Electrochromic Material Containing Unsymmetrical Substituted *N,N,N′,N′*-Tetraaryl-1,4-phenylenediamine: Synthesis and Their Optical, Electrochemical, and Electrochromic Properties

HAN-YU WU,[1] KUN-LI WANG,[2] DER-JANG LIAW,[1] KUEIR-RARN LEE,[3] JUIN-YIH LAI[3]

[1]Department of Chemical Engineering, National Taiwan University of Science and Technology, 10607, Taipei, Taiwan

[2]Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, 10608, Taipei, Taiwan

[3]R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, 32023, Chung-Li, Taiwan

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ABSTRACT: A novel dibromo compound containing unsymmetrical substituted bi-triarylamine was synthesized. A conjugated polymer was prepared via the Suzuki coupling from the newly prepared dibromo compound and 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate). The glass transition temperature (T_g) of the conjugated polymer was 140 °C, 10% weight-loss temperatures (T_{d10}) in nitrogen was 458 °C, and char yield at 800 °C in nitrogen higher than 64%. Cyclic voltammogram of the polymer film cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.70 and 1.10 V versus Ag/Ag$^+$ in acetonitrile solution. The polymer films revealed excellent stability of electrochromic characteristics, with a color change from yellow green of the neutral form to the dark green and blue of oxidized forms at applied potentials ranging from 0 to 1.3 V. The color switching time and bleaching time were 4.25 and 7.22 s for 860 nm and 5.51 s and 6.48 s for 560 nm. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1469–1476, 2010

KEYWORDS: conjugated polymers; electrochemistry; electrochromic; naphthalene; synthesis

INTRODUCTION In the last two decades, π-conjugated polymers have attracted considerable interests because of their potential applications in electrochromics,[1–4] light emitting diodes,[5–9] organic thin film transistors,[10–14] photovoltaics,[15–18] and polymer memories.[19–20] Fluorene and its analogous derivatives have drawn much attention of optoelectronics because they generally have good solubility, high luminescent efficiency, and very good charge-transfer mobility in both neutral and doped states.[21–24] However, it is also known that they have drawbacks such as unsatisfied thermal stability and excimers formation in the solid state.[25,26] The applications for electrochromic conjugated polymers are quite diverse due to several favorable properties of these materials, like stable oxidation state, fast switching times, and excellent switching reproducibility.[27] This excellent properties led to the development of many technological applications such as self-darkening rear-view mirrors, adjustably darkening windows, large-scale electrochromic screens, and chameleon materials.[28–30] Electron-rich triarylamines are known to be easily oxidized to form stable polarons, and the oxidation process is always associated with a noticeable change of the coloration. Furthermore, triarylamine-based polymers are not only widely used as the hole-transport layer in electroluminescent diodes but also show interesting electrochromic behavior.[31–33]

In this article, we, therefore, synthesized a new dibromo monomer containing unsymmetrical *N,N,N′,N′*-tetraaryl-substituted 1,4-phenylenediamine moiety. The unsymmetric structure with naphthalene in the dibromo compound was designed to enhance the thermal stability and solubility. A conjugated polymer derived from the dibromide via Suzuki coupling reaction with a fluorene derivative was prepared, and its general properties such as thermal and optical properties as well as electrochemical and electrochromic property were investigated and discussed in detail in this study.

EXPERIMENTAL

Materials

N-Phenyl-1-naphthylamine was purchased from Ouchi Shinko Chemical Industrial, 1-bromo-4-iodobenzene, iodobenzene, bis(dibenzylideneacetone) palladium [Pd(dba)$_2$], 1,1′-bis(diphenylphosphino)-ferrocene (DPPF), sodium *tert*-butoxide and tetrakis(triphenylphosphine) palladium(0) [Pd(PPh$_3$)$_4$] were purchased from Acros, 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) was purchased from Aldrich and recrystallized from ethyl acetate and *n*-hexane before used. Tetrabutylammonium perchlorate (TBAP) was purchased from Acros and recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. DMSO was dried and distilled over calcium hydride

Additional Supporting Information may be found in the online version of this article. Correspondence to: K.-L. Wang (E-mail: klwang@ntut.edu.tw) or D.-J. Liaw (E-mail: liawdj@mail.ntust.edu.tw)

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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.

Measurements

Infrared (IR) spectra were recorded in the range 400–4000 cm^{-1} for the synthesized monomers and polymer in a KBr disk (Bio-Rad Digilab FTS-3500). Elemental analysis was made on a Perkin-Elmer 2400 instrument. Nuclear magnetic resonance (NMR) spectra were recorded using a BRUKER AVANCE 500 NMR. Weight-average molecular weights (M_w) and number-average molecular weights (M_n) were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns (300 × 7.7 mm^2, guard, 105, 104, 103, and 500 Å in series) were used for GPC analysis with tetrahydrofuran (THF; 1 mL min^{-1}) as the eluent. The eluents were monitored with a UV detector (JMST Systems, VUV-24) at 254 nm. Polystyrene was used as the standard. Thermogravimetric data were obtained on a TA instrument Dynamic thermogravimetric analysis (TGA) 2950 under nitrogen flowing condition at a rate of 20 cm^3 min^{-1} and a heating rate of 10 °C min^{-1}. Differential scanning calorimetric analysis was performed on a differential scanning calorimeter (DSC; TA instrument TA 910) under nitrogen flowing condition at a rate of 50 cm^3 min^{-1} and a heating rate of 10 °C min^{-1}. UV–vis spectra of the polymer films or solutions were recorded on a JASCO V-550 spectrophotometer at room temperature in air. The fluorescence spectra were recorded by a Shimadzu RF-5031 spectrophotometer. Cyclic voltammetry (CV) was performed with CHI model 619A with 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^{-1} against a Ag/Ag$^+$ reference electrode in a solution of 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile (CH$_3$CN). 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. Photoluminescence spectra were measured with a Jasco FP-6300 spectrofluorometer.

