

Polyfluorene Containing Diphenylquinoline Pendants and Their Applications in Organic Light Emitting Diodes

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ABSTRACT: We present a short, efficient synthetic route for the preparation of a novel polyfluorene copolymer (PF-Q) containing two electron-deficient, 2,4-diphenylquinoline groups functionalized at the C-9 positions of alternate fluorene units that form a three-dimensional cardostructure. The presence of the rigid bulky pendent groups leads to a polyfluorene possessing a high glass-transition temperature (207 °C) and very good thermal stability (5% weight loss observed at 460 °C). A photoluminescence study revealed that the Förster energy transfer from the excited quinoline groups to the polyfluorene backbone is very efficient; it also demonstrated that the commonly observed aggregate/excimer formation in polyfluorenes is suppressed very effectively in this polymer, even after it has been annealed at 150 °C for 20 h. A light emitting diode (LED) device prepared with PF-Q as the emitting layer exhibits a stable blue emission with a maximum brightness of 1121 cd/m² at 12 V and a maximum external quantum efficiency of 0.80% at 250 cd/m². We also used PF-Q, which contains diphenylquinoline units that behave as electron-transporting side chains, as a host material and doped it with 2.4 wt % of a red-emitting phosphorescent dye, Os(fppz), to realize a red electroluminescence with CIE color coordinates of (0.66, 0.34). The doped device exhibits a maximum external quantum efficiency of 6.63% (corresponding a luminance efficiency of 8.71 cd/A) at a current density of 47.8 mA/cm², together with a maximum brightness of 10457 cd/m². © 2005 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 43: 859–869, 2005

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INTRODUCTION

Since poly(phenylene vinylene) (PPV) was first employed in a polymer-based light-emitting diode (PLED) in 1990,¹ the synthesis and properties of light-emitting polymers and their applications in PLEDs have been studied intensively.^{2–5} The

main advantages of organic polymers, when compared with inorganic or molecular organic materials, are the ability to fine-tune the luminescence properties of polymers by manipulating their chemical structure and the feasibility of spin-coating and ink-jet printing processes for preparing large-area display devices. Most electroluminescent conjugated polymers, however, such as PPV and polyfluorene (PF), have a π -excessive nature, that is, they are typical *p*-dope-type polymers, and are hole-transport-dominated materi-

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als.^{6–8} Because the electroluminescent (EL) light in PLEDs arises from the recombination of electrons and holes in active polymer layers, any unipolar characteristics of these conjugated polymers may result in an imbalance in hole and electron injection and/or transport that would lead to a lowering of the efficiency of the device.

To achieve high electroluminescent efficiency, it is necessary to balance the injection and transport of electrons and holes.^{9–17} In this article, we report the synthesis of a fluorene copolymer containing two electron-deficient, 2,4-diphenylquinoline groups functionalized on the C-9 position of the alternating fluorene unit. This polymer design has the advantage of permitting the incorporation of a high concentration of quinoline groups while retaining the conjugation and integrity of the emission spectrum of the PF main chain. We chose PF as the polymer backbone because PFs and their copolymers are very promising candidates for blue light-emitting materials because of their high photoluminescence (PL) and EL efficiencies and good thermal stability, solubility, and film-forming capability.^{18–24} In addition, the facile methods for functionalizing the C-9 position of the fluorene unit also offer the ability to tune the optoelectronic properties of PFs through macromolecular engineering.^{14,15,25–31} We chose to use diphenylquinoline units as the pendent groups because of their electron-deficient nature³² and because several polyquinolines and their copolymers have been demonstrated to be electron injecting/transporting materials in organic light emitting diode (OLED) devices.^{33–38} The incorporation of electron-deficient quinoline groups into fluorene units will result in an increased electron affinity and increased transporting properties of the PF polymer, which will result in a more balanced charge recombination in the polymer emissive layer. Moreover, the presence of sterically demanding substituents may prevent the occurrence of π -stacking between polymer chains and suppress the formation of excimers in the solid state. Taking all of these features into account, we expected that such a PF copolymer would possess good solubility, excellent thermal stability, a low-lying lowest unoccupied molecular orbital (LUMO) energy level, and an efficient and stable blue emission that is highly desirable to serve as a blue emitter by itself or even as a host material to generate the high efficiency saturated red phosphorescence.

EXPERIMENTAL

Materials

2,7-Dibromofluorene (**1**),³⁹ 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctylfluorene (**4**),⁴⁰ 2,4-diphenylquinoline (DPQ),⁴¹ and 1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI)⁴² were prepared according to reported procedures. The solvents were dried with standard procedures. All other reagents were used as received from commercial sources unless otherwise stated.

