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New electron-accepting π-conjugated polyquinoxalines with fluorene unit: synthesis and light-emitting properties

S. H. Jung[1], D. H. Suh[2], H. N. Cho[1](✉)

[1]Polymer Materials Laboratory, KIST, P.O. Box 131, Cheongryang, Seoul, 130-650, Korea
[2]Department of Chemical Technology, College of Engineering, Hanyang University, Haengdang 1-dong, Seongdong-gu, Seoul 133-791, Korea
E-mail: hncho@kist.re.kr, Tel: +82-2-958-5321, Fax: +82-2-958-5309

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Summary

New fluorene-linked π-conjugated polyquinoxaline PFQx Ⅰ and PFQx Ⅱ have been synthesized and characterized. The PFQx polymers are prepared by the polycondensation of the 2,7-bis(phenyloxoacetyl)-9,9'-di-n-hexylfluorene or 2,7-bis(4-benzil)-9,9'-di-n-hexylfluorene and 3,3'-diaminobenzidine leading to the PFQx Ⅰ and PFQx Ⅱ. The polycondensation is usually carried out in *m*-Cresol. These polymers possess relatively good solubility and thermal stability. The resulting polymers exhibit a UV-visible absorption band in the range of 397-407 nm in both chloroform solution and the film state. Upon photo-excitation around the absorption maximum wavelength, their PL spectra show a maximum peaks around at 447-467 nm. Multilayered light-emitting diode with the device structure of ITO/PEDOT/PFQx Ⅰ/PVK blend(2:8)/LiF/Al gives a highest EL peak in the blue region of 460 nm. *J*-*V* curve shows a turn-on voltage of 13 V.

Introduction

A unique research field was opened up for polymers with conjugated double bonds when poly (*p*-phenylenevinylene) (PPV) sandwiched between indium-tin oxide (ITO)-coated glass and aluminum electrodes emitted light with a green color on a forward bias potential [1]. Blue is the color most sought after in light-emitting diodes (LEDs) since it is one of the main colors, and easily converted into green or red with a small intensity loss when color dyes are employed.

For the most of conjugated polymers, the barrier of electron injection is much higher than that of hole injection. To improve efficiency of PLEDs, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device [2]. Therefore, many high electron affinity substituents such as quinoxaline [3-5], oxadiazole [6], triazole [7] and quinoline [8] have been introduced.

Poly(phenylquinoxalines) (PPQx) are known already since 1967 when their synthesis was first described by Hergenrother [9]. They are a class of high-temperature/high-performance thermoplastics that have many desirable properties such as high glass transition temperatures, low dielectric constants, high chemical resistance, and high thermo-oxidative stability. Recently, new π-conjugated poly (quinoxaline-5,8-diyl) (PQx) and its 2,3-disubstituted derivatives have been synthesized [3]. These polymers are expected to be good electroluminescent (EL) materials by combining them with other hole transporting polymers such as PPV. In addition, thiophene-linked polyquinoxaline was reported as an excellent electron transport (ET) material for polymer LEDs [4].

In this work, we describe the preparation of new electron-accepting π-conjugated polyquinoxalines based on fluorene moiety in hope of combining both excellent electron-affinitive and light-emitting properties into the polymers.

Experimental

Materials

Syntheses of 9,9'-di-n-hexylfluorene and 2,7-dibromo-9,9'-di-n-hexylfluorene were prepared according to the literature [10]. All other chemicals were purchased from the Aldrich, TCI, and Acros were used without further purification.