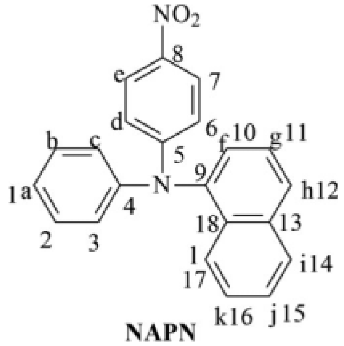
Synthesis of *N*-(4-Nitrophenyl)-*N*-phenyl-1-naphthalylamine (NAPN)

In a 500-mL three-neck round-bottom flask was placed *N*-phenyl-1-naphthylamine (10 g, 45.6 mmol), 4-fluoro-nitrobenzene (8 g, 45.6 mmol), sodium hydride (2 g, 83 mmol), and dimethyl sulfoxide (DMSO, 120 mL). The mixture was heated with stirring at 120 °C for 24 h. The reaction mixture was cooled and then poured into 1 L of saturated sodium chloride solution. The crude product was purified by silica gel column chromatography (*n*-hexane: toluene = 4:1) to afford pure product with MP 163 °C measured by DSC at 10 °C/min. IR (KBr): 2924 (Ar—H), 1598 (—NO$_2$ assymetric), 1313 (—NO$_2$ symetric), 810 (C—N strech).

^{1}H NMR (CDCl$_3$): δ (ppm) = 6.82–6.84 (d, 2H, H$_d$, J = 10.41 Hz); 7.18–7.20 (m, 1H, H$_{a,}$); 7.31–7.37 (m, 4H, H$_b$ and H$_c$); 7.44–7.48 (m, 2H, H$_g$ and H$_j$); 7.52–7.56 (m, 2H, H$_h$ and H$_k$); 7.90–7.93 (t, 2H, H$_f$ and H$_i$, J = 7.50 Hz); 7.96–7.98 (d, 1H, H$_l$, J = 10.41 Hz); 8.02–8.04 (d, 2H, H$_{e,}$ J = 10.41 Hz).

^{13}C NMR (CDCl$_3$): δ (ppm) = 116.47 (C$_6$), 123.20 (C$_9$), 124.94 (C$_3$), 125.25(C$_1$), 125.93 (C$_7$), 126.28 (C$_{11}$), 126.49 (C$_{15}$), 127.06 (C$_{14}$), 127.38 (C$_{10}$), 127.98 (C$_{13}$), 128.64 (C$_{16}$), 129.65 (C$_2$), 130.46 (C$_{17}$), 135.14 (C$_{12}$), 139.64 (C$_4$), 141.15 (C$_{18}$), 145.50 (C$_8$), 153.70 (C$_5$)

Elem Anal. Calcd. for $C_{22}H_{16}N_2O_2$: C, 76.63% : H, 4.74%; N, 8.23%. Found: C, 76.16%; H, 4.66%; N, 8.35%.



NAPN

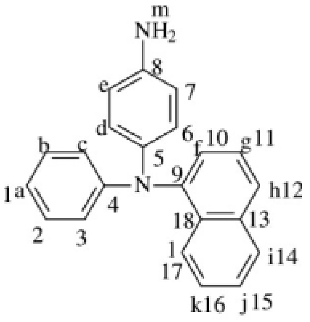
Synthesis of *N*-(4-Aminophenyl)-*N*-phenyl-1-naphthalylamine (NAPA)

In a 500-mL three-neck round-bottom flask equipped with a stirrer bar under nitrogen atmosphere, nitro compound (**NAPN**; 8 g, 23 mmol), Pd/C (0.2g), ethanol 200 mL were added. After 7 mL hydrazine monohydrate was slowly added to the mixture from a dropping funnel, the solution was stirred at reflux temperature for 12 h. Then the solution was cooled down to room temperature, the solution was filtered to remove the catalyst, and the crude product was recrystallized from ethanol to afford green solid with a 75% yield. MP = 129 °C measured by DSC at 10 °C/min; IR (KBr) 3356, 3445 cm^{-1} (NH$_2$ stretch).

^{1}H NMR.(CDCl$_3$): δ (ppm) = 3.54 (s, 2H, H$_m$); 6.60–6.63 (m, 2H, H$_{e,}$); 6.83–6.87 (m, 3H, H$_a$ andH$_c$); 7.02–7.04 (d, 2H, H$_d$, J = 9.96 Hz); 7.14–7.17 (m, 2H, H$_b$); 7.32–7.34 (d, 1H, H$_f$, J = 9.96 Hz); 7.37–7.39 (m, 1H, H$_j$); 7.45–7.48 (t, 2H, H$_g$ andH$_k$, J = 7.47 Hz); 7.73–7.75 (d, 1H, H$_l$, J = 9.96 Hz); 7.88–7.90 (d, 1H, H$_h$, J = 9.96 Hz); 8.02–8.04 (d, 1H, H$_{i,}$ J = 9.96 Hz).

