

New Fluorene–Pyrazino[2,3-g]quinoxaline-Conjugated Copolymers: Synthesis, Optoelectronic Properties, and Electroluminescence Characteristics

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ABSTRACT: New donor–acceptor conjugated copolymers called poly[2,7-(9,9'-dihexylfluorene)-*co*-5,10-[pyrazino(2,3-g)quinoxaline]s or PFPQs [where F represents the 2,7-(9,9'-dihexylfluorene) moiety and PQ represents the 5,10-(pyrazino[2,3-g]quinoxaline) moiety], synthesized by the palladium-catalyzed Suzuki coupling reaction, are reported. The PQ contents in the PFPQ copolymers were 0.3, 1, 5, and 50 mol %, and the resulting copolymers were named PFPQ0.3, PFPQ01, PFPQ05, and PFPQ50, respectively. Absorption spectra showed a progressive redshift as the PQ acceptor content increased. The relatively small optical band gap of 2.08 eV for PFPQ50 suggested strong intramolecular charge transfer (ICT) between the F and PQ moieties. The photoluminescence emission peaks of the PFPQ copolymer films also exhibited a large redshift with enhanced PQ contents, ranging from 551 nm for PFPQ0.3 to 592 nm for PFPQ50. However, the PFPQ copolymer based electroluminescence (EL) devices showed poor device performances probably due to the strong confinement of the electrons in the PQ moiety or significant ICT. This problem

was resolved with a binary blend of poly[2,7-(9,9-dihexylfluorene)] (PF) and PFPQ with a volume ratio of 95/5 (BPQ05). Multiple emission peaks were observed at 421, 444, 480, 516, and 567 nm in the BPQ05-based EL devices because the low PQ content led to incomplete energy transfer. The Commission Internationale de L'Eclairage 1931 coordinates of the BPQ05-based EL device were (0.31, 0.32), which were very close to the standard white emission of (0.33, 0.33). Furthermore, the maximum luminescence intensity and luminescence yield were 524 cd/m² and 0.33 cd/A, respectively. This study suggested that a pure white light emission was achieved with the PFPQ copolymers or PF/PFPQ blends through the control of the energy transfer between F and PQ. Such PFPQ copolymers or PF/PFPQ blends would be interesting for electronic and optoelectronic devices. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2094–2101, 2009

Key words: conjugated polymers; light-emitting diodes (LED); luminescence; photophysics; thin films

INTRODUCTION

Scientific interest in conjugated polymers remains high because of their potential optoelectronic applications, including light-emitting diodes (LEDs),¹ thin-film transistors,² and photovoltaic devices.³ The electronic structure of conjugated polymers is one of the most important factors controlling their device applications. Donor–acceptor conjugated polymers have been extensively studied recently because their electronic and optoelectronic properties can be tuned through efficient intramolecular charge transfer (ICT).^{4–6}

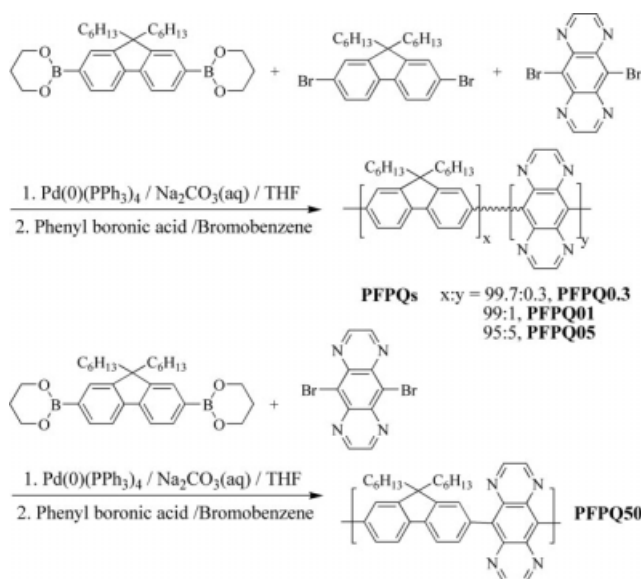
Polyfluorene is one of the promising candidates for polymer LEDs^{4(a,b),7} because of its processability and charge transport characteristics.⁸ Fluorene-based

copolymers with various acceptors can not only improve the electron-transport properties but also tune the emission colors.^{4(a,b),9} By the incorporation of acceptors with different acceptor strengths or contents, full-color and pure white emissions have been achieved in various fluorene-based copolymers and blends.⁹ In our reported theoretical results, an alternating fluorene–pyrazinoquinoxaline copolymer showed a relatively small band gap and high electronic affinity.¹⁰ However, the synthesis and optoelectronic properties of fluorene–pyrazinoquinoxaline copolymers and blends have not been fully explored yet.

In this article, the synthesis, properties, and electroluminescence (EL) characteristics of new conjugated copolymers called poly[2,7-(9,9'-dihexylfluorene)-*co*-5,10-[pyrazino(2,3-g)quinoxaline]s or PFPQs [where F represents the 2,7-(9,9'-dihexylfluorene) moiety and PQ represents the 5,10-(pyrazino[2,3-g]quinoxaline) moiety] and their blends are reported. PFPQs were synthesized by a palladium-catalyzed Suzuki coupling reaction, as shown in Scheme 1.

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Scheme 1 Synthesis of the fluorine-PQ copolymers, PFPQ0.3–PFPQ50.

The copolymers containing 0.3, 1, 5, and 50 mol % concentrations of the PQ moieties were denoted PFPQ0.3, PFPQ01, PFPQ05, and PFPQ50, respectively. Moreover, BPQ05, a blend of poly[2,7-(9,9-dihexylfluorene)] (PF) and PFPQ05 with a volume ratio of 95/5, was also prepared, and its application for pure white emissions was explored. The photophysical properties of the synthesized PFPQ copolymers were compared with those of the parent PF. EL devices fabricated from the synthesized PFPQ copolymer and BPQ05 blend as emissive layers were characterized. The experimental results suggested that the photophysical properties and EL characteristics of the PFPQ copolymers varied significantly with the acceptor contents, and pure white light emissions were obtained with the PFPQ copolymer or PF/PFPQ blend.