Instruments

Varian 200 was used for the ^{1}H NMR measurements. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) with polystyrene standards calibration (Water high-pressure GPC assembly Model M590 pump, μ -Styragel columns of 10^5, 10^4, 10^3, 500, and 100Å, a refractive index detector, solvent: THF). Fourier transform Infrared spectra (FT-IR) were measured with the specimens in the form of KBr pellets on a Thermo-Nicolet Spectrometer. Differential scanning calorimetric (DSC) analyses were performed with a Perkin Elmer Pyris1 at a heating rate of 10°C/min and thermo-gravimetric (TGA) analyses were conducted with a TA Q50-0075 at a heating rate of 10°C/min under nitrogen gas flow. UV-visible absorption spectra were recorded on a HP8452A Diode Array Spectrophotometer. The photoluminescence (PL) and electroluminescence (EL) spectra were obtained using an ISS PL-1 spectrofluorometer equipped with a 300W-xenon arc lamp. The I-V-L characteristics were recorded with a Keithely 236 source/measure unit and by a Newport power meter (model 1830-C)

Synthesis of monomers

Synthesis of 2,7-bis(phenylethynyl)-9,9'-di-n-hexylfluorene (1)

To a 500 mL Schlenk type flask charged with 200 mL diisopropylamine were added 2,7-dibromo-9,9'-di-n-hexylfluorene (20.00 g, 40.0 mmol), phenylacetylene (9.12 g, 89.0 mmol), bis(triphenylphosphine)palladium(II)chloride (1.42 g, 2.0 mmol), and a catalytic amount of copper(I) iodide (0.38 g, 2.0 mmol), in that order. The mixture was then refluxed overnight under an atmosphere of argon. The solution was allowed to cool to room temperature and was filtered to remove the precipitate of diisopropylamine hydrobromide salts. The solvent was removed at reduced pressure and the residue was taken up in methylene chloride. Extraction with 5% HCl followed by extraction with water, drying of the oranic layer, and removal of the solvent yielded the crude product as dark oil. The oil was purified by chromatography on silica using a 7:1 mixture of hexane and ethyl acetate, and further purified by recrystallization from hexan and ethyl acetate, affording a white crystalline solid. Yield: 13 g (60%). mp 92-94 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.5(br, 4H, CH_2), 0.71-0.78(t, 6H, CH_3), 0.9-1.1(m, br, 12H, CH_2), 1.95-2.05(t, br, 4H, CCH_2), 7.25 -8.05 (m, 16H, Aromatic)

Synthesis of 2,7-bis(phenyloxoacetyl)-9,9'-di-n-hexylfluorene (2)

To a solution of compound 1 (30.00 g, 56.0 mmol) in 250 mL of dichloromethane was added 3 g of tetrabutylammonium bromide, 500 mL water, 12.00 g of $NaHCO_3$, and 60 g of $KMnO_4$. After vigorous stirring at room temperature for 48 h, 80.00 g of sodium bisulfite and 40 mL of concenturated HCl were slowly added to reduce excess oxidizing agents . The mixture was extracted with dichloromethane and washed with water, and the organic layer was dried over $MgSO_4$. The solvent was evaporated to afford a yellow viscous oil. The yellow oil was purified by recrystallization from ethyl acetate, affording a yellow crystalline product. Yield: 23 g (68%). mp: 91-93 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.5(br, 4H, CH_2), 0.71-0.78(t, 6H, CH_3), 0.9-1.1(m, br, 12H, CH_2), 1.95-2.05(t, br, 4H, CCH_2), 7.50-8.05 (m, 16H, Aromatic)

Synthesis of 2,7-diphenyl-9,9'-di-n-hexylfluorene (3)

$Pd(PPh_3)_4$ (3.34 g, 2.9 mmol) and 2 M aqueous Na_2CO_3 (150 mL) were added to a solution of 2,7-dibromo-9,9'-di-n-hexylfluorene (57.00 g, 115.8 mmol) and phenylboronic acid (35.20 g, 231.6mmol) in toluene (300 mL). The mixture was heated at reflux for 48h under an atmosphere of argon and then cooled to room temperature. The solution was extracted with toluene, and the organic layer was washed with water a several times, dried over $MgSO_4$, and evaporated to give a viscouse oil. Purification of the crude product by silica gel column chromatography (hexane as eluent), and further purified by recrystallization from hexane, affording a white crystalline solid. Yield: 43 g (76%). mp: 65-66 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.77-0.83(t, 10H, CH_2, CH_3), 1.11(s, 12H, CH_2), 2.06-2.14(t, br, 4H, CCH_2), 7.37-7.84(m, 16H, Aromatic)

