New Alternative Copolymer Constituted of Fluorene and Triphenylamine Units with a Tunable −CHO Group in the Side Chain. Quantitative Transformation of the −CHO Group to −CH═CHAr Groups and Optical and Electrochemical Properties of the Polymers

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Received December 16, 2003; Revised Manuscript Received May 5, 2004

ABSTRACT: A new alternative functional copolymer, **PFT**, comprising of fluorene and triphenylamine units with a tunable −CHO group in the side chain was synthesized by the polycondensation of 4-[*N*,*N*-di(4-bromophenyl)amino]benzaldehyde with 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) using Pd(PPh_3)$_4$ as the catalyst. The polymer was soluble in organic solvents and gave a number-average molecular weight, M_n, of 10 000 and a weight-average molecular weight, M_w, of 17 700. **PFT** had an intrinsic viscosity [η] of 0.24 dL g^{-1} in toluene and exhibited the photoluminescence (PL) peak strongly influenced by the kind of the solvents, e.g., at 462 nm in toluene and at 528 nm in NMP. The quantum yield of the PL of **PFT** also varied from 12% in toluene to less than 1% in NMP. A cast film of **PFT** showed the emission peak at 497 nm. By using the Wittig reaction, the −CHO group of **PFT** was quantitatively transformed into trans −CH═CHAr groups. The modified products, **MPa** (Ar = $-C_6H_6$) and **MPb** (Ar = $-C_6H_4OCH_3$-*p*), showed a UV−vis peak at 390 nm in solutions and in the solid. **MPa** and **MPb** showed PL peaks at 433 and 457 nm, respectively, in toluene. The quantum yields of **MPa** and **MPb** rose to 64% and 51%, respectively, from 12% of **PFT**. A cast film of **MPa** gave a quantum yield comparable to that of poly(9,9-dioctylfluorene-2,7-diyl). **PFT**, **MPa**, and **MPb** were electrochemically active and received electrochemical oxidation, which was followed by cyclic voltammetry and UV−vis spectroscopy.

Introduction

Since excellent hole-transporting properties of triphenylamine (TPA) in organic light-emitting diodes (OLEDs) were revealed,[1] efforts have been made to synthesize its derivatives and to reveal chemical properties of the derivatives.[2−8] In recent years, strong interest in fabrication and development of the OLEDs using single-layer polymeric or supramolecular electroluminescent materials has promoted many research efforts[8−18] to focus on preparation of the copolymers consisting of the TPA unit and other units such as phenylethylene,[10,11] thiophene,[13] oxadiazole,[14] and 1,3,5-triazine units.[12] Among these copolymers, copolymers consisting of TPA and fluorene units are particularly important[9] because they show both the hole-transporting and light-emitting properties.[7,8,9d]

For further development of such a polymeric OLED material, obtaining a mother polymer with tunable reactive chemical groups such as carbonyl group is attractive. Physical properties of the polymer will be adjusted by chemical transformation of the reactive group. Studies on the polymers with variously transformed chemical groups will render basis for better understanding of the relationship between the chemical structure of the polymer and chemical properties of the polymer. Promoted by these situations, we have prepared a new alternative copolymer comprising of fluorene and triphenylamine units with a reactive −CHO group and found that the −CHO group undergoes quantitative transformation reaction to −CH═CH−Ar groups. Herein, we report the results.

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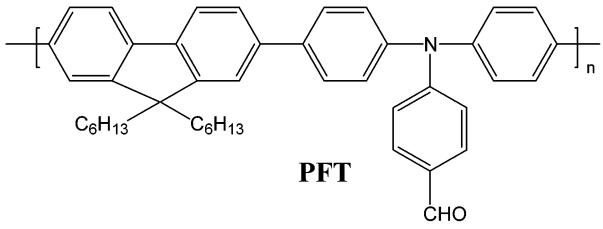
Chart 1. Structure of the Copolymer, PFT[a]



PFT

[a] C_6H_{13} = hexyl. The −CHO group undergoes quantative Wittig reaction.