EXPERIMENTAL

Materials

2,1,3-Benzothiadiazole, bromine, glacial acetic acid, zinc dust, glyoxal (40 wt % in water), 1,2,4,5-tetraaminobenzene tetrahydrochloride, *N*-bromosuccinimide, 9,9-dihexylfluorene-2,7-bis(trimethyleneborate), 9,9-dihexyl-2,7-dibromofluorene, tetrakis(triphenylphosphine)-palladium(0), potassium carbonate, sodium carbonate, sodium acetate hydrate, sodium hydrogen carbonate, and trioctylmethylammonium chloride (Aliquot 336) were purchased from Aldrich (St. Louis, MO) or Acros (Geel, Belgium) and used without further purification. Ultra-anhydrous solvents used in the reactions were purchased from Tedia (Fairfield, Ohio). 5,10-Dibromopyrazino[2,3-g]quinoxaline (PQBr)¹¹

and poly[2,7-(9'-9-dihexylfluorene)]^{9(d)} were prepared according to the literature procedures.

General polymerization procedure

The general procedure for synthesizing fluorene-acceptor copolymers is shown in Scheme 1. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate), 9,9-dihexyl-2,7-dibromofluorene, PQBr, tetrakis(triphenylphosphine) palladium(0) (2 mol % with respect to the diborate monomer), and several drops of Aliquot 336 were dissolved in tetrahydrofuran (THF) to obtain PFPQ copolymers. To the reaction mixture, degassed and aqueous 2M Na₂CO₃ (3.3 equiv with respect to the diborate monomer) was added. The mixture was refluxed with vigorous stirring for 72 h under a nitrogen atmosphere. The end groups were capped by refluxing for 12 h each with phenyl boronic acid and bromobenzene in sequence (both 1.1 equiv with respect to the diborate monomer). After end capping, the mixture was cooled and poured into a mixture of methanol and water. The precipitated product was dissolved into a small amount of THF and then reprecipitated into methanol to afford its crude polymer. The crude polymer was washed for 24 h with acetone to remove oligomers and catalyst residues and then dried *in vacuo* to obtain the polymer product.

PFPQ0.3

9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (502 mg, 1 mmol), 2.0 mg of PQBr (0.006 mmol), 489.4 mg of 9,9-dihexyl-2,7-dibromofluorene (0.994 mmol), and 15 mL of THF were used to afford 489 mg of a gray solid. The molecular weight data for the polymer obtained from gel permeation chromatography (GPC) were as follows: a weight-average molecular weight (M_w) of 15,920, a number-average molecular weight (M_n) of 8580, and a polydispersity index (PDI) of 1.86.

¹H-NMR (CD₂Cl₂, δ , ppm): 0.79 (br, 10H), 1.14 (br, 12H), 2.15 (br, 4H), 7.62–7.86 (m, br, 6H). FTIR (KBr pellet, cm⁻¹): 3059, 3025, 2931, 2850, 1882, 1780, 1605, 1455, 1401, 1377, 1341, 1287, 1251, 1221, 1161, 1137, 1095, 1018, 999, 885, 813, 753, 723. ANAL. Calcd for C_{23.958}H_{31.916}N_{0.012}: C, 89.96 wt %; H, 9.99 wt %; N, 0.053 wt %. Found: C, 87.32 wt %; H, 9.57 wt %; N, 0.06 wt %.

PFPQ01

9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (502 mg, 1 mmol), 6.8 mg of 5,10-dibromopyrazino[2,3-g]quinoxaline (0.02 mmol), 482.5 mg of 9,9-dihexyl-2,7-dibromofluorene (0.98 mmol), and 15 mL of THF were used to afford 588 mg of a pale yellow solid.

The molecular weight data for the polymer obtained from GPC were as follows: $M_w = 11,740$, $M_n = 7580$, and PDI = 1.55.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 0.79 (br, 10H), 1.17 (br, 12H), 2.15 (br, 4H), 7.63–7.88 (m, br, 6H). FTIR (KBr pellet, cm^{-1}): 3060, 3032, 2924, 2857, 1890, 1775, 1606, 1457, 1403, 1377, 1337, 1255, 1133, 1039, 998, 944, 890, 809, 755, 728, 700. ANAL. calcd for $\text{C}_{23.86}\text{H}_{31.72}\text{N}_{0.04}$: C, 89.87 wt %; H, 9.96 wt %; N, 0.18 wt %. Found: C, 88.43 wt %; H, 9.03 wt %; N, 0.16 wt %.

PFPQ05

9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (502 mg, 1 mmol), 34 mg of PQBr (0.1 mmol), 443 mg of 9,9-dihexyl-2,7-dibromofluorene (0.9 mmol), and 15 mL of THF were used to afford 570 mg of a pale yellow solid. The molecular weight data for the polymer estimated from GPC were as follows: $M_w = 46,650$, $M_n = 19,740$, and PDI = 2.36.

$^1\text{H-NMR}$ (CD_2Cl_2 , δ , ppm): 0.79 (br, 10H), 1.15 (br, 12H), 2.17 (br, 4H), 7.63–7.88 (m, br, 6H), 8.96 (m, br, 0.09H). FTIR (KBr pellet, cm^{-1}): 3060, 3016, 2931, 2850, 1890, 1782, 1606, 1457, 1403, 1376, 1336, 1254, 1134, 1106, 1039, 998, 971, 890, 809, 755, 728. ANAL. calcd for $\text{C}_{23.3}\text{H}_{30.6}\text{N}_{0.6}$: C, 89.32 wt %; H, 9.78 wt %; N, 0.89 wt %. Found: C, 89.19 wt %; H, 8.83 wt %; N, 0.81 wt %.