Synthesis of 2,7-bis(4-phenacetylphenyl)-9,9'-di-n-hexylfluorene (4)

A solution of compound 3 (30.00 g, 61.6 mmol) and phenylacetyl chloride (22.00 g, 141.0 mmol) in 100 mL of carbon disulfide was slowly added to an ice cold suspension of anhydrous aluminum chloride (19.00 g, 142.0 mmol) and carbon disulfide (400 mL). The reaction mixture was stirred at room temperature for 24 h under an atmosphere. The flask was cooled in ice bath and the aluminum chloride complex decomposed by slow addtion of 20% HCl followed by the addition of methylene chloride (200 mL). The organic layer was separated, washed with water, a 10% $NaHCO_3$ solution, and water again, and dried over $MgSO_4$. The crude product was purified by recrystallization from methylene chloride and ethanol. White crystalline solid was obtained. Yield: 36 g (81%). mp: 129-131 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.65-0.75(m, 10H, CH_2CH_3), 1.05-1.15(m, 12H, CH_2), 2.01-2.07(t, br, 4H, CCH_2), 4.35(s, 4H, CH_2), 7.22-8.15(m, 24H, Aromatic)

Synthesis of 2,7-bis(4-benzil)-9,9'-di-n-hexylfluorene (5)

Aqueous HBr (14 mL of a 48 weight percent solution) was added to compound 4 (12.00 g, 16.5 mmol) in DMSO (250 mL) and the resulting mixture was heated to 100

°C. for five hours, then cooled to ambient temperature. The mixture was partitioned between toluene (250 mL) and water (500 mL). The organic layer was washed with water, followed by washing with brine, and concentration to gave a viscous oil. Recrystallization from hexane and ethyl acetate gave 10 g (yield: 80%) of the title compound as bright yellow crystalline solid. mp: 138-139 °C. ^{1}H NMR ($CDCl_3$, ppm): 0.65-0.75(m, 10H, CH_2CH_3), 1.05-1.15(m, 12H, CH_2), 2.01-2.07(t, br, 4H, CCH_2), 7.50-8.10(m, 24H, Aromatic)

Polymerization

Poly{[9,9'-bis(n-hexyl)fluorene-2,7-diyl]-alt-[6,6'-bis(3-phenylquinoxaline)-2,2'-diyl]} (PFQx Ⅰ)

