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ARTICLE

N,N,N′,N′- Tetraphenyl-1,4-phenylenediamine−Fluorene Alternating Conjugated Polymer: Synthesis, Characterization, and Electrochromic Application

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ABSTRACT: A novel *N,N,N′,N′*-tetraphenyl-1,4-phenylenediamine (TPPA)-containing aromatic dibromide (**3**), *N,N*-bis(4-bromophenyl)-*N′,N′*-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)-1,4-phenylenediamine, was successfully synthesized. The novel conjugated polymer (**4**) having number-average molecular weight of 2.05×10^4 was prepared via Suzuki coupling from the dibromide (**3**) with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. The conjugated polymer (**4**) exhibited excellent solubility in common organic solvents such as *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran, chloroform, and toluene at room temperature. The conjugated polymer (**4**) had useful levels of thermal stability associated with their relatively high glass transition temperature (T_g = 144 °C), 10% weight-loss temperatures (T_{d10}) in nitrogen (T_{d10} = 445 °C), and char yields at 800 °C in nitrogen (59.0%). The hole-transporting and electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltammograms of the conjugated polymer films cast onto indium−tin oxide (ITO)-coated glass substrates exhibited two reversible oxidation redox couples at $E_{1/2}$ value of 0.67 and 1.05 V vs Ag/Ag^+ in acetonitrile solution. The conjugated polymer film (**4**) revealed better stability of electrochromic characteristics and more rapid switching time than model polymers **M2** which has no electron-donating bis(4-(2,4,4-trimethylpentan-2-yl) phenyl)amine group and **M3** without electron-donating 2,4,4-trimethylpentan-2-yl substituent. The conjugated polymer film (**4**) also showed high contrast with color change from pale yellowish to green and then to blue at applied potentials ranging from 0.00 to 1.18 V.

Introduction

Electrochromism is known as the reversible electromagnetic absorbance/transmittance and color change resulting from the oxidation or the reduction of the material in response to an externally applied potential by electrochemical means.[1] This interesting property led to the development of many technological applications such as automatic antiglazing mirror,[2] smart windows,[3] electrochromic displays,[4] and chameleon materials.[5] Hitherto, a wide variety of electrochromic materials showing high coloration efficiencies, low operating voltage, and fast switching capabilities[6] have been developed, which can be classified into several distinct categories such as metal oxides [tungsten trioxide (WO_3) or iridium dioxide (IrO_2)],[7] mixed-valence metal complexes (Prussian blue),[8] small organic molecules (viologens, bipyridinium, and phthalocyanines),[9] and conjugated polymers.[10] Conjugated organic polymers[11] have received significant attention throughout the course of the past two decades, stemming not only from their high conductivities in the doped state but also from a variety of optoelectronic and redox properties for advanced technological applications such as light-emitting diodes, photovoltaic cells, and electrochromic cells. Moreover, the most important features of conjugated polymers are the possibilities to fine-tune the color through chemical structure modification of the conjugated backbone and to get multichromism from the same material.[12]

Recently, triphenylamine (TPA) derivative materials, including small molecules and macromolecules, have extensively been investigated for hole transporters,[13] light emitters,[14] and polymer electronic memories.[15] For instance, Kang et al.[13k] reported that triphenylamine−fluorene alternating conjugated copolymers with pendant acceptor groups (aldehyde, monocyano, and dicyano group) were applied for solar cell field. On the other hand, Chen et al.[14d] reported that copolyfluorenes containing bipolar groups (hole-transporting triphenylamine and electron-transporting 1,2,4-triazole group) were useful for enhancing electroluminescence of MEH-PPV {poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene]}. Thus, different functional substituents on triphenylamine had diverse properties and applications. TPA can also be considered as a good electrochromic material as it easily oxidizes to form radical cation with a noticeable change of coloration.[16] Although TPA has many advantages, Adams and co-workers[17] reported that TPA could be easily dimerized to form tetraphenylbenzidine during the anodic oxidation pathway. For electrochromic materials, this dimerization could be considered as an undesired side reaction, which might cause irreversible defect after several redox switches. To avoid this behavior, incorporating electron-donating substituents such as alkyl or alkoxy group at the para-position of the TPA group could prevent the coupling reactions and afford stable cationic radicals with lower potential.[18] The redox

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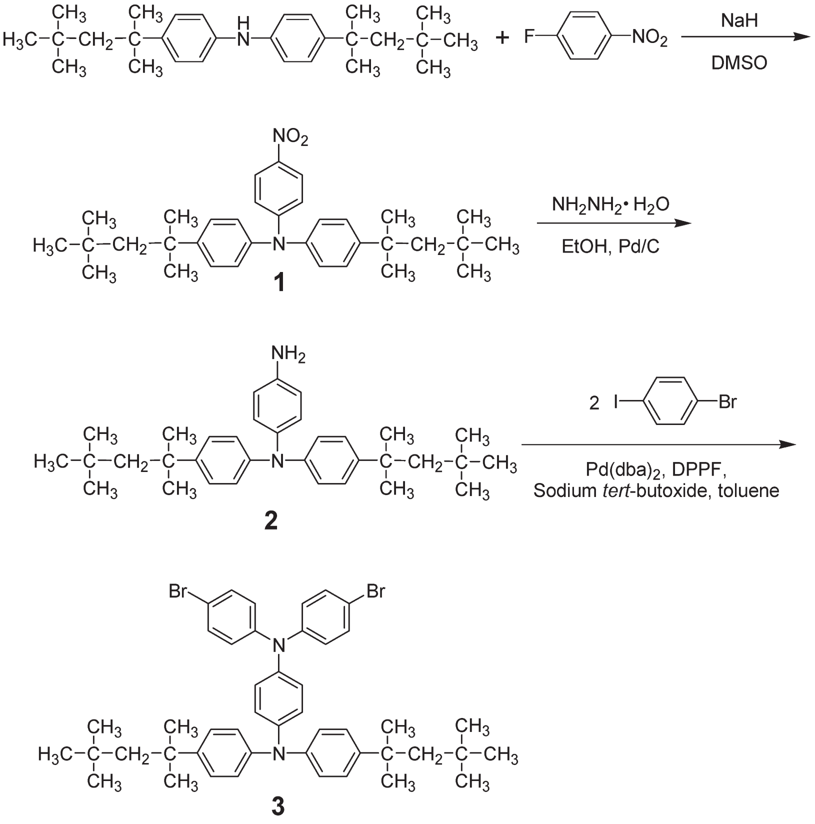
Scheme 1. Synthesis Route of *N*,*N*-Bis(4-bromophenyl)-*N*′,*N*′-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)-1,4-phenylenediamine (3)



