Novel Triarylamine-Based Alternating Conjugated Polymer with High Hole Mobility: Synthesis, Electro-Optical, and Electronic Properties

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ABSTRACT: Novel bis-triphenylamine-containing aromatic dibromide M3, N,N-bis(4-bromophenyl)-N',N'-diphenyl-1,4-phenylene-diamine, was successfully synthesized. The novel conjugated polymer P1 having number-average molecular weight of 1.31 × 105 was prepared via Suzuki coupling from the dibromide M3 and 9,9-diocetylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester. Polymer P1 had excellent thermal stability associated with a high glass-transition temperature (Tg = 141 °C). The hole-transporting and UV-vis-near-infrared electrochromic properties were examined by electrochemical and spectroelectrochemical methods. Cyclic voltamograms of the conjugated polymer films cast onto indium-tin oxide-coated glass substrates exhibited two reversible oxidation redox couples at E1/2 values of 0.73 and 1.13 V versus Ag/Ag+ in acetonitrile solution. The hole mobility of the conjugated polymer P1 revealed ~10−3 cm2 V−1 s−1, which is much higher than that of other conjugated polymer systems. The observed UV-vis-near-infrared absorption change in the conjugated polymer film P1 at applied potentials ranging from 0.00 to 1.23 V are fully reversible and associated with strong color changes from pale yellowish in its neutral form to green and blue in its oxidized form. Using a combination of experimental study and theoretical investigation, we proposed an oxidation mechanism based on molecular orbital theory, which explains the cyclic voltammetry experimental results well. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 4654–4667, 2010

KEYWORDS: conjugated polymers; electrochemistry; high performance polymers; hole mobility; Suzuki coupling; triarylamine

INTRODUCTION Conjugated organic polymers1 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 properties1 for advanced technological applications such as light-emitting diodes, photovoltaic cells, and electrochromic cells.2 In addition, the most important features of conjugated polymers are the ability to fine-tune the color through chemical structure modification of the conjugated backbone and to get multichromism from the same material.3 However, creating conjugated polymers that possess good film-forming properties, strong absorption abilities, and high hole mobility is a critical challenge when developing ideal p-type materials. Increasingly, near-infrared (NIR)-absorbing electrochromic materials are receiving more attention because of their potential applications in biological sensing, optical communication, data storage, and thermal control and thermal emission detectors for spacecrafts.4

Triphenylamine (TPA) derivatives, including small molecules and macromolecules, are well known for their photo and electroactive properties that find optoelectronic applications as hole transporters,5 light emitters,6 and polymer electronic memories.7 Molecules containing TPA moieties,8 such as N,N′-diphenyl-N,N′-di(m-tolyl) benzidine (TPD) and N,N′-di(naphthalene-1-yl)-N,N′-diphenyl-benzidine have been used widely as hole-transport materials in multilayer organic light-emitting diodes (OLEDs)11 and in xerography12 because of their high hole mobility. However, there are few publications that produced conjugated polymer systems with a hole mobility exceeding 10−3 cm2 V−1 s−1. Liao et al.14 reported that spatial hindrance has a crucial effect on the hole transport behavior. Therefore, we tried to design and
synthesize a conjugated polymer containing a triarylamine group without any substituents to obtain greater intermolecular interactions between polymer chains, thereby enhancing the hole mobility. TPA can be easily oxidized to form radical cations, and the oxidation process is always associated with a noticeable change in coloration. In addition, N,N,N,N0,N0-tetrasubstituted-1,4-phenylenediamines exhibiting excellent redox properties, electron-transfer process, multicoloring electrochromism, and photoelectrochemical behavior are good candidates for technological applications such as smart windows, automatic antiglazing mirrors, large-scale electrochromic screens, and chameleon materials.

In this study, we created a new propeller-shaped bi-triphenylamine (BTPA)-containing dibromo monomer without any substituents that was expected to create a corresponding conjugated polymer with high hole mobility through Suzuki coupling. The basic properties of the conjugated polymer such as thermal, optical, and electrochemical properties and solubility, especially hole mobility, were characterized. In addition, the electro-optical properties were applied to polymer light-emitting diodes and electrochromic devices. Lastly, investigation of the oxidation mechanism for the conjugated polymer was done using theoretical analysis based on molecular orbital theory.