^{13}C NMR (CDCl$_3$): δ (ppm) = 116.01 (C$_7$), 119.31 (C$_3$), 119.71 (C$_1$), 124.46 (C$_{14}$), 125.75 (C$_{17}$), 125.83 (C$_6$), 125.92 (C$_{11}$), 126.04 (C$_5$), 126.27 (C$_{16}$), 126.45 (C$_{10}$), 128.26 (C$_{12}$), 128.80 (C$_2$), 131.06 (C$_{13}$), 135.18 (C$_9$), 139.82 (C$_{15}$), 142.25 (C$_8$), 144.01 (C$_{18}$), 149.58 (C$_4$).

Elem Anal. Calcd. for $C_{22}H_{18}N_2$: C, 85.13% : H, 5.85%; N, 9.02%. Found: C, 85.27%; H, 5.83%; N, 9.03%.



NAPA

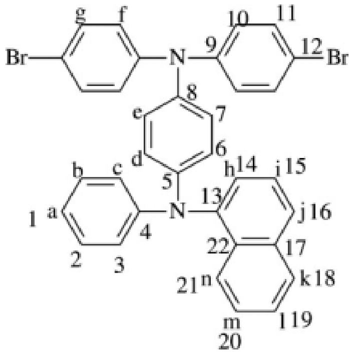
Synthesis of *N,N*-Bis(4-bromophenyl)-*N*′-phenyl-*N*′-(naphthalen-1-yl)-1,4-phenylenediamine (NAPHDIBr)

1-Bromo-4-iodobenzene (13 g, 48 mmol), **NAPA** (7.5 g, 24 mmol), Pd(dba)$_2$ (0.4 g, 0.72 mmol), DPPF (0.39 g, 0.72 mmol), sodium *tert*-butoxide (7 g, 72 mmol) and dry toluene (100 mL) were charged in a three-necked flask kept under nitrogen. The mixture was heated to reflux for 6 h. After the completion of the reaction, the solvent was removed under vacuum and the residue was extracted with dichloromethane–water. The organic layer was dried over MgSO$_4$ and filtered. After removing the solvent, the residue was purified by silica gel column chromatography (toluene: *n*-hexane = 1 : 4). Then the product was recrystallized from *n*-hexane and ethyl acetate (V/V = 4/1), and the light yellow solid was obtained. MP = 166 °C measured by DSC at 10 °C/min; IR (KBr) 1070 cm^{-1} (Ar—Br); 1282 cm^{-1} (Ar—N); 3034 cm^{-1} (Ar—H stretch).

^{1}H NMR (CDCl$_3$): δ (ppm) = 6.89–6.98 (m, 9H, $H_{a,}H_d$, H_e and H_f); 7.02–7.04 (d, 2H, H_c, J = 10.05 Hz); 7.19–7.22 (t, 2H, H_b, J = 7.54 Hz); 7.32–7.34 (d, 4H, H_g, J = 10.05 Hz); 7.36–7.41 (m, 2H, H_h and H_l); 7.47–7.52 (m, 2H, H_i and H_m); 7.78–7.80 (d, 1H, $H_{n,}$ J = 10.05 Hz); 7.89–7.91 (d, 1H, $H_{j,}$ J = 10 Hz); 7.96–7.98 (d, 1H, $H_{k,}$ J = 10.15 Hz).

^{13}C NMR (CDCl$_3$): δ (ppm) = 114.88 (C$_{12}$), 122.41 (C$_1$), 121.57 (C$_3$), 122.98 (C$_{17}$), 124.76 (C$_7$), 126.06 (C$_{19}$), 126.16 (C$_6$), 126.32 (C$_{14}$), 126.38 (C$_{13}$), 126.59 (C$_{20}$), 127.20 (C$_{18}$), 128.44 (C$_{15}$), 129.09 (C$_2$), 131.26 (C$_{21}$), 132.20 (C$_{11}$), 135.30 (C$_{22}$), 140.52 (C$_5$), 143.25 (C$_{16}$), 144.77 (C$_8$), 146.55 (C$_9$), 148.22 (C$_4$).

Elem Anal. Calcd. for C$_{34}$H$_{24}$Br$_2$N$_2$: C, 65.83% : H, 3.90%; N, 4.52%. Found: C, 65.99%; H, 4.07%; N, 4.50%.