Experimental Section

Materials. 9,9-Dihexylfluorene-2,7-bis(trimethyleneborate), **3**, purchased from Aldrich, was recrystallized from hexane before use. Bis(4-bromophenyl)phenylamine, **1**, was prepared according to the reported procedure.[18]

Synthesis of 4-[*N*,*N*-Di(4-bromophenyl)amino]benzaldehyde, 2. To a mixture of **1** (12 g, 30 mmol), 1,2-dichloroethane (100 mL), and DMF (3.3 g, 45 mmol) was added $POCl_3$ (7.0 g, 46 mmol) under nitrogen. The deep red solution was heated to reflux, and the temperature was maintained for 18 h. After cooling to room temperature, the dark solution was poured into a mixture of crushed ice and water (200 mL). The resulting mixture was stirred at room temperature for 1 h and then neutralized to pH = 7 using powdery $NaHCO_3$. The dark green solution was extracted with chloroform (4 × 80 mL). The organic layer was washed with water (3 × 50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography on silica by using ethyl acetate/hexane mixtures (first a 1:6 mixture (v/v) and second a 1:1 mixture (v/v)) as the eluent to give **2** as yellow crystalline needles with green photoluminescence; 5.5 g, yield, 43%. IR (KBr pellet, cm^{-1}): 1694, 2724. ^{1}H NMR ($CDCl_3$): δ 6.97−7.03 (m, 6H), 7.41 (d, 4H), 7.68 (d, 2H), 9.82 (s, 1H). Anal. Calcd for $C_{19}H_{13}NBr_2O$: C, 52.93; H, 3.04; N, 3.25; Br, 37.07. Found: C, 52.92; H, 3.19; N, 3.29; Br, 37.16.

10.1021/ma0359133 CCC: $27.50 © 2004 American Chemical Society
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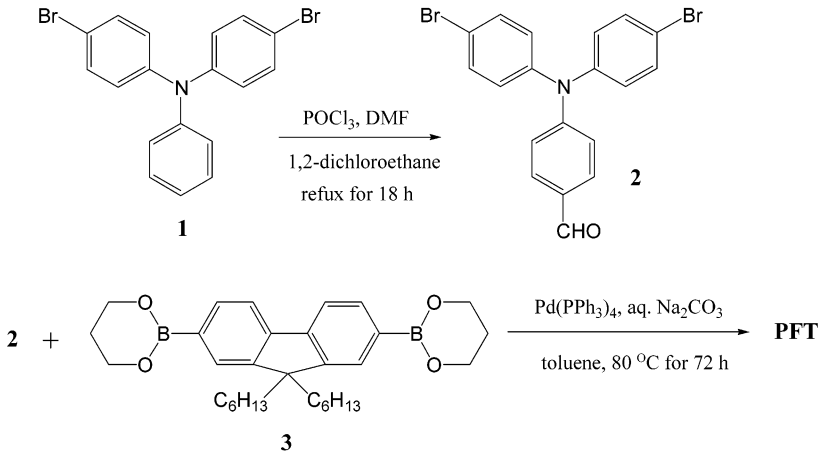
Scheme 1. Procedure for Preparation of PFT



Polymerization. The polycondensation between monomers **2** and **3** under Suzuki coupling conditions was carried out according to the analogue procedures reported in the literature.[19] To a 200 mL Schlenk tube charged with **2** (587 mg, 1.36 mmol), 9,9-dihexylfluorene-2,7-bis(trimethyleneborate) (683 mg, 1.36 mmol), and $Pd(PPh_3)_4$ (50 mg, 0.043 mmol) was added 100 mL of degassed toluene, and the mixture was stirred for 20 min at room temperature under N_2. Then, 20 mL of a 2 M K_2CO_3 aqueous solution (40 mmol, bubbled by N_2 through the solution for 0.5 h) was added, and the reaction mixture was heated to 80 °C. After maintaining this temperature for 72 h under intensive stirring, the mixture was cooled to room temperature and diluted with 200 mL of toluene. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was redissolved in 10 mL of chloroform, and the solution was poured into 200 mL of a mixture of acetone and ethanol (1:1, v/v) to give a polymer precipitate. After filtration and drying under vacuum, **PFT** was obtained as a yellow powder (640 mg, 78% yield). M_n = 10 000 (GPC, $CHCl_3$); M_w = 17 700. Intrinsic viscosity: $[\eta]$ = 0.24 dL g^{-1} (toluene, 30 °C). IR (KBr pellet, cm^{-1}): 2925, 1694, 2724. ^1H NMR (CD_2Cl_2): δ 0.74−0.78 (m, 10H, $-CH_3$ and β-CH_2), 1.07 (m, 12H, $-CH_2$), 2.06 (t, 4H, α-CH_2), 7.17 (d, 2H), 7.32 (d, 4H), 7.63 (d, 4H), 7.70−7.76 (m, 6H, aromatic H at fluorene ring), 7.80 (d, 2H), 9.84 (s, 1H, −CHO). Anal. Calcd for $C_{25}H_{34}BO_2$−($C_{44}H_{45}NO$ $0.1H_2O)_{17}$−$B(OH)_2$: C, 86.66; H, 7.52; N, 2.22. Found: C, 86.41; H, 7.41; N, 2.39; Br, 0.