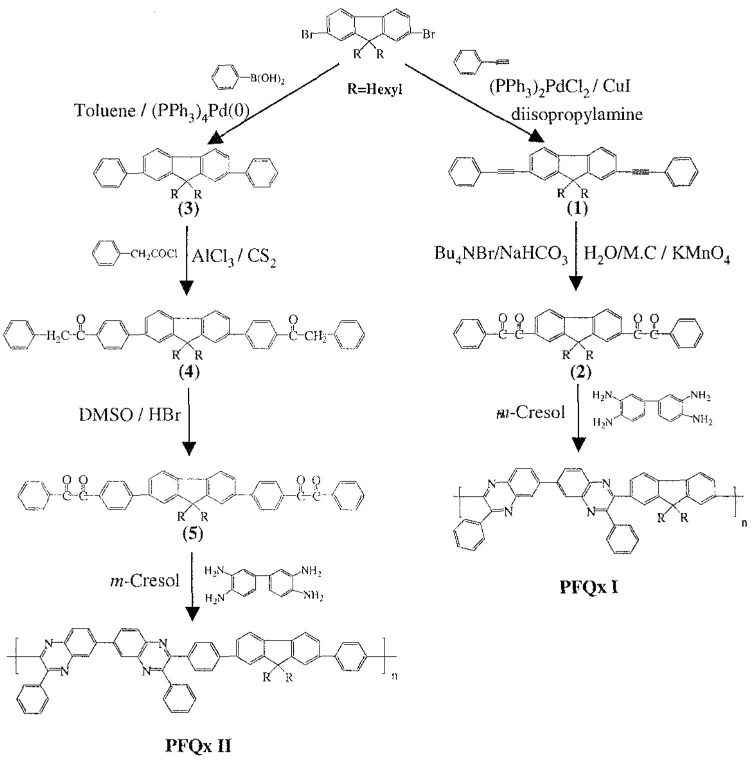
Equimolar amounts of compound 2 (1.00 g, 1.67 mmol) and 3,3'-diaminobenzidine (357 mg, 1.67 mmol) were dissolved in 7 mL of *m*-cresol in a 50 mL glass reactor fitted with a mechanical stirrer. The reaction mixture was stirred under argon purge at 100 °C for 48 h during which progressive increase of the solution viscosity was observed. The reaction mixture was poured into 600 mL methanol, precipitating a yellow polymer product which was collected by suction filtration and redissolved chloroform. The solution was filtered through a micro filter to remove residual particles and precipitated in methanol. The obtained polymer was dried in a vaccum oven at 40 °C for 2 days. 1.2 g

Poly{[9,9'-bis(n-hexyl)fluorene-2,7-diphenyl-4,4'-diyl]-alt-[6,6'-bis(3-phenylquinoxaline)-2,2'-diyl]} (PFQx Ⅱ)

Equimolar amounts of compound 2 (1.00 g, 1.33 mmol) and 3,3'-diaminobenzidine (285 mg, 1.33 mmol) were dissolved in 6 mL of *m*-cresol in a 50 mL glass reactor fitted with a mechanical stirrer. The reaction mixture was stirred under argon purge at 100 °C for 48 h during which progressive increase of the solution viscosity was observed. The reaction mixture was poured into 600 mL methanol, precipitating a yellow polymer product which was collected by suction filtration and redissolved chloroform. The solution was filtered through a micro filter to remove residual particles and precipitated in methanol. The obtained polymer was dried in a vaccum oven at 40 °C for 2 days. 1.1 g

Results and discussion

We used a different synthetic approach which is showed in Scheme 1. The 2,7-bis(phenylethynyl)-9,9'-di-n-hexylfluorene could easily be oxidized to the tetraketones with $KMnO_4$ in CH_2Cl_2 according to the procedure for the oxidation of 2,5-bis(phenylethynyl)thiophene described by Jenekhe. The 2,7-bis(4-benzil)-9,9'-di-n-hexylfluorene is usually prepared by HBr (48% solution) oxidation of 2,7-bis(4-phenacetylphenyl)-9,9'-di-n-hexylfluorene which is obtained by Friedel Crafts acylation. The PFQx polymers are prepared by the polycondensation of the 2,7-bis(phenyloxoacetyl)-9,9'-di-n-hexylfluorene and 2,7-bis(4-benzil)-9,9'-di-n-hexylfluorene with 3,3'-diaminobenzidine in *m*-cresol, leading to the PFQx Ⅰ and PFQx Ⅱ.



Scheme 1. Synthetic routes to monomers and polymers.

Table 1. Molecular weights and thermal properties of the polymers

polymer	yield (%)	M_n ($\times10^{-3}$)	M_w ($\times10^{-3}$)	PDI	T_g (^oC)	T_d[a] (^oC)
PFQx I	97	16.2	59.4	4.2	235	450
PFQx II	93	61.8	165.4	3.6	255	440

[a] Temperature resulting in 5% weight loss based on initial weight.

