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Novel White Electroluminescent Single Polymer Derived from Fluorene and Quinacridone

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ABSTRACT: A novel series of white light emitting single polymers are prepared by incorporating low contents of quinacridone into the main chain of polyfluorene. This is the first report of quinacridone-containing conjugated polymer. Single layer devices (ITO/PEDOT:PSS/polymer/Ca/Al) are fabricated with these polymers. Energy transfer from fluorene segments to quinacridone unit is observed. Moreover, in the EL process, quinacridone unit can trap electrons and cannot trap holes from fluorene segments. Electroluminescence (EL) spectra of these polymers exhibit simultaneous blue emission (λ_{max} = 425 nm/445 nm) from the fluorene segments and yellow emission (λ_{max} = 540 nm/580 nm) from the quinacridone unit. The latter one comes from the partial energy transfer and charge trapping from the fluorene segments to the quinacridone unit. With the increase of the quinacridone unit's content in the copolymers, the relative intensity of the orange emission band in the EL spectra becomes stronger owing to the more complete energy transfer and charge trapping. For the polymer (**PFQA3**) with the quinacridone unit's content of 0.03 mol %, its EL spectrum shows balanced intensities of blue emission and orange emission, leading to white emission with CIE coordinates of (0.27, 0.35). Single layer device of this polymer exhibits the turn-on voltage of 3.5 V, luminous efficiency of 3.47 cd/A, power efficiency of 2.18 lm/W, external quantum efficiency of 1.33% and maximum brightness of 9062 cd/m^2. Increase of the quinacridone unit's content results in increased turn-on voltages and decreased EL efficiencies of the resulting devices owing to the serious trap of electrons by quinacridone unit and exciton quenching of quinacridone unit at high concentration, respectively.

Introduction

Polymer light-emitting diodes (PLEDs) have attracted considerable attention because of their potential application in large-area flat-panel displays.[1] After nearly two decades' effort, light emitting polymers with three primary colors (blue, green and red) have been developed. Devices based on them exhibit not only high efficiencies and brightness but also improving operational lifetime. However, white light emitting polymers, which are very desirable for full color displays with color filters, backlights and lighting applications, are very scarce.[2−7]

Several polymers have been described to show white electroluminescence (EL) because of the blue emission from the polymer itself and orange emission from aggregates/excimers/exciplex/electromer.[3] However, devices of these polymers always have low EL efficiencies because the formation of aggregates/excimers/exciplex/electromer reduces radiative decay rates of excitons. Our group has proposed two strategies to develop white light emitting single polymers by incorporating an orange emissive unit to a blue light emitting polymer host[4a−e] and by attaching both a green chromophore and a red chromophore to a blue light emitting polymer host.[5] Highly efficient white EL with bias-independent EL spectra has been achieved with both the two strategies. For white electroluminescent polymers based on the first strategy, polyfluorene is often selected as the blue polymer host but we find that orange emissive units play a very important role in the resulting polymers' EL performance. For example, the color purity of white emission is dependent on the emission wavelength of the orange emissive unit.[4b] Furthermore, the EL efficiencies of the white light emitting polymer can be enhanced by improving the photoluminescence (PL) quantum efficiency of the orange emissive unit.[4c] However, until now, only 1,8-naphthalimide derivative unit,[4a,b] 2,1,3-benzothiadiazole derivative unit,[4c−e] 2,3-dimethyl-5,8-dithien-2-ylquinoxaline unit,[4f] malononitrile derivative unit,[4g] and benzoselenadiazole unit[4h] have been used as the orange emissive unit in white light emitting polymers. Therefore, it is still very desirable to develop new orange chromophores for white light emitting polymers, especially orange chromophores with high PL quantum efficiencies.

Quinacridone and its derivatives are well-known chemically stable organic pigments.[8] They have also been used in supramolecular assemblies and as photovoltaic and photoconductive materials.[9] In particular, quinacridone has been demonstrated to be an excellent dopant in vacuum-deposited organic light-emitting diodes (OLEDs) because of its PL quantum efficiency of unity.[10] Devices based on quinacridone achieve power efficiencies as high as 20 lm/W.[10a] However, there is no report of use of quinacridone in solution-processed PLEDs although solution processing has the great advantage of low cost and ease of covering large area. This is due to quinacridone's poor solubility and great tendency to aggregate resulting from its intermolecular hydrogen bonding and strong $\pi-\pi$ interaction.