Preparation of the −CH=CHAr Polymers, MPa and MPb. To a 100 mL Schlenk tube charged with a magnetic bar, benzyltriphenylphosphonium bromide (1.0 g, 95%, 2.19 mmol), and THF (30 mL) was added sodium *tert*-butoxide (210 mg, 2.19 mmol) under N_2. The suspended mixture was stirred for 1 h at room temperature (rt); then, a solution of **PFT** (150 mg, 0.25 mmol based on the repeating unit) in THF was added dropwise to the tube. After stirring for 72 h at rt, the resultant mixture was allowed to heat to 60 °C, and the temperature was kept for 2 h. The orange mixture being cooled to rt was concentrated to about 20 mL and poured into 200 mL of methanol containing 10 mL of 20% HCl to give a precipitate. After filtration, the solid was washed with water and methanol and dried under vacuum to give **MPa** as a green-yellow powder; 150 mg, 89% yield. M_n = 9600 (GPC, $CHCl_3$); M_w = 17 500. IR (KBr pellet, cm^{-1}): 957. ^1H NMR (CD_2Cl_2): δ 0.74−0.78 (m, 10H), 1.07 (m, 12H), 2.04 (t, 4H), 7.01−7.70 (m, 25H, aromatic H and vinylic H). Anal. Calcd for $C_{25}H_{34}BO_2$−($C_{51}H_{51}N$ $0.3H_2O)_{17}$−$B(OH)_2$: C, 89.03; H, 7.60; N, 1.98. Found: C, 88.90; H, 7.69; N, 2.11. Similarly, **MPb** was obtained in 63% yield by using the corresponding phosphonium salt prepared by refluxing a mixture of 4-methoxybenzyl chloride and triphenylphosphine in toluene for 16 h. M_n = 11 500 (GPC, $CHCl_3$); M_w = 21 500. IR (KBr pellet, cm^{-1}): 957. ^1H NMR (CD_2Cl_2): δ 0.73−0.78 (m, 10H), 1.07 (m, 12H), 2.07 (t, 4H), 3.78 (s, 3H), 6.79−7.79 (m, 24H, aromatic H and vinylic H). Anal. Calcd for $C_{25}H_{34}BO_2$−($C_{52}H_{53}NO$ $0.1H_2O)_{17}$−$B(OH)_2$: C, 87.46; H, 7.54; N, 1.91. Found: C, 87.23; H, 7.33; N, 2.18.

Measurements. IR and NMR spectra were taken with a JASCO FT/IR 410 plus spectrophotometer and a JEOL P-300 spectrometer, respectively. Elemental analyses were carried out with a Yanagimoto type MT-2 CHN autocorder. Molecular weights were measured by gel permeation chromatography (GPC) using a Shimadzu LC-9A liquid chromatograph equipped with a UV detector (eluent = chloroform). The data were relative to polystyrene standards. UV−vis absorption spectra were obtained with a Shimadzu UV 3000 spectrophotometer. Photoluminescence was measured with a Hitachi F-4500 fluorescence spectrophotometer. X-ray diffraction patterns were recorded on a Rigaku RINT 2000 Ultima +/PC X-ray diffractometer with Cu Kα (1.54 Å) radiation. Thermal stability of the polymers was determined with a Shimadzu TGA-50 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} in nitrogen. Cyclic voltammetry of cast films of the polymers on Pt plates was performed in an acetonitrile solution of $[Bu_4N]$-BF_4 (0.10 M, Bu = butyl)) under N_2 using (0.10 M $AgNO_3$)/Ag and platinum wire as reference and counter electrodes, respectively. A Solartron S-1260 analyzer was used for the cyclic voltammetry. Viscosity was measured with an Ubbelohde viscometer using toluene at 30 °C.

Results and Discussion

Synthesis and Characterization. The monomers **2** and **PFT** were prepared according to the procedure shown in Scheme 1. Because of the presence of the −CHO group, which may cause expansion of the π-conjugation system and/or bring about a charge-transferred (CT) electronic state in the molecule, **2** showed a UV−vis peak red-shifted by about 50 nm from 308 nm of its precursor **1**. **2** showed a photoluminescence (PL) peak at 493 nm in CH_2Cl_2, whereas **1** was not photoluminescent.