Poly[2,7-(9,9'-dihexylfluorene)-*alt*-5,10-(pyrazino[2,3-*g*]quinoxaline)] (PFPQ50)

9,9-Dihexylfluorene-2,7-bis(trimethyleneborate) (250 mg, 0.5 mmol), 170 mg of PQBr (0.5 mmol), and 80 mL of THF were used to afford 135 mg of an orange solid (52.73%). The molecular weight data for the polymer estimated from GPC were as follows: $M_w = 4505$, $M_n = 3270$, and PDI = 1.38.

$^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 0.78 (br, 10H), 1.17 (br, 12H), 2.03 (br, 4H), 7.68–8.02 (m, br, 6H), 8.98 (m, br, 4H). FTIR (KBr pellet, cm^{-1}): 3031, 2957, 2925, 2843, 1931, 1687, 1605, 1499, 1450, 1377, 1336, 1312, 1255, 1092, 1045, 1019, 970, 864, 807, 750. ANAL. calcd for $\text{C}_{35}\text{H}_{36}\text{N}_4$: C, 82.03 wt %; H, 7.03 wt %; N, 10.94 wt %. Found: C, 79.25 wt %; H, 7.16 wt %; N, 9.04 wt %.

Preparation of the PF/PFPQ blend

PF and PFPQ05 in THF were prepared at a concentration of 1 wt % (10 mg of the polymer in 1 g of THF) individually. Then, they were mixed at the volume ratio of 95/5 to obtain a PF/PFPQ05 polymer blend solution called BPQ05.

Characterization

$^1\text{H-NMR}$ data were obtained with a Bruker (Rheinstetten/Karlsruhe, Germany) AV 500-MHz spec-

trometer. GPC analysis was performed on a Lab Alliance (State College, PA) RI2000 instrument (two columns, mixed C and D, from Polymer Laboratories, Shropshire, England) connected to one refractive-index detector from Schambeck SFD GmbH (Babbonnef, Germany). All GPC analyses were performed with a polymer/THF solution at a flow rate of 1 mL/min at 40°C and were calibrated with polystyrene standards.

Thermogravimetric analysis (TGA) measurements were performed under a nitrogen atmosphere at a heating rate of 20°C/min with a TA Instruments (New Castle, DE) TGA-951. Differential scanning calorimetry (DSC) measurements were performed under a nitrogen atmosphere at a heating rate of 10°C/min from 0 to 300°C with a TA Instruments DSC-910S. UV-vis absorption and photoluminescence (PL) spectra were recorded on a Jasco (Tokyo, Japan) V-570 UV-vis/near-infrared spectrometer and a Fluorolog-3 spectrofluorometer (Jobin Yvon, North Edison, NJ), respectively. For the solution spectra, polymers were dissolved in chloroform (ca. 10^{-5} M) and then put into a quartz cell for measurement. For the thin-film spectra, polymers were first dissolved in chloroform (1 wt %) and then spin-coated onto a glass substrate at 1000 rpm for 60 s. Then, the thin-film samples were dried at 60°C *in vacuo*.

The electrochemical properties of the polymer films were investigated with a Princeton Applied Research (Oak Ridge, TN) model 273A potentiostat/galvanostat with a 0.1M acetonitrile solution (>99.5%; Tedia) containing tetrabutylammonium hexafluoroborate (Fluka, Buche, Switzerland; >99.9%) as the electrolyte. Platinum wire and rod-tip electrodes were used as the counter and working electrodes, respectively. Silver/silver ion [silver in 0.1M AgNO_3 (Acros; 99.8%) in the supporting electrolyte solutions] was used as a reference electrode. A 3 wt % solution of the polymer in THF was used to prepare the polymer film on the platinum rod-tip electrode. Then, the cyclic voltammetry (CV) of the films was performed on a three-electrode cell. The reference electrode was calibrated with the CV of ferrocene without any polymer added to the solution. The cyclic voltammograms were obtained at a voltage scan rate of 50 mV/s. The potential values obtained versus an Fc^+/Fc standard were converted to the saturated calomel electrode (SCE) scale by the addition of a constant voltage to them. The energy parameters, the ionization potential (EA) and electron affinity (IP), were estimated from the measured redox potentials on the basis of previous work on conjugated polymers that has shown the following: $\text{IP} = (E_{\text{onset}}^{\text{ox}} + 4.4)$ and $\text{EA} = (E_{\text{onset}}^{\text{red}} + 4.4)$, where the onset potentials for oxidation ($E_{\text{onset}}^{\text{ox}}$) and reduction ($E_{\text{onset}}^{\text{red}}$) are in volts (vs SCE) and IP and EA are in electron volts. The constant of 4.4 eV in the relation