Considering quinacridone's great PL quantum efficiency of unity, we report here the utilization of quinacridone unit as the orange emissive unit in white light emitting polymers by incorporating a low content of quinacridone unit into the main chain of polyfluorene. Since quinacridone unit is fixed in the matrix of polyfluorene with good solubility,[11] quinacridone's

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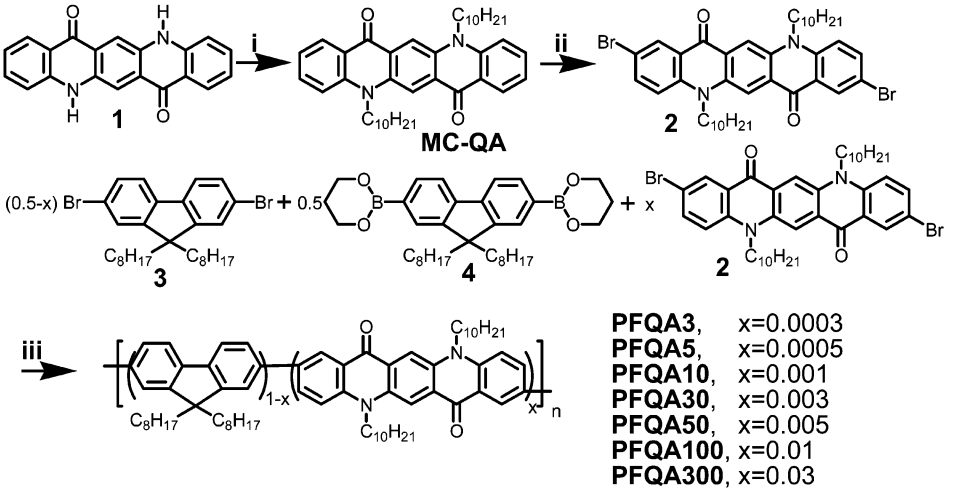
Scheme 1. Chemical Structures and Synthetic Routes of the Monomers and Polymers[a]



[a] Reagents and conditions: (i) NaH, DMF, n-$C_{10}H_{21}Br$, 120 °C; (ii) Br_2, CH_3COONa, CH_3COOH, reflux; (iii) $Pd(PPh_3)_4$, K_2CO_3 (aq. 2 M), aliquot 336, toluene, 90 °C.

problem of poor solubility and tendency to aggregate can be dissolved, making it applicable in PLEDs.[12] The chemical structures of the resulting polymers are shown in Scheme 1. As to the best of our knowledge, this is the first quinacridone-containing conjugated polymer. In the EL process, partial energy transfer and charge trapping from the fluorene segments to the quinacridone unit are observed and leads to simultaneous blue emission from the fluorene segments and yellow emission from the quinacridone unit. By adjusting the content of the quinacridone unit, we tune the relative intensity of the blue emission band and the yellow emission band in the EL spectra and realize white EL.

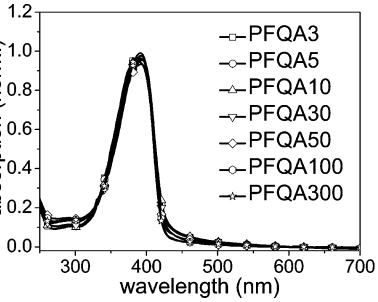


Figure 1. Absorption spectra of the polymers in solid films.

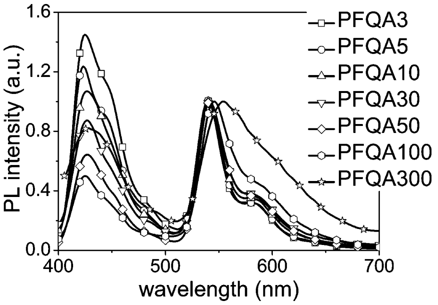


Figure 2. PL spectra of the polymers in solid films.

Results and Discussion

Synthesis. The synthetic routes of the model compounds, monomer and polymers are outlined in Scheme 1. Alkylation of quinacridone afforded the model compound, **MC-QA**. Owing to the poor solubility of quinacridone, the yield of **MC-QA** was very low. The introduction of the two alkyl chains completely prevented the formation of intermolecular hydrogen bonding of quinacridone. Monomer **2**, 2,9-dibromo-*N,N′*-didecylquinacridone, was prepared by the bromination of **MC-QA** at the presence of Br_2. Both the two alkyl chains and the two bromo substitutes in **2** are helpful to diminish the $\pi-\pi$ interaction of quinacridone skeleton. [10e] Hence, monomer **2** exhibits good solubility in common organic solvent, such as toluene, chloroform, etc. The good solubility of monomer **2** makes it applicable in the following polymerization. The polymers were synthesized from 2,7-dibromo-9,9-dioctylfluorene (**3**), 2,7-bis(trimethyleneborate)-9,9-dioctylfluorene (**4**) and **2** using Suzuki polycondensation with different feed ratios. All these polymers are soluble in common organic solvents, such as toluene, chloroform, and tetrahedronfuran (THF), etc. Their number-average molecular weights, as determined by gel permeation chromatography (GPC) with polystyrene standards, range from 20900 to 39200 with polydispersities (PDI) varying from 2.22 to 2.42. These polymers' chemical structures are verified by ^1H NMR and elemental analysis. The signal at 4.58 ppm in ^1H NMR spectra is attributed to the quinacridone unit and we can calculate quinacridone unit's actual content according to this peak. The actual content of quinacridone unit in **PFQA300** is 0.015, which is to some extent close to the feed ration of the monomer **2** in the polymerization. For **PFQA3**, **PFQA5**, **PFQA10**, **PFQA30**, **PFQA50**, and **PFQA100,** the contents of quinacridone unit are too low to give signals in ^1H NMR. All these polymers exhibit good thermal stability with degradation temperature higher than 420 °C.