Characterization

¹H and ¹³C NMR spectra were recorded on a Varian Unity 300 MHz or a Bruker-DRX 300 MHz spectrometer. Mass spectra were obtained on a JEOL JMS-HX 110 mass spectrometer. Size exclusion chromatography (SEC) was performed with a Waters chromatography unit interfaced to a Waters 410 differential refractometer; three 5- μ m Waters styragel columns (300 \times 7.8 mm) were connected in series in order of decreasing pore size (10⁴, 10³, and 10² Å); tetrahydrofuran (THF) was the eluent. Standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed on a Seiko EXSTAR 6000 DSC unit at a heating rate of 20 °C min⁻¹ and a cooling rate of 40 °C min⁻¹. Samples were scanned from 30 to 350 °C, cooled to 0 °C, and then scanned again from 30 to 300 °C. The glass-transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken on a DuPont TGA 2950 instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min⁻¹. UV-visible (UV-vis) spectra were measured with an HP 8453 diode-array spectrophotometer. PL spectra were obtained on a Hitachi F-4500 luminescence spectrometer. Cyclic voltammetry (CV) measurements were performed with a BAS 100 B/W electrochemical analyzer in anhydrous acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at a scanning rate of 50 mV/s. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode with ferrocene as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising and background current of the cyclic

voltammogram. Single-crystal X-ray diffraction data were obtained from a Bruker Smart Apex-CCD diffractometer with $\lambda(\text{Mo-K}\alpha)$ radiation ($\lambda = 0.71073 \text{ \AA}$); data collection was executed with the SMART program. Cell refinement and data reduction were undertaken with the SAINT program. The structure was determined with the SHELXTL/PC program and refined with full-matrix least squares methods.

Fabrication of LEDs

We fabricated LED devices with the structure ITO/poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) (35 nm)/polymer emitting layer (50–70 nm)/TPBI (30 nm)/Mg:Ag (100 nm)/Ag(100 nm). The PEDOT was spin-coated directly onto the indium tin oxide (ITO) glass and dried at 80 °C for 12 h *in vacuo* to improve hole injection and the smoothness of the substrate. The light-emitting layer was spin-coated on top of the PEDOT layer with chlorobenzene as the solvent and the sample was then dried for 3 h at 60 °C *in vacuo*. Before film casting, the polymer solution was filtered through a Teflon filter (0.45 μm). The TPBI layer, which we used as an electron transporting layer that would also block holes and confine excitons, was grown by thermal sublimation in a vacuum of 3×10^{-6} torr.⁴³ Subsequently, the cathode Mg:Ag (10:1, 100 nm) alloy was deposited by coevaporation onto the TPBI layer; this process was followed by placing an additional layer of Ag (100 nm) onto the alloy as a protection layer. The current–voltage–luminance relationships were measured under ambient conditions with a Keithley 2400 source meter and a Newport 1835C optical meter equipped with an 818ST silicon photodiode.

2,7-Dibromo-9,9-bis(4-acetylphenyl)fluorene (2)

A mixture of **1** (3.47 g, 10.7 mmol), 4-fluoroacetophenone (3.40 g, 24.6 mmol), K_2CO_3 (4.43 g, 32.1 mmol), and dimethylformamide (DMF; 18 mL) was heated under reflux for 27 h. The mixture was then poured into water (200 mL). The precipitated product was purified by column chromatography (hexane/EtOAc, 6:1) to yield **2** (3.94 g, 65.8%).

^1H NMR (300 MHz, CDCl_3 , δ): 2.55 (s, 6H), 7.20 (dd, $J = 6.7, 1.8$ Hz, 4H), 7.43 (d, $J = 1.6$ Hz, 2H), 7.52 (dd, $J = 8.1, 1.8$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.85 (dd, $J = 6.8, 1.8$ Hz, 4H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 26.6, 65.5, 121.9, 122.1,

128.0, 128.8, 129.1, 131.6, 136.2, 138.1, 149.0, 151.4, 197.4. High-resolution mass spectrometry (HRMS) [M^+] calcd. for $\text{C}_{29}\text{H}_{21}\text{Br}_2\text{O}_2$ 558.9908, found 558.9908. Anal. Calcd. for $\text{C}_{29}\text{H}_{20}\text{Br}_2\text{O}_2$: C, 62.17; H, 3.60. Found: C, 62.30; H, 3.89.