property, electron-transfer process, multicoloring electrochromism, and photoelectrochemical behavior of *N*,*N*,*N*′,*N*′-tetrasubstituted-1,4-phenylenediamines (TPPA) are important for technological application.[19]

In this report, we prepared TPPA-containing dibromo monomer with electron-donating group (2,4,4-trimethylpentan-2-yl substituted), and their corresponding conjugated polymers were obtained by Suzuki coupling. The basic properties of the conjugated polymer such as solubility as well as thermal and optical properties are described. The electrochemical and electrochromic characteristics of the conjugated polymer are also investigated herein. For comparing the stability and switching time of electrochromic characteristics with synthesized conjugated polymer, the model polymers **M2** and **M3** were synthesized as well.

Experimental Section

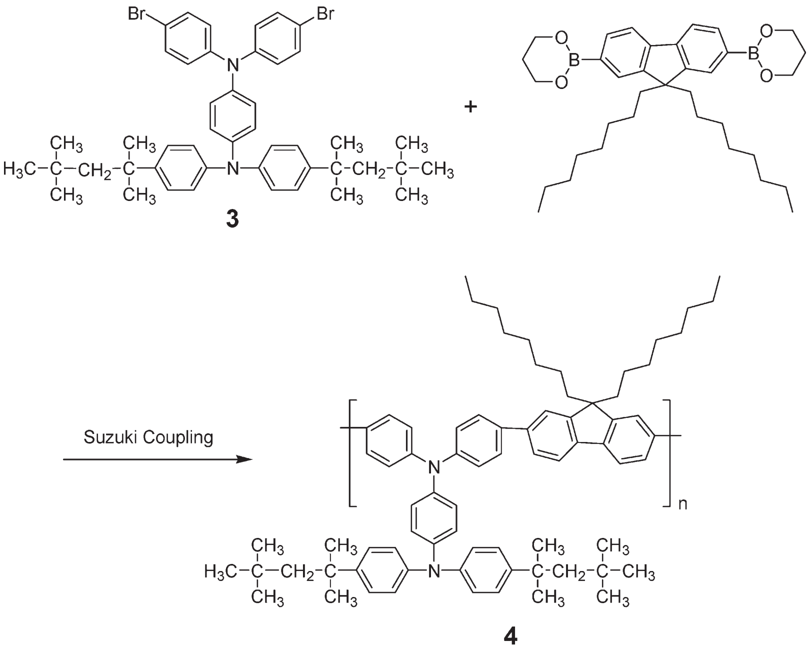
Materials. The chemical bis(4-(2,4,4-trimethylpentan-2-yl)-phenyl)amine was purchased from Ouchi Shinko Chemical Industrial. 4-Fluoronitrobenzene (Acros, 99%), sodium hydride (Aldrich), hydrazine monohydrate (Merck), 10% palladium on activated carbon (10% Pd/C) (Merck), 1-bromo-4-iodobenzene (Acros, 98%), bis(dibenzylideneacetone)palladium [Pd(dba)$_2$] (Acros), 1,1′-bis(diphenylphosphino)ferrocene (DPPF) (Acros, 98%), anhydrous potassium carbonate (Merck), and sodium *tert*-butoxide (Aldrich, 98%) were used without further purification. Tetrabutylammonium perchlorate (TBAP) was obtained from Fluka and recrystallized twice from ethyl acetate and then dried in vacuum prior to use. The catalyst tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) was purchased from Acros. 9,9-Dioctylfluorene-2,7-diboronic acid bis-(1,3-propanediol) ester was purchased from Aldrich and recrystallized from mixture of ethyl acetate and *n*-hexane prior to use. DMSO was dried and distilled over calcium hydride under an inert atmosphere. Toluene was dried and distilled over sodium under an inert argon atmosphere. All other reagents were used as received from commercial sources.

Monomer and Polymer Synthesis. *Synthesis of 4-Nitro-N,N-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)aniline* (***1***) (*Scheme 1*). In a 500 mL three-neck round-bottom flask was placed bis-(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine (30.00 g, 76.20 mmol), 4-fluoronitrobenzene (12.90 g, 91.45 mmol), sodium hydride (2.74 g, 114.31 mmol), and dimethyl sulfoxide (DMSO, 120 mL). The mixture was heated with stirring at 120 °C for 48 h. The reaction mixture was cooled and then poured into 1 L of methanol. The yellow precipitate was collected by filtration and dried under vacuum. The product was purified by silica gel column chromatography (dichloromethane:*n*-hexane = 1:3) and recrystallized from ethyl acetate to afford yellow crystals, 4-nitro-*N*,*N*-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)aniline (**1**), in a 60% yield; mp 167 °C (by DSC at a scan rate of 10 °C min^{-1}).