Photophysical Properties. Figure 1 shows the absorption spectra of the polymers in solid films. **PFQA3**, **PFQA5**, **PFQA10**, **PFQA30**, **PFQA50**, **PFQA100**, and **PFQA300** all exhibit an absorption band at 390 nm attributed to the $\pi-\pi^*$ transition of the fluorene segments.[13] The absorption band at 480 nm/514 nm of the quinacridone unit cannot be observed because of its low contents. Figure 2 shows the PL spectra of the polymers in solid films with an excitation wavelength of 370 nm. All the PL spectra of the polymers exhibit two emission bands at 425/445 and 540/580 nm, which are assigned to the fluorene segments and the quinacridone unit, respectively. The emission band of quinacridone unit comes from the Förster energy transfer from polyfluorene to the quinacridone unit due to the overlap of the emission spectrum of polyfluorene and absorption spectrum of the model compound **MC-QA** (see Figure 3). With the increase of the quinacridone unit's content, the relative intensity of the band at 540/580 nm increases

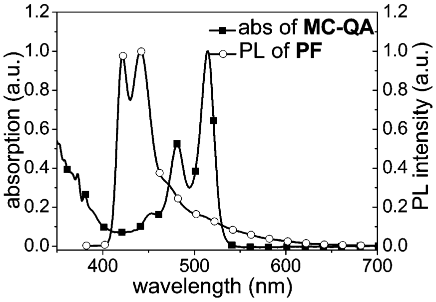


Figure 3. Absorption spectrum of **MC-QA** and emission spectrum of **PF**.

because of the more efficient energy transfer. In the PL spectrum of **PFQA300,** the relative intensity of the orange emission band is exceptionally weak probably due to the fluorescence quenching of the quinacridone unit at high concentration. The orange emission band in the PL spectra of **PFQA100** and **PFQA300** are red-shifted and become structureless when compared with that of other polymers because of the aggregation of quinacridone unit at high concentration.

Electrochemical and Charge Transporting Properties. The electrochemical behaviors of the polymers were investigated by cyclic voltammetry (CV). **PFQA3**, **PFQA5**, **PFQA10**, **PFQA30**, **PFQA50**, **PFQA100**, and **PFQA300** all show the same redox properties with one oxidation process and one reduction process. Their onset potentials are +1.43 and −2.15 eV, respectively, which are very close to the data reported for polyfluorene homopolymer.[14] Therefore, the oxidation process and the reduction process are due to the fluorene segments. No signal of quinacridone unit is observed. According to the formula, ($E_{\mathrm{HOMO}} = -(E^{\mathrm{ox}}+4.34)$ eV and $E_{\mathrm{LUMO}} = -(E^{\mathrm{red}}+4.34)$ eV),[15] we estimate the HOMO and LUMO energy levels of the polymers to be −5.77 and −2.19 eV, respectively.

Owing to the poor solubility of the model compound **MC-QA**, we are unable to measure its electrochemical properties. It is reported that a similar compound, *N*,*N'*-diisoamyl quinadricone, shows a LUMO of −3.5 eV and HOMO of −5.9 eV.[11b] Since the LUMO of **MC-QA** is below that of polyfluorene (relative to vacuum energy levels) and the HOMO of **MC-QA** is not higher than that of polyfluorene, the quinacridone unit will only trap electrons and cannot trap holes from polyfluorene for the quinacridone-containing polymers in EL process.[16]