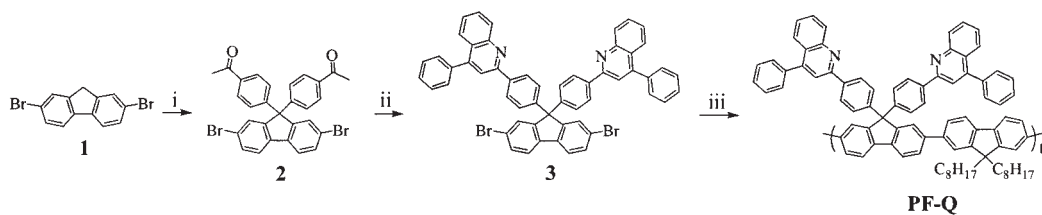
Synthesis of Monomer 3

A mixture of **2** (1.00 g, 1.79 mmol), 2-aminobenzophenone (739 mg, 3.75 mmol), diphenyl phosphate (DPP; 2.23 g, 8.93 mmol), and freshly distilled *m*-cresol (1.0 mL) was flushed with nitrogen while stirring at 65 °C for about 30 min and then heated under nitrogen at 140 °C for 3 h. After cooling, the reaction mixture was added to a solution of 10% (v/v) triethylamine in methanol. The precipitated product was purified by column chromatography (toluene/EtOAc, 10:1) to yield **3** (530 mg, 67.3%).

^1H NMR (300 MHz, CDCl_3 , δ): 7.35 (d, $J = 8.4$ Hz, 4H), 7.43–7.54 (m, 14H), 7.58 (d, $J = 1.6$ Hz, 2H), 7.61 (d, $J = 8.1$ Hz, 2H), 7.71 (ddd, $J = 8.4, 7.0, 1.3$ Hz, 2H), 7.76 (s, 2H), 7.90 (d, $J = 7.6$ Hz, 2H), 8.07 (d, $J = 8.4$ Hz, 4H), 8.23 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3 , δ): 65.4, 119.3, 121.7, 122.0, 125.6, 125.7, 126.4, 127.9, 128.5, 128.6, 129.45, 129.53, 131.2, 138.1, 138.2, 138.8, 145.4, 148.7, 149.3, 152.5, 156.4. HRMS [M^+] calcd. for $\text{C}_{55}\text{H}_{35}\text{N}_2^{79}\text{Br}_2$ 881.1167, found 881.1163. Anal. Calcd. for $\text{C}_{55}\text{H}_{34}\text{N}_2\text{Br}_2$: C, 74.84; H, 3.88; N, 3.17. Found: C, 74.67; H, 4.02; N, 3.09.

Preparation of PF-Q

Aqueous K_2CO_3 (2.0 M, 2.0 mL) and aliquat® 336 (ca. 28 mg) were added to a mixture of monomers **3** (200 mg, 227 μmol) and **4** (146 mg, 227 μmol) in distilled toluene (3.5 mL). The mixture was degassed and tetrakis(triphenylphosphine)palladium (6 mg, 2.5 mol %) was added in one portion under N_2 . The solution was heated at 110 °C for 72 h. The end groups were then capped by heating under reflux for 12 h with benzenboronic acid (58.9 mg, 480 μmol) and then for 12 h with bromobenzene (76 mg, 480 μmol). The reaction mixture was cooled to room temperature and precipitated into a mixture of MeOH and H_2O (1:1 v/v, 100 mL). The crude polymer was collected, washed with excess MeOH, dissolved in chloroform, and then reprecipitated into MeOH. Finally, the polymer was washed with acetone for 48 h with a Soxhlet apparatus and then dried *in vacuo* to yield PF-Q (194 mg, 78.9%).



Reagents: (i) 4-fluoroacetophenone, K_2CO_3 , DMF; (ii) 2-aminobenzophenone, DPP/*m*-cresol; (iii) diboronate **4**, $Pd(PPh_3)_4/K_2CO_3$, toluene/ H_2O /aliquate 336.

Scheme 1

1H NMR (300 MHz, $CDCl_3$, δ): 0.64–0.74 (m, 10H), 1.03 (br, 20H), 2.03 (br, 4H), 7.42–7.58 (m, 20H), 7.67–7.76 (m, 10H), 7.86–7.94 (m, 4H), 8.09 (d, $J = 8.0$ Hz, 4H), 8.20 (d, 2 H, $J = 8.0$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 13.4, 22.5, 23.8, 29.1, 30.0, 31.6, 40.3, 55.3, 65.6, 119.4, 120.0, 120.6, 120.9, 121.3, 124.9, 125.0, 125.6, 125.7, 126.3, 127.2, 127.4, 127.8, 128.4, 128.5, 128.9, 129.5, 130.1, 138.3, 138.5, 139.0, 140.1, 141.5, 147.1, 148.8, 149.1, 151.5, 151.8, 156.8.