**EXPERIMENTAL**

**Materials**

The chemicals, diphenylamine (Acros, 99%), 4-fluoro-nitrobenzene (Acros, 99%), sodium hydride (Aldrich, St. Louis, MO), 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 (Acros, 98%), anhydrous potassium carbonate (Merck), and sodium tert-butoxide (Aldrich, 98%) were used without further purification. Tetrabutylammonium perchlorate (TBAP; Fluka) was recrystallized twice from ethyl acetate and then dried under vacuum before use. The catalyst, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh3)4) was purchased from Acros. 9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (Aldrich) was recrystallized from a mixture of ethyl acetate and n-hexane before use. Dimethyl sulfoxide 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 N,N-bis(4-bromophenyl)-N,N-diphenyl-1,4-phenylenediamine (M3) was carried out using the Buchwald-Hartwig reaction (Scheme 1). 4-Nitrotiphenylamine (M1) and 4-aminotiphenylamine (M2) were prepared according to reported procedures. A mixture of 3.54 g (13.60 mmol) of 4-nitrotiphenylamine, 7.69 g (27.20 mmol) of 1-bromo-4-iodobenzene, 156.4 mg (2.72 × 10⁻³ mmol) of Pd(dba)2, 301.3 mg (5.44 × 10⁻³ mmol) of 1,1'-bis(diphenylphosphino)ferrocene, 3.92 g (40.79 mmol) of sodium tert-butoxide, and 18 mL of dry toluene were charged in a three-necked flask kept under nitrogen atmosphere. The mixture was heated and stirred 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 MgSO₄ overnight and then filtered to remove MgSO₄. The solvent from the filtrate was then removed using vacuum distillation, and the residue was purified by silica gel column chromatography (dichloromethane:n-hexane = 1:3). This was followed by recrystallization using hexane to obtain white crystals (71% yield, 5.51 g); mp 166 °C (by differential scanning calorimetry).
calorimetry [DSC] at a scan rate of 10 °C min⁻¹. ν/cm⁻¹ (KBr) 3035 (Ar-H stretch), 1484 (C=O), 1269 (Ar-N), and 1002 (Ar-Br). δH (ppm) (500 MHz, CDCl₃, Me₄Si) 7.75 (d, J = 8.55 Hz, 4H, H₆), 7.27 (t, J = 7.70 Hz, 4H, H₅), 7.12 (d, J = 7.95 Hz, 4H, H₄), 7.04 ~ 7.00 (m, 4H, H₃, H₂), 6.97 ~ 6.94 (m, 6H, H₁, H₂); δC (ppm) (125 MHz, CDCl₃, Me₄Si) 147.63 (C₀), 146.54 (C₁₁), 144.94 (C₃), 141.38 (C₁₀), 132.27 (C₇), 129.25 (C₂), 125.87 (C₃), 124.98, 124.92 (C₄ and C₁), 124.06 (C₉), 122.77 (C₁), 115.05 (C₁₂).

ELEM. ANAL. Calcd. for C₃₀H₂₂Br₂N₂, 63.18%; H, 3.89%; N, 4.91%; Found: C, 63.78%; H, 4.32%; N, 4.91%.

Synthesis and Identification of Ref(P2) and Ref(P3)
The synthetic procedures and characterization data of these polymers are reported in the Supporting Information.

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 ¹H- and ¹³C-NMR spectra were recorded on a Bruker DRX-500 instrument operating at 500 MHz for proton and 125 MHz for carbon. Weight-average (Mₙ) and number-average (Mₓ) molecular weight were determined by gel permeation chromatography (GPC). Five Waters (Ultrastraygel) columns 300 × 7.7 mm (guard, 500, 10³, 10⁴, and 10⁵ Å in a series) were chained with a refractive index detector (RI 2000), using tetrahydrofuran (THF; 1 mL min⁻¹) as the eluent and polystyrene as the standard for GPC analysis. The melting temperature (Tₘ) and glass-transition temperature (Tg) were measured on a Du Pont 9000 differential scanning calorimeter (TA instrument TA 910) at a heating rate of 10 °C min⁻¹ from 50 to 250 °C under a steady flow of nitrogen. The Tg was recorded on the second heating run. The differential scanning calorimeter was calibrated using indium as the standard. Thermogravimetric (TG) data were obtained on a Perkin-Elmer TG/DTA (Diamond TG/DTA). Experiments were carried out using 3–5 mg samples at a heating rate of 10 °C min⁻¹ from 50 to 800 °C under flowing nitrogen or air (20 cm³ min⁻¹). UV-vis spectra of the polymer films and solutions were recorded on a Jasco V-550 spectrophotometer at room temperature in air. Photoluminescence (PL) spectra were measured with a HORIBA Jobin Yvon FluoroMax-3 spectrophotometer. Fluorescence quantum yield (Φf) of samples in THF were measured using 9,10-diphenylanthracene in THF as a reference standard (Φf = 0.9) with excitation at 346 nm. All corrected fluorescence excitation spectra were found to be equivalent to their respective absorption spectra. Cyclic voltammetry (CHI model 619A) was conducted with the use of a three-electrode cell in which indium-tin oxide (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 0.1M TBAP/acetonitrile (CH₃CN). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downward. The
The synthesis route of conjugated polymer P1, Ref(P2) ~ Ref(P5) via Suzuki coupling.