To further investigate the charge trapping ability of quinacridone unit, "electron-only" devices and "hole-only" devices of the polymers were fabricated with the configuration of Al (60 nm)/polymer (90 nm)/Ca (10 nm) /Al (100 nm) and indium−tin oxide (ITO)/poly(ethylenedioxythiophene) doped with poly(styrene sulfonic acid) (PEDOT:PSS) (40 nm)/polymer (90 nm)/MoO_3 (5 nm) /Al (100 nm), respectively. The voltage−current density curves (*V*−*I*) of the devices of **PFQA5**, **PFQA30** and **PFQA300** are depicted in Figure 4. In the former device structure, owing to the relatively high work function of Al (−4.3 eV) anode, there is large energy barrier for hole injection. Moreover, there is small energy barrier for electron injection due to the high work function of Ca/Al cathode (−2.9 eV). Therefore, the *V*−*I* characteristics of these devices are only related to the bulk electron conduction of polymer films. As shown in Figure 4a, with the increase of the quinacridone unit's content from 0.05 to 3 mol %, the current densities at the same voltage greatly decrease, indicating that quinacridone unit is an electron trap. For the latter device structure, because of the low function of MoO_3/Al (−5.3 eV) and large energy barrier for electron injection as well as the low work function of PEDOT-modified ITO (−5.2 eV) and small energy barrier for hole injection, the devices' *V*−*I* characteristics are only related to the bulk hole conduction of polymer films. It can be seen in Figure 4b that with the increase of the quinacridone unit's content, the *V*−*I* curves keep almost unchanged, indicating that quinacridone unit canot trap holes. The "electron-only" device and "hole-only" device characterization results are in accordance with the aforementioned estimation of the LUMO and HOMO energy levels of the quinacridone unit.

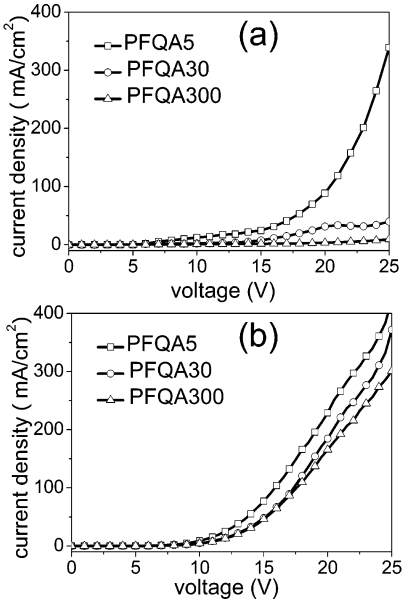


Figure 4. *V*−*I* characteristics of the "electron-only" devices (a) and "hole-only" devices (b) of **PFQA5**, **PFQA30**, and **PFQA300**.

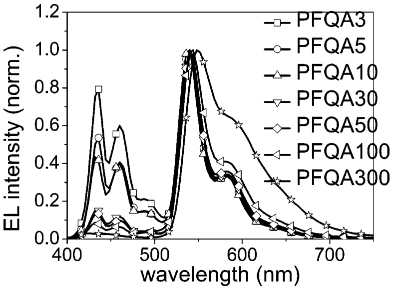


Figure 5. EL spectra of the electroluminescent devices of the polymers.

Table 1. Contents of the Quinacridone Unit, Number Average Molecular Weights (M_n), Polydispersities (PDI), and Thermal Degradation Temperatures (T_d) of the Polymers

polymer	content	M_n	PDI	T_d (°C)
PFQA3	0.0003	31 200	2.30	430
PFQA5	0.0005	29 600	2.29	431
PFQA10	0.0010	32 500	2.43	428
PFQA30	0.003	39 200	2.26	429
PFQA50	0.005	32 100	2.42	426
PFQA100	0.01	27 800	2.33	430
PFQA300	0.03	20 900	2.22	428

Electroluminescence Properties. The EL properties of these polymers were examined with the device configuration of ITO/PEDOT:PSS (40 nm)/polymer (90 nm)/Ca (10 nm)/Al (100 nm). Figure 5 shows the EL spectra of the devices, and Table 2 lists the corresponding CIE coordinates. The EL spectra of **PFQA3**, **PFQA5**, **PFQA10**, **PFQA30**, **PFQA50**, and **PFQA100** all show two emission bands at 436/460 and at 540/580 nm, which are attributed to the fluorene segments and the quinacridone unit, respectively. Moreover, the relatively intensity of the orange emission band is larger in the EL spectra compared to in the

Table 2. EL Performance of the Device of the Polymers

polymer	turn-on voltage (V)	luminous efficiency (cd/A)	power efficiency (lm/W)	external quantum efficiency	maximum brightness (cd/m^2)	CIE coordinates (x, y)
PFQA3	3.5	3.47	2.18	1.33%	9062	(0.27, 0.35)
PFQA5	3.5	4.00	1.94	1.32%	12 470	(0.29, 0.40)
PFQA10	3.5	4.14	2.15	1.34%	14 110	(0.29, 0.43)
PFQA30	4.0	3.17	1.17	0.88%	10 190	(0.34, 0.51)
PFQA50	5.0	2.21	0.73	0.61%	7121	(0.36, 0.53)
PFQA100	8.0	0.54	0.13	0.21%	2207	(0.38, 0.54)
PFQA300	10.0	0.10	0.02	0.03%	317	(0.46, 0.54)

PL spectra. We attribute it to the charge trapping effect of quinacridone unit.[11b,17] With the increase of the quinacridone unit's content, the relative intensity of the yellow emission band at 540 nm/580 nm increased because of the more complete energy transfer and charge trapping. In the EL spectra of **PFQA3**, the intensities of the blue emission band and the orange emission band are fairly balanced, resulting in near-white emission with the CIE coordinates of (0.27, 0.35). Furthermore, the EL spectral shape of the electroluminescent device of **PFQA3** keeps almost unchanged when the bias increases from 6 to 10 V (see Figure 6).