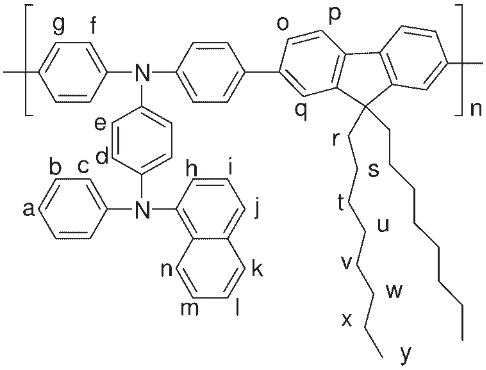
NAPHDIBr

Synthesis of the Conjugated Polymer, NAPHFL

To a three-necked flask was added 9,9-dioctylfluorene-2,7-bis (trimethyleneboronate) (138.4 mg, 0.25 mmol), **NAPHDIBr** (200 mg, 0.25 mmol). The flask equipped with a condenser was then evacuated and filled with nitrogen several times to remove traces of air, then the degassed toluene (5 mL) was added. Once the two monomers were dissolved, tetrakis(triphenyl-phosphine)palladium (0) [Pd(PPh$_3$)$_4$], 8.6 mg, (0.007 mmol) and 3 M aqueous sodium carbonate solution (2 mL) was added, and the mixture was stirred for 48 h at 105 °C under nitrogen. The reaction mixture was cooled to room temperature, and the organic layer was separated, washed with water, and precipitated into methanol. The green polymer sample was filtered, washed with excess methanol, dried, and purified by a Soxhlet extraction with methanol for 2 days. IR (KBr) 1261 cm^{-1} (Ar—N); 3031 cm^{-1} (Ar—H stretch).

^{1}H NMR (CDCl$_3$): δ (ppm) = 0.75 (s, 4H, H_s); 0.85–0.88 (m, 6H, H_y); 1.08–1.28 (m, 20H, H_t, H_u, H_v, H_w, and H_x); 2.00–2.05 (br, 4H, H_r); 6.93–6.96 (t, 1H, H_a, J = 7.5 Hz); 7.05–7.11 (br, 6H, $H_{c,}$ H_e, and H_g); 7.21–7.29 (m, 4H, H_b, and H_d); 7.38–7.45 (m, 2H, H_h, and H_l); 7.47–7.55 (m, 3H, H_i, and H_p); 7.58–7.62 (m, 8H, H_g, H_m, H_n, and H_o); 7.75–7.77 (m, 4H, H_f); 7.91–7.93 (d, 1H, $H_{j,}$ J = 10 Hz); 8.03–8.05 (d, 1H, $H_{k,}$ J = 10 Hz).

^{13}C NMR (CDCl$_3$): δ (ppm) = 14.09, 22.64, 23.84, 25.60, 29.26, 29.28, 29.57, 30.07, 31.86, 40.47, 40.53, 55.20, 67.95, 119.86, 120.89, 121.61,122.83, 123.39, 123.59, 124.15, 124.28, 125.48, 126.13, 126.35, 127.03, 127.17, 127.25, 127.77, 128.31, 128.43, 128.75, 129.13, 135.32, 139.55, 139.91, 141.51, 143.51, 144.24, 146.95, 148.58, 151.61.



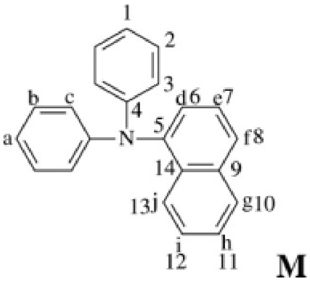
Synthesis of the Model Compound, M1

Iodobenzene (1.4 g, 7 mmol), *N*-phenyl-1-naphthylamine (1.3 g, 6 mmol), Pd(dba)$_2$ (0.2 g, 0.36 mmol), DPPF (0.72 mmol), sodium *tert*-butoxide (27 mmol) and dry toluene (10 mL) were charged in a three-necked flask kept under nitrogen. The mixture was heated to reflux for 8 h. After the completion of the reaction, the solvent was removed under vacuum and the residue was extracted with dichloromethane and water. The organic layer was dried over MgSO$_4$ and filtered. After removing the solvent, the residue was purified by silica gel column chromatography (toluene: *n*-hexane = 1:2). Then the light green solid product was obtained in a 71% yield.

^{1}H NMR (CDCl$_3$): δ (ppm) = 6.95–6.98 (t, 2H, H_a, J = 7.5 Hz); 7.07–7.09 (d, 4H, $H_{c,}$ J = 10 Hz); 7.21–7.24 (t, 4H, H_b, J = 7.5 Hz); 7.36–7.40 (m, 2H, H_h and H_d); 7.47–7.52 (t, 2H, H_e and H_i, J = 7.5 Hz); 7.80–7.81 (d, 1H, H_j, J = 5 Hz); 7.91–7.93 (d, 1H, $H_{f,}$ J = 8 Hz); 7.99–8.00 (d, 1H, H_g, J = 5 Hz).

^{13}C NMR (CDCl$_3$): δ (ppm) = 121.62 (C$_1$), 121.83 (C$_3$), 124.26 (C$_{10}$), 126.08(C$_{12}$), 126.32 (C$_7$), 126.34 (C$_6$), 126.39

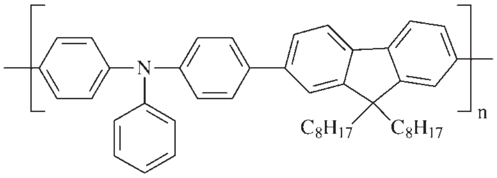
(C_{13}), 127.21 (C_{11}), 128.34 (C_8), 129.05 (C_2), 131.27 (C_5), 135.27 (C_9), 143.57 (C_{14}), 148.44 (C_4).



