Solution-Processable Transmissive-to-Green Switching Electrochromic Polyamides Bearing 2,7-*Bis*(Diphenylamino)Naphthalene Units

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ABSTRACT: A new 2,7-*bis*(diphenylamino)naphthalene-based diamine monomer, *N,N'-bis*(4-aminophenyl)-*N,N'-bis*(4-metho-xyphenyl)-2,7-naphthalenediamine, was synthesized and polymerized with various aromatic dicarboxylic acids via the phosphorylation polyamidation reaction leading to a new series of redox-active and electrochromic aromatic polyamides. The polyamides exhibited high solubility in many polar aprotic solvents, good film-forming ability, and high thermal stability. They also showed stable electrochemical stability and anodically green coloring when oxidized. The two arylamino centers

INTRODUCTION Electrochromism (EC), first termed in 1961 by Platt,¹ is a process by which a material changes its electrooptic properties through the application of an electric potential across the material. Typically, these electrooptic changes occur in the visible region of the spectrum with the material switching colors upon a change in applied potential. EC technology and EC devices are drawing attention for their high potentiality in solar control,² display,³ and camouflage⁴ applications. A number of different organic and inorganic materials have been described and used in the construction of EC devices, such as transition metal oxides, viologens, conjugated polymers, metal coordination complexes, and Prussian blue.⁵ In particular, conjugated polymers have been popularly used as active layers in EC devices due to their unique properties such as solution processability, fast response times, high optical contrasts, and easy tuning of their colors through structural modifications.⁶ However, most of conjugated polymers are colored in their neutral state and can be converted to colorless and transmissive state upon electro-oxidation.⁷ In order to gain transparency when needed, this type electrochromic materials must be continuously kept at their oxidized state, which requires consumption of energy and may cause the degradation of the electrochromic material. In addition, long alkyl chains are usually needed to be attached on the backbone of conjugated polymers in order to achieve solution processability, which decreases

showed a weak electronic interaction via the 2,7-naphthalenediyl bridge, and thus they started to oxidize almost at the same time. No intervalence charge transfer (IVCT) absorption was observed during the oxidation processes of these polyamides. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2017**, *00*, 000–000

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heat and UV resistance of the electrochromic material. Thus, the use of neutral state colorless electrochromic polymers may be a better choice for the fabrication of EC devices.

Aromatic polyamides are known as highly thermally stable polymers with a favorable balance of physical and chemical properties.8 However, rigidity of the backbone and strong interchain interactions result in high melting or glass transition temperatures and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their wide spread applications. To overcome such a drawback, polymer-structure modification becomes necessary. One of the common approaches for increasing solubility and processability of aromatic polyamides without much sacrificing high thermal stability is the introduction of bulky, packing-disruptive groups into the polymer backbone.9-11 It has been demonstrated that aromatic polyamides containing threedimensional, propeller-shaped triphenylamine (TPA) unit are amorphous, have good solubility in organic solvents and good film-forming capability, and exhibit high thermal stability.¹² Moreover, the incorporation of bulky groups increases the interchain spacing and reduces the packing efficiency thereby increasing the intrinsic microporosity. This ultimate behavior finds application in gas separation membrane technology, where much effort has been focused to enhance gas

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FIGURE 1 Structures of the synthesized compounds and codes of the hydrogen and carbon atoms for the assignments of NMR signals. [Color figure can be viewed at wileyonlinelibrary.com]

permeability through an increment in intrinsic free volume which could be achieved by chemical modification of the polymer chain.¹³

Triarylamine derivatives and polymers are well known for photo- and electroactive properties that find optoelectronic applications as photoconductors, hole-transporters, lightemitters, and electrochromics.¹⁴ Many conjugated systems containing triphenylamine units have been synthesized as active materials for EC devices.¹⁵ During the last decade, a vast number of condensation-type polymers (e.g., aromatic polyamides and polyimides) with triarylamine units have been developed as potential electrochromic materials.^{16,17} It has been demonstrated by Yen and Liou¹⁸ that aromatic polyamides prepared from N,N'-bis(4-aminophenyl)-N,N'-bis(4-methoxyphenyl)-1,4-phenylenediamine [**(OMe)₂TPPA**]