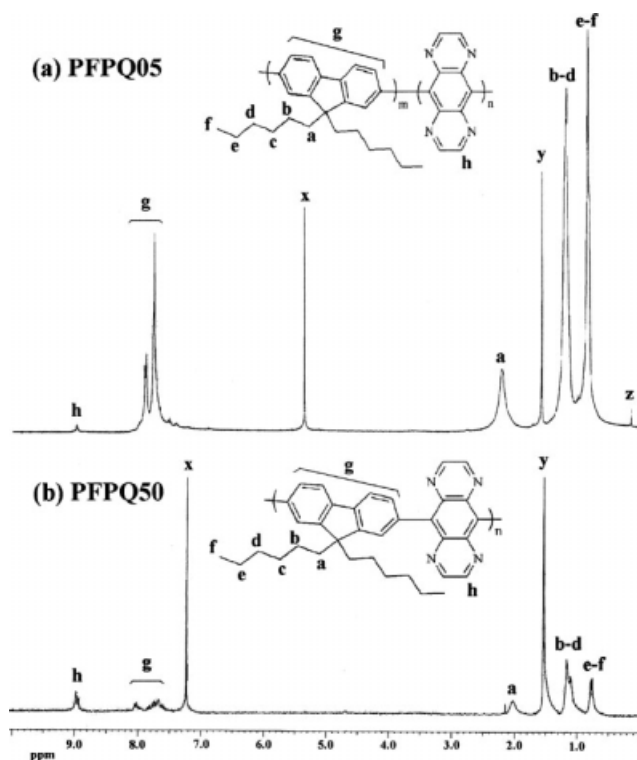


Figure 1 $^1\text{H-NMR}$ spectra of (a) PFPQ05 and (b) PFPQ50 ($x = d$ -solvent; $y = \text{H}_2\text{O}$; $z = \text{TMS}$).

of the IP, EA, and redox potentials is the SCE energy level versus a vacuum. The electronic structure parameters, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), were estimated with the relation of $\text{HOMO} = -\text{IP}$ and $\text{LUMO} = -\text{EA}$ by the assumption of no configuration interactions.

Device fabrication and testing

The EL devices were fabricated on a indium tin oxide (ITO) coated glass substrate with a sheet resistance of 20–30 Ω/Sq . The substrate was ultrasonically cleaned with detergent, deionized water, acetone, and methanol subsequently. On the ITO glass, a layer of poly(ethylene dioxythiophene) (PEDOT):poly(styrene sulfonate) (PSS), measured to be 50–60 nm thick (probed with an Alpha-Step 500 surface profiler from Tencor, San Jose, CA), was formed via spin coating from its aqueous solution (Baytron P 8000, Bayer, Leverkusen, Germany). The emissive layer was spin-coated at 1500 rpm from the corresponding *p*-xylene solution (1.5 wt %) on top of the vacuum-dried PEDOT:PSS layer. The nominal thickness of the emissive layer was 60–70 nm. Under a base pressure below 2×10^{-4} Torr, a layer of calcium (10 nm) was vacuum-deposited as a cathode, and a thick layer of silver (100 nm) was deposited subsequently as the protecting layer. The cathode

area defines the active area of the device, which was 0.1256 cm^2 in this study.

Current–voltage characteristics were measured with a Keithley (Cleveland, OH) 2400 computerized source measure unit. The luminance and Commission Internationale de L'Eclairage (CIE) coordinates of the device were measured with a Konica-Minolta (Tokyo, Japan) CS-100A chroma meter. The EL spectrum of the device was recorded on a Fluorolog-3 spectrofluorometer (Jobin Yvon).

RESULTS AND DISCUSSION

Synthesis and characterization

Figure 1(a,b) shows the $^1\text{H-NMR}$ spectra of PFPQ05 in CD_2Cl_2 and PFPQ50 in CDCl_3 , respectively. The signals in the ranges of 0.79–2.17 and 7.39–7.88 ppm are assigned to the hexyl and phenylene protons of the fluorene moiety, respectively. The proton signal around 8.96–8.98 ppm is attributed to the PQ moiety, and its intensity increases from PFPQ05 to PFPQ50 as expected. However, for PFPQ0.3 and PFPQ01 with very low PQ contents, only the signals contributing to the fluorene moiety can be observed. Figure 2 illustrates the FTIR spectra of PFPQ05 and PFPQ50. A comparison of the FTIR spectra of PFPQ05 and PFPQ50 shows only small peaks with weak intensities in the region of $1700\text{--}1600 \text{ cm}^{-1}$ for the former but relatively intense peaks for the later. Hence, the small peaks are attributed to C=C stretching because the FTIR spectra of PF and PFPQ05 are almost the same. However, the large peaks in the region of $1700\text{--}1600 \text{ cm}^{-1}$ of the PFPQ50 spectrum can probably be attributed to the C=N group of the PQ moiety. Note that the FTIR spectrum of PFPQ05 is almost the same as that of PF^{9(d)} because of the relatively low acceptor content. The experimental

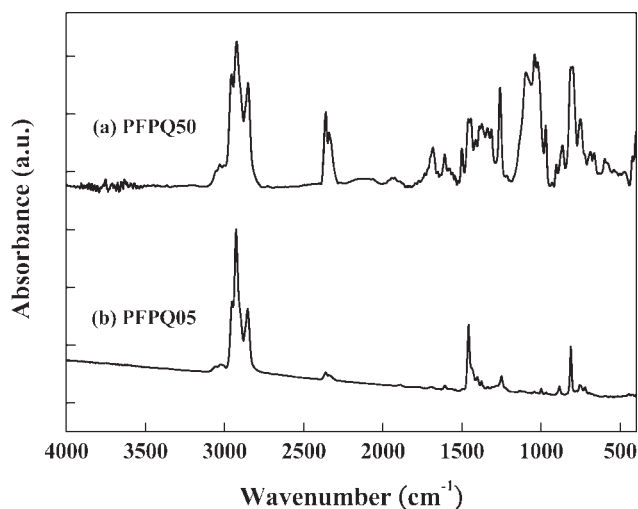


Figure 2 FTIR spectra of (a) PFPQ50 and (b) PFPQ05 on KBr.