M 1

Synthesis of the Model Compound, M2

The model compound was prepared according to the procedures published in the paper.[34]

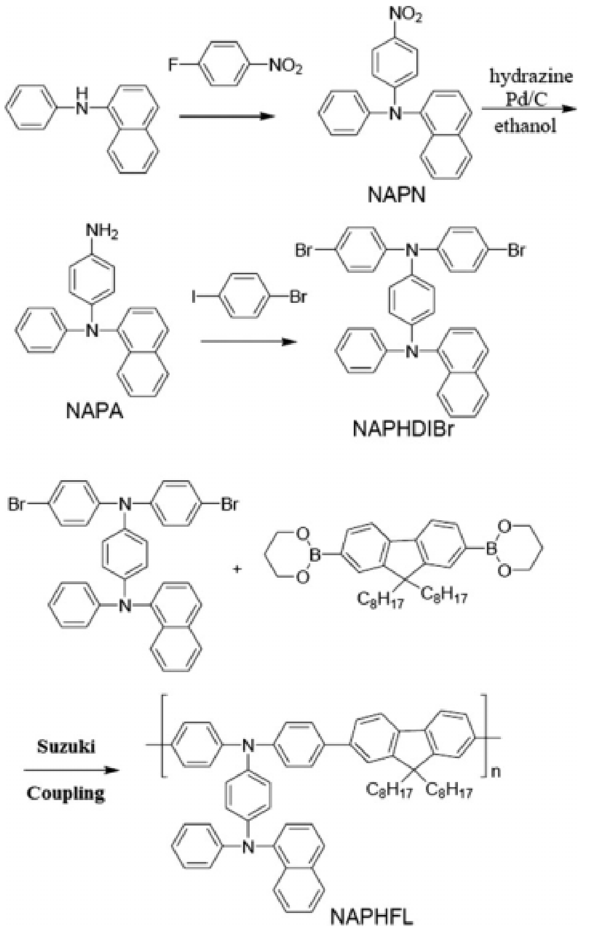


M 2

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis procedures of dibromo monomer (**NAPHDIBr**) containing unsymmetrical bi-triarylamine structure were outlined in Scheme 1. The precursor, *N*-(4-aminophenyl)-*N*-phenyl-naphthalen-1-amine (**NAPA**), was obtained with hydrazine monohydrate under a nitrogen atmosphere by Pd/C-catalytic reduction of compound *N*-(4-nitrophenyl)-*N*-phenylnaphthalen-1-amine (**NAPN**), which was prepared from *N*-phenyl-1-naphthylamine and 4-fluoro-nitrobenzene in the presence of sodium hydride. The new aromatic dibromo compound, **NAPHDIBr**, having ditriarylamine and naphthalene groups was successfully synthesized by the Buchwald-Hartwig reaction with 1-bromo-4-iodobenzene. Elemental analysis, Fourier transform IR (FTIR), ^{1}H NMR, and ^{13}C NMR spectra as well as two dimensional NMR techniques were used to identify structures of the intermediates **NAPN**, **NAPA**, and the desired dibromo compound, **NAPHDIBr**. The FTIR spectrum of **NAPN** showed nitro characteristic bands at 1313 and 1598 cm^{-1}. After reduction, the characteristic band of the **NAPA** showed the typical NH_2 stretch at 3356 and 3445 cm^{-1}, and the nitro characteristic bands disappeared. The characteristic band for the aryl bromide group of **NAPHDIBr** monomer was observed at 1070 cm^{-1} in the FTIR spectrum. The ^{1}H NMR and ^{13}C NMR spectra as well as two dimensional spectra including COSY and HMQC of the dibromo monomer were showed in the Supporting Information. All aromatic protons of the **NAPHDIBr** are in the range of 6.89–7.98 ppm. Elemental analysis, IR, and NMR spectra clearly confirm that the compounds, **NAPN**, **NAPA**, and **NAPHDIBr** were consistent with the proposed structures. The conjugated polymer, **NAPHFL**, was synthesized by Suzuki coupling polymerization of an equimolecular mixture of the dibromide (**NAPHDIBr**) and 9,9-dioctylfluorene-2,7-bis(trimethyleneboronate) as shown in Scheme 1. The polymerization was carried out for 48 h using 3 mol % $Pd(PPh_3)_4$ as the catalyst in a two-phase mixture of degassed toluene and aqueous K_2CO_3 (3 M). The chemical structure of the polymer was verified by FTIR and NMR spectra. Figure 1 shows the aromatic part ^{1}H NMR spectra of **NAPHFL** in $CDCl_3$, where all the peaks are consistent with the expected structure. The aliphatic hydrogens attached on the fluorene appear at the range of 0.5–2.2 ppm and the integrations of the peaks are consistent with the structure. The M_n of the prepared polymer was as high as about17,200 and the polydispersity index was 2.99.



SCHEME 1 Synthesis of the dibromo monomer and conjugated polymer.