**Time-of-Flight Mobility Measurement**

Time-of-flight (TOF) samples were prepared by dissolving appropriate weight ratios (up to 10 wt %) of the conjugated polymers P1, Ref(P4) and Ref(P5) in chlorobenzene and then dip-coating the solutions onto an ITO substrate within a glove box. The films were subsequently dried by baking at 130 °C for 30 min to remove the residual solvent. The device samples were then completed through thermal deposition of the back electrode Ag (100 nm) through a shadow mask.

For the TOF measurements, the samples were mounted in a cryostat under vacuum (~10⁻⁴ torr). A sheet of charge carriers in the organic layer was generated by radiating a short excitation pulse (nitrogen laser) through the semitransparent ITO electrode. Under an applied DC voltage, these charge carriers swept over the organic sample toward the counter electrode (Ag) and discharged, resulting in a transient photocurrent. When the carriers reached the counter electrode, the current dropped to zero; the time at which this event occurred corresponded to the transit time of the carriers. The photocurrent signal was detected using a digital storage oscilloscope. Selected carriers (holes or electrons) drifted across the sample on switching the polarity of the applied bias. The carrier mobility (μ) was calculated from the transit time (tᵣ), the sample thickness (d), and the applied voltage (V) using the expression $\mu = d^2 / tᵣ V$.

**OLED Device Fabrication**

ITO substrates were cleaned in an ultrasonic detergent bath and then washed sequentially in acetone and methanol. The substrates were subsequently treated in a UV-ozone cleaner to remove any residual organic contaminants. A hole-injection layer of poly(3,4-ethylenedioxythiophene)-poly(4-styrenesulfonate) (PEDOT:PSS) was first spin-coated onto the ITO substrate to a thickness of 30 nm and then dried at 120 °C for 30 min to remove any residual solvent. After direct dip-
coating of a solution of the conjugated polymers P1 and Ref(P4) (~1 wt % in chlorobenzene) onto the PEDOT:PSS/ITO substrate, the system was baked at 130 °C for 30 min to remove residual solvent. A 60-nm-thick layer of Alq3 was then vacuum-deposited on top of the conjugated polymers P1 and Ref(P4) at a deposition rate of 2–3 Å s⁻¹. Finally, a 0.5-nm-thick layer of LiF and a 100-nm-thick Al cathode were deposited through a shadow mask. The current-voltage-luminance (I-V-L) characteristics of the devices were measured simultaneously using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode. EL spectra were measured using an Ocean Optics spectrometer.

RESULTS AND DISCUSSION

Synthesis

Novel BTPA-containing dibromo compound M3 and the conjugated polymer P1 containing BTPA 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 ¹H-NMR, ¹³C-NMR, heteronuclear multiple quantum coherence, and correlation spectroscopy were used to identify structures of the intermediate compounds, the dibromo monomer M3, and the conjugated polymer P1. The confirmation data are shown in the Experimental section and Supporting Information. The results from the elemental analyses of the intermediate compounds and target dibromo monomer M3 agree with the proposed structures. The NMR spectra also agree well with the proposed molecular structures of compound M3 and the conjugated polymer P1.

Basic Characterization

The solubility behavior of conjugated polymer P1 was tested qualitatively. The conjugated polymer P1 was highly soluble in common organic solvents at room temperature such as N-methyl-2-pyrrolidinone, THF, dichloromethane, chloroform, toluene, xylene, and benzene. This enhanced solubility could be attributed to the introduction of the bulky pendant BTPA moiety and the alkyl chain of the fluorene group into the repeating unit. Thus, the excellent solubility makes the conjugated polymer P1 a potential candidate for practical applications for optoelectronic devices through spin-coating, dip-coating, or inkjet-printing processes to obtain thin films.

The molecular weight of the conjugated polymers was determined by GPC using polystyrene as the standard and is summarized in Table 1. The number-average molecular weight of the prepared conjugated polymers P1, Ref(P2), and Ref(P3) were as high as 1.31 × 10⁴, 1.75 × 10⁴, and 1.77 × 10⁴, respectively, with a polydispersity index of 1.77, 1.80, and 1.74, respectively.

