorption and emission spectra of PSF66 and P2F66, and the spectral properties of polyquinolines are summarized in Table 2. As the chain rigidity and conjugation length increase, the PL emission for dilute solution (in THF, $10^{-5}$ M) increases from 404 nm (POF66) to 446 nm (P2F66), and the PL emission of thin film shows the same tendency. The UV−vis maximum absorption peak of PSF66 was 400 nm, which is attributed to the $\pi-\pi^*$ transition, and the PL spectra of PSF66 showed emission maxima at 422 nm for dilute solution and 434 nm for thin film when excited at 365 nm. As a result of the richer electron density of the sulfur atom than that of oxygen, the absorption (∼12 nm) and emission (∼20 nm) maxima were shifted bathochromically. The PL spectrum of thin film of P2F66 had two peaks at 494 and 534 nm and showed green emission (Figure 2). This broad peak around 534 nm was likely due to interchain excimer emission.[21] To investigate the excimer formation of P2F66 in the solid state, P2F66 was blended with PVK (20/80 by weight).[22] But the P2F66/PVK blend film exhibited two emission maxima, one at 410 nm and the

**Table 2. Optical and Electrochemical Properties of Polyquinolines**

| polymer | absorption | fluorescence $\lambda_{max}$(nm) solution[b] | film[c] | blend[d] | band gap[e] (eV) | HOMO[f] (eV) | LUMO[g] (eV) |
|---|---|---|---|---|---|---|---|
| POF66 | 388 | 404 | 414 (490) | | 3.02 | −6.1 | −3.08 |
| PSF66 | 400 | 422 | 434 (525) | | 2.86 | −5.99 | −3.13 |
| P1F66 | 404 | 434 | 446 (480, 525) | 440 (460) | 2.79 | −6.0 | −3.21 |
| P2F66 | 384 | 446 | 494, 534 | 450 (410) | 2.76 | −5.54 | −2.78 |

[a] Obtained from solid films, numbers in parentheses are the wavelengths of subpeaks or shoulders. [b] In THF, $10^{-5}$ M, excited at 365 nm. [c] Excited at 365 nm. [d] Polymer/PVK = 20/80 by weight, excited at 340 nm. [e] Calculated from the absorption edge of the UV−vis spectrum. [f] Measured by cyclic voltammetry [g] Estimated from the HOMO and band gap.

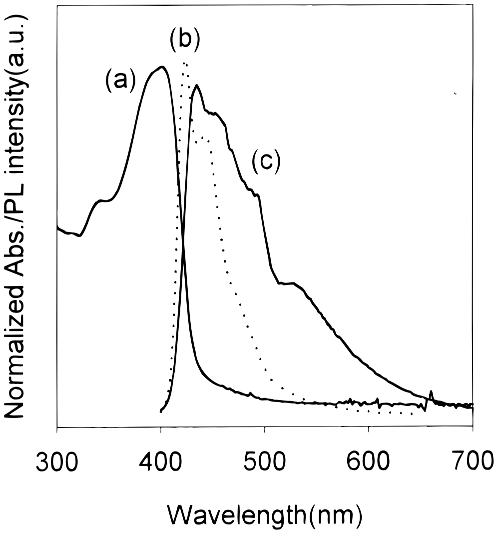


**Figure 1.** (a) UV absorption spectrum, (b) PL spectrum of solution ($10^{-5}$ M), and (c) PL spectrum of film of PSF66.

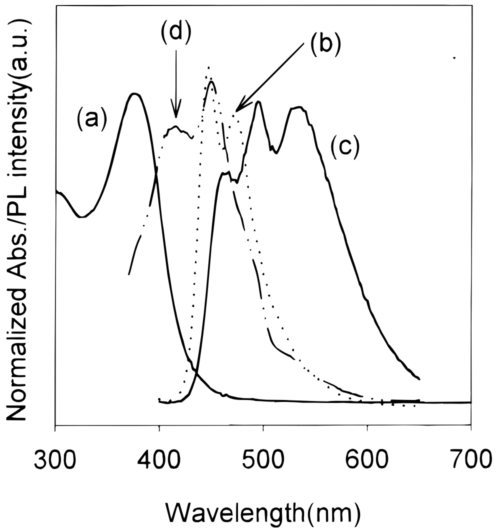


**Figure 2.** (a) UV absorption spectrum, (b) PL spectrum of solution ($10^{-5}$ M), (c) PL spectrum of film of PSF66, and (d) PL spectrum of the P2F66/PVK blend film.

other 450 nm, which was quite different behavior compared with that of the P1F66/PVK blend.[18] Though the broad excimer peak around 534 nm disappeared, another peak at 410 nm which originated from the PVK emission was observed. This might be owing to the phase separation when the P2F66/PVK blend film was spin-coated from solution. It is supposed that the different precipitation rates of the two polymers (P2F66, PVK) in DMAc solution during spin-coating cause the phase separation of blend film. Since the emission intensity of P2F66 was not strong enough to dwarf the PVK emission to the noise level due to the poor film quality, P2F66/PVK blend film had two emission maxima, one from P2F66 (450 nm) and the other from PVK emission (410 nm).