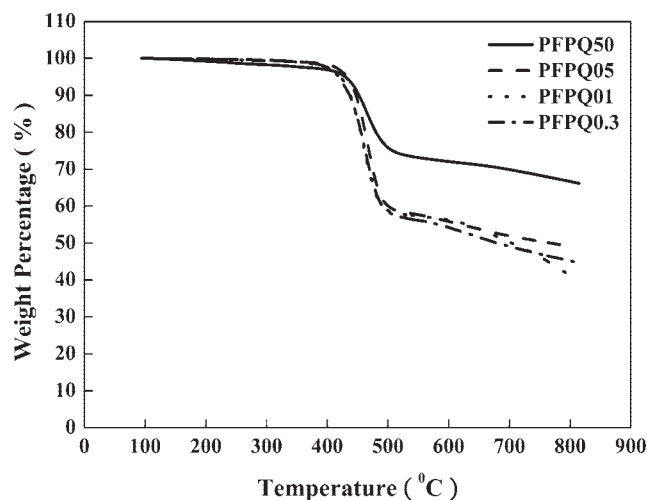


Figure 3 TGA curves of the PFPQs.

carbon, hydrogen, and nitrogen contents of the synthesized polymers, except for PFPQ50, are in good agreement with the theoretical values, and the 2.8% difference in the carbon content of PFPQ50 could be due to the end-group effect of the low-molecular-weight polymer. In summary, these results suggest the successful preparation of the target copolymers.

All the prepared copolymers are readily soluble in common organic solvents such as chloroform, THF, and toluene. The M_w and PDI values of the chloroform-soluble fractions PFPQ0.3, PFPQ01, PFPQ05, and PFPQ50 are 15,920 and 1.86, 11,740 and 1.55, 46,650 and 2.36, and 4505 and 1.38, respectively. The poor solubility of the rigid PQ structure could limit the production of a high molecular weight during polymerization.

Thermal properties

Figure 3 shows the TGA curves of the prepared polymers at a heating rate of 20°C/min under a nitrogen atmosphere. The onset decomposition temperatures of PFPQ50, PFPQ05, PFPQ01, and PFPQ0.3 can be observed at 432, 450, 445, and 423°C, respectively. The high decomposition temper-

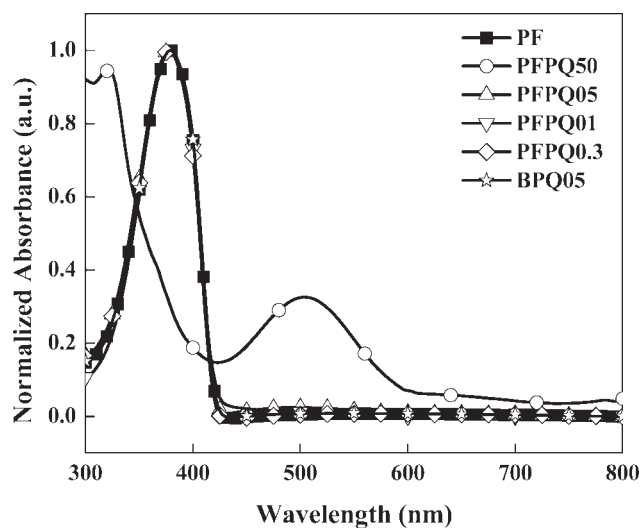


Figure 4 Optical absorption spectra of PF, PFPQ series copolymers, and binary blends (BPQ05 : PF/PFPQ05 = 95 : 5) in thin films.

atures indicate that PFPQ copolymers possess considerable thermal stability. The glass-transition temperatures of PFPQ0.3, PFPQ01, and PFPQ05, as measured by DSC, are 65, 67, and 72°C, respectively, and they increase with the PQ content increasing. However, the DSC curve of PFPQ50 does not show any significant transition, and this indicates that the polymer chain mobility is suppressed by the rigid backbone.

Optical absorption properties

The normalized optical absorption spectra of thin films of PFPQ copolymers are shown in Figure 4, and the corresponding absorption maximum ($\lambda_{\max}^{\text{abs}}$) values are summarized in Table I. The absorption spectra of all the random copolymers and blend systems display one major $\lambda_{\max}^{\text{abs}}$ value at 384 nm attributed to the π - π^* transition of the conjugated fluorene segments in the polymer chains. As the acceptor content increases to 5%, small absorption shoulders can be observed around 488 nm for

TABLE I
Optical and Electrochemical Properties of the Polymers

	$\lambda_{\max}^{\text{abs}}$ (nm)	E_g^{opt} (eV)	$\lambda_{\max}^{\text{PL}}$ (nm)		Oxidation (vs SCE)		Reduction (vs SCE)		E_g^{ec} (eV)
			Solution	Thin film	$E_{\text{onset}}^{\text{ox}}$ (V)	HOMO (eV)	$E_{\text{onset}}^{\text{red}}$ (V)	LUMO (eV)	
PF	368	2.95	412, 437	424, 445	0.99	-5.39	—	-2.44 ^a	—
PFPQ50	506	2.08	580	592	0.89	-5.29	-1.35	-3.05	2.24
PFPQ05	380	2.17	413, 439, 471, 580	422, 445, 582	0.95	-5.35	-1.34	-3.06	2.29
PFPQ01	380	2.95	413, 439, 471	418, 442, 473, 559	0.94	-5.34	-1.41	-2.99	2.35
PFPQ0.3	380	2.95	413, 439, 471	418, 443, 475, 551	—	—	—	—	—
BPQ05	380	—	—	424, 447, 556	—	—	—	—	—

^a Estimated by the following relation: LUMO = E_g^{opt} + HOMO.

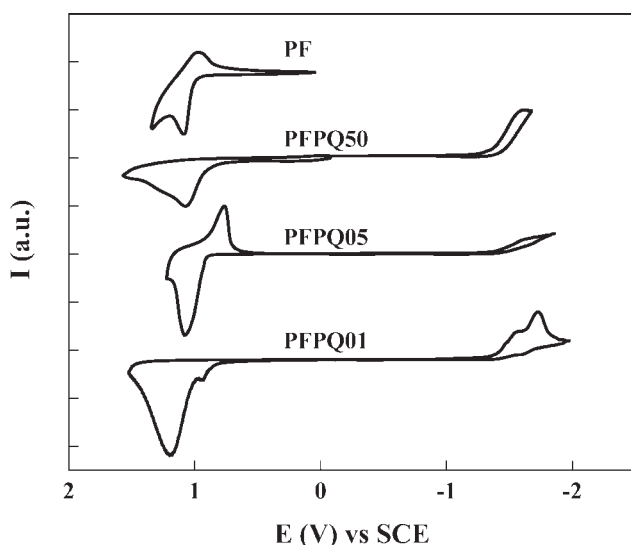


Figure 5 CV of the PF and PFPQs. I, current; E, potential.