PFT was obtained in a good yield by using standard Suzuki polycondensation procedure from the monomers **2** and **3**, as shown in Scheme 1. **PFT** had a number-average molecular weight, M_n, of 10 000 and a weight-average molecular weight, M_w, of 17 700 and exhibited an intrinsic viscosity $[\eta]$ of 0.24 dL g^{-1} in toluene at 30 °C. According to number-average molecular weight (M_n), the number of the repeating unit of the polymer was estimated at about 17. The polymer had good solubility in common organic solvents such as toluene, chloroform, and THF and had good film-forming ability when cast from either THF or toluene solutions. Formation of a free-standing film was possible.

The chemical structure of **PFT** was confirmed by IR, ^1H NMR, and elemental analysis. The characteristic

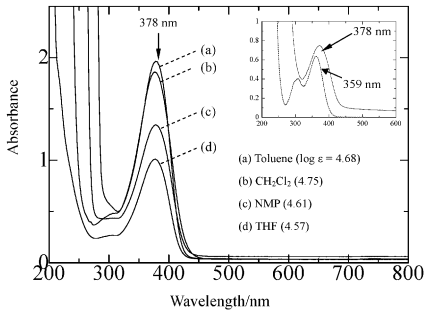


Figure 1. UV−vis spectra of **PFT** in organic solvents. The values in parentheses are molar absorption coefficients (log ϵ); molarity is based on the repeating unit, $-C_{44}H_{45}NO-$. The inset shows the UV−vis spectrum of **PFT** on a quartz glass plate (solid line) and that of monomer **2** in dichloromethane (dotted line).

υ(C═O) and υ(C−H) peaks of the −CHO group appeared at 1694 and 2724 cm^{-1}, respectively. The ^1H NMR spectrum showed the −CHO peak at δ 9.84 with reasonable peak area. These data indicated that the aldehyde group was neither reduced nor oxidized under the polymerization conditions. The elemental analysis showed no content of bromine, indicating that the terminal groups were the fluorene unit, although polycondensations of aromatic dihalogenated compounds using transition metals as catalysts sometimes gave polymers with halogenated terminal groups.[20] Monomer **3** is considered to have a higher reactivity than monomer **2**.

Optical and Thermal Properties and Crystallinity. Figure 1 shows the UV−vis spectra of **PFT** in organic solvents and in the solid state. **PFT** shows essentially the same UV−vis absorption peak and molar absorption coefficient (ϵ) in the different solvents. The maximum absorption peak of **PFT** in dichloromethane has a red shift of about 20 nm from those of **2** (**PFT**: 378 nm; **2**: 359 nm). Cast film of **PFT** on a quartz glass plate shows the same UV−vis absorption peak as its dichloromethane solution, similar to the case of the triphenylamine (TPA)-type polymers, which are not able to form π-stacked structure in the solid due to the twisted TPA units.[18]

PL spectra of **PFT** are exhibited in Figure 2. It is evident that there is a strong effect of the solvent polarity on the emission wavelength of **PFT**; such a phenomenon has sometimes been observed with aromatic polymers, especially when the polymer has a CT structure.[21] In Figure 2, the maximum emission peak of **PFT** shifts to a longer wavelength with increase in the polarity of the solvents, for example, from 462 nm (blue) in toluene (dielectric constant[22] $D_k = 2.4$ at 25 °C) to 528 nm (green) in NMP ($D_k = 32.2$ at 25 °C). This solvatochromism observed for the PL suggests that the photoexcited state has a polar structure (presumably a positive center at N and a negative center at the −CHO unit), which is stabilized by solvation, and the light emission takes place from the stabilized molecule. The shift of the PL peak in toluene (462 nm) from the onset position of the UV−vis absorption band (about 430 nm; cf. Figure 1) suggests that even the PL in toluene receives such a stabilization effect. The quantum yield of **PFT** falls with increase in the Stokes shift as indicated in Figure 2. Similar results were reported for PL of some π-conjugated polymers.[21]

TGA showed that **PFT** had good thermal stability with 5 wt % loss temperature of 344 °C under N_2.