Cyclic voltammetry (CV) was employed to investigate the redox behaviors of polyquinolines and to estimate the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) levels of the materials. The characteristic data of AB type polyquinolines measured at a ITO electrode versus a Ag/AgCl reference electrode at a scan rate of 20 mV/s at room temperature are listed in Table 2. Each measurement was calibrated against an internal standard, the ferrocene/ferrocenium redox system (−4.8 eV), according to the method described in the literature.[23] Our polyquinolines were electrochemically inert in the reduction region and exhibited irreversible oxidation onset from −5.54 to −6.1 eV. With the exception of P2F66, other polyquinolines showed an HOMO level of $\sim-6.0$ eV, having a slightly increased HOMO level compared with that of quinoline ($\sim-6.28$ eV, estimated from the reduction half-potential obtained by CV measurements in solution, $\sim 10^{-3}$ M in acetonitrile). The LUMO level varied according to the band gap (−3.08 to −3.21 eV), while maintaining the HOMO level in the vicinity of −6.0 eV. These reduction potentials are lower than those of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) ($\sim-2.4$ eV),[24] one of the most widely used electron-transporting/hole-blocking materials, and other 1,3,4-oxadiazole-containing materials.[25] These values are comparable with that of poly(cyanoterephthalyidene) (CN−PPV) (−3.10 eV), which shows good electron-transporting ability in polymeric LED devices. It is believed that the low-lying LUMO level of polyquinolines originates from the electron-deficient nature of the quinoline ring. Thus, the results suggest that LUMO energy levels of the polymers may be lower than those conventional p-dope-type electroluminescence polymers. Such energy levels may provide a closer match to the work function of Al when they are used as electron-transporting/hole-blocking materials in polymer LEDs.

To investigate the electron-transporting/hole-blocking properties of polyquinolines, POF66 and P1F66 were chosen for further study. As the emissive polymers P-3 (Chart 1),[12] the statistical copolymer with fluorene as one unit and a mixture of *p*- and *m*-divinylbenzene (3:7) as the other synthesized by the Heck reaction were chosen. Because of excellent film-forming properties of polyquinolines, homogeneous transparent films could be spin-cast from their formic acid solutions, which were applied in double- and three-layer LEDs together with P-3 as emissive layer. Because P-3 does not dissolve or swell in formic acid, heterojuctions with relatively sharp polymer/polymer interfaces were obtained. Reasons for achieving such sharp interfaces include the relatively short solution contact time and high solvent evaporation

**Table 3. Summary of EL Quantum Efficiencies, Luminances, and Turn-On Voltages for the Multilayer LEDs**

| | P-3:PVK blend/polyquinoline | | | PVK/P-3/polyquinoline | | |
|---|---|---|---|---|---|---|
| | rel efficiency | luminance ($\mu$W) | turn-on (V) | rel efficiency | luminance ($\mu$W) | turn-on (V) |
| control | 1 (0.0045%) | 6 | 14 | 1 (0.0008%) | 1 | 10 |
| POF66 | ~9.1 | 4.5 | 14 | ~17.5 | 3.4 | 8 |
| P1F66 | ~11.6 | 16 | 14 | ~15.6 | 8.2 | 12 |

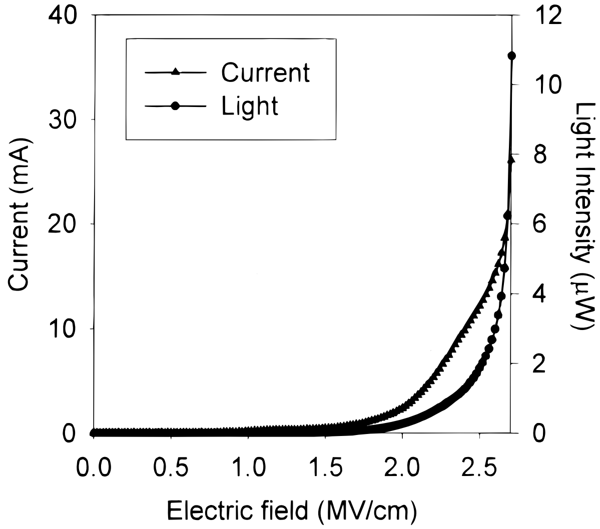
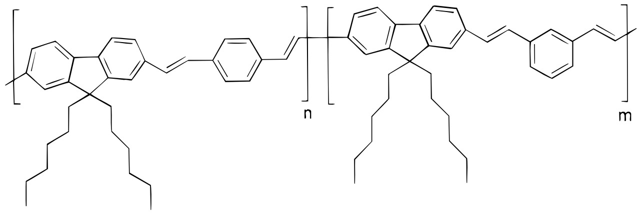