RESULTS AND DISCUSSION

Synthesis

Scheme 1 illustrates the synthetic route we followed for the preparation of the PF-Q. Starting from 2,7-dibromofluorene (**1**), which contains an activated methylene group at the C-9 position, our synthetic strategy was based on the nucleophilic aromatic substitution of 4-fluoroacetophenone with the fluorenyl anion generated by the action of K_2CO_3 in DMF. This approach is a simple and direct method for introducing two 4-acetylphenyl groups to the C-9 position of fluorene, that is, for the preparation of 9,9-bis(4-acetylphenyl)-2,7-dibromofluorene (**2**); in comparison, previously reported methods for the synthesis of 9,9-bis(4-acetylphenyl)fluorene require several synthetic steps.^{44,45} Subsequent condensation of **2** with 2-aminobenzophenone, under the conditions of an acid-catalyzed Friedländer reaction, furnished the desired dibromo monomer **3**.^{46,47} The alternating polyfluorene copolymer PF-Q was synthesized by performing a Suzuki coupling reaction between dibromide **3** and the diboronate **4**,⁴⁰ with $Pd(PPh_3)_4$ as the catalyst in a mixture of toluene and aqueous K_2CO_3 (2.0 M) in the presence of Aliquat 336 as a phase transfer reagent. The structure of the polymer we obtained was confirmed by 1H and ^{13}C NMR spectroscopy.

In the ^{13}C NMR spectrum, two signals that superimpose with the signals of the C-9 carbon atom of monomers **3** and **4** appear at $\delta = 65.6$ and 55.3; we ascribed these signals to the C-9 carbon atoms of the two different fluorene units in the copolymer.

To examine the steric requirements of the diphenylquinoline pendent groups, we elucidated the molecular structure of monomer **3** in the solid state by X-ray crystallographic analysis. Single crystals were obtained by slow diffusion of hexane into a chloroform solution of **3**; this monomer cocrystallized with a chloroform solvated molecule. Figure 1 displays the ORTEP plot of **3** determined by X-ray diffraction at 295 K. The aromatic units of the diphenylquinoline group are aligned in a nonplanar arrangement: the substituted phenyl group at the C-4 position is significantly twisted out of the plane of the quinoline ring, as evidenced by the large dihedral angle of about 50° . The key feature of this solid-state structure is that the incorporation of the two 2,4-diphenylquinoline groups at the C-9 position of the fluorene ring results in a rigid three-dimensional cardostructure that may prevent π -stacking or excimer formation.

PF-Q is readily soluble in organic solvents such as chloroform and chlorobenzene, but it is soluble

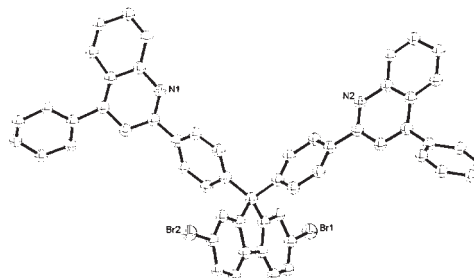


Figure 1. ORTEP diagram of monomer **3** determined by X-ray crystallography. All hydrogen atoms have been omitted for clarity.

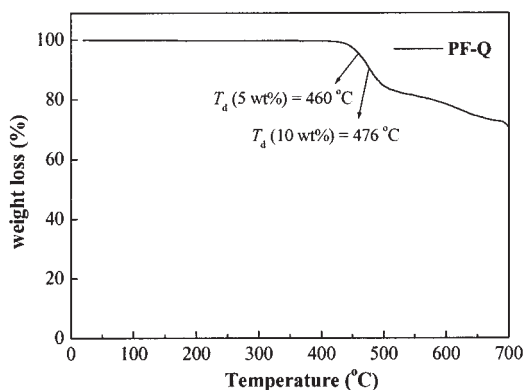


Figure 2. TGA thermogram of PF-Q.

in THF and toluene only on heating. The molecular weight of the polymer was determined by SEC analysis, with THF as the eluent and calibrating against polystyrene standards. The polymer possesses a number-average molecular weight (M_n) of about 2.0×10^4 and a polydispersity index of 3.2. The thermal properties of PF-Q were investigated by TGA and DSC. As revealed by a TGA thermogram (Fig. 2), PF-Q exhibits good thermal stability, with 5% weight loss occurring at 460 °C. In the DSC measurements, we observed a distinct T_g at 207 °C (Fig. 3); in contrast, poly(9,9-dioctylfluorene) (POF), which contains two flexible *n*-octyl chains at the C-9 position of each repeating fluorene unit, exhibited its T_g at 75 °C.⁴⁸ These results indicate clearly that the incorporation of the two rigid, nonplanar diphenylquinoline moieties at the C-9 position of every alternate fluorene unit in the polymer backbone does enhance the chain rigidity of PF-Q and restricts its segmental mobility, which significantly increases both the T_g and the thermal sta-

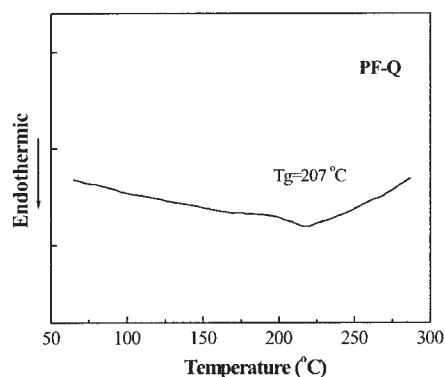


Figure 3. DSC data of PF-Q (heating rate, 20 °C/min) under nitrogen.