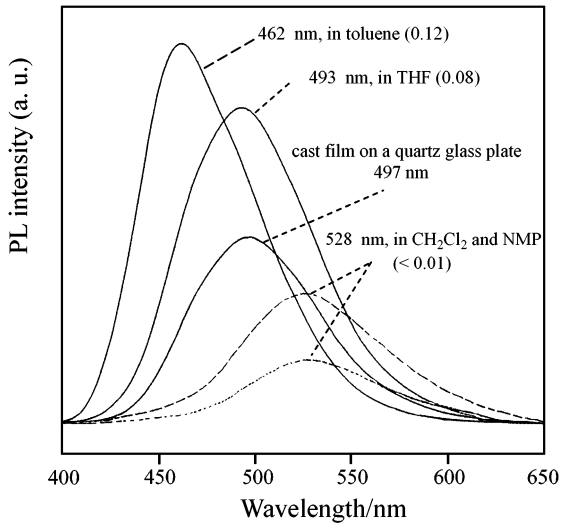


Figure 2. PL spectra of **PFT** in solvents and in a film cast on a quartz glass plate. The values in parentheses are quantum yields (Φ) of PL of **PFT** in the solvents estimated by using a 0.5 M H_2SO_4 solution of quinine (10^{-5} M, $\Phi = 0.55$) as a reference. In all cases the exciting wavelength was 378 nm (UV−vis peak of **PFT**).

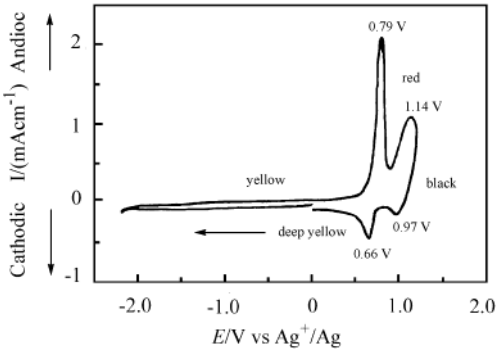
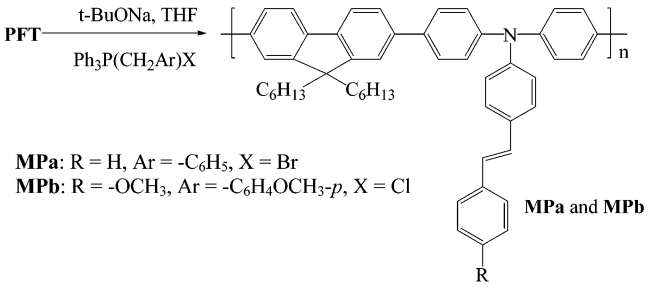


Figure 3. CV curve of a cast film of **PFT** on a Pt plate. In a 1:3 (v/v) solution of CH_3CN and CH_2Cl_2 containing 0.10 M $[Bu_4N]BF_4$. Sweep rate = 50 mV s^{-1}.

The powder X-ray diffraction (XRD) pattern of **PFT** given in the Supporting Information indicates that **PFT** is essentially amorphous, revealing that **PFT** does not form a well-packed structure, similar to the case of TPA (triphenylamine) type polymers,[18] as discussed above.

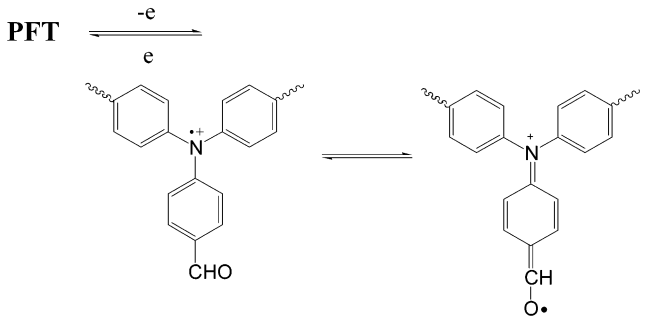
Electrochemical Properties. Electrochemical behavior of **PFT** was characterized by cyclic voltammetry (CV) with its dichloromethane solution and with a cast film on a Pt plate in a 1:3 (v/v) solution of CH_3CN (poor solvent) and CH_2Cl_2. Figure 3 gives the CV curve of the film of **PFT**. As depicted in Figure 3, the electrochemical oxidation of **PFT** gives two peaks at 0.79 and 1.14 V vs Ag^+/Ag, respectively, accompanied by the color change of yellow to black through red. This electrochemical behavior of **PFT** is similar to that of the copolymers consisting of fluorene units and triphenylamine units, in which triphenylamine shows oxidation peaks at 0.6−0.8 V vs Ag^+/Ag and fluorene units give the oxidation peaks about 1.08 V vs Ag^+/Ag.[9c,e] Aromatic aldehyde groups are stable in this region and do not give oxidation peaks in nonaqueous media in the range from 0 to 2.5 V vs Ag^+/Ag.[23] Therefore, the electrochemical oxidation peak which appears at 0.79 V vs Ag^+/Ag is mainly associated with oxidation of the triphenylamine unit, whereas the peak at 1.14 V vs Ag^+/Ag is assigned to oxidation of the fluorene unit of **PFT**. The electrochemi-