The thermal properties of the conjugated polymers were investigated by DSC and thermogravimetric analysis (TGA) techniques, and the results are summarized in Table 1. All the polymers showed no clear melting endotherms up to the decomposition temperatures on the DSC thermograms (Fig. 1). This supports the proposed amorphous nature of these TPA-containing polymers. In Figure 1, the T₆₅'s of the conjugated polymers P1, Ref(P2), and Ref(P3) were observed at 141, 133, and 112 °C, respectively, which were much higher than that of poly(9,9-dioctylfluorene) (T₆₅ = 75 °C) and TPD (T₆₅ = 60 °C), indicating that the

![Figure 1](https://www.wileyonlinelibrary.com/journal/pola)
use of these conjugated polymers may greatly improve the device durability, which is related to the $T_g$'s of the materials as reported by Tokito et al.$^{23}$ The relatively high $T_g$ is an advantage for electronic material applications.$^{24}$ Also, the $T_g$ of the model polymer Ref(P2) ($T_g = 133$ °C) was higher than that of the model polymer Ref(P3) ($T_g = 112$ °C). This is due to the flexibility of the 4-butoxy-substituted group in the model polymer Ref(P3), which causes a decrease in steric hindrance, increasing chain mobility. The typical TGA spectra of conjugated polymers [P1, Ref(P2), and Ref(P3)] in nitrogen atmosphere are shown in Figure 1. The conjugated polymers P1 and Ref(P2) exhibited a similar TGA pattern with no significant weight loss below 400 °C in nitrogen atmosphere. The decomposition temperatures at 10% weight loss ($T_{10}$) and char yield (59.0%) than those of conjugated polymer P1 also exhibited similar TGA pattern with no significant weight loss below 400 °C in nitrogen atmosphere. The decomposition temperatures at 10% weight loss ($T_{10}$) and char yield of the conjugated polymers P1 and Ref(P2), examined by TG analysis, were 446 and 438 °C in nitrogen, 432 and 417 °C in air, and 69.7% and 63.9% in nitrogen, respectively. It can be observed that the conjugated polymer P1 was more thermally stable than the model polymer Ref(P2) because of incorporation of the bulky BTPA moiety into the conjugated polymer and higher aromatic content. In addition, the model polymer Ref(P2) was more thermally stable than the model polymer Ref(P3) because of the flexibility of the 4-butoxy-substituted group in the model polymer Ref(P3) and higher aromatic content of the model polymer Ref(P2). The conjugated polymer Ref(P4)$^{30}$ showed lower $T_{10}$ in nitrogen (445 °C) and air (412 °C) and lower char yield (59.0%) than those of conjugated polymer P1 because of the less-stable aliphatic segment (2,4,4-trimethylpentan-2-yl substituted) and lower aromatic content.

### Optical and Electrochemical Properties

The optical properties of the conjugated polymers were investigated by UV-vis and PL spectroscopy when in the solid state and when dissolved in toluene (ca. $1 \times 10^{-5} M$ solution). The results are summarized in Table 2.

The UV-vis absorption of the conjugated polymer P1 exhibited a strong absorption around 385 nm and a minor absorption around 310 nm in toluene solution. By comparing the absorption spectra of monomer M3 (Fig. 2), the minor absorption around 310 nm was ascribed to a $\pi-\pi^*$ transition resulting from the conjugation between the aromatic rings and nitrogen atoms (BTPA unit). Because the maximum absorption peak for poly(9,9-diocotyfluorene) is 391 nm,$^{21}$ the strong absorption around 385 nm was assigned to $\pi-\pi^*$ transition derived from the conjugated fluorene backbone. The model polymer Ref(P2) and Ref(P3) also exhibited similar results. The UV absorption peaks of the solid film were observed at 314 and 378 nm for P1, 303 and 379 nm for Ref(P2), and 312 and 390 nm for Ref(P3). As shown in Figure 2, the absorption wavelength from a dilute solution to a solid-state film causes a bathochromic shift of the high-energy transition band (310 nm) and a hypsochromic shift of the low-energy transition band (385 nm). The hypsochromic shift of the low-energy transition band may be attributed to the more disordered morphology of the backbone, resulting from conformational fluctuations of the highly twisted and bulky BTPA units in the polymer backbone.$^{25}$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solution λ (nm)</th>
<th>PL Max.</th>
<th>φ&lt;sub&gt;PL&lt;/sub&gt; (%)</th>
<th>Φ&lt;sub&gt;onset&lt;/sub&gt;</th>
<th>Φ&lt;sub&gt;abs&lt;/sub&gt;</th>
<th>E&lt;sub&gt;onset&lt;/sub&gt;</th>
<th>E&lt;sub&gt;opt&lt;/sub&gt;</th>
<th>d&lt;sub&gt;film&lt;/sub&gt; (nm)</th>
<th>$E_{g,s}$ (eV)</th>
<th>$E_{g,C}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>303, 379</td>
<td>430</td>
<td>64.1</td>
<td>61.5</td>
<td>430</td>
<td>4.30</td>
<td>4.06</td>
<td>435</td>
<td>2.88</td>
<td>2.84</td>
</tr>
<tr>
<td>Ref(P2)</td>
<td>299, 386</td>
<td>429</td>
<td>64.1</td>
<td>61.5</td>
<td>430</td>
<td>4.30</td>
<td>4.06</td>
<td>435</td>
<td>2.88</td>
<td>2.84</td>
</tr>
<tr>
<td>Ref(P3)</td>
<td>299, 386</td>
<td>429</td>
<td>64.1</td>
<td>61.5</td>
<td>430</td>
<td>4.30</td>
<td>4.06</td>
<td>435</td>
<td>2.88</td>
<td>2.84</td>
</tr>
</tbody>
</table>