PFPQ05, and these are attributed to the PQ unit. In comparison with the random copolymers, the alternating copolymer of PFPQ50 exhibits a main absorption peak at 506 nm. The significantly redshifted absorption peaks versus that of PF at 368 nm suggest efficient ICT between the electron-donating fluorene moiety and the electron-accepting PQ moiety.

The optical band gap [E_g^{opt} (eV)] values of the studied copolymers, estimated from the absorption edges in Figure 4, are listed in Table I. The trend of the band gap variation versus the PQ contents shows that a lower band gap is obtained with an increasing acceptor percentage for PFPQ copolymers. As the acceptor content increases to 50%, the corresponding E_g^{opt} value, as low as 2.08 eV for PFPQ50, is obtained. E_g^{opt} of PFPQ50 is much lower than that of PF (2.95 eV) or poly[2,7-(9,9'-dihexylfluorene)-*alt*-5,8-quinoxaline] (2.64 eV).^{9(d)} The much smaller band gap of PFPQ50 results from the strong accepting characteristic of the PQ moiety, which lead to the efficient ICT between the fluorene and PQ moiety. The aforementioned trend of E_g^{opt} is in good agreement with the theoretical prediction reported previously by our group.¹⁰

Electrochemical properties

The oxidation and reduction potentials of these polymers were investigated with CV. Figure 5 shows the cyclic voltammograms of PFPQ copolymers, and the corresponding electrochemical properties are listed in Table I. The HOMO levels of the studied polymers determined by CV are in the range of -5.29 to -5.51 eV, and this is similar to the level of PF (-5.39 eV). However, the LUMO levels of the studied polymers (-2.99 to -3.05 eV) are much lower than the level of PF (-2.44 eV). The decreasing LUMO level

with increasing acceptor content indicates that the incorporation of the PQ acceptor significantly enhances the IP of the studied copolymers. The electrochemical band gap [E_g^{ec} (eV)] values, estimated from the gap between LUMO and HOMO, show a trend similar to that of E_g^{opt} . This again demonstrates the significance of ICT through the incorporation of the acceptor segment into the polyfluorene-based polymer.

PL properties

The normalized PL emission spectra of PFPQ copolymers in dilute chloroform solutions (ca. 10^{-5} M) excited at the wavelength of 380 nm (except for PFPQ50, which was excited at 490 nm) are shown in Figure 6; the corresponding emission maxima ($\lambda_{\text{max}}^{\text{PL}}$) are summarized in Table I. The PL spectra of all the random copolymers exhibit the characteristic emission bands assigned to the polyfluorene segment in the copolymers: the 0–0 transition emission band located at 413 nm, followed by the 0–1 and 0–2 transitions at 439 and 471 nm, respectively. With increasing acceptor content, an additional emission band can be observed around 580 nm for the PFPQ copolymer, which can be attributed to the PQ segment.

Figure 7 shows the PL emission spectra of the copolymer thin films excited at the wavelength of 380 nm; the corresponding $\lambda_{\text{max}}^{\text{PL}}$ values are summarized in Table I. The PL emission spectra of the PFPQ copolymers show that the long-wavelength peak maxima increase with the PQ content increasing from 0.3 to 50%, ranging from 551 nm for PFPQ0.3 to 592 nm for PFPQ50. The emissive peak at 551 nm can be observed at the relatively low PQ content of 0.3% in the solid state but is not shown in a dilute solution. This result suggests that the interchain

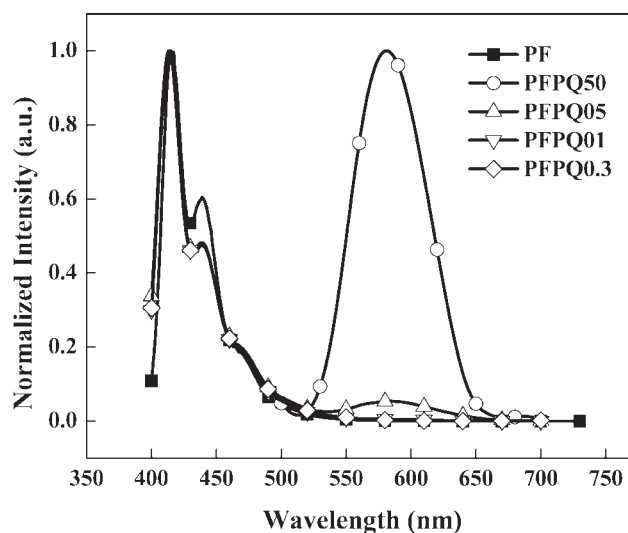


Figure 6 Normalized PL spectra of the PF and PFPQs in dilute CHCl_3 solutions.