Scheme 2. Procedure for Preparation of MPa



cally oxidized **PFT** seems to be neutralized in the reverse scanning with the corresponding p-dedoping peaks at 0.97 and 0.66 V vs Ag^+/Ag. However, the color of the film did not come back to the original (yellow) after a cyclic sweep, suggesting some irreversibility of the redox reaction of **PFT**. In the CH_2Cl_2 solution of 0.10 M $[BuN_4]BF_4$, **PFT** (0.5 mM, based on the repeating unit) showed two broad oxidation peaks at about 0.65 and 1.0 V vs Ag^+/Ag.

The cast film of **PFT** was partly dissolved in the 1:3 mixture of CH_3CN and CH_2Cl_2 (v/v) after the electrochemical oxidation. The increase in the solubility may be due to formation of a strongly polarized product:



In the reduction region, no peaks were observed in the range from 0 to −2.2 V vs Ag^+/Ag, similar to the behavior of poly(9,9-alkylfluorene-*alt*-triphenylamine)s,[9c] although aromatic aldehyde derivatives often show reduction peaks at about −1.7 V vs Ag^+/Ag.[23] This inertness of the −CHO group for the electrochemical reduction may arise from the strong electron-donating action of the amine group at the para position of the −CHO group.

Transformation of the −CHO Group to −CH═CHAr Groups. As depicted in Scheme 2, the −CHO group of **PFT** was transformed to −CH═CHAr groups by the Wittig reaction.

The transformation reaction proceeded quantitatively, and chemical structures of the obtained polymers, **MPa** and **MPb**, were characterized by IR, ^1H NMR, and elemental analysis. IR spectra of **MPa** and **MPb** showed that the peaks of the −CHO group at 1694 and 2724 cm^{-1} of **PFT** disappeared, and a new out-of-plane δ (CH) peak of a *trans*-vinylene group[12,24] appeared at about 957 cm^{-1}, as indicated in the Supporting Information. ^1H NMR spectra did not show the −CHO peak at δ 9.84. For **MPa**, two doublet peaks were observed at δ 7.08 and 7.13 ppm (cf. Supporting Information), which were assigned to the protons of the trans vinylic group.[25] The Wittig reaction often gives both cis and trans geometric structures;[26] however, in our case, no δ (CH) peak of a cis vinylene group peak[26b] at 853 cm^{-1} was observed in the IR spectra of **MPa** and **MPb**, as seen from Figure S3 in the Supporting Information.

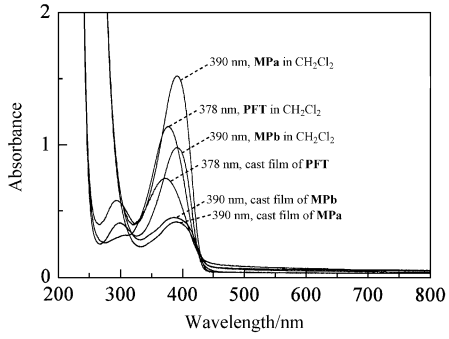


Figure 4. UV−vis spectra of **MPa** and **MPb** in dichloromethane and films cast on a quartz glass plate.

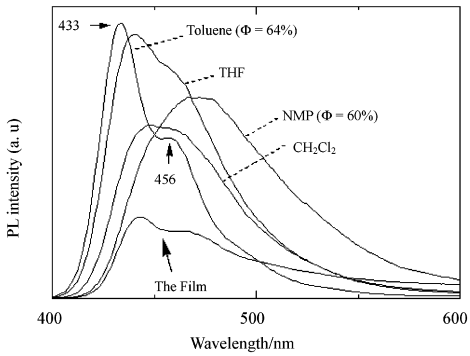


Figure 5. PL spectra of **MPb** in different solvents and in a film cast on a quartz glass plate. Irradiated at 390 nm (UV−vis peak).

Optical Properties of MPa and MPb. Because of expansion of the π-conjugation system, the UV−vis absorption peaks of **MPa** and **MPb** shifted to 390 nm from 378 nm of **PFT**, as depicted in Figure 4.**MPa** and **MPb** give a similar PL spectrum, and the PL spectra of **MPb** in organic solvents and in the solid are depicted in Figure 5. In toluene, **MPb** gives a main peak at 433 nm and a shoulder peak at 456 nm; such a couple of PL peaks appears for various fluorene polymers.[7,8] The PL data of **MPa** and **MPb** are listed in Table 1 together with those of **PFT**.