### References

1. ref1
2. ref2
3. ref3
4. ref4
5. ref5
6. ref6
7. ref7
8. ref8
9. ref9
10. ref10
11. ref11
12. ref12
13. ref13
14. ref14
15. ref15
16. ref16
17. ref17
18. ref18
19. ref19
20. ref20
21. ref21
22. ref22
23. ref23
24. ref24
25. ref25
26. ref26
27. ref27
28. ref28
29. ref29
30. ref30
The bathochromic shift of the high-energy transition (band) may be attributed to the intrachain and/or interchain mobility of the excitons. In addition, the dibromo monomer M3 also exhibited similar results (Fig. 2).

The fluorescence emission of the conjugated polymers P1, Ref(P2), and Ref(P3) exhibited a maximum emission peak at 445, 423, and 433 nm, respectively, when in toluene. The fluorescence quantum yield (ΦF) of the conjugated polymers P1, Ref(P2), and Ref(P3) in THF was estimated by comparing with the standard, 9,10-diphenylanthracene (ca. 1 x 10^-5 M solution). The fluorescent quantum yield for the conjugated polymers P1, Ref(P2), and Ref(P3) in THF were 90.0%, 69.5%, and 64.1%, respectively. As quantum calculation results (see below), the nonbonded electron pair of the nitrogen atoms involves in the π-conjugation with the attached benzences, indicating that the bond between nitrogen and benzene ring is partial double bond, which makes the molecule more planar and rigid. It is well known that fluorescence is particularly favored in molecules with rigid structures. The conjugated polymer P1 has two pairs of electrons, and the model polymer Ref(P2) has only one pair of electrons involved in π-conjugation. Therefore, polymer P1 showed higher quantum yield than polymer Ref(P2) in this study. Moreover, the quantum yield for Ref(P3) is lower than that of Ref(P2) because of the flexible 4-butoxy-substituted group in Ref(P3). The PL emission peaks of the solid film were observed at 454 nm for P1, 429 nm for Ref(P2), and 440 nm for Ref(P3). The solid-state PL spectrum of the conjugated copolymers P1, Ref(P2), and Ref(P3) is red-shifted by about 9, 6, and 7 nm, respectively, from the corresponding solution spectra (Fig. 2). This phenomenon is probably attributable to intermolecular interactions, leading to aggregation and possible excimer formation.26

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 (CH3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. The typical cyclic voltammograms for the conjugated polymers P1, Ref(P2), and Ref(P3) are shown in Figure 3 for comparison. There are two reversible oxidation redox couples at E1/2 values of 0.73 (Eonset = 0.65 V) and 1.13 V for the conjugated polymer P1, and one reversible oxidation redox couples at E1/2 = 1.03 V (Eonset = 0.89 V) for model polymer Ref(P2) and E1/2 = 0.98 V (Eonset = 0.85 V) for model polymer Ref(P3) in the oxidative scan. Comparing the electrochemical data, the model polymer Ref(P3) is much more easily oxidized than the model polymer Ref(P2) (E1/2 = 0.98 versus 1.03 V). The introduction of electron-donating 4-butoxy group of the electroactive model polymer Ref(P3) lowers the oxidation potential compared with the corresponding model polymer Ref(P2).

The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the investigated conjugated polymers P1, Ref(P2), and Ref(P3) was determined from the oxidation onset potentials and the onset absorption wavelength of the polymer films. The results are summarized in Table 2. For instance, the oxidation onset potential for the conjugated polymer P1 (Fig. 3) was determined to be 0.65 V versus Ag/Ag⁺. The external ferrocene/ferrocenium (Fc/Fc⁺) redox standard Eonset (Fc/Fc⁺) was 0.42 V versus Ag/Ag⁺ in CH3CN. 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 P1 was evaluated to be -5.03 eV. The LUMO level of the conjugated polymers was calculated according to the equation: LUMO =...
HOMO $+ E_g$. From the optical bandgap, the LUMO level for the conjugated polymer $P_1$ was $-2.19$ eV.