Synthesis of 4-Amino-N,N-bis(4-(2,4,4-trimethylpentan-2-yl)-phenyl)aniline (***2***) (*Scheme 1*). In a 500 mL three-neck round-bottom flask equipped with a stirrer bar under nitrogen atmosphere, 7.00 g (13.60 mmol) of nitro compound (**1**) and 0.22 g of 10% Pd/C were suspended in 150 mL of ethanol. The suspension solution was heated to reflux, and 7 mL of hydrazine monohydrate was added slowly to the mixture from a dropping funnel over a period of 1 h under dry nitrogen. After a further 12 h of reflux, the mixture solution was filtered to remove Pd/C, and the filtrate was cooled to precipitate. The crude product was collected by filtration and recrystallization from ethanol to afford white crystals (80% yield); mp 95 °C (by DSC at a scan rate of 10 °C min^{-1}).

Synthesis of N,N-Bis(4-bromophenyl)-N′,N′-bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)-1,4-phenylenediamine (***3***) (*Scheme 1*) *by Buchwald–Hartwig Reaction*[20]. A mixture of 1.00 g (2.06 mmol) of amino compound **2**, 1.17 g (4.13 mmol) of 1-bromo-4-iodobenzene, 23.72 mg (4.13 × 10^{-2} mmol) of Pd(dba)$_2$, 45.71 mg (8.25 × 10^{-2} mmol) of DPPF, 0.59 g (6.19 mmol) of sodium *tert*-butoxide, and 6 mL of dry toluene was charged in a three-necked flask kept under a nitrogen atmosphere. The mixture

Scheme 2. Synthesis Route of Conjugated Polymer 4 via Suzuki Coupling



was heated to reflux for 6 h. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was extracted with dichloromethane/water. The collected organic layer was dried over $MgSO_4$ overnight and then filtered to remove $MgSO_4$. After removing the solvent of filtrate, the residue was purified by silica gel column chromatography (dichloromethane:*n*-hexane = 1:3) and recrystallized from hexane to obtain white crystals (61% yield); mp 205 °C (by DSC at a scan rate of 10 °C min^{-1}).

Synthesis of Model Compound 4,4′-Bis(2,4,4-trimethylpentan-2-yl)triphenylamine (***M1***). A mixture of 3.00 g (7.62 mmol) of bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine, 1.55 g (7.62 mmol) of 1-iodobenzene, 87.6 mg (1.52×10^{-1} mmol) of Pd(dba)$_2$, 168.9 mg (3.05×10^{-1} mmol) of DPPF, 1.10 g (11.43 mmol) of sodium *tert*-butoxide, and 10 mL of dry toluene was charged in a three-necked flask kept under a nitrogen atmosphere. The mixture was heated to reflux for 12 h. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was extracted with dichloromethane/water. The collected organic layer was dried over $MgSO_4$ overnight and then filtered to remove $MgSO_4$. After removing the solvent of filtrate, the residue was purified by silica gel column chromatography (*n*-hexane) to obtain colorless liquid (65% yield).

Synthesis of the Conjugated Polymers 4 via Suzuki Coupling (*Scheme 2*). To a three-necked flask was added 0.1757 g (0.3146 mmol) of 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester and 0.25 g (0.3146 mmol) of dibromo compound **3**. The flask equipped with a condenser was then evacuated and filled with nitrogen several times to remove traces of air, and then 5 mL of the degassed toluene was added. Once the two monomers were dissolved, 10.9 mg (9.4369×10^{-3} mmol) of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and 5 mL of 3 M aqueous sodium carbonate solution were added, and the mixture was stirred for 48 h at 105 °C under a nitrogen atmosphere. After completing the reaction, the reaction mixture was cooled to room temperature, and the organic layer was separated, washed with water, and precipitated into methanol. The light yellow-green fibrous polymer sample was filtered, washed with excess methanol, dried, and purified by a Soxhlet extraction with acetone for 2 days. Yield: 92%.

Synthesis of Bis(4-bromophenyl)phenylamine and Model Polymer ***M2***. A mixture of 1.00 g (10.74 mmol) of aniline, 6.08 g (21.48 mmol) of 1-bromo-4-iodobenzene, 123.5 mg (2.15×10^{-1} mmol) of Pd(dba)$_2$, 237.9 mg (4.30×10^{-1} mmol) of DPPF, 3.10 g (32.21 mmol) of sodium *tert*-butoxide, and 10 mL of dry toluene was charged in a three-necked flask kept under a nitrogen atmosphere. The mixture was heated to reflux for 12 h. After the completion of the reaction, the solvent was removed under reduced pressure, and the residue was extracted with dichloromethane/water. The collected organic layer was dried over $MgSO_4$ overnight and then filtered to remove $MgSO_4$. After removing the solvent of filtrate, the residue was purified by silica gel column chromatography (*n*-hexane) to obtain colorless viscous liquid (bis(4-bromophenyl)phenylamine, 85% yield).

The model polymer **M2** was prepared analogously as the conjugated polymer **4**. Yield: 88%.