**Figure 3.** *I*−*V* and *L*−*V* characteristics of the ITO/P-3:PVK blend/Al device.

**Chart 1. Chemical Structure of P-3 Used as Emissive Material in Multilayer EL Devices**



P-3 ( n : m = 3 : 7)

rate during spin-coating and the rodlike nature of the polyquinolines which preclude ready diffusion into the underlying emissive film.[3b]

We fabricated two kinds of polymer/polymer heterojunction LEDs of the form ITO/P-3:PVK blend/polyquinoline (PQ)/Al and ITO/PVK/P-3/PQ/Al to evaluate the potential of polyquinolines as an electron transport materials for EL device. The EL quantum efficiencies, luminances, and turn-on voltages for double- and three-layer LEDs are summarized in Table 3. Figures 3 and 4 present the current−voltage and luminance−voltage characteristics of the ITO/P-3:PVK blend(20/80 by weight, 100 nm)/Al and ITO/P-3:PVK blend(100 nm)/P1F66(30 nm)/Al devices. Since introducing an electron transport layer would lead to an increase in device thickness, it is more convenient to plot the current versus electric field than versus applied voltage for understanding the device characteristics. The turn-on voltages (determined from the onset of luminance in the log−log plot of light intensity vs voltage) of both the devices are 14 V, while considering the device thickness, the turn-on voltage was reduced by ~23% (~1.4 to ~ 1.08 MV/cm) when polyquinoline was introduced as an electron-transporting layer. The quantum efficiency of the ITO/P-3:PVK blend/P1F66/Al device (0.052%) was increased by a factor of 11.6, compared with a single layer P-3:PVK blend device. Introduction of POF66 also exhibited increase of quantum efficiency (9.1 times increase). Introduction of P1F66 as electron transport layer increased the luminance by a factor of 2.7, but in the case of POF66, the luminance decreased slightly compared to the single-layer ITO/P-3:PVK blend/Al device. The EL spectra of the LEDs with and without P1F66 layer (operated at 20 and 12 V, respectively) are shown in Figure 5. The EL spectrum of the double-layer LED (emission maximum at 480 nm), ITO/P-3:PVK blend/P1F66/Al device, is very close to that of single-layer P-3:PVK blend device (emission maximum at 476 nm), indicating that the P-3:PVK blend acts as the emitting layer in the double-layer device, and no exciplex formation[21,26] occurs.

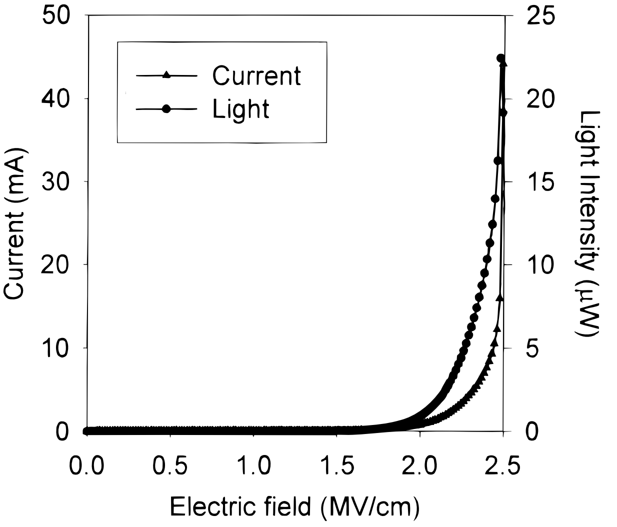


**Figure 4.** *I*−*V* and *L*−*V* characteristics of the ITO/P-3:PVK blend/P1F66/Al device.

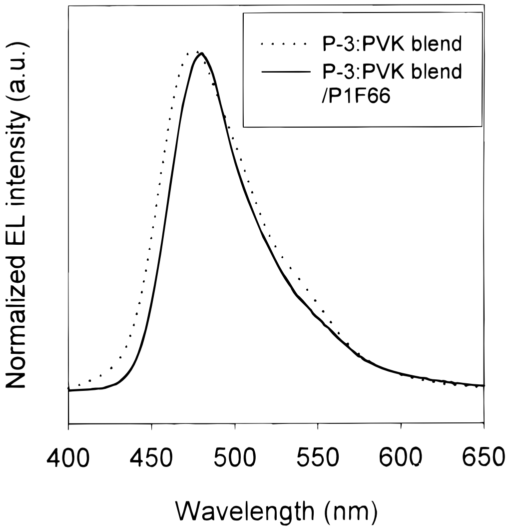


**Figure 5.** EL spectra of ITO/P-3:PVK blend/Al and ITO/P-3:PVK blend/P1F66/Al device.

The current−voltage and luminance−voltage characteristics of ITO/PVK(60 nm)/P-3(18 nm)/Al and ITO/