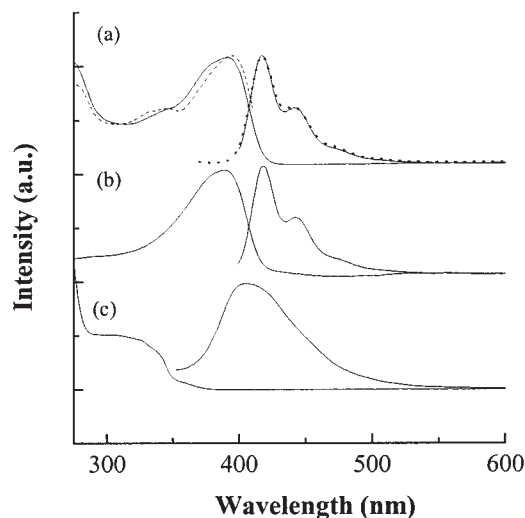


Figure 4. (a) UV-vis absorption (solid line), excitation (dashed line), and PL (solid and dotted line, excited at 390 and 347 nm, respectively) spectra of PF-Q in CHCl_3 solution. UV-vis absorption and PL spectra of (b) POF and (c) DPQ in CHCl_3 .

bility. Such a relatively high T_g , which could prevent morphological change and suppress the formation of aggregates and excimers upon exposure to heat, is desirable for polymers used as emissive materials for light-emitting applications.⁴⁹

Photophysical Properties

The optical properties of the quinoline-containing fluorene copolymer were investigated both in dilute solution and in the solid state (Table 1). Figure 4 presents the absorption and PL spectra of PF-Q, POF, and DPQ, which serves as a model compound in studying the optical properties of the quinoline pendants. In a chloroform solution, PF-Q exhibits its main absorption peak at 391 nm, with an absorption shoulder appearing at 347 nm. In comparison to the absorption spectra of POF and the model compound DPQ, we ascribe the band at 391 nm to a π - π^* transition derived from the conjugated polyfluorene backbone and the shorter-wavelength shoulder to an absorption originating from the pendent quinoline groups. On excitation of the PF main chain at 390 nm, the emission spectrum displays a vibronic fine structure with two sharp bands appearing at 418 and 441 nm. This PL spectrum is nearly identical to that obtained from POF, which indicates that linking quinoline groups to fluorene units through their C-9 carbon atoms does not cause

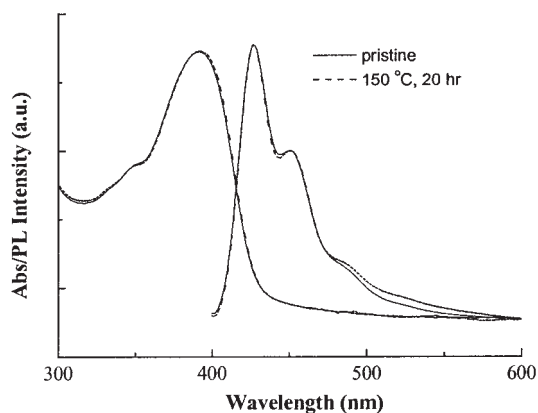


Figure 5. UV-vis absorption and PL spectra of PF-Q film before and after annealing at 150 °C for 20 h under a nitrogen atmosphere.

perturbation of the main chain's conjugation. In addition, the good spectral overlap between the emission bands of the DPQ pendants ($\lambda_{\text{max}} = 405 \text{ nm}$) and the absorption band of the conjugated main chain of PF-Q suggests that most of the excitons formed in the pendant groups by direct photoexcitation are likely to migrate to the PF main chain, from which emission occurs. As a result, the PL spectrum obtained on excitation of the DPQ moieties at 347 nm is the same as that obtained under excitation of the PF backbone at 390 nm; in contrast, no luminescence from the DPQ side chains was detected in the deep-blue region (350–400 nm). Furthermore, the excitation spectrum of PF-Q, monitored at 450 nm, is perfectly superimposed with its absorption spectrum. This observation reveals that the Förster energy transfer from the excited pendant groups to the PF backbone is very efficient. PF-Q exhibits a high quantum yield (Φ_f) in a diluted solution. The PL quantum yield in toluene excited at 365 nm, was 1.0 as measured relative to 9,10-diphenylanthracene ($\Phi_f = 0.9$) as a standard⁵⁰; this value is even higher than that measured for POF ($\Phi_f = 0.85$).