Measurements. FT-IR spectra were recorded in the range 4000−400 cm^{-1} on a Bio-Rad FTS-3500 spectrometer. Elemental analyses were performed on Perkin-Elmer 2400 C, H, and N analyzer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument operating at 500 MHz for proton and 125 MHz for carbon. Weight-average ($\overline{M_w}$) and number-average ($\overline{M_n}$) molecular weight were determined by gel permeation chromatography (GPC). Five Waters (Ultrastyragel) columns 300 × 7.7 mm (guard, 500, 10^3, 10^4, 10^5 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 mL min^{-1}) as an eluent. The eluents were monitored with a refractive index detector (RI 2000). Polystyrene was used as a standard. The melting temperature (T_m) and glass transition temperature (T_g) were measured on a DuPont 9000 differential scanning calorimeter (TA Instruments TA 910) at a heating rate of 10 °C min^{-1} from 50 to 250 °C under a steady flow of nitrogen. The glass transition temperature (T_g) was recorded on second run heating. The recorded temperatures were calibrated using indium as standard. Thermogravimetric data were obtained on a Perkin-Elmer TG/DTA (Diamond TG/DTA). Experiments were carried out on approximately 3−5 mg samples at a heating rate of 10 °C min^{-1} from 50 to 800 °C under nitrogen or air flowing conditions (20 cm^3 min^{-1}). UV−vis spectra of the polymer films or solutions were recorded on a JASCO V-550 spectrophotometer at room temperature in air. Photoluminescence spectra were measured with a HORIBA Jobin Yvon FluoroMax-3 spectrofluorometer. Fluorescence quantum yield (Φ_F) values of the samples in THF were measured by using 9,10-diphenylanthracence in THF as a reference standard ($\Phi_F = 0.9$) with excitation at 346 nm. All corrected

Table 1. Molecular Weight and Thermal Properties of the Conjugated Polymers

polymer	yield[a] (%)	$\overline{M}_n \times 10^{-4\,b}$	$\overline{M}_w \times 10^{-4\,b}$	PDI[b]	T_g[c] (°C)	T_{d10}[d] (°C) N$_2$	T_{d10}[d] (°C) air	char yield[e] (%)
4	92	2.05	3.52	1.72	144	445	412	59.0
M2	88	1.75	3.16	1.80	133	438	417	63.9

[a] Yield was determined gravimetrically. [b] Determined by gel permeation chromatography (GPC) in THF using polystyrene as a standard. [c] T_g was determined by DSC at a heating rate of 10 °C min^{-1}. [d] The decomposition temperature at 10% weight loss (T_{d10}) was determined by TG at a heating rate of 10 °C min^{-1}. [e] Residual weight percentage at 800 °C in nitrogen.

fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. Cyclic voltammetry (CV; CHI model 619A) was conducted with the use of a three-electrode cell in which ITO was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 50 mV/s against a Ag/Ag$^+$ reference electrode in a solution of 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH_3CN). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. The spectroelectrochemical cell was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/Ag$^+$ reference electrode. Absorption spectra in spectroelectrochemical analysis were measured with a JASCO V-550 spectrophotometer.

Results and Discussion

Synthesis. Novel *N,N,N′,N′*-tetraphenyl-1,4-phenylenediamine (TPPA)-containing dibromo compound **3** and the conjugated polymer **4** containing TPPA and fluorene groups were synthesized according to the synthetic route outlined in Schemes 1 and 2, respectively. The identification techniques such as elemental analysis, IR, and NMR spectra including ^{1}H NMR, ^{13}C NMR, HMQC, and COSY were used to identify structures of the intermediate compounds, the dibromo monomer **3**, and the conjugated polymer **4**. The confirmation data are shown in the Supporting Information. The results of the elemental analyses for the intermediate compounds and the target dibromo monomer **3** are in good agreement with the proposed structures. The NMR spectra also agree well with the proposed molecular structures of compound **3** and the conjugated polymer **4**.

Basic Characterization. The solubility behavior of conjugated polymer **4** was tested qualitatively. The conjugated polymer **4** was highly soluble in comment organic solvent such as *N*-methyl-2-pyrrolidinone (NMP), tetrahydrofuran (THF), dichloromethane, chloroform, toluene, xylene, and benzene at room temperature, and the enhanced solubility could be attributed to the introduction of the bulky pendent *N,N,N′,N′*-tetraphenyl-1,4-phenylenediamine (TPPA) moiety and alkyl chain including fluorene group and 2,4,4-trimethylpentan-2-yl substituted into the repeating unit. Thus, the excellent solubility makes the conjugated polymer **4** potential candidates for practical applications by spin-coating, dip-coating, or inject-printing processes to obtain thin films for optoelectronic devices.

The molecular weights of the conjugated polymers were determined by gel permeation chromatography (GPC) using the polystyrene as the standard and are summarized in Table 1. The number-average molecular weight of the prepared conjugated polymers **4** and **M2** was as high as 2.05 × 10^4 and 1.75 × 10^4 with polydispersity index of 1.72 and 1.80, respectively.