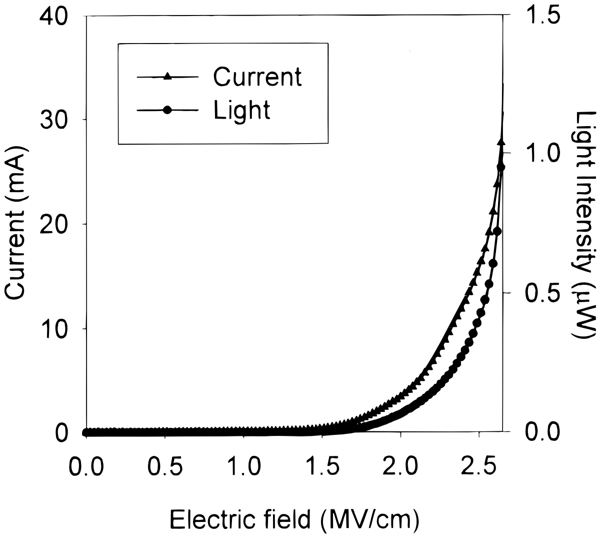


**Figure 6.** *I*−*V* and *L*−*V* characteristics of the ITO/P-3/PVK/Al device.

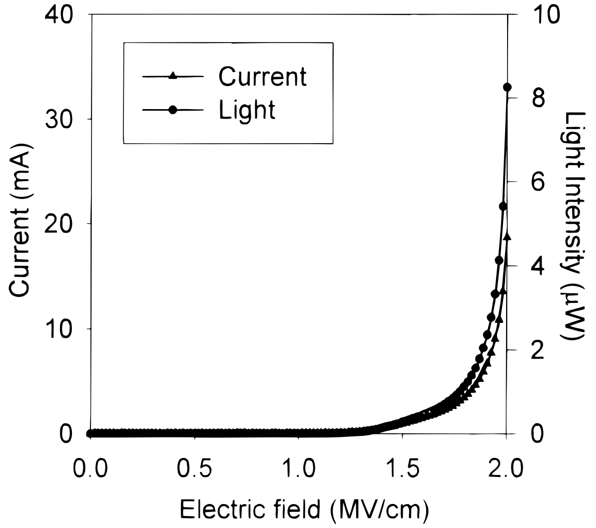


**Figure 7.** *I*−*V* and *L*−*V* characteristics of the ITO/P-3/PVK/P1F66/Al device.

PVK(60 nm)/P-3(18 nm)/P1F66(30 nm)/Al devices are shown in Figures 6 and 7, respectively. Introduction of PVK as hole-transporting layer and polyquinoline as electron-transporting layer resulted in significant reduction of turn-on voltages (13−42%), compared to that of the ITO/PVK/P-3/Al device (1.28 MV/cm). Both the light intensity (3.4 and 8.2 times) and quantum efficiency (17.5 and 15.6 times) are significantly increased compared to those of the control device. The light output is approximately proportional to the current as seen with typical current−luminance characteristics of three different LEDs (Figure 8).

In summary, we synthesized a series of polyquinolines having a 9,9-di-*n*-hexylfluorene moiety in the main chain using Friedländer quinoline synthesis. These polyquinolines were found to be thermally stable with initial decomposition temperatures over 388 °C and together with high glass transition temperatures (195−243 °C), which may improve the operating lifetime of the EL device. Optical and fluorescent behaviors of these polyquinolines varied with conjugation length. POF66 and P1F66 showed good hole-blocking/electron-transporting properties in double- and three-layer EL devices.

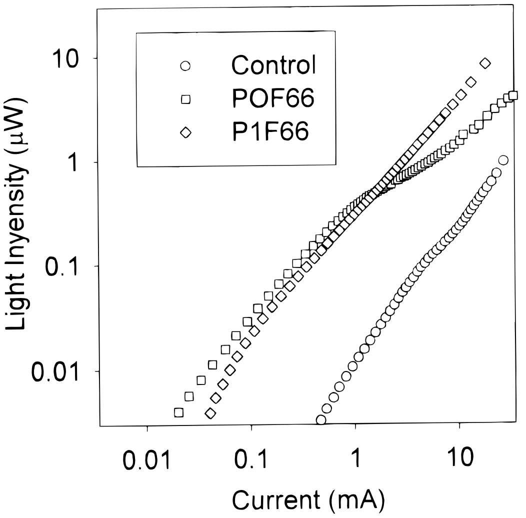


**Figure 8.** Plot of light intensity vs current for ITO/P-3/PVK/polyquinoline/Al devices.

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