Figure 5 presents the absorption and PL spectra of a PF-Q film spin-coated from a toluene solution onto a quartz plate. In comparison to the dilute solution, the absorption spectrum of the thin film is slightly broadened, whereas the emission spectrum displays a redshift of 8–10 nm. The PL quantum yield of the film was estimated to be 0.54 by comparing its fluorescence intensity with that of the POF polymer thin film sample excited at 380 nm ($\Phi_f = 0.55$).⁵¹ It has been demonstrated that a thin film of POF containing flexible alkyl

chains exhibits poor spectral stability upon exposure to heat.^{48–54} To examine the effect that incorporating rigid and bulky DPQ pendant groups has on the thermal stability of PF-Q, the polymer film was heated for 20 h on a hot plate at 150 °C under a nitrogen atmosphere. The absorption and PL spectra were recorded when the films had cooled to room temperature. As indicated in Figure 5, both the absorption and PL spectra remained almost unchanged after this thermal treatment. In contrast, previous reports have shown that the annealing of a POF film results not only in a bathochromic shift in the PL wavelength and a significant reduction in emission intensity but also in the appearance of an additional emission band between 500 and 600 nm.^{28,59} The cause of the undesirable emissive color instability of the POF film has been attributed to the formation of aggregates and interchain excimers or to keto defects.^{52–58} In the case of PF-Q, because of the presence of the rigid, nonplanar DPQ pendant groups—the steric demand of which restricts close packing of the polymer chains and reduces the probability of interchain interactions—the tendency to form aggregates and excimers in the polymer film on thermal treatment is suppressed. The higher value of the T_g of PF-Q also accounts for the enhanced thermal stability of the polymer film.

Electrochemical Studies

We employed CV to investigate the redox behavior of PF-Q and to estimate its highest occupied molecular orbital (HOMO) and LUMO energy levels. The electrochemical processes of this polymer film coated on a glassy carbon electrode were monitored in a standard three-electrode electrochemical cell with ferrocene as the internal standard in an electrolyte of 0.1 M TBAPF₆ in acetonitrile at a scanning rate of 50 mV/s. By knowing the energy level of the ferrocene/ferrocenium reference, one can calculate the LUMO and HOMO energies with the assumption that the energy level of ferrocene is 4.8 eV below a vacuum.⁶⁰ On the basis of the onset potentials of the oxidation and reduction, which were 0.93 and –2.52 V, respectively, we estimated the HOMO and LUMO energy levels of PF-Q to be 5.73 and 2.28 eV, respectively. For comparison, the same electrochemical experiments were conducted with POF. The onset potentials of the oxidation and reduction of POF were 0.96 and –2.74 V, respectively, and, in turn, we calculated the HOMO and LUMO

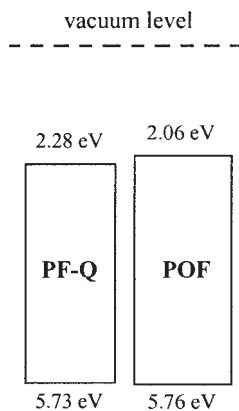


Figure 6. Relative HOMO/LUMO energy levels of PF-Q and POF.

energy levels of POF to be 5.76 and 2.06 eV, respectively; these values are in good agreement with the data reported previously for POF ($I_p = 5.8$ eV; $E_a = 2.12$ eV).⁶¹ Figure 6 depicts the relative HOMO/LUMO energy levels of PF-Q and POF. The markedly lower LUMO energy level of PF-Q that originates from the electron-deficient nature of the quinoline substituents, suggests there may be an increase in the electron affinity and an improvement in the electron injection of the polymer.

EL Properties of LED Devices

To evaluate the potential of PF-Q to behave as a blue emissive material in polymer LED applications, we fabricated a polymer LED with the configuration ITO/PEDOT/PF-Q/TPBI/Mg:Ag. As indicated in the inset of Figure 7, the EL spectrum of PF-Q displays a maximum peak at 428 nm with a shoulder at 451 nm; no undesirable excimer/aggregate emission is observed at a long wavelength as has been reported in the literature for the spectrum of POF. The EL spectrum is almost identical to the corresponding PL spectrum presented in Figure 5; this finding indicates that both the PL and EL originate from the same radiative decay process of the singlet exciton. As displayed in Figure 7, the device based on PF-Q reaches its maximum brightness of 1121 cd/m^2 at 12 V and its maximum external quantum efficiency of 0.80% at 250 cd/m^2 , with a bias of 9.5 V. This device demonstrates a much higher brightness and efficiency than does the device prepared from the unmodified POF that had a maximum brightness of about 600 cd/m^2 and an external quantum efficiency of 0.2%.⁵¹ We attribute the