As seen from Table 1, **MPa** and **MPb** show much higher quantum yields in the solvents than **PFT**. The quantum yields of **MPb** and **MPa** in toluene are 64% and 51%, respectively, whereas the value for **PFT** is 12% as described above. The emission peak of **MPa** and **MPb** shifts to a large wavelength with increase in the polarity of the solvent, similar to the case of **PFT**. However, the degree of the shift is smaller compared with that observed with **PFT**, presumably due to the less polar structure of **MPa** and **MPb**, and the high quantum yield is maintained even in the polar solvents. Cast films of **MPa** and **MPb** show the PL peaks near the position observed with the toluene solution, revealing that **MPa** and **MPb** do not form an excimer-like adduct between the excited polymer molecule and the polymer molecule in the ground state. Such an excimer-like adduct is often formed for aromatic polymers. The cast film of **MPa** gave a quantum yield (Φ = 0.51) comparable to that (Φ = 0.55)[27] of poly(9,9-dialkylfluorene-2,7-diyl).

Electrochemical Response of MPa and MPb. The CV curves of the films of **MPa** and **MPb** cast on platinum plates are shown in Figure 6. Electrochemical

Table 1. PL Data of MPa and MPb[a]

	λ_{em} (nm)[b]				
	in organic solvents				
polymer	toluene	THF	CH_2Cl_2	NMP	in film[c]
MPa	433, 457 (0.51)	441, 457 (0.50)	449 (0.43)	466 (0.50)	443, 465 (0.51)
MPb	433, 457 (0.64)	441, 457 (0.52)	448 (0.49)	466 (0.60)	443, 465 (0.09)
PFT	462 (0.12)	493 (0.08)	528 (<0.01)	528 (<0.01)	497 (0.24)

[a] In all cases, excited at the UV−vis λ_{max} position (e.g., 390 nm for **MPa** and **MPb**). For comparison, data of **PFT** are also included. [b] Position of the emission peak, λ_{em}. The values in parentheses are quantum yield (Φ) estimated by using a 0.5 M H_2SO_4 solution of quinine (10^{-5} M, $\Phi = 0.55$) as a reference. [c] Cast film on a quartz glass plate. The values in parentheses are quantum yield estimated by using a film of poly(9,9-dialkylfluorene-2,7-diyl) ($\Phi = 0.55$) as a reference.[27]

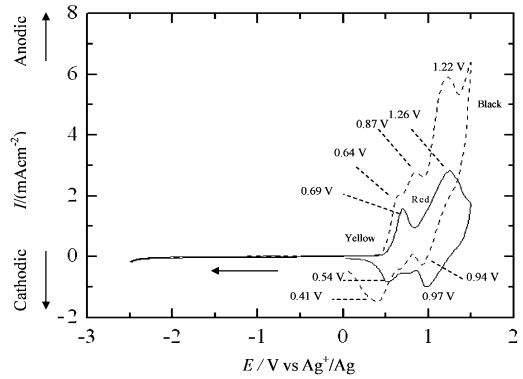


Figure 6. CV curves ofthe cast films of **MPa** (solid line) and **MPb** (dashed line) on Pt electrodes (1 cm × 1 cm) with a sweep rate of 50 mV s^{-1} in an acetonitrile solution of 0.10 M $[Bu_4N]$-BF_4 (Bu = butyl).

Table 2. Electrochemical Data of the Polymers[a]

	redox potential, E/V vs Ag^+/Ag					
	first cycle		second cycle		third cycle	
polymer	ox[b]	red[c]	ox	red	ox	red
PFT	0.79	0.66	1.14	0.97		
MPa	0.69	0.54	1.26	0.97		
MPb	0.64	0.41	0.87	0.68	1.22	0.94

[a] Measure with the cast film on a Pt plate. In an acetonitrile solution of $[Bu_4N]BF_4$ (0.10 M). [b] Oxidation peak. [c] Reduction peak coupled with the oxidation peak.