The obtained polymers are almost completely soluble in common organic solvents, such as THF, chloroform, chlorobenzene, *m*-cresol. Chemical structure has been checked by FT-IR analysis (Figure 1). Intense absorption peaks at 1664-1667 cm^{-1}, attributed to the carbonyl groups in monomers disappeared after polycondensation.

The molecular weights of these polymers were determined by GPC using THF as an eluent and polystyrene as a standard and are listed in Table 1. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) of the polymers were 16,200-61,800 and 59,400-165,400 with a polydispersity of 4.2-3.6, respectively. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10 °C/min. Figure 2 shows thermo-gravimetric curve of the resulting polymers. TGA reveals good thermal stability of these polymers with the onset decomposition temperature (T_d) range from 440 °C to 450 °C under nitrogen. PFQx Ⅰ and PFQx Ⅱ showed very high glass transition temperature (T_g) of 235 °C and 255 °C, respectively.

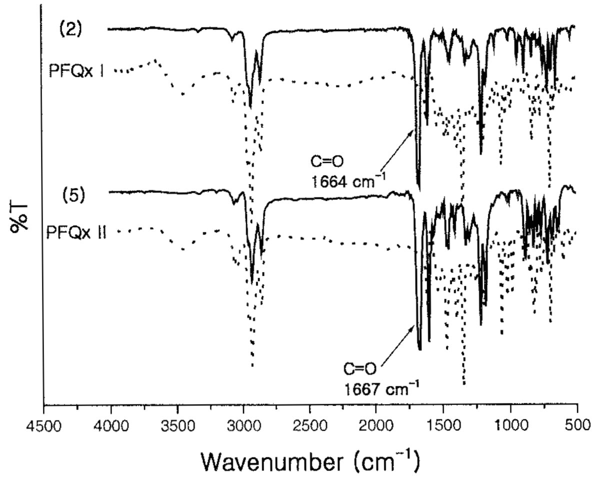


Figure 1. IR spectra of compound (2), compound (5), PFQx Ⅰ and PFQx Ⅱ.

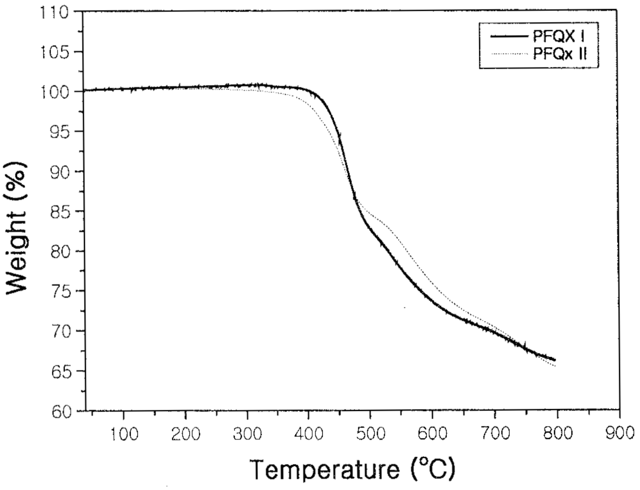


Figure 2. TGA traces (10 °C/min) of PFQx Ⅰ and PFQx Ⅱ under nitrogen.

The UV-vis absorption spectra and photoluminescence (PL) spectra of PFQx Ⅰ and PFQx Ⅱ in dilute solution of chloroform and as thin films are shown in Figure 3. The UV-vis absorption maxima of PFQx Ⅰ and PFQx Ⅱ appear at 407 and 397 nm for the chloroform solutions and at 406 and 404 nm for the thin films, respectively. The PL spectrum of the PFQx I in thin film exhibits a maximum at 460 nm and a weak eximer peak at 523 nm. On the other hand, The PFQx II showed blue emission with the PL maxima at 467 nm in chloroform solution and at 460 nm in thin film with a eximer peak at 523 nm.