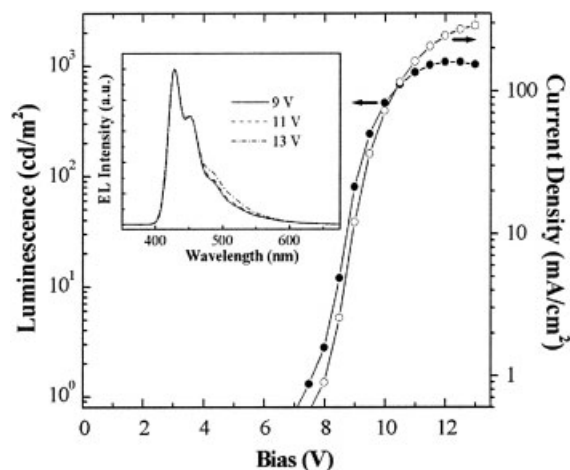


Figure 7. Current density–voltage–luminance characteristics of ITO/PEDOT/PF-Q/TPBI/Mg:Ag. Inset: the corresponding EL spectra recorded at different applied voltages.

improved device performance to the better charge injection and transport from PF-Q and to the efficient energy transfer from the quinoline side chains to the PF main chains. In addition, the introduction of an electron injecting and transporting TPBI layer that is also used for hole blocking and exciton confinement may contribute to the high performance, even though we have used a high-work-function alloy of Mg:Ag as the cathode, rather than Ca. Moreover, the EL spectra of PF-Q exhibited no significant changes as the applied voltage was increased. Thus, the phenylquinoline pendent groups in PF-Q do simultaneously provide both the functions of suppressing the aggregation and improving the charge injection.

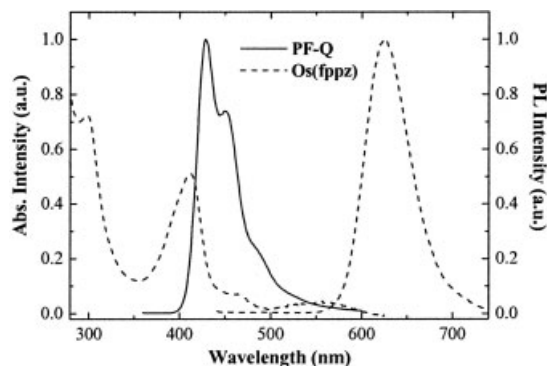


Figure 8. Solid-state PL of the PF-Q film and the normalized absorption and PL spectra of Os(fppz) recorded in a CH_2Cl_2 solution.

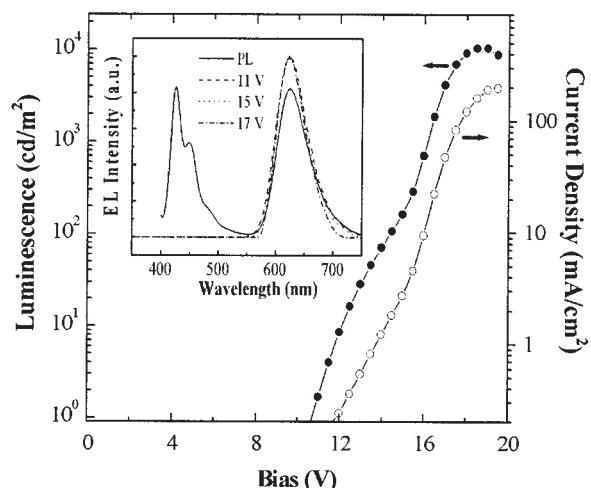
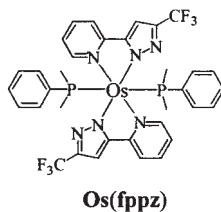


Figure 9. Current density–voltage–luminance characteristics of ITO/PEDOT/Os(fppz):PF-Q/TPBI/Mg:Ag. Inset: the PL spectrum of Os(fppz):PF-Q and the corresponding EL spectra recorded at different applied voltages.



The preparation of electrophosphorescent LEDs that use polymers as the host materials for their emitting layers is an attractive prospect because such devices have the potential for applications, among other things, in large-area devices prepared with simple processes. Efficient EL polymer-based devices have been prepared by