oxidation (or p-doping) of **MPa** and **MPb** starts at about 0.4 V vs Ag^+/Ag, and **MPa** gives two p-doping peaks at 0.69 and 1.26 V vs Ag^+/Ag, respectively. **MPb** gives somewhat complicated CV chart with three p-doping peaks at 0.64, 0.87, and 1.22 V vs Ag^+/Ag, respectively. The two peaks of **MPa** at 0.69 and 1.26 V vs Ag^+/Ag are assigned to oxidation of the triphenylamine and fluorene units, respectively,[9c] as discussed above. The potential of the first oxidation peak reflects the electronic effect of the group at the para position. Thus, the first oxidation potential is in the following order: **PFT** (−CHO; 0.79 V) > **MPa** (−CH═CH−C_6H_5; 0.69 V) > **MPb** (−CH═CH−$C_6H_4OCH_3$-*p*; 0.64 V). Table 2 summarizes the electrochemical data of the polymers. In the reverse scanning, the color of the film of **MPa** comes well back to the original color (yellow), similar to the poly(phenylenevinylene)s containing triphenylamine units;[10,11] however, the film of **MPb** does not give such a color reversibility, suggesting the presence of certain irreversible process in the oxidation of **MPb**. Similar electrochemical irreversibility has been observed with poly(*p*-phenylene)s and poly(aryleneethynylene)s with alkyloxy side chains[28,29] and attributed to a strong interaction of the anion dopant (BF_4^- in the present case) with the alkoxy side chain. The oxidation peak of

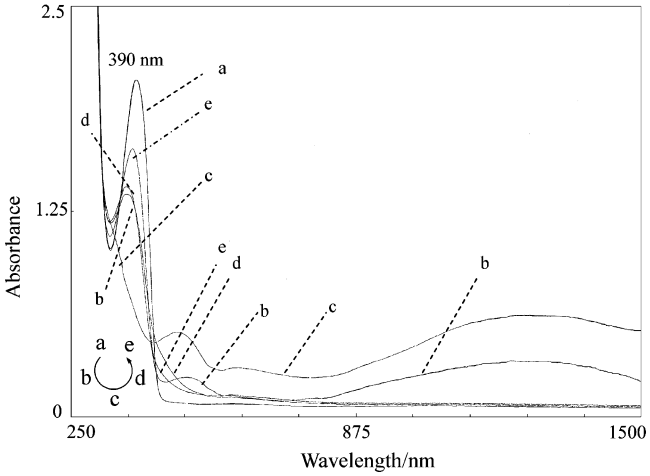


Figure 7. Changes in the UV−vis spectrum of a film of **MPa** on an ITO glass electrode at various applied potentials vs Ag^+/Ag. The curve a shows the UV−vis spectrum of the cast film of **MPa**. Applied potential (V): chart a (0.0) → b (1.0) → c (1.5) → d (1.0) → e (0.0). In a CH_3CN solution of $[Bu_4N][BF_4]$ (0.10 M).

MPb at 0.87 V vs Ag^+/Ag may be related to this type of irreversible oxidation.

Since the film of **MPa** did not show dissolution in the supporting electrolyte during the CV cycle, optoelectrochemical changes of the cast film of **MPa** on an ITO (indium−tin oxide) glass plate can be followed UV−vis spectroscopically, and the data are shown in Figure 7. On application of a potential of 1.0 V (chart b), the peak of the chart a at 390 nm shifts to about 365 nm and two new absorption bands, which are assigned to polaron and/or bipolaron bands,[30] appear at about 500 and 1200 nm. The yellow color of the film turns to red, as shown in Figure 6. When the potential further increases to 1.5 V (chart c), the absorption peak of the chart b at about 365 nm almost disappears, and the two new peaks become stronger. The color of the film changes from red to black, as shown in Figure 6. On applying a reverse potential of 1.0 V, the absorption peaks of the chart c at about 500 and 1400 nm disappear, Finally, when the potential returns to 0 V (chart e), the original peak at 390 nm is recovered.

Conclusions

A new alternative copolymer comprised of fluorene and triphenylamine units with a tunable reactive −CHO group in the side chain was prepared. The polymer, **PFT**, showed good solubility in common organic solvents and exhibited photoluminescence with the emission peak depending on the kind of the solvent. By using the Wittig reaction, the −CHO group of **PFT** was quantitatively converted into the trans −CH═CHAr

group. The Wittig reaction products, **MPa** and **MPb**, showed improved quantum yields in PL. All of the polymers were electrochemically active. Studies in this line are expected to give polymers with better chemical properties.

Acknowledgment. Financial support from Japan Society for Promotion of Science (JSPS) is gratefully acknowledged.

Supporting Information Available: ^{1}H NMR spectrum of **PFT** (Figure S1), XRD powder patterns of **PFT** (Figure S2), IR spectra of **PFT**, **MPa**, and **MPb** (Figure S3), and ^{1}H NMR spectrum of **MPa** (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0359133