Basic Properties

The polymer has good solubility in common organic solvents, such as NMP, THF, dichloromethane, chloroform, toluene, xylene, and benzene at room temperature. The excellent solubility may result from the aliphatic segment and the propeller structure of the noncoplanar bi-triarylamine moiety. The TPA-based compounds are noncoplanar and propeller shape,

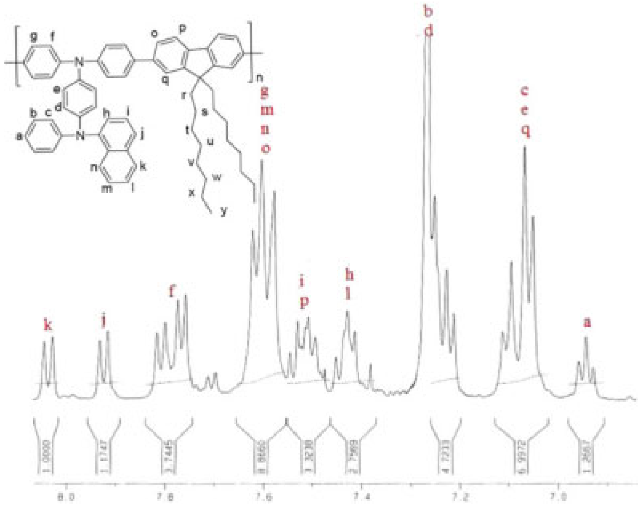


FIGURE 1 ^{1}H NMR spectrum of the conjugated polymer, **NAPHFL**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

so that they have more space than coplanar structures to let solvent penetrate (or swelling). On the other hand, the rigid structure of triphenylamine can enhance the T_g and thermal stability as studied by many researches.[35–37] The thermal stability of **NAPHFL** under nitrogen was determined by TGA, and their phase transition behavior was evaluated with DSC. The **NAPHFL** showed excellent thermal stability with decomposition temperatures 448 and 458 °C in air and nitrogen, respectively. The glass transition temperature of **NAPHFL** was 140 °C which is much higher than that of poly(9,9-dioctylfluorene) (**POF**; $T_g = 66$ °C).[34] The high transition temperature may result from the rigid *N,N*-diphenyl-*N*′-phenyl-*N*′-naphthalen-1-yl-1,4-phenylene diamine structure.

Optical Properties

The optical absorption and emission spectra of **NAPHFL** in toluene and **NAPHDIBR** in toluene and solid film state are shown in Figure 2, and their photophysical properties were summarized in Table 1. For **NAPHFL** in toluene solution, a major absorption at around 381 nm and a minor absorption at 307 nm were observed. Because of the maximum absorption (324 nm) of **NAPHDIBr** in toluene is near the minor absorption (307 nm) of **NAPHFL**, we ascribe the peak at 307 nm to π–π* transition of *N,N*-bis(4-bromophenyl)-*N*-phenyl-*N*-naphthalen1-yl-1,4-phenylene-diamine moieties group. Since the maximum absorption peak for **POF** is 387 nm,[34] we ascribe the major absorption to π-π* transition derived from the conjugated polymer backbone. The absorption spectra in solid state were similar to that in toluene solution. The band edge of absorption peak of the polymer film exists around 460 nm, which is ~20 nm longer than that of the solution. This fact indicates the existence of interchain interaction in the solid-state polymer. On excitation at the maximum absorption wavelength, the **NAPHFL** and **NAPHDIBr** exhibit blue emission color in toluene solution with the emission peaks at 473 and 454 nm. The fluorescent quantum yield for **NAPHFL** is 79% in toluene solution. The PL spectra of the polymer (**NAPHFL**) and the monomer (**NAPHDIBr**) in solid state were red-shifted by 43 and 5 nm for from the corresponding solution spectra. This phenomenon is probably attributable to intermolecular interactions that planarize segments in the monomers/polymers leading to better conjugation in the solid state[38,39] The emissions of **NAPHFL** was red-shifted both in solution and solid state as compared to **NAPHDIBr** because of the enhanced conjugated length by Suzuki coupling reaction.

Electrochemical Properties

The electrochemical behavior of **NAPHFL** was investigated by CV conducted by film cast on an ITO-coated glass substrate as the working electrode in dry CH_3CN containing 0.1 M of **TBAP** as electrolyte under nitrogen atmosphere. Oxidative and reductive cycles of the polymer and model compounds are shown in Figure 3. The **NAPHFL** show two reversible oxidation redox couples at $E_{1/2}$ values of 0.72 ($E_{\text{onset}} = 0.68$) and 1.11 V in the oxidative scan. For understanding the oxidation order of the two nitrogen atoms in the polymer, model compounds (**M1** and **M2**) were prepared and their electrochemical behaviors are also shown in Figure 3. The **M1** and **M2** have reversible oxidation peak at 1.27 V ($E_{\text{onset}} = 1.01$ V) and 1.46 V ($E_{\text{onset}} = 1.03$ V), respectively. Comparing the electhochemical data, we could find that **M1** was more easily oxidized than **M2**, and prove the oxidation order of nitrogen atoms for **NAPHFL** according to the electron density among the two nitrogen atoms on different triphenylamine structures in each repeating unit (Table 2). From these electrochemical data, the first electron removal for **NAPHFL** could be assumed to occur at the nitrogen atom on the pendent *N,N*-diphenyl-naphthalene-1-amine unit, which was more electron-rich than the nitrogen atom on the main-chain triphenylamine units (Scheme 2). From the oxidation potential relative to ferrocene/ferrocenenium, which can correspond to −4.8 eV for ferrocene below the vacuum level,[40] we can approximately calculate the HOMO energy level of the conjugated polymer. The LUMO level of the polymer was calculated according to the equation: LUMO = HOMO + E_g. The electrochemical properties of **NAPHFL** and