**Oxidation Mechanism of Conjugated Polymer $P_1$ by Theoretical Study**

Cyclic voltammograms of Ref($P_2$) and conjugated polymer $P_1$ are shown in Figure 3. The position of oxidation peaks of Ref($P_2$) were very different from those of conjugated polymer $P_1$, indicating that the oxidations were not a result of electron removal only from the nitrogen atoms. Many previous literatures proposed the oxidation mechanism of triarylamine derivatives. They proposed that the first electron was removed from the nitrogen atom with larger electron density, whereas the second electron was removed from the other nitrogen atom, which is close to atomic orbital theory. However, from the electrochemical comparison of model compounds and the conjugated polymer $P_1$ as mentioned above, it is not suitable to explain the mechanism using atomic orbital theory. If the oxidations occurred only in the nitrogen atoms, the oxidation peaks should have appeared in the same bias potential. A more reasonable oxidation mechanism reported in previous literature (see Supporting Information) is that the first electron was removed from the HOMO of the molecule instead of the lone pair electron of the nitrogen atom. The first electron was removed from the HOMO to form single occupied molecular orbital (SOMO), and the second electron was removed from the SOMO to form the second oxidation state.

All theoretical calculations in this study are carried out using Gaussian 03. Equilibrium structure for each fluorene-based polymer is determined using DFT with the B3LYP functional.
TABLE 3 Atomic Charge Distribution of Selected Atoms in Ground State, First Oxidation State, Second Oxidation State, and the Charge Difference of ΔQ1 and ΔQ2

<table>
<thead>
<tr>
<th>Atom</th>
<th>GS</th>
<th>Ox1</th>
<th>Ox2</th>
<th>ΔQ1</th>
<th>ΔQ2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 N</td>
<td>-0.658887</td>
<td>-0.612556</td>
<td>-0.599882</td>
<td>0.046331</td>
<td>0.012674</td>
</tr>
<tr>
<td>2 C</td>
<td>0.291559</td>
<td>0.257828</td>
<td>0.264351</td>
<td>-0.03733</td>
<td>0.006523</td>
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<tr>
<td>12 C</td>
<td>0.274123</td>
<td>0.302011</td>
<td>0.287970</td>
<td>0.027888</td>
<td>-0.01404</td>
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<tr>
<td>19 C</td>
<td>0.289397</td>
<td>0.329864</td>
<td>0.329696</td>
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<td>-0.00017</td>
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<tr>
<td>22 C</td>
<td>0.289406</td>
<td>0.253692</td>
<td>0.257264</td>
<td>-0.03571</td>
<td>0.003572</td>
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<tr>
<td>32 N</td>
<td>-0.657661</td>
<td>-0.628458</td>
<td>-0.609706</td>
<td>0.029203</td>
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<tr>
<td>33 C</td>
<td>0.280021</td>
<td>0.247172</td>
<td>0.238079</td>
<td>-0.03285</td>
<td>-0.00909</td>
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<tr>
<td>43 C</td>
<td>0.273850</td>
<td>0.240603</td>
<td>0.235941</td>
<td>-0.03325</td>
<td>-0.00466</td>
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<tr>
<td>56 C</td>
<td>-0.198009</td>
<td>-0.191910</td>
<td>-0.176815</td>
<td>0.006099</td>
<td>0.015095</td>
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<tr>
<td>63 C</td>
<td>-0.192892</td>
<td>-0.185598</td>
<td>-0.169031</td>
<td>0.007294</td>
<td>0.016567</td>
</tr>
<tr>
<td>84 C</td>
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<tr>
<td>95 C</td>
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<td>-0.169468</td>
<td>0.006895</td>
<td>0.016431</td>
</tr>
</tbody>
</table>

a GS, ground state.
b Ox1, losing one electron.
c Ox2, losing two electrons.
d ΔQ1 = atomic charge difference of Ox1 and GS.
e ΔQ2 = atomic charge difference of Ox2 and Ox1.

and the 6-31G(d) basis set. It has been shown that B3LYP/6-31G(d) gives decent ground state structures of conjugated polymers. The atomic charge was determined by Mulliken population analysis herein. The sketch map containing the studied basic structure and optimized structure by B3LYP/6-31G(d) are plotted in Figure 4. The electronic states of the neutral structure and oxidized structures of the conjugated polymer P1 were simulated, and the main results are summarized in Table 3 (see detailed distribution in Table S1 in the Supporting Information). The main atomic charge differences were located on 1N, 2C, 12C, 19C, 22C, 32N, 33C, and 43C atoms. For the first oxidation (losing first electron), the 1N, 12C, 19C, and 32N atoms contributed 4.6%, 2.8%, 4.0%, and 2.9% of an electron, whereas the 2C, 22C, 33C, and 43C got 3.4%, 3.6%, 3.3%, and 3.3% of an electron, respectively. For the second oxidation, the 1N, 32N, 56C, 63C, 84C, and 95C atoms contributed 1.3%, 1.9%, 1.5%, 1.7%, 1.5%, and 1.6% of an electron, respectively, whereas the 12C got 1.4% of an electron. The electron density contour of the ground state and oxidation states are plotted by Gauss View as shown in Figure 5, which illustrates that the electron density distribution of the HOMO state of the basic unit (ground state) was mainly located on N,N,N,N'-tetraphenyl phenylene diamine moiety and extended to the fluorene moiety for the SOMO electronic state of the first oxidation state. From the Figure 5, it is obvious that the electronic density contours show that the electron lone pair of the nitrogen atoms have strong coupling with π electrons.