doping PF or poly(*N*-vinylcarbazole) (PVK) with triplet complexes.^{62–64} For charge balance purposes, some electron-transporting materials, such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) or 3-(4-biphenyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ), have also been introduced to compensate for the poor electron-transporting ability of the host polymers.^{65,66} In this study, we used PF-Q, which is possessed of PF backbones and DPQ as electron-transporting side chains, as the host material and doped it with 2.4 wt % of an efficient red-emitting phosphorescent dye, Os(fppz),⁶⁷ to realize red EL. The Os complex is chelated by two anions of 3-trifluoromethyl-5-(2-pyridyl) pyrazole (fppzH) to balance the +2 charge on the metal center and two phosphine donors to complete the coordination requirement. Its lifetime (0.7 μ s) is shorter than typical red emitting Ir(III) complexes.⁶⁸ This shorter triplet lifetime can help to minimize the exciton quenching by triplet–triplet annihilation at a high current density.⁶⁹ The PL spectrum of PF-Q and the absorption spectrum of Os(fppz) (Fig. 8) overlap to a moderate extent in the region 400–500 nm, which meets the requirement for efficient energy transfer. On photoexcitation at the absorption maximum of PF-Q, the PL profile of the blend contains two emission bands: one centered at about 440 nm that originates from the remaining emission of the PF-Q host, whereas the other, at about 624 nm, corresponds to the emission of Os(fppz) (see the inset in Fig. 9). In contrast, the host emission is quenched completely when stimulated by an electric field; this process resulted in red triplet emission from the Os complex that had Commission Internationale de L’Eclairage (CIE) color coordinates of (0.66, 0.34)

Table 1. Photophysical Properties of PF-Q, POF, and DPQ

	Solution ^a			Film ^b		
	Abs (nm)	PL (nm) ^c	Φ_f^d	Abs (nm)	PL (nm) ^c	Φ_f
PF-Q	(347) 391	418 (441)	1.00	(349) 390	428 (449)	0.54
POF	389	418 (442)	0.85	387	424 (448)	0.55 ^e
DPQ	340	405				

^a Evaluated in chloroform.

^b Evaluated in the solid state and prepared from toluene solutions.

^c Excited at 390 nm.

^d Quantum yield (Φ_f) determined in toluene, relative to 9,10-diphenylanthracene in cyclohexane, with excitation at 365 nm.

^e The thin film quantum efficiency of POF, as measured in an integrating sphere, was 0.55.

^f Peaks that appear as shoulders or weak bands are provided in parentheses.

Table 2. The Performance of Devices with the Structure ITO/PEDOT/EML/ TPBI/Mg:Ag

Device	PF-Q	Os(fppz) (2.4 wt%):PF-Q
Turn-on voltage (V) ^a	7.2	10.7
Voltage (V) ^b	9.2 (10.3)	16.4 (17.7)
Brightness (cd/m ²) ^b	138 (622)	1675 (7935)
Luminance efficiency (cd/A) ^b	0.69 (0.63)	8.28 (8.01)
External quantum efficiency (%) ^b	0.80 (0.73)	6.31 (6.10)
Maximum brightness (cd/m ²)	1121 (@ 12V)	10457 (@ 18.5V)
Maximum luminance efficiency	0.69	8.71
Maximum external quantum efficiency (%)	0.80	6.63
EL maximum (nm) ^d	428	622
CIE coordinates, x and y ^d	0.16 and 0.10	0.66 and 0.34

^a Recorded at 1 cd/m².^b Recorded at 20 mA/cm².^c The data in parentheses were recorded at 100 mA/cm².^d Recorded at 11 V.

at 11 V. These results suggest that both Förster energy transfer and direct charge trapping/recombination on the Os(fppz) guest are responsible for the observed EL.^{63,64} Table 2 summarizes the characteristics of the devices based on the doped and undoped polymers. The maximum external quantum efficiency of 6.63% (corresponding a luminance efficiency of 8.71 cd/A) is obtained from the doped device at a current density of 47.8 mA/cm², together with a brightness of 4163 cd/m². The maximum luminance for bright red emission, as depicted in Figure 9, is found to be 10,457 cd/m², at a bias of 18.5 V and a current density of 161 mA/cm². Furthermore, the turn-on voltage for the host-only device is 7.2 V, whereas that for the doped device increased to 10.7 V. This observation also supports the proposed charge trapping mechanism.^{63,64}

In summary, we have developed a direct and simple method for the synthesis of a PF copolymer, PF-Q, that contains two electron-deficient, 2,4-diphenylquinoline groups functionalized on the C-9 position of alternate fluorene units. Because of the 3-D cardostructure, the PF exhibits a high T_g and very good thermal and spectral stability. The incorporation of pendent quinoline groups also results in improved electron injection and transport in PF-Q, without significantly altering the electronic properties of the conjugated backbone. An EL device based on PF-Q exhibited a stable blue emission with color coordinates of (0.16, 0.10), a maximum brightness of 1121 cd/m², and a maximum external quantum efficiency of 0.80%. Moreover, with PF-Q as the host material

and doping it with 2.4 wt % of a red-emitting osmium complex, we realized a red electroluminescent device with a maximum brightness of 10,457 cd/m² and CIE coordinates of (0.66, 0.34); these coordinates are very close to those of the standard red (0.67, 0.33) demanded by the National Television System Committee (NTSC).

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