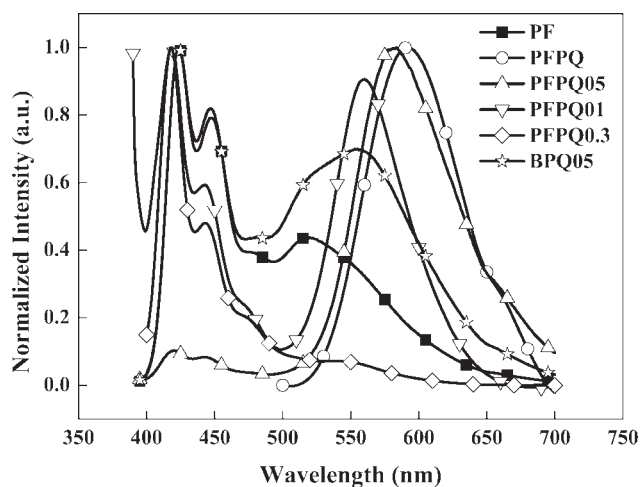


Figure 7 Normalized PL spectra of the PF, PFPQs, and binary blends (BPQ05 : PF/PFPQ05 = 95 : 5) in thin films.

interaction is much stronger in the solid-state film and leads to efficient Förster energy transfer from the PF segment to the PQ acceptor segment. On the other hand, the incomplete Förster energy transfer of PFPQ0.3 leads to the multiple emission peaks at 418, 443, 475, and 551 nm. In the BPQ05 blend with the PQ content of 0.25%, the PL spectrum exhibits emission peaks at 424, 447, and 556 nm. The emission spectra of PFPQ0.3 and BPQ05 cover the entire visible region and thus suggest their potential applications for white light emissions.

EL properties

EL devices based on the PFPQ copolymers and BPQ05 blend as emissive layers were fabricated with the configuration ITO/PEDOT: PSS/Ca/Ag. Figure 8 shows the EL spectra of the PFPQ-based devices, and the corresponding performance parameters are summarized in Table II. Similarly to the PL spectra, the PF emission decreases gradually with increasing PQ content because of energy transfer, and the peak intensity is much lower in the case of EL. Such a sig-

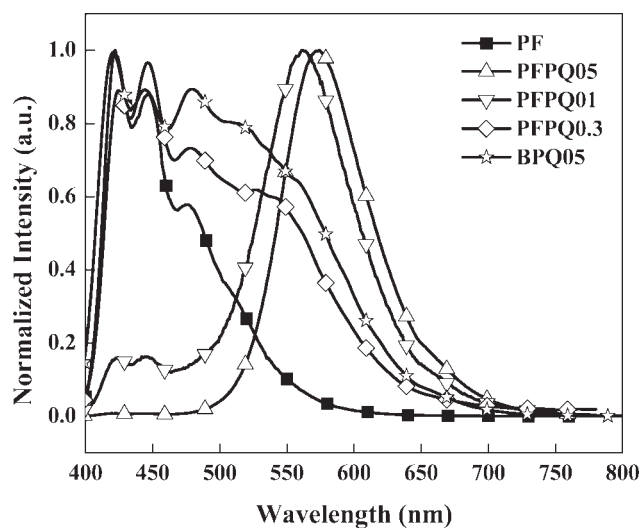


Figure 8 Normalized EL spectra of the PF, PFPQs, and binary blends (BPQ05 : PF/PFPQ05 = 95 : 5) as emissive layers.

nificant difference between PL and EL spectra is attributed to the difference between the emission mechanisms of photo and electric excitations.^{12,13} In the case of PL spectra, the long-wavelength emission of PFPQ01 is not dominant because of the significant steric hindrance of the PQ moiety along the copolymer backbone and the incomplete Förster energy transfer from PF to PQ. The LUMO levels of the PFPQ copolymers are around 2.99–3.10 eV, and this is much lower than the level of the PF homopolymer (by 2.12 eV). Therefore, the strong emission from the PQ segment in EL is probably dominated by the charge trapping mechanism.¹³ Because of the strong acceptor ability of the PQ segment in the copolymers, the electron injection from Ca/Ag electrodes would be confined in PQ segments efficiently, and thus the dominant EL emission from the PQ segment can be observed.

Table II lists the EL characteristics of the studied copolymers. The luminance intensities of PFPQ05, PFPQ01, and PFPQ0.3 are 71, 145, and 15 cd/m², respectively, under the condition of the maximum

TABLE II
Luminescence Characteristics of the Studied Polymers

	$\lambda_{\text{max}}^{\text{EL}}$ (nm)	Bias (V)	Luminance (cd/m ²)	Luminance yield (cd/A)	Chromaticity coordinates ^a	
					X	y
PF	425, 445, 475	10.5	103	0.188	0.221	0.264
PFPQ05	574	14	71.1	0.045	0.536	0.461
PFPQ01	564, 446, 422	9.5	145	0.148	0.468	0.468
PFPQ0.3	540, 481, 446, 423	12	15.3	0.030	0.341	0.391
BPQ05	421, 444, 480, 516, 567	10	524	0.33	0.310	0.322

The device structure was as follows: ITO/PEDOT : PSS/emissive layer/Ca/Ag. The values were measured at the maximum luminance yield.

^a CIE 1931 coordinates.

luminance yield. The CIE 1931 coordinates of the LED with PFPQ copolymers changes from (0.341, 0.391) for PFPQ0.3 to (0.536, 0.461) for PFPQ05. The EL emissive color changes from white to orange with increasing PQ content. This result indicates that the color tuning of the EL devices through the incorporation of different contents of the acceptor is feasible. However, in comparison with the luminescence intensity of 103 cd/m² of the PF-based EL device, no improvement in the luminescence intensities of the PFPQ-based EL device has been observed. The poor LED performances can be explained as followed: although the PQ moiety improves the electron transport properties in contrast to PF, the much lower LUMO level of the PFPQs probably leads to the confinement of electrons in the PQ moiety and the reduction of exciton formation. In addition, the PQ moiety with four nitrogen atoms as a strong acceptor enhances the ICT effect and leads to the reduction of the luminescence efficiency.^{9(d)} Fortunately, such poor device performance could be significantly improved by a PF/PFPQ binary blend. An EL device with the binary blend BPQ05 as the emissive layer showed a spectrum with multiple emission peaks at 421, 444, 480, 516, and 567 nm because the low PQ content led to incomplete energy transfer. Such a wide-wavelength-range emissive performance would be of interest for pure white emissions. The CIE 1931 coordinates of the BPQ05-based EL device are (0.31, 0.32), which are very close to those of the standard white emission, (0.33, 0.33). The maximum luminescence intensity and luminescence yield are 524 cd/m² and 0.33 cd/A, respectively. The experimental results suggest that the photophysical properties and EL characteristics of the PFPQ copolymers vary significantly with the acceptor content. Also, a pure white light emission could be obtained with the PFPQ copolymer or BPQ05 blend.