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, 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 used for the UV-vis-NIR spectrophotometer. This procedure allowed us to obtain electronic absorption spectra with controlled voltage in a 0.1M TBAP/CH3CN solution. The typical electronic absorption spectra of the conjugated polymer P1 film are presented in Figure 6 as a series of UV-vis-NIR absorbance curves correlated to electrode potentials. In the neutral form (0 V), the conjugated polymer P1 (Fig. 6) film exhibited strong absorption at wavelength around 313 and 385 nm characteristic of a BTPA and fluorene group, respectively, but it was almost transparent in the visible region. During oxidation of the conjugated polymer P1 film (increasing applied voltage from 0 to 0.99 V), the characteristic peak of absorbance at 385 nm decreased gradually, whereas a new broadband having its maximum absorption wavelength at 990 nm in the NIR region gradually increased in intensity because of the first-stage oxidation. As the applied potential became more anodic to 1.23 V, corresponding to the second-step oxidation, a new broadband with two peaks centered around 582 nm and 869 nm rose.

The observed UV-vis-NIR absorption changes in the film for the conjugated polymer P1 at various potentials are fully reversible and are associated with strong color changes, which can even be seen easily by the naked eye. From the inset shown in Figure 6, it can be seen that the film of conjugated polymer P1 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 Ref(P2) are shown in Supporting Information. When the applied potential increased positively from 0 to 1.08 V, the characteristic peak of absorbance at 385 nm for model polymer Ref(P2)
above, and each film was alternated repeatedly between its neutral (0 V) and oxidized (1.23 V) state. Although the films were switched, the absorbance at 869 nm was monitored as a function of time with UV-vis spectroscopy. Optical switching data for the cast film of the conjugated polymer P1 (at 869 nm) are shown in Figure 7. The switching time was defined as the time required to reach 90% of the full change in absorbance after the switching of the potential. The thin film from the conjugated polymer P1 required a switching time of 11.8 s and a bleaching time of 3.4 s at 1.23 V for 869 nm. The switching times are slower than that for general electrochromic polymer films. It seems that the TPA-based conjugated polymers\textsuperscript{5e–g,27c,28} showed slower switching times than other conjugated systems such as polypyrrole and polypyrrole. This may be due to slow ion permeation or relatively high internal resistance compared with those of conducting polymers such as polypyrrole or polypyrrole derivatives.\textsuperscript{31}

**Hole Mobility Measurement**

To characterize the hole transport in the conjugated polymers P1, Ref(P4),\textsuperscript{5e} and Ref(P5)\textsuperscript{28} and to quantify their mobilities, we used TOF techniques\textsuperscript{32} to measure the charge carrier mobility, which has been successfully applied to investigate the charge transport behavior of a wide range of polymers and small molecules. Figure 8(a–c) displays the TOF transients of the conjugated polymer films P1, Ref(P4), and Ref(P5). We observed photocurrents that did not display any distinct constant current plateau; instead, the current decayed significantly, resulting in dispersive charge transport, suggesting that the charge carriers were trapped and could not attain dynamic equilibrium while migrating across the sample. The transit times \( t_T \) were obtained from the intersection point of two asymptotes in the double-logarithmic representations [insets of Fig. 8(a–c)]. The hole mobility was determined using the relation \( \mu = d^2/V t_T \) where \( d \) is the organic film thickness, \( V \) is the applied voltage, and \( t_T \) is the transit time.