(Fig. 1) and aromatic dicarboxylic acids exhibited good solubility, high thermal stability, and several advantageous electrochromic characteristics such as high optical contrast, low switching times, high coloration efficiency, and excellent electrochemical/electrochromic stability. Bis(diphenylamino)naphthalene derivatives have been characterized as redoxswitchable high-spin organic molecules¹⁹ or host materials.²⁰ To our knowledge, there is little information about the synthesis and electrochromic properties of triarylamine-based high-performance polymers containing naphthalene units in the backbone. In this work, a new bis(diphenylamino)naphthalene-based diamine monomer, namely N,N'-bis(4-aminophenyl)-*N*,*N'-bis*(4-methoxyphenyl)-2,7-naphthalenediamine (Structure 3 in Fig. 1) was synthesized and led to a new series of aromatic polyamides with 2,7-bis(diphenylamino)naphthalene moieties in the main chain. Incorporation of the naphthalene-2,7-diyl core on the electrochemical and electrochromic properties of the polyamides was investigated by comparing with those of **(OMe)**₂**TPPA**-derived polyamides.

EXPERIMENTAL

Materials

N,*N*'-*Bis*(4-methoxyphenyl)-2,7-naphthalenediamine (1)(m.p. = 175 - 177 °C) was synthesized by condensation of 2,7-dihydroxynaphthalene (Acros) with *p*-anisidine (Acros) in the presence of catalytic amounts of iodine by the Knoevenagel's method.²¹ p-Fluoronitrobenzene (Acros), cesium fluoride (CsF) (Acros), 10% palladium on charcoal (Pd/C) (Acros), and 99% hydrazine monohydrate (TCI) were used without further purification. Dimethyl sulfoxide (DMSO) (Tedia), N,N-dimethylacetamide (DMAc) (Tedia), pyridine (Py) (Wako), and N-methyl-2-pyrrolidone (NMP) (Tedia) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in sealed bottles. Triphenyl phosphite (TPP) (TCI) was used as received from the supplier. Commercially obtained calcium chloride (CaCl₂) was dried under vacuum at 180 °C for 3 h prior to use. The aromatic dicarboxylic acid monomers including 4,4'-biphenyldicarboxylic acid (4a) (Aldrich), 4,4'dicarboxydiphenyl ether (4b) (TCI), *bis*(4-carboxyphenyl) sulfone (4c) (TCI), and 2,2-bis(4-carboxyphenyl)hexafluoropropane (4d) (TCI) were used as received from commercial sources. Tetrabutylammonium perchlorate (Bu₄NClO₄) (TCl) was recrystallized twice from ethyl acetate under nitrogen atmosphere and then dried in vacuo prior to use. All other reagents and solvents were used as received from commercial sources.

Monomer Synthesis

N,N'-Bis(4-Methoxyphenyl)-2,7-Naphthalenediamine (1)

In a 100-mL three-necked round-bottom flask equipped with a Dean-Stark trap, a mixture of 16 g (0.1 mol) of 2,7-dihydroxynaphthalene, 24 g (0.2 mol) of *p*-anisidine and 1.0 g (7 mmol) of iodine in 40 mL of xylene was heated at 160 °C for about 24 h. After cooling to around 90 to 100 °C, the mixture was poured into 200 mL of ethanol, and the precipitated product was collected by filtration. Recrystallization from ethanol yielded 30 g (81%) of gray crystals with melting point of 176 to 179 °C (by DSC). IR (KBr): 3411 (-NH- stretch), 2950, 2835 cm⁻¹ (methoxy, C-H stretch).

¹H NMR (600 MHz, DMSO- d_6 , δ , ppm) (Codes of the hydrogen atoms: see Fig. 1): 7.94 (s, 2H, -NH-), 7.52 (d, J = 8.4 Hz, 2H, H_a), 7.14 (d, J = 8.4 Hz, 4H, H_d), 6.99 (d, J = 1.8 Hz, 2H, H_c), 6.89 - 6.92 (m, 6H, H_b + H_e), 3.72 (s, 6H, $-OCH_3$).