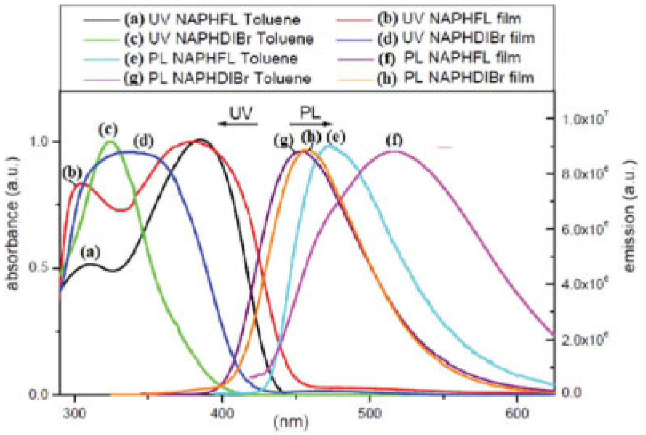


FIGURE 2 UV–vis and PL spectra of **NAPHDIBr** and **NAPHFL**. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE 1 Photophysical Properties of Conjugated Polymers and the Monomers

	Solution (Toluene)			Film	
Compound	Abs (nm)	PL (nm)	$\Phi_{PL}(\%)^a$	Abs (nm)	PL (nm)
NAPHFL	307, 381	473	79	310, 385	516
NAPHDIBr	324	454	–	326, 363	459
POF[37]	387	414	85	389	435

[a] Quantum yield (within an error margin of ±3%) in Toluene solution was calculated in an integrating sphere with 9,10-diphenylanthracene as the standard ($\Phi_F = 0.9$).

model compounds are summarized in Table 2. The onset oxidation potentials are situated from 0.68 to 1.03 V, from which their HOMO levels are estimated in the range of −4.86 to −5.21 eV. From the optical bandgap, the LUMO levels are calculated in the range of −2.08 to −2.39 eV. Because of the stability of the film and the good adhesion between the polymer and ITO substrate, the **NAPHFL** exhibited excellent reversibility of electrochromic characteristics in 1200 s continuous cyclic scans (measuring time limit of the instrument) between 0.0 and 1.2 V, changing color from light green to deep green and then blue. The electrochromic characteristics will be discussed below.

Electrochromic Characteristics

Electrochromism of the polymer thin film was examined by an optically transparent thin-layer electrode coupled with UV–vis spectroscopy. The electrode preparations and solution conditions were identical to those used in CV. The typical electrochromic absorbance spectra of **NAPHFL** are shown in Figure 4. When the applied potentials increased positively from 0 to 1.0 V, the characteristic peak of absorbance at 385 nm for neutral form **NAPHFL** decreased gradually and shifts to 344 nm, and then a new band grows up at 860 nm due to first oxidation. When the potential was adjusted to a more positive value of 1.2 V, corresponding to the second step oxidation, the peak at 860 nm keep to raise and a new band at 560 nm slowly grow up. Meanwhile, the film changed from original yellow green to dark green and then to a dark blue oxidized form as shown in Figure 4. The color switching times were estimated by applying a potential step, and the absorbance profiles were followed in Figure 5. The switching time was calculated at 90% of the full switch because it is difficult to perceive any further color change with naked eye beyond this point. Thin **NAPHFL** film requires 4.25 s at 1.2 V for switching and 7.22 s for bleaching at 860 nm, 5.51 s for switching and 6.48 s for bleaching at 560 nm. Continuous cyclic scans between 0.0 and 1.2 V, the polymer films still exhibited good stability of electrochromic characteristics.

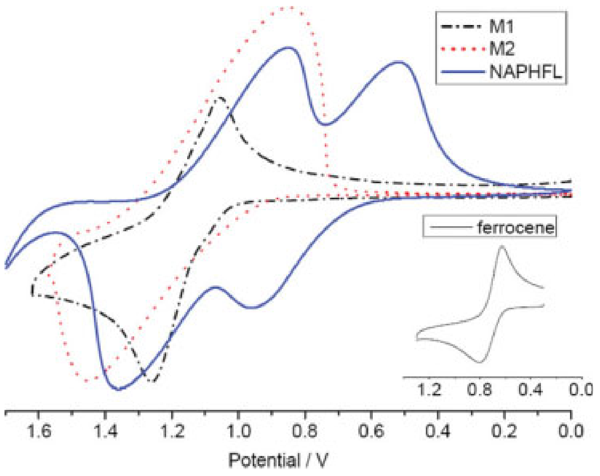


FIGURE 3 Cyclic voltammograms of **NAPHFL**, **M1**, and **M2** in film cast on an indium-tin oxide (ITO)-coated glass substrate in CH_3CN containing 0.1 M TBAP. The scanning rate is 0.1 V/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