Table 2 outlined the EL performance of the single-layer devices. The device of **PFQA3** emits near-white light with the turn-on voltage of 3.5 V, luminous efficiency of 3.47 cd/A, power efficiency of 2.18 lm/W, external quantum efficiency of 1.33%, maximum brightness of 9062 cd/m^2 and CIE coordinates of (0.27, 0.35). Figure 7 shows the typical voltage−current density-brightness (V−I−B) characteristic and current density-luminous efficincy-power efficiency curve of this electroluminescent device. This performance is somewhat worse than that of other white electroluminescent polymers[4−7] probably because the quinacridone unit is not able to trap both electrons and holes and cannot enhance the recombination rate of positive and negative charge carriers. For **PFQA10**, **PFQA30**, **PFQA50**, **PFQA100**, and **PFQA300,** with the increase of the quinacridone unit's content, the turn-on voltages of the resulting devices increase while the external quantum efficiencies decrease. The increased turn-on voltage is due to the charge trapping effect of the quinacridone unit. In these devices, electrons are the dominant charge carriers because of the large energy barrier for hole injection from PEDOT:PSS layer to the emitting layer.[18] Quinacridone unit is a serious electron trap. At low voltage, the small amount of electrons injected from the cathode are trapped by quinacridone unit in the emitting layer and cannot migrate to the PEDOT/polymer interface to recombination with holes. Hence, higher voltage is required for the injection of more electrons and for the migration of electrons and thus for the combination of electrons and holes. The decrease of EL efficiencies with increased quinacridone unit's content is probably due to the exciton quenching effect of the quinacridone unit.

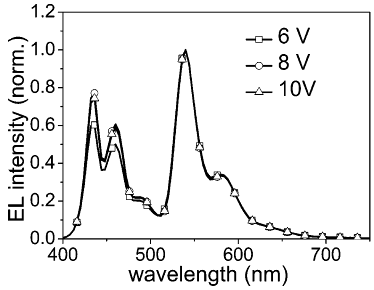


Figure 6. EL spectra of the electrouminescent device of **PFQA3** under different biases.

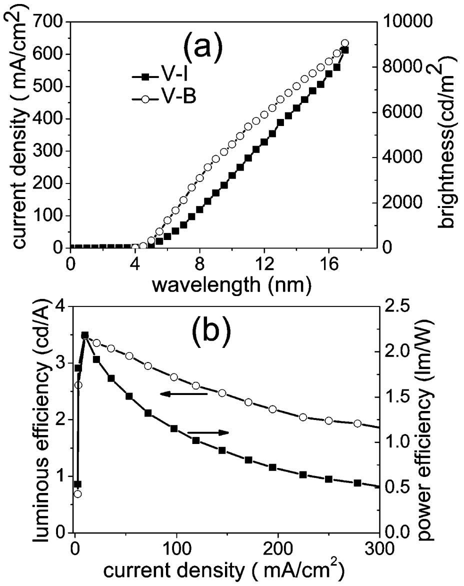


Figure 7. (a) V−I−B characteristic of the electroluminescent device of **PFQA3**. (b) Dependence of luminous efficincy and power efficiency on current density of the electroluminescent device of **PFQA3**.

Conclusion

In summary, we have successfully developed a novel series of conjugated polymers by incorporating quinacridone to the main chain of polyfluorene. The EL spectra of these polymers exhibit both blue emission (λ_{max} = 425/445 nm) from the fluorene segments and yellow emission (λ_{max} = 540/580 nm) from the quinacridone unit due to the energy transfer and charge trapping from the fluorene segments to the quinacridone unit. The relative intensities of the two emission bands can be tuned by adjusting the content of the quinacridone unit. For the polymer with the quinacridone unit's content of 0.03 mol %, the intensities of the blue emission and the orange emission in the EL spectrum are balanced, leading to white emission. Single layer device of this polymer emits white light with the CIE coordinates of (0.27, 0.35), luminous efficiency of 3.47 cd/A and power efficiency of 2.18 lm/W.

Experimental Section

Materials. All reagents were purchased from Aldrich, Acros or TCI companies. 2,7-dibromo-9,9-dioctylfluorene (**3**)[12b] and 2,7-bis-(trimethyleneborate)-9,9-dioctylfluorene (**4**)[12b] were prepared according to the literature procedure.