Figure 8(d) displays the hole mobilities of the conjugated polymer films P1, Ref(P4), and Ref(P5) plotted as a function of the square root of the electric field. The linear correlation follows the universal Poole–Frenkel relationship, \( \mu \propto \exp(\beta E^{1/2}) \), where \( \beta \) is the Poole–Frenkel factor and \( E \) is the electric field.\textsuperscript{33} Carrier transport in an amorphous organic solid can be commonly described by Marcus theory.\textsuperscript{34} Marcus theory is generally associated with charge carriers hopping along the channel of localized hopping sites. The conjugated polymer P1 exhibited hole mobilities in the range from \( 6 \times 10^{-4} \) to \( 2 \times 10^{-3} \) cm\(^2\)/V s\(^-1\) at electric fields between \( 6 \times 10^5 \) and \( 2 \times 10^5 \) V cm\(^-1\); the conjugated polymer Ref(P4) exhibited hole mobilities in the range from \( 1.5 \times 10^{-4} \) to \( 4 \times 10^{-4} \) cm\(^2\)/V s\(^-1\) at electric fields between \( 1.6 \times 10^5 \) and \( 5.3 \times 10^5 \) V cm\(^-1\); and the conjugated polymer Ref(P5) exhibited hole mobilities in the range from \( 5 \times 10^{-5} \) to \( 1 \times 10^{-4} \) cm\(^2\)/V s\(^-1\) at electric fields between \( 2.7 \times 10^5 \) and \( 4.1 \times 10^5 \) V cm\(^-1\). The observed hole mobility of the conjugated polymer film P1 \( (\mu_h = 10^{-3} \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}) \) was one order of magnitude higher than that of the conjugated polymer films Ref(P4) \( (\mu_h = 10^{-4} \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}) \) and Ref(P5) \( (\mu_h = 8 \times 10^{-5} \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}) \) under the same electric field \( (~2 \times 10^5 \text{ V cm}^{-1}) \). We ascribe this phenomenon to the presence of the bulky 2,4,4-trimethylpentan-2-yl-substituted group of the conjugated polymer Ref(P4) and bulky 2-phenyl-2-isopropyl-substituted group of the conjugated polymer Ref(P5), which increased...
the carrier hopping distance, thus retarding hole migration.\(^\text{14,35}\) Furthermore, the hole mobility of the conjugated polymer \(P1\) revealed \(10^{10}\) cm\(^2\) V\(^{-1}\) s\(^{-1}\), which is much higher than that of other conjugated polymer systems.\(^\text{36}\)

**Device**

To assess the feasibility of using \(P1\) and \(\text{Ref}(P4)\) polymeric thin films as hole transporting layers, we fabricated hybrid OLEDs having the device structure ITO/PEDOT:PSS/\(P1\) or \(\text{Ref}(P4)\) (50 nm)/Alq3 (60 nm)/LiF (0.5 nm)/Al (100 nm), in which vacuum-deposited conventional tris(8-quinolino-tol)aluminum (Alq3) acted as the electron transport/emissive layer. The current-voltage-luminance (I-V-L) characteristics, as well as plots of device efficiency versus current density, for the devices incorporating the conjugated polymers \(P1\) and \(\text{Ref}(P4)\) are displayed in Supporting Information. Both devices exhibited a voltage-independent pure emission from Alq3, implying that charge recombination occurred exclusively within the Alq3 layer. The hybrid OLED with the conjugated polymer \(P1\) exhibited a turn-on voltage of 2.5 V, a maximum brightness of 25,700 cd m\(^{-2}\), and a power efficiency of 1 lm W\(^{-1}\). Another device with the conjugated polymer \(\text{Ref}(P4)\) exhibited a turn-on voltage of 2.5 V, a higher brightness of 34,300 cd m\(^{-2}\), and a power efficiency of 1.1 lm W\(^{-1}\). Interestingly, the device based on \(\text{Ref}(P4)\) exhibited superior performance relative to that based on \(P1\); we ascribe this behavior to the relatively lower hole mobility of the \(\text{Ref}(P4)\) polymeric thin film. Thus, a more balanced recombination of holes and electrons can be achieved with a high EQE of 0.88%, even at a high-driving current.

**CONCLUSIONS**

The new BTPA-containing aromatic dibromo monomer, \(N,N\text{-bis}(4\text{-bromophenyl})\text{-N,N'-diphenyl-1,4-phenylenediamine} \ (M3)\), was successfully synthesized in high purity and high yields from available reagents. A novel NIR propeller-shape BTPA-containing electrochromic conjugated polymer with high hole mobility was readily prepared from the newly synthesized dibromo monomer \(M3\) with 9,9-diocytfluorene-2,7-diboronic acid bis(1,3-propanediol) ester via Suzuki coupling. Introduction of extremely electron-donating BTPA group to the polymer chain leads to good solubility and
film-forming properties of the conjugated polymer. In addition to high $T_T$ and excellent thermal stability, the conjugated polymer P1 also revealed 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 has great potential for use in optoelectronics applications. Combining the experiments and theoretical computation, we proposed a new oxidation mechanism of the conjugated polymer P1. The first electron was removed from the HOMO instead of specific atoms like the nitrogen atom.

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REFERENCES AND NOTES