N,N'-Bis(4-Methoxyphenyl)-N,N'-Bis(4-Nitrophenyl)-2,7-Naphthalenediamine (2)

In a 50-mL round-bottom flask equipped with a stirring bar, a mixture of 7.4 g (0.02 mol) of *N*,*N'-bis*(4-methoxyphenyl)-2,7-naphthalenediamine **(1)**, 6.4 g (0.045 mol) of *p*-fluoroni-trobenzene, and 6.8 g (0.045 mol) of cesium fluoride (CsF) in 35 mL of dimethyl sulfoxide (DMSO) was heated at 140 °C

¹H NMR (600 MHz, DMSO- d_6 , δ , ppm): 8.05 (d, J = 9.6 Hz, 4H, H_g), 7.95 (d, J = 9.0 Hz, 2H, H_a), 7.65 (d, J = 2.4 Hz, 2H, H_c), 7.35 (dd, J = 9.0 Hz, 4H, H_b), 7.24 (d, J = 9.0 Hz, 4H, H_d), 7.02 (d, J = 9.0 Hz, 4H, H_e), 6.84 (d, J = 9.6 Hz, 4H, H_f), 3.78 (s, 6H, - OCH₃). ¹³C NMR (150 MHz, DMSO- d_6 , δ , ppm): 157.68, 153.41, 143.43, 138.89, 137.47, 134.83, 129.61, 128.79, 128.70, 125.56, 124.71, 122.98, 116.72, 115.51, 55.30 (codes of the hydrogen and carbon atoms: see Fig. 1). ANAL. CALCD. for C₃₆H₂₈N₄O₆ (612.64): C, 70.58%; H, 4.61%, N, 9.14%. Found: C, 70.02%; H, 4.35%; N, 8.95%.

N,N'-Bis(4-Aminophenyl)-N,N'-Bis(4-Methoxyphenyl)-2,7-Naphthalenediamine (3)

In a 250-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 2.00 g (3.26 mmol) of dinitro compound **2** and 0.15 g of 10% Pd/C were dispersed in 150 mL of ethanol. The suspension solution was heated to reflux, and 2 mL of hydrazine monohydrate was added slowly to the mixture. After a further 24 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled under nitrogen atmosphere. The precipitated product was collected by filtration and dried in vacuo at 80 °C to give 1.44 g (80% in yield) of pale yellow-green powder; mp = 188 – 190 °C (by DSC). IR (KBr): 3448, 3368 cm⁻¹ (–NH₂ stretch).

¹H NMR (600 MHz, DMSO- d_6 , δ , ppm): 7.46 (d, J = 8.9 Hz, 2H, H_a), 6.98 (d, J = 8.9 Hz, 4H, H_d), 6.86 (d, J = 9.0 Hz, 4H, H_e), 6.80 (d, J = 8.6 Hz, 4H, H_f), 6.78 (dd, J = 8.9, 2.3 Hz, 2H, H_b), 6.56 (d, J = 2.3 Hz, 2H, H_c), 6.55 (d, J = 8.6 Hz, 4H, H_g), 5.00 (s, 4H, -NH₂), 3.73 (s, 6H, -OCH₃). ¹³C NMR (150 MHz, DMSO- d_6 , δ , ppm): 155.20, 147.14, 145.81, 140.58, 135.73, 135.25, 127.92, 127.49, 125.88, 122.83, 117.99, 114.90, 114.66, 111.83, 55.13 (codes of the hydrogen and carbon atoms: see Fig. 1). ANAL. CALCD. for C₃₆H₃₂N₄O₂ (552.91): C, 78.20%; H, 5.83%, N, 10.13%. Found: C, 78.02%; H, 5.35%; N, 9.87%.

Synthesis of Model Compound

A mixture of 0.1105 g (0.2 mmol) of diamine monomer **3**, 0.0488 g (0.4 mmol) of benzoic acid, 0.15 g of anhydrous calcium chloride, 0.4 mL of triphenyl phosphite (TPP), 0.15 mL of pyridine, and 0.3 mL of NMP was heated with stirring at 120 °C for 3 h. The resulting solution was poured with stirring into methanol/H₂O. The precipitated product was washed repeatedly with methanol and hot water, and dried to give a quantitative yield of model compound **M**. IR spectrum of **M**: 3255 (amide N–H stretch), 1648 cm⁻¹ (amide carbonyl stretch). ¹H NMR (600 MHz, DMSO-*d*₆, δ , ppm): 10.20 (s, 2H, amide protons), 7.94 (d, *J* = 7.4 Hz, 4H, H_h), 7.69 (d, *J* = 8.6 Hz, 4H, H_g), 7.51 (t, *J* = 7.4 Hz, 4H, H_i), 7.04 (d, *J* = 8.7 Hz, 4H, H_d), 7.00 (d, *J* = 8.6 Hz, 4H, H_f), 6.96 (d,





SCHEME 1 Synthetic route to the diamine monomer 3.