The thermal properties of the conjugated polymers were investigated by DSC and TGA techniques, and the results are summarized in Table 1. All the polymers indicated no clear melting endotherms up to the decomposition temperatures on the DSC thermograms (Figure 1). This result supports the amorphous nature of these triphenylamine-containing polymers.[21] In Figure 1, the glass transition temperature of the conjugated polymer **4** were observed at 144 °C, which is much higher than that of poly(9,9-dioctylfluorene) (POF) (POF; T_g = 75 °C)[22,23] and 4,4′-bis-[*N,N*-(*m*-tolyl)phenylamino]biphenyl (TPD; T_g = 60 °C),[24] indicating that the use of these conjugated polymers may greatly improve the device durability, which related to the T_g's of the materials as reported by Tokito et al.[24] The relatively high glass transition temperature has the thermal advantage for the application of electronic materials.[25] It also observed that the glass transition temperature of the model polymer **M2** (T_g = 133 °C) was slightly lower than that of conjugated polymer **4** (T_g = 144 °C) due to incorporation of bulky *N,N,N′,N′*-tetraphenyl-1,4-phenylenediamine (TPPA) moiety into the conjugated polymer. Tokito et al.[24] investigated that the oligomerization of triphenylamine brought about increase of the T_g. Typical TGA spectra of conjugated polymers **4** and **M2** in a nitrogen atmosphere are shown in Figure 1. The conjugated polymers **4** and **M2** exhibited a similar TGA pattern with no significant weight loss below 400 °C in a nitrogen atmosphere. The decomposition temperatures at 10% weight loss (T_{d10}) and char yield of the conjugated polymers **4** and **M2**, examined by TG analysis, were 445 and 438 °C in nitrogen, 412 and 417 °C in air, and 59.0% and 63.9% in nitrogen, respectively. Because of lower aromatic content, the conjugated polymer **4** was lower char yield than that of conjugated polymer **M2**.

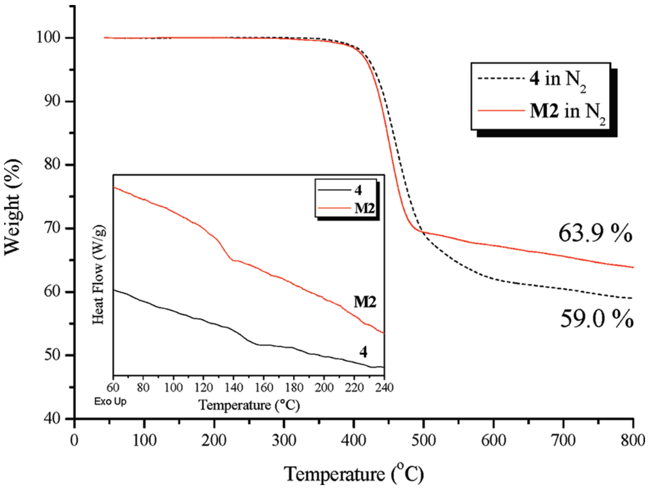


Figure 1. TGA and DSC curve of the conjugated polymers **4** and **M2** with a heating rate of 10 °C min^{-1}.

Optical and Electrochemical Properties. The optical properties of the conjugated polymers were investigated by UV−vis and photoluminescence spectroscopy in solid state and toluene (ca. 1 × 10^{-5} M solution). The results are summarized in Table 2.

The UV−vis absorption of the conjugated polymer **4** exhibited a strong absorption around 387 nm and a minor absorption around 314 nm in toluene solution. By

Table 2. Optical and Electrochemical Properties of the Conjugated Polymers

	solution λ (nm)[a]			film λ (nm)				oxidation (V; vs Ag/Ag$^+$ in CH_3CN)		
polymer	abs max	PL max[b]	Φ_{PL} (%)[c]	abs max	abs onset	PL max[b]	E_g^{opt} (eV)[d]	$E_{ox/onset}$ (V)[e]	HOMO (eV)[f]	LUMO (eV)[f]
4	314, 387	452	84.3	318, 381	440	462	2.82	0.57	−4.95	−2.13
M2	299, 386	423, 444 (s)[g]	69.5	303, 379	430	429, 454 (s)[g]	2.88	0.89	−5.28	−2.40

[a] Polymer solution in toluene (ca. 1×10^{-5} M solution). [b] Excited at the abs_{max} for both the solution and solid states. [c] Fluorescence quantum yields (Φ_F) values of the samples in dilute THF solution were measured in an integrating sphere using 9,10-diphenylanthracence in THF as a reference standard (Φ_F = 0.9) with excitation at 346 nm. [d] Calculated from UV absorption spectrum of polymer films by the equation: band gap = $1240/\lambda_{onset}^{abs}$. [e] The oxidation potential versus Ag/Ag$^+$ calculated from CV spectrum using ferrocene as internal standard. [f] Calculated from the equation HOMO = $-(E_{onset}^{ox} - E_{onset}^{Fc}) - 4.8$, LUMO = HOMO + band gap. [g] "s" means shoulder.

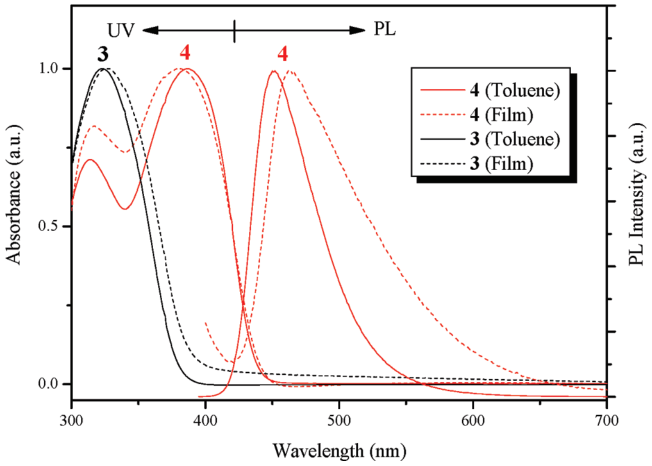


Figure 2. UV spectrum of the conjugated polymer **4** and the dibromo compound **3** and PL spectrum of the conjugated polymer **4** in solution and in film state.