CONCLUSIONS

New fluorene pyrazino[2,3-*g*]quinoxaline copolymers were successfully synthesized through a palladium-catalyzed Suzuki coupling reaction. The absorption or luminescence spectra showed a progressive redshift as the PQ acceptor content increased. The relatively small E_g^{opt} value of 2.08 eV of PFPQ50 suggested strong ICT between the fluorene and pyrazino[2,3-*g*]quinoxaline. A pure white light emission could be achieved with PFPQ copolymers or blends with a relatively low PQ content (~ 0.25–0.3%) through the control of the energy transfer between F and PQ. This study suggests that the tunable electronic and optoelectronic properties of PFPQ copolymers and blends may have potential device applications.

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References

- (a) Braun, D.; Heeger, A. J. *Appl Phys Lett* 1991, 58, 1982; (b) Zhu, Y.; Alam, M. M.; Jenekhe, S. A. *Macromolecules* 2003, 36, 8958; (c) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. *Adv Mater* 2000, 12, 1737.
- (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* 1998, 280, 1741; (b) Sirringhaus, H.; Kawase, T.; Friend, R. H.; Shimoda, T.; Inbasekaran, M.; Wu, W.; Woo, E. P. *Science* 2000, 290, 2123; (c) Bao, Z.; Lovinger, A. J. *Chem Mater* 1999, 11, 2607.
- (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* 1995, 270, 1789; (b) Granström, M.; Petritsch, K.; Arias, A. C.; Lux, A.; Andersson, M. R.; Friend, R. H. *Nature* 1998, 395, 257; (c) Halls, J. J. M.; Pichler, K.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Appl Phys Lett* 1996, 68, 3120.
- (a) Chen, M.; Perzon, E.; Andersson, M. R.; Marcinkevicius, S.; Jönsson, S. K. M.; Fahlman, M.; Berggren, M. *Appl Phys Lett* 2004, 84, 3570; (b) Wu, W. C.; Lee, W. Y.; Chen, W. C. *Macromol Chem Phys* 2006, 207, 1131; (c) Hancock, J. M.; Gifford, A. P.; Zhu, Y.; Lou, Y.; Jenekhe, S. A. *Chem Mater* 2006, 18, 4924; (d) Sonmez, G.; Sonmez, H. B.; Shen, C. K. F.; Jost, R. W.; Rubin, Y.; Wudl, F. *Macromolecules* 2005, 38, 669.
- (a) Babel, A.; Wind, J. D.; Jenekhe, S. A. *Adv Funct Mater* 2004, 14, 891; (b) Yamamoto, T.; Yasuda, T.; Sakai, Y.; Aramaki, S. *Macromol Rapid Commun* 2005, 26, 1214; (c) Yamamoto, T.; Kokubo, H.; Kobashi, M.; Sakai, Y. *Chem Mater* 2004, 16, 4616; (d) Zhu, Y.; Champion, R. D.; Jenekhe, S. A. *Macromolecules* 2006, 39, 8712.
- (a) Brabec, C. J.; Winder, C.; Sariciftci, N. S.; Hummelen, J. C.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Adv Funct Mater* 2002, 12, 709; (b) Zhou, Q.; Hou, Q.; Zheng, L.; Deng, X.; Yu, G.; Cao, Y. *Appl Phys Lett* 2004, 84, 1653; (c) Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganäs, O.; Andersson, M. R. *Adv Mater* 2003, 15, 988; (d) Scharber, M. C.; Mühlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv Mater* 2006, 18, 789.
- Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn J Appl Phys* 1991, 30, L1941.
- (a) Snaith, H. J.; Greenham, N. G.; Friend, R. H. *Adv Mater* 2004, 16, 1640; (b) Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C.-W.; Ho, Peter, K. H.; Friend, R. H. *Nature* 2005, 434, 194.
- (a) Herguth, P.; Jiang, X.; Liu, M. S.; Jen, A. K. Y. *Macromolecules* 2002, 35, 62094; (b) Hou, Q.; Zhou, Q.; Zhang, Y.; Yang, W.; Yang, R.; Cao, Y. *Macromolecules* 2004, 37, 6299; (c) Kulkarni, A. P.; Zhu, Y.; Jenekhe, S. A. *Macromolecules* 2005, 38, 1553; (d) Wu, W.-C.; Liu, C.-L.; Chen, W.-C. *Polymer* 2006, 47, 527; (e) Gadisa, A.; Perzon, E.; Andersson, M. R.; Inganäs, O. *Appl Phys Lett* 2007, 90, 113510; (f) Kinder, L.; Kanicki, J.; Petroff, P. *Synth Met* 2004, 146, 181.
- Wu, W.-C.; Chen, W.-C. *J Polym Res* 2006, 13, 441.
- (a) Kobayashi, T.; Kobayashi, S. *Eur J Org Chem* 2002, 13, 2066; (b) Ono, K.; Okazaki, Y.; Ohkita, M.; Saito, K.; Yamashita, Y. *Heterocycles* 2004, 63, 2207.
- McGehee, M. D.; Bergstedt, T.; Zhang, C.; Saab, A. P.; O'Regan, M. B.; Bazan, G. C.; Srdanov, V. I.; Heeger, A. J. *Adv Mater* 1999, 11, 1349.
- Gong, X.; Ostrowski, J. C.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv Funct Mater* 2003, 13, 439.