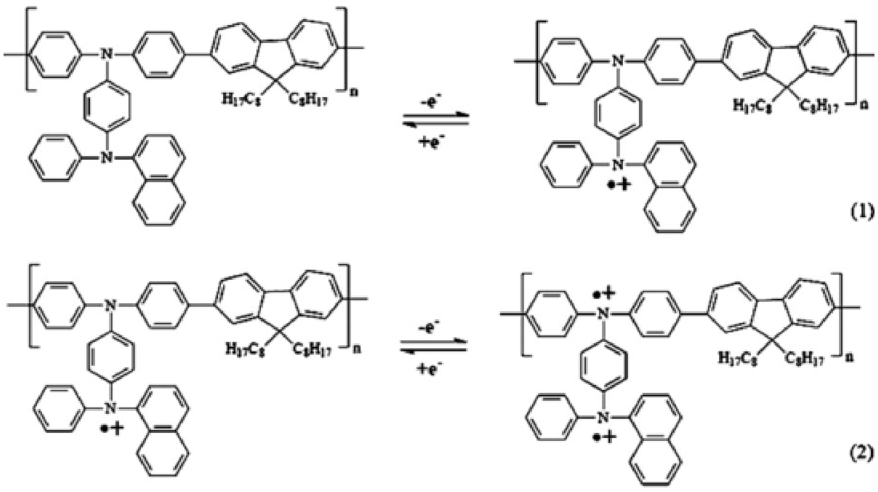
CONCLUSIONS

A novel conjugated polymer, **NAPHFL**, was successfully prepared via Suzuki coupling reaction from a fluorene derivative and a novel dibromo monomer containing unsymmetrical *N,N,N′,N′*-tetraaryl-substituted 1,4-phenylenediamine. The polymer exhibits excellent solubility in common organic solvent, and has high thermal stability such as T_{d10} at 453 °C in nitrogen atmosphere and T_g at about 140 °C. In electrochromic behavior, it revealed excellent continuous cyclic stability of electrochromic characteristic in 1200 s.

TABLE 2 Electrochemical Properties of **NAPHFL** and Model Compounds

	$E_{1/2}{}^a$ (V)					
Compound	First	Second	$E_{onset}{}^d$	$E_g{}^b$ (eV)	HOMO[c] (eV)	LUMO[c] (eV)
NAPHFL	0.72	1.11	0.68	2.78	−4.86	−2.08
M1	1.15	–	1.01	3.05	−5.19	−2.14
M2	1.16	–	1.03	2.88	−5.21	−2.39

[a] $E_{1/2}$ (average potential of the redox couple peaks).
[b] The data were calculated from polymer films by the equation $E_g = 1240/\lambda$onset.
[c] Calculated from the equation: HOMO $= -(E^{ox}_{onset} - E^{Fc}_{onset}) - 4.8$, LUMO = HOMO + band gap.
[d] $E_{ox/onset}$ (Fc/Fc vs. Ag/Ag+) = 0.62 V.



SCHEME 2 Supposed redox process of **NAPHFL** from its neutral state, radical cation state to dication.

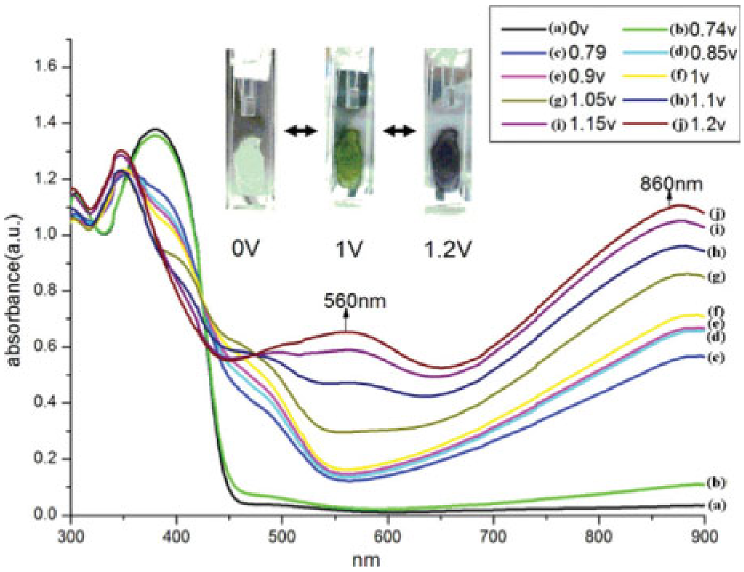


FIGURE 4 Electrochromic behavior of **NAPHFL** thin film (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) from 0 to 1.2 V.

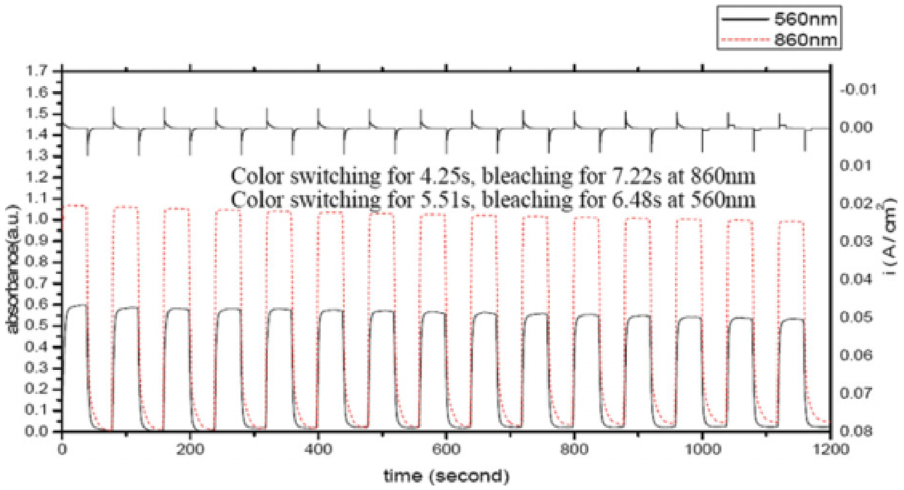


FIGURE 5 Current consumption and potential step absorptometry of **NAPHFL** (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step (0.00–1.20 V).

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