J = 8.9 Hz, 2H, H_b), 6.92 (d, J = 8.7 Hz, 4H, H_e), 6.88 (s, 2H, H_c), 3.73 (s, 6H, -OCH₃).

¹³C NMR (150 MHz, DMSO- d_6 , δ, ppm): 165.20, 155.87, 146.24, 143.12, 139.97, 135.21, 134.97, 134.37, 131.40, 128.43, 128.30, 127.55, 126.91, 124.60, 124.01, 121.61, 120.23, 115.33, 114.98, 55.18 (codes of the hydrogen and carbon atoms: see Fig. 1). ANAL. CALCD. for C₅₀H₄₀N₄O₄ (760.89): C, 78.93%; H, 5.30%, N, 7.36%. Found: C, 78.42%; H, 5.03%; N, 7.03%.

Synthesis of Polyamides

The synthesis of polyamide 5b was used as an example to illustrate the general synthetic route used to produce the polyamides. A mixture of 0.3316 g (0.6 mmol) of diamine monomer 3, 0.1549 g (0.6 mmol) of 4,4'-dicarboxydiphenyl ether (4b), 0.15 g of anhydrous calcium chloride, 0.7 mL of triphenyl phosphite (TPP), 0.2 mL of pyridine, and 0.4 mL of NMP was heated with stirring at 120 °C for 3 h. The polymerization proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solution. The resulting viscous solution was poured slowly with stirring into 150 mL of methanol, giving rise to a tough, fibrous precipitate. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried to give a quantitative yield of polyamide 5b. The inherent viscosity of polymer was 0.45 dL/g, measured in DMAc (containing 5 wt % LiCl) at a concentration of 0.5 g/dL at 30 °C.

IR spectrum of **5b** (film): 3313 (amide N–H), 2835, 2950 (methoxy C–H stretch), 1650 cm⁻¹ (amide carbonyl stretch).

¹H NMR (600 MHz, DMSO- d_6 , δ , ppm) (assignments of the NMR signals to the structure: see Supporting Information Fig. S8): 10.18 (2H, amide protons), 8.00 (4H, H_h), 7.65 (4H, H_g), 7.59 (2H, H_a), 7.15 (4H, H_i), 6.98 (10H, H_b, H_d, H_f), 6.89 (6H, H_c, H_e), 3.71 (6H, $-\text{OCH}_3$).

Measurements

Infrared (IR) spectra were recorded on a Horiba FT-720 FT-IR spectrometer. ¹H and ¹³C NMR spectra were measured on a Bruker Avance III HD-600 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analyses were run in a Heraeus Vario EL III CHNS elemental analyzer. The inherent viscosities were determined with a Cannon-Fenske viscometer at 30 °C. Gel permeation chromatography (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector at 3 mg/mL concentration. Two Waters 5 μ m Styragel HR-2 and HR-4 columns (7.8 mm I. D. \times 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 mL/min at 40 °C and were calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA. Experiments were carried out on approximately 3 to 5 mg of polymer film samples heated in flowing nitrogen or air (flow



FIGURE 2 (a) ¹H NMR and (b) COSY spectra of the target diamine monomer **3** in DMSO- d_6 . [Color figure can be viewed at wileyonlinelibrary.com]

rate = 40 cm³/min) at a heating rate of 20 °C/min. DSC analyses were performed on a Perkin-Elmer DSC 4000 at a scan rate of 20 °C/min in flowing nitrogen. Ultraviolet-visible (UV-Vis) spectra of the polymer films were recorded on an Agilent 8453 or a Hitachi U-4100 UV-visible spectrometer. Electrochemistry was performed with a CHI 750A electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about 0.5 cm \times 2.0 cm) was used as a working electrode. All cell potentials were taken with the use of a home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.44 V vs. Ag/AgCl). Spectroelectrochemistry analyses were carried out with an electrolytic cell, which was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a home-made Ag/AgCl, KCl (sat.) reference electrode. Absorption spectra in the spectroelectrochemical experiments were also measured with an Agilent 8453 UV-visible photodiode array spectrophotometer.