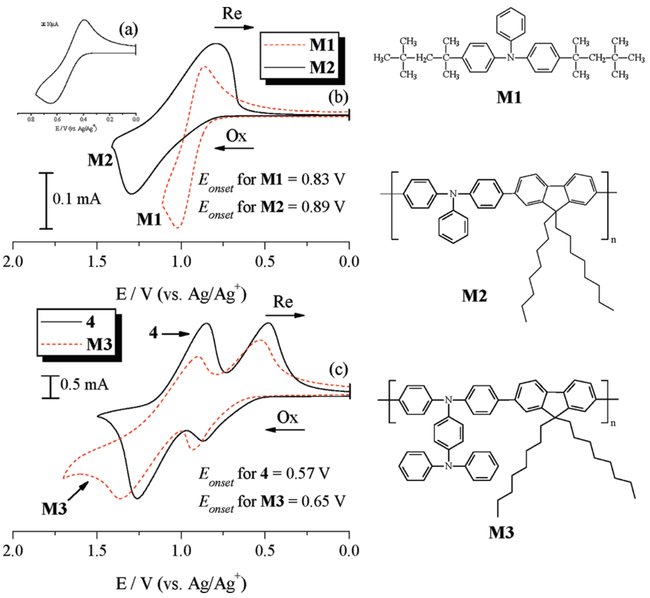


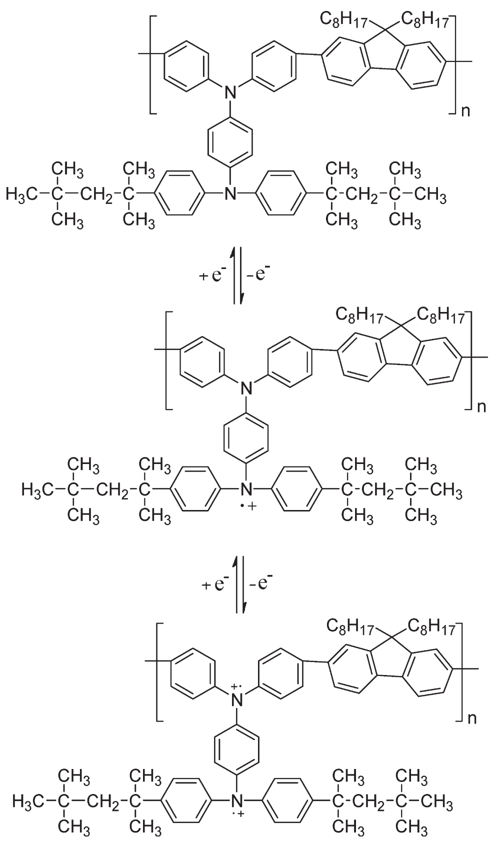
Figure 3. Cyclic voltammograms of the conjugated polymers **4**, **M2**, and **M3** films and model compound **M1** on an ITO-coated glass substrate in CH_3CN solutions containing 0.1 M TBAP. Scan rate = 50 mV/s. Oxidation redoxs of (a) ferrocene, (b) the conjugated polymer **M2** film and model compound **M1**, and (c) the conjugated polymers **4** and **M3** films.

comparing the absorption spectra of monomer **3** (Figure 2), the minor absorption around 314 nm was ascribed to a $\pi-\pi^*$ transition resulting from the conjugation between the aromatic rings and nitrogen atoms (TPPA unit). Since the maximum absorption peak for poly(9,9-dioctylfluorene) (POF) is 391 nm,[22] the strong absorption around 387 nm was assigned to $\pi-\pi^*$ transition derived from the conjugated fluorene backbone. The model polymer **M2** also exhibited the similar results. The UV absorption peaks of the solid film were observed at 318 and 381 nm for **4** and 303 and 379 nm for **M2**. As shown in Figure 2, it is clearly observed that the absorption wavelength is given a simultaneous bathochromic shift of the high-energy transition (314 nm) and hypsochromic shift of the low-energy transition (387 nm) from a dilute solution to a solid state thin film in UV spectrum. For hypsochromic shift of the low-energy transition, it may be attributed to the more disordered morphology of the backbone, resulting from conformational fluctuations of the highly twisted and bulky TPPA units in the polymer backbone.[26] For bathochromic shift of the high-energy transition, it may be due to the intrachain and/or interchain mobility of the excitons. In addition, the dibromo monomer **3** also exhibited the similar results (Figure 2).

The fluorescence emission of the conjugated polymers **4** and **M2** exhibited a maximum emission peak at 452 and 423 nm in toluene solutions, respectively. The fluorescence quantum yield (Φ_F) of the conjugated polymers **4** and **M2** in THF was estimated by comparing with the standard of 9,10-diphenylanthracene (ca. 1×10^{-5} M solution). The fluorescent quantum yield for the conjugated polymers **4** and **M2** was 84.3% and 69.5% in THF solution, respectively. The PL emission peaks of the solid film were observed at 462 nm for **4** and 429 nm for **M2**. The solid-state PL spectrum of the conjugated copolymers **4** and **M2** is red-shifted by about 10 and 6 nm, respectively, from the corresponding solution spectra (Figure 2). This phenomenon is probably attributable to intermolecular interactions, leading to aggregation and possible excimer formation.[13k,27]

The electrochemical behavior of the conjugated polymers was investigated by cyclic voltammetry conducted by film cast on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under a nitrogen atmosphere. The typical cyclic voltammograms for the conjugated polymer **4** (with substituted 2,4,4-trimethylpentan-2-yl group), **M3** (without substituted 2,4,4-trimethylpentan-2-yl group), **M2**, and model compound **M1** are shown in Figure 3 for comparison. There are two reversible oxidation redox couples at $E_{1/2}$ values of 0.67 and 1.05 V for the conjugated polymer **4** and 0.73 and 1.13 V for model polymer **M3** and one reversible oxidation redox couples at $E_{1/2}$ = 0.93 for moldel compound **M1** and 1.03 for model polymer **M2** in the oxidative scan. From these electrochemical data between the conjugated polymers **4** and **M2** and model compound **M1**, the first electron removal for the conjugated polymer **4** could be assumed to occur at the N atom on the pendent 4,4′-bis(2,4,4-trimethylpentan-2-yl)triphenylamine groups, which was more electron-rich than the N atom on the main-chain triphenylamine unit. The anodic oxidation pathway of the conjugated polymer **4** was postulated as in Scheme 3. Comparing the electrochemical data in Figure 3c, we found that