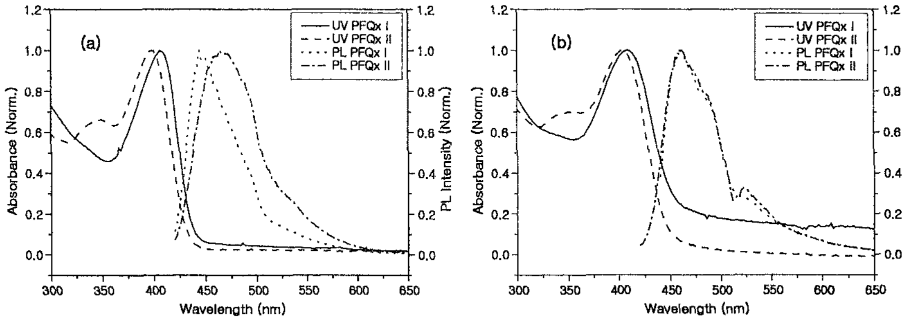


Figure 3. Absorption spectra and photoluminescence spectra of the polymers in (a) chloroform solution (10^{-5} M) and (b) thin films.

Multilayered light-emitting diode with the device structure of ITO/PEDOT/PFQx I /PVK blend(2:8)/LiF/Al was fabricated to investigate the electroluminescent properties and the current-voltage characteristic of PFQx I. Polymer film of thickness approximately 100 nm was spin-cast onto a PEDOT layer of thickness approximately 30 nm, which had been pre-cast on the ITO substrate. The electroluminescence from the polymer in the device was blue. As shown in Figure 4(a), the EL spectrum of PFQx I shows maximum peak at 460 nm. This feature is similar to that observed in the PL spectra of the corresponding polymer film. The turn-on voltage is 13 V from *J*-*V* curve. The external quantum efficiency of this device was 0.013% photons per electron.

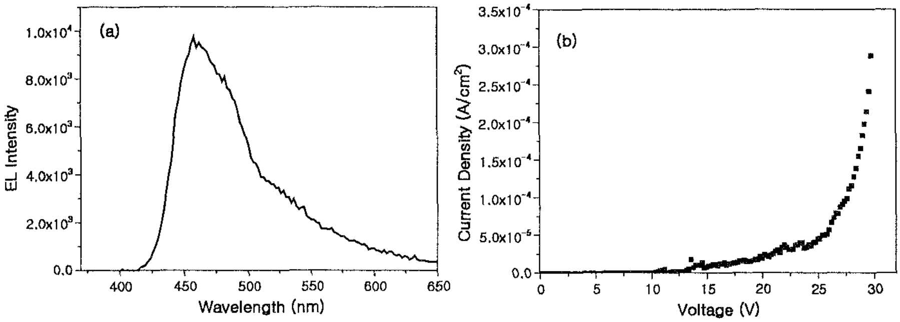


Figure 4. (a) EL spectrum of PFQx I in device of configuration ITO/PEDOT/PFQx I /PVK blend(2:8)/LiF/Al and (b) *J*-*V* curve of PFQx I.

Conclusions

New fluorene-linked π-conjugated polyquinoxaline PFQx I and PFQx II have been synthesized and characterized. These polymers possess relatively good solubility and thermal stability. The resulting polymers exhibit a UV-visible absorption band in the range 397-407 nm in chloroform solution and in the film state. Upon photo-excitation around the absorption maximum wavelength, their PL spectra show a maximum band around 447-467 nm in the blue region. The light-emitting diode of ITO/PEDOT/PFQx I /PVK blend(2:8)/LiF/Al was successfully fabricated. *J-V* curve shows a turn-on voltage of 13 V. The EL spectrum of PFQx I gives a highest peak in the blue EL emissive band at 460 nm. The external quantum efficiency of this device was found to be 0.013% photons per electron. Intensive studies on the electron-transporting/hole-blocking properties of these polymers in LED devices are in progress.

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