***N,N′*-Didecylquinacridone (MC-QA).** To a stirred mixture of quinacridone (**1**) (0.93 g, 3.0 mmol) in DMF (80 mL) at 120 °C was added 50% NaH (0.36 g, 7.5 mmol). The mixture was stirred for 30 min, followed by addition of *n*-$C_{10}H_{21}Br$ (10.0 mL, 48 mmol). The resulting mixture was stirred for another 24 h. After cooled, the mixture was poured into brine and extracted with ethyl acetate (EA). The organic layer was washed with brine for three times and then dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified with silica gel column using CH_2Cl_2/EA (4/1) as eluent. Yield: 0.12 g (7%). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.80 (s, 2H), 8.60 (dd, 2H), 7.77 (m, 2H), 7.53 (d, 2H), 7.29 (t, 2H). 4.50 (t, 4H), 1.99 (m, 4H), 1.62−1.07 (m, 28H), 0.86 (t, 6H). Anal. Calcd: C, 81.04; H, 8.84; N, 4.73. Found: C, 80.89; H, 8.43; N, 4.53.

2,9-Dibromo-*N,N′*-didecylquinacridone (2). A mixture of *N,N′*-didecylquinacridone (0.12 g, 0.2 mmol), CH_3COONa (0.043 g, 0.52 mmol) and acetic acid (5 mL) was heated to reflux with stirring. A solution of Br_2 (0.025 mL, 0.46 mmol) in acetic acid (5 mL) was added dropwise to the mixture, followed by stirring for 1 h. After the mixture had cooled, the precipitated solid was collected by filtration and was washed with aqueous $NaHSO_3$ and water. Recrystallization of the crude product in EA afforded the title compound as red crystal. Yield: 0.11 g (79%). ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 8.60 (s, 2H), 8.55 (d, 2H), 7.76 (dd, 2H), 7.35 (d, 2H). Anal. Calcd: C, 64.00; H, 6.71; N, 3.73. Found: C, 63.44; H, 6.36; N, 3.55.

General Procedure of the Suzuki Polymerization. To a mixture of 2,7-dibromo-9,9-dioctylfluorene (**3**), 2,7-bis(trimethyleneborate)-9,9-dioctylfluorene (**4**) and 2,9-dibromo-*N,N′*-didecylquinacridone (**2**) with corresponding feed ratios, aliquot 336 (0.10 g, 0.25 mmol), and $Pd(PPh_3)_4$ (11.0 mg, 0.01 mmol) under argon were added 2 M degassed aqueous K_2CO_3 (2.5 mL) and degassed toluene (7 mL). The mixture was heated to 90 °C and stirred in the dark for 48 h. After workup, the mixture was poured to methanol. The precipitated fibers were collected by filtration and then dissolved in CH_2Cl_2. The solution was then washed with water for four times and then dried with anhydrous Na_2SO_4. After filtration, the solution was concentrated to an approximate volume and then poured into methanol to give polymer fibers. The polymer was purified by Soxhlet extraction in acetone for 24 h. The reprecipitation procedure in dichloromethane/methanol was then repeated for several times. The final product was obtained after drying in vacuum with a yield of 45−60%.

PFQA3. 3 (0.2740 g, 0.4997 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (0.6 mL 5×10^{-4} solution in toluene, 3×10^{-4} mmol) were used in the polymerization.

PFQA5. 3 (0.2739 g, 0.4995 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (1.0 mL 5×10^{-4} solution in toluene, 5×10^{-4} mmol) were used in the polymerization.

PFQA10. 3 (0.2736 g, 0.4990 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (2.0 mL 5×10^{-4} solution in toluene, 1×10^{-3} mmol) were used in the polymerization.

PFQA30. 3 (0.2725 g, 0.4970 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (0.0022 mg, 0.003 mmol) were used in the polymerization.

PFQA50. 3 (0.2713 g, 0.4950 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (0.0038 mg, 0.005 mmol) were used in the polymerization.

PFQA100. 3 (0.2683 g, 0.4900 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (0.0075 mg, 0.010 mmol) were used in the polymerization.

PFQA300. 3 (0.2580 g, 0.4700 mmol), **4** (0.2792 g, 0.5000 mmol), and **2** (0.0221 mg, 0.030 mmol) were used in the polymerization.

PFQA3, PFQA5, PFQA10, PFQA30, PFQA50 and **PFQA100** all showed similar ^1H NMR and elemental analysis results.

For example: **PFQA100.** ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.88 (d, 2H), 7.73 (br, 4H), 2.15 (br, 4H), 1.17 (br, 24H), 0.85 (t, 6H). Anal. Calcd: C, 89.68; H, 10.31. Found: C, 88.98; H, 10.11.

PFQA300. ^1H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.84 (d, 2H), 7.68 (br, 4H), 4.58 (br, 0.06H), 2.11 (br, 4H), 1.14 (br, 24H), 0.82 (t, 6H). Anal. Calcd: C, 89.66; H, 10.30; N, 0.02, Found: C, 89.02; H, 10.06, N, 0.33.