Scheme 3. Simplified Redox Process of Conjugate Polymer 4 from Its Neutral State and Radical Cation State to Dication State



the conjugated polymer **4** ($E_{1/2} = 0.67$ V) was much more easily oxidized than the model polymer **M3** ($E_{1/2} = 0.73$ V). The introduction of electron-donating 2,4,4-trimethylpentan-2-yl group not only greatly prevented the coupling reaction but also lowered the oxidation potentials of the electroactive conjugated polymer **4** as compared with the corresponding model polymer **M3** which has no electron-donating 2,4,4-trimethylpentan-2-yl substituent.[18]

The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated the conjugated polymers **4** and **M2** could be determined from the oxidation onset potentials and the onset absorption wavelength of polymer films, and the results are summarized in Table 2. For instance (Figure 3), the oxidation onset potential for the conjugated polymer **4** was determined to be 0.57 V vs Ag/Ag$^+$. The external ferrocene/ferrocenium (Fc/Fc$^+$) redox standard E_{onset}(Fc/Fc$^+$) was 0.42 V vs Ag/Ag$^+$ in CH_3CN. Under the assumption that the HOMO energy for the ferrocene standard was −4.80 eV with respect to the zero vacuum level, the HOMO energy for the conjugated polymer **4** was evaluated to be −4.95 eV.

Spectroelectrochemical and Electrochromic Characteristics. Spectroelectrochemistry experiments were conducted to elucidate the optical properties of the electrochromic films. For these investigations, the conjugate polymer film was cast on an ITO-coated glass slide (a piece that fit in the commercial UV−vis cuvette), and a homemade electrochemical cell was built from a commercial UV−vis cuvette. The cell was placed in the optical path of the sample light beam in a commercial diode array spectrophotometer. This procedure allowed us to obtain electronic absorption spectra under potential control in a 0.1 M TBAP/CH_3CN solution.

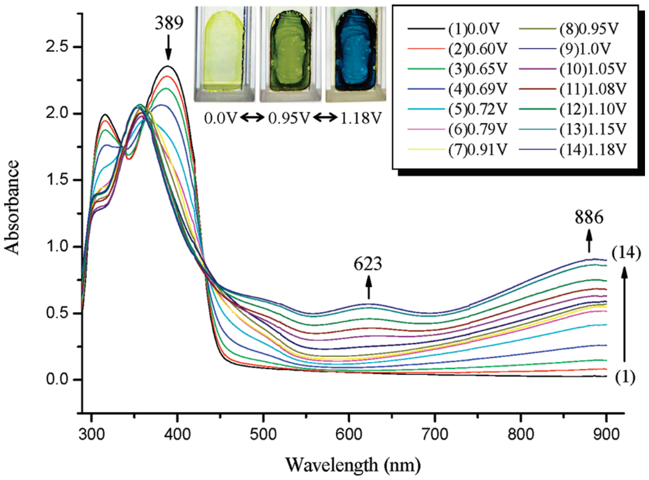


Figure 4. Spectral change of **4** thin film on the ITO-coated glass substrate (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage: 0−1.18 V vs Ag/Ag$^+$ couple as reference. The inset shows the photographic images of the film at indicated applied voltages.

The typical electrochromic absorption spectra of the conjugated polymer **4** film are presented in Figure 4 as a series of UV−vis absorbance curves correlated to electrode potentials. In the neutral form of conjugated polymer **4** (Figure 4), at 0 V, the film exhibited strong absorption at wavelength around 316 and 389 nm characteristic for TPPA and fluorene group, respectively, but it was almost transparent in the visible region. Upon oxidation of the conjugated polymer **4** film (increasing applied voltage from 0 to 0.95 V), the intensity of the absorption peak at 316 and 389 nm gradually decreased, while a new broad band at around 700−900 nm gradually increased in intensity due to the first stage oxidation. As the applied potential became more anodic to 1.18 V, corresponding to the second step oxidation, the two new peaks at 623 and 886 nm gradually increased in intensity.

The observed UV−vis absorption changes in the film of conjugated polymer **4** at various potentials are fully reversible and are associated with strong color changes; indeed, they even can be seen readily by the naked eye. From the inset shown in Figure 4, it can be seen that the film of conjugated polymer **4** switches from a transmissive neutral state (pale yellow) to a highly absorbing semioxidized state (green) and a fully oxidized state (blue). The spectroelectrochemistry characteristics of the model polymer **M2** are also shown in Figure 5. When the applied potential increased positively from 0 to 1.04 V, the peak of characteristic absorbance at 385 nm for model polymer **M2** decreased gradually, while a new band grew up at 495 nm and a broad band rose at around 700−900 nm. The new spectrum was assigned to the formation of a cationic radical TPA moiety which appeared the red color after oxidation. According to this result, it was also proven that the second electron removal for the conjugated polymer **4** would be occurred at the N atom on the main-chain triphenylamine unit. From the inset shown in Figure 5, it can be seen that the film of **M2** switches from a transmissive neutral state (pale yellow) to a fully oxidized state (red).

For optical switching studies, polymer films were cast on ITO-coated glass slides in the same manner as described above, and each film was potential stepped between its neutral (0 V) and oxidized (+1.18 V) state. While the films were switched, the absorbance at 389 and 886 nm was monitored as a function of time with UV−vis spectroscopy. Optical switching data for the cast film of the conjugated

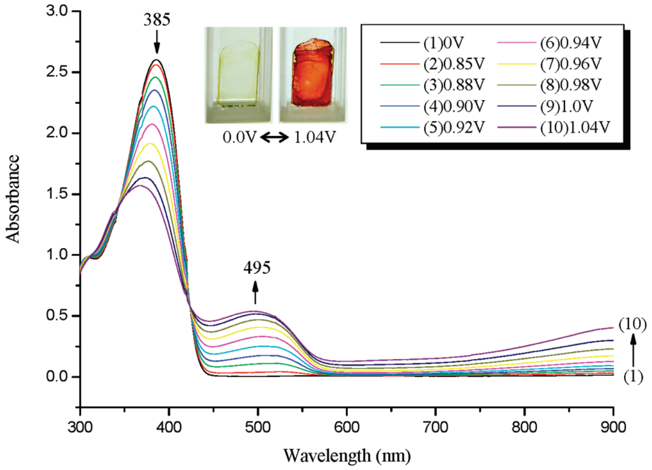


Figure 5. Spectral change of model polymer **M2** thin film on the ITO-coated glass substrate (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage: 0−1.04 V vs Ag/Ag^+ couple as reference. The inset shows the photographic images of the film at indicated applied voltages.

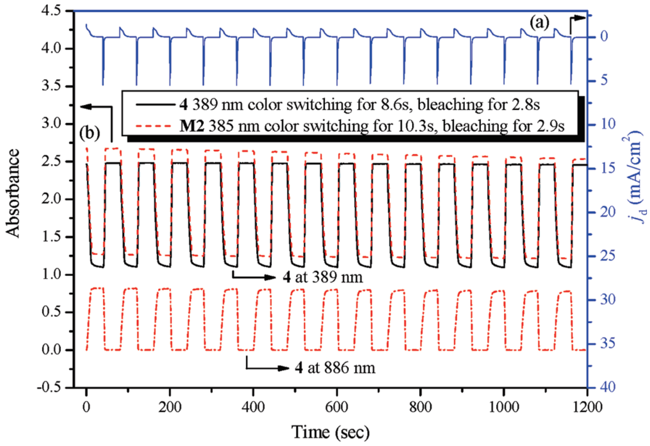


Figure 6. (a) Current consumption and (b) potential step absorptometry of the conjugated polymers **4** (at 389 and 886 nm) and **M2** (at 385 nm) (in 0.1 M TBAP/CH_3CN as the supporting electrolyte) by applying a potential step (0.00 ↔ 1.18 V) (coated area: 1 cm^2) with a cycle time of 80 s.

polymer **4** (at 389 and 886 nm) are shown in Figure 6. The switching time was defined as the time required for reach 90% of the full change in absorbance after the switching of the potential. The thin film casted from the conjugated polymer **4** required 8.6 s at 1.18 V for color switching at 389 and 886 nm and 2.8 s for bleaching. The switching times shown above are somewhat slower than the typical switching time of 1−2 s for electrochromic polymer films. This may be due to slow ion permeation or relatively high internal resistance in comparison to those of conducting polymers such as polythiophene or polypyrrole derivatives.[28] Comparing the electrochromic data, the film of the conjugated polymer **4** (8.6 s for color switching and 2.8 s for bleaching) showed more rapid switching time than the conjugated polymers **M2** which has no electron-donating bis(4-(2,4,4-trimethylpentan-2-yl)phenyl)amine group (10.3 s for color switching and 2.9 s for bleaching) and **M3** without electron-donating 2,4,4-trimethylpentan-2-yl substituent (11.8 s for color switching and 3.4 s for bleaching). After switching 15 times between 0 and 1.23 V, the film of the conjugated polymer **4** showed higher electrochromic stability and faster switching time than the conjugated polymers **M2** and **M3**. Therefore, the results of these experiments revealed that the introduction of the electron-donating bis(4-(2,4,4-trimethylpentan-2-yl) phenyl)amine group at the active sites of the TPA or 2,4,4-trimethylpentan-2-yl substituent at the active sites of the TPPA unit enhanced the redox and electrochromic stability of the conjugated polymer **4**, which could be a good candidate as anodic electrochromic materials due to their proper oxidation potentials, lower switching time, and thin film formability.

Conclusions

A novel TPPA-containing conjugated polymer **4** was readily prepared from the newly synthesized dibromo monomer **3** with 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester via Suzuki coupling. Introduction of extremely electron-donating TPPA group and 2,4,4-trimethylpentan-2-yl substituent to the polymer chain not only greatly prevented the coupling reaction and lowered the oxidation potentials of the electroactive conjugated polymer but also led to good solubility and film-forming properties of the conjugated polymer. In addition to high T_g and good thermal stability, the conjugated polymer **4** also reveal valuable electrochromic characteristics such as high contrast (pale yellowish neutral form to oxidized blue forms) and good electrochromic reversibility. Thus, these characteristics suggest that the conjugated polymer have great potential for use in optoelectronics applications.

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Supporting Information Available: Identification data such as IR, elemental analysis and NMR spectroscopy for monomers and conjugated polymers, and NMR spectrum such as ^1H NMR, ^{13}C NMR, HMQC, and HMBC for dibromo compound **3** and conjugated polymer **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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