Instruments. ^1H NMR spectra were obtained with a Bruke Avance 300 NMR spectrometer. Elemental analysis was performed using a Bio-Rad elemental analysis system. Number- and weight-average molecular weights of the polymers were determined by gel permeation chomotagraphy (GPC) on a Waters 410 instrument with polystyrene as standards and THF as eluent. Thermal properties of the polymers were analyzed with a Perkin-Elmer-TGA 7 instrument under nitrogen at a heating rate of 10 °C min^{-1}. UV−vis absorption spectra were recorded by a Perkin-Elmer Lambda 35 UV/vis spectrometer. PL spectra were recorded with a Perkin-Elmer LS50B spectrofluorometer. Cyclic voltammetry of polymer films on a glassy carbon electrode were conducted on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system with a working electrode (glassy carbon), a counter electrode (Pt wire) and a reference electrode (Ag/AgCl) at room temperature in a solution of *n*-Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 100 mV/s. EL spectra, CIE coordinates, current−voltage and brightness−voltage characteristics of devices were measured with a Spectrascan PR650 spectrophotometer at the forward direction and a computer-controlled Keithley 2400 under ambient condition.

Device Fabrication. The indium−tin oxide (ITO) glass plates were cleaned in ultrasonic solvent bath and then baked in a heating chamber at 120 °C. A 40 nm thick ITO-modifying layer of PEDOT:PSS was spincoated on top of ITO at 3000 rpm for 60 s and then baked for 15 min at 120 °C. Thin films (90 nm) of the polymers were spincoated from their solution in toluene (15 mg/mL). The substrate was then thermally annealed in vacuum at 80 °C for 1 h, After being cooled, the substrate was transferred to a vacuum thermal evaporator. A layer of 10 nm thick Ca was deposited at a pressure of 3×10^{-3} Pa through a mask, and another layer of 100 nm thick Al was deposited on the top as a protecting layer for Ca. The active emissive area defined by the two electrodes was 10 mm^2.

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References and Notes

(1) (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature (London)* **1990**, *347*, 539. (b) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.

(2) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585.

(3) (a) Chen, S. A.; Chuang, K. R.; Chao, C. I.; Lee, H. T. *Synth. Met.* **1996**, *82*, 207. (b) Tsai, M. L.; Liu, C.-Y.; Hsu, M.-A.; Chow, T. J. *Appl. Phys. Lett.* **2003**, *82*, 550. (c) Lee, Y.-Z.; Chen, X. W.; Chen, M. C.; Chen, S.-A.; Hsu, J.-H.; Fann, W. S. *Appl. Phys. Lett.* **2001**, *79*, 308. (d) Paik, K. L.; Baek, N. S.; Kim, H. K.; Lee, J.-H.; Lee, H. *Macromolecules* **2002**, *35*, 6782. (e) Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Fréchet, J. M. *J. Am. Chem. Soc.***2003**, *125*, 13165.

(4) (a) Tu, G. L.; Zhou, Q. G.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Appl. Phys. Lett.* **2004**, *85*, 2172. (b) Tu, G. L.; Mei, C. Y.; Zhou, Q. G.; Cheng, Y. X.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Adv. Funct. Mater.* **2006**, *16*, 101. (c) Liu, J.; Zhou, Q. G.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Adv. Funct. Mater.* **2006**, *16*, 957. (d) Liu, J.; Guo, X.; Bu, L. J.; Xie, Z. Y.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Adv. Funct. Mater.* **2007**, *17*, 1917. (e) Liu, J.; Shao, S. Y.; Chen, L.; Xie, Z. Y.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Adv. Mater.* **2007**, *19*, 1859. (f) Sun, M. L.; Niu, Q. L.; Du B.; Peng, J. B.; Yang, W.; Cao Y. *Macromol. Chem. Phys.* **2007**, *208*, 988. (g) Lee, S. K.; Jung, B.-J.; Ahn, T.; Jung, Y. K.; Lee, J.-I.; Kang, I.-N.; Lee, J.; Park, J.-H.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 3380. (h) Chien, C.-H.; Shih, P.-I.; Shu C.-F. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2938.

(5) (a) Liu, J.; Zhou, Q. G.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Adv. Mater.* **2005**, *17*, 2974. (b) Liu, J.; Xie, Z. Y.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma, D. G.; Jing, X. B.; Wang, F. S. *Adv. Mater.* **2007**, *19*, 531. (c) Liu, J.;

Chen, L.; Shao, S. Y.; Xie, Z. Y.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Adv. Mater.* **2007**, *19*, 4224.

(6) (a) Jiang, J. X.; Xu, Y. H.; Yang, W.; Guan, R.; Liu, Z. Q.; Zhen, H. Y.; Cao, Y. *Adv. Mater.* **2006**, *18*, 1769. (b) Wu, F.-I.; Yang, X.-H.; Neher, D.; Dodda, R.; Tseng, Y.-H.; Shu, C. F. *Adv. Funct. Mater.* **2007**, *17*, 1085.

(7) (a) Luo, J. Li, X. Z.; Hou, Q.; Peng, J. B.; Yang, W.; Cao, Y. *Adv. Mater.* **2007**, *19*, 1113. (b) Chuang, C.-Y.; Shih, P.-I.; Chien, C.-H.; Wu, F.-I.; Shu, C.-F. *Macromolecules*, **2007**, *40*, 247. (c) Lee, S. K.; Hwang, D.-H.; Jung, B.-J.; Cho, N. S.; Lee, J.; Lee, J.-D.; Shim, H.-K. *Adv. Funct. Mater.* **2005**, *15*, 1647. (d) Lee, P.-I.; Hsu, S. L.-C.; Lee, R.-F. *Polymer* **2007**, *48*, 110. (e) Wu, W.-C.; Lee, W.-Y.; Chen, W.-C. *Macromol. Chem. Phys.* **2006**, *207*, 1131.

(8) Lincke, G. *Dyes Pigm.* **2002**, *52*, 169.

(9) (a) De Feyter, S.; Gesquière, A.; De Schryver, F. C.; Keller, U.; Müllen, K. *Chem. Mater.* **2002**, *14*, 989. (b) Hiramoto, M.; Kawase, S.; Yokoyama, M. *Jpn. J. Appl. Phys. Part 2* **1996**, *35*, L349. (c) Manabe, K.; Kusabayashi, S.; Yokoyama, M. *Chem. Lett.* **1987**, 609. (d) Mu, Z. C.; Wang, Z. Q.; Zhang, X.; Ye K. Q.; Wang, Y. *J. Phys. Chem. B* **2004**, *108*, 19955. (e) Yang, X. Y.; Mu, Z. C.; Wang, Z. Q.; Zhang, X.; Wang, J.; Wang, Y. *Langmuir* **2005**, *21*, 7225.

(10) (a) Shaheen, S. E.; Jabbour, G. E.; Kippelen, B.; Peyghambarian, N.; Anderson, J. D.; Marder, S. R.; Armstrong, N. R.; Bellmann, E.; Grubbs, R. H. *Appl. Phys. Lett.* **1999**, *74*, 3212. (b) Shaheen, S. E.; Kippelen, B.; Peyghambarian, N.; Wang, J. F.; Anderson, J. D.; Mash, E. A.; Lee, P. A.; Armstrong, N. R.; Kawabe, Y. *J. Appl. Phys.* **1999**, *85*, 7939. (c) Shi, J.; Tang, C. W. *Appl. Phys. Lett.* **1997**, *70*, 1665−1667. (d) Flora, W. H.; Hall, H. K.; Armstrong, N. R. *J. Phys. Chem. B* **2003**, *107*, 1142. (e) Ye, K. Q.; Wang, J.; Sun, H.; Liu, Y.; Mu, Z. C.; Li, F.; Jiang, S. M.; Zhang, J. Y.; Zhang, H. X.; Wang, Y.; Che, C.-M. *J. Phys. Chem. B* **2005**, *109*, 8008.

(11) (a) Bernius, M. T.; Inbasekaran, M.; O'Brien, J.; Wu, W. S. *Adv. Mater.* **2000**, *12*, 1737. (b) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365. (c) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.

(12) (a) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Müllen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437. (b) Chen, X. W.; Liao, J. L.; Liang, Y. M.; Ahmed, M. O.; Tseng, H. E.; Chen, S.-A. *J. Am. Chem. Soc.* **2003**, *125*, 636.

(13) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *32*, 3306.

(14) Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebeler, C.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 2453.

(15) Bard, A. J.; Faulkner, L. A. *Electrochemcal Methods: Fundamentals and Applications*; Wiley: New York, 1984.

(16) (a) Utsugi, K.; Takano, S. *J. Electrochem. Soc.* **1992**, *139*, 3610. (b) Suzuki, H.; Hoshino, S. *J. Appl. Phys.* **1996**, *79*, 8816.

(17) Liu, J.; Tu, G. L.; Zhou, Q. G.; Cheng, Y. X.; Geng, Y. H.; Wang, L. X.; Ma D. G.; Jing, X. B.; Wang, F. S. *J. Mater. Chem.* **2006**, *16*, 1431.

(18) Woudenbergh, T.; Wildeman, J.; Blom, P. W. M.; Bastiaansen, J. J. A. M.; Langeveld-Voss, B. M. W. *Adv. Funct. Mater.* **2004**, *14*, 677.

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