RESULTS AND DISCUSSION

Monomer Synthesis

The diamine monomer 3 was synthesized by a three-step reaction sequence as shown in Scheme 1. In the first step,

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FIGURE 3 (a) ¹³C NMR and (b) C-H COSY spectra of the target diamine monomer **3** in DMSO- d_6 (the methoxy carbon at 55.13 ppm is not shown). [Color figure can be viewed at wileyonlinelibrary.com]

N,*N*'-*bis*(4-methoxyphenyl)-2,7-naphthalenediamine (**1**) was synthesized by condensation of 2,7-dihydroxynaphthlene with *p*-anisidine in the presence of small amounts of iodine according to the Knoevenagel synthesis of aromatic secondary amines.²¹ In the second step, the intermediate

dinitro compound, N,N'-bis(4-methoxyphenyl)-N,N'-bis(4nitrophenyl)-2,7-naphthalenediamine (**2**) was obtained by the nucleophilic aromatic fluoro-displacement reaction of *p*fluoronitrobenzene with the secondary amine **1** in the presence of cesium fluoride (CsF).^{12(a),22} Finally, the target



SCHEME 2 Synthesis of polyamides 5a to 5d.

diamine monomer **3** was prepared by hydrazine Pd/C-catalyzed reduction of dinitro compound **2**. The yield of each step was generally higher than 80%.

Supporting Information Figure S1 illustrates FT-IR spectra of all the synthesized compounds 1-3. The IR spectrum of compound 1 gives rise to a sharp, medium absorption at about 3411 cm⁻¹ ascribed to the aryl secondary amine N-H stretching vibration. The dinitro compound 2 shows the characterisic absorption of nitro groups at around 1585 and 1308 cm^{-1} (-NO₂ asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared and the amino group shows the typical $-NH_2$ stretching absorption pair at 3448 and 3368 cm⁻¹ as shown in the IR spectrum of diamine monomer 3. The 1 H NMR and COSY spectra of the secondary amine 1 are compiled in Supporting Information Figure S2. The resonance signal of aromatic -NH- groups appears at 7.94 ppm as a sharp singlet, and the tall singlet at 3.72 ppm is attributed to the methoxy protons. The resonance signals of aromatic hydrogens appear in the range of 6.89 to 7.53 ppm. The ¹H and ¹³C NMR together with the COSY spectra of the dinitro compound 2 are included in Supporting Information Figures S3 and S4, and those of the target diamine monomer 3 are illustrated in Figures 2 and 3. The ¹H NMR spectra confirm that the nitro groups bave been completely converted into amino groups by the high field shift of the aromatic protons, especially for protons H_g, ortho to the amino group, and the resonance signal at about 5.00 ppm corresponding to the aryl primary amino protons. The assignments of aromatic hydrogen and carbon atoms are assisted by two-dimensional (2D) NMR spectra and are in good agreement with the proposed molecular structures of compounds 2 and 3.

Synthesis of Model Compound

The model compound **M** was synthesized from the phosphorylation condensation reaction of diamine monomer **3** with two equivalent amount of benzoic acid by using triphenyl phosphite (TPP) and pyridine as condensing agents. The structure of the model compound **M** was confirmed by IR and NMR spectroscopy. Its IR spectrum is shown in Supporting Information Figure S5. The appearance of the characteristic absorption bands at around 3255 cm⁻¹ (amide N-H

stretch) and 1648 cm⁻¹ (amide carbonyl stretch) confirms the formation of the amide linkages. Supporting Information Figures S6 and S7 shows the ¹H and ¹³C NMR spectra of the model compound **M** in deuterated dimethyl sulfoxide (DMSO- d_6). The signal appearing at the farthest downfield at 10.21 ppm is ascribed to the amide protons, and that appearing at the farthest upfield at 3.74 ppm can be easily assigned to the methoxy protons. Assignments of all the protons and carbons are assisted by the 2-D COSY NMR spectra, and the spectra agree well with the proposed molecular structure of this compound.

Synthesis of Polyamides

According to the phosphorylation polyamidation technique described by Yamazaki et al.,23 some novel aromatic polyamides 5a to 5d were synthesized from the polycondensation reactions of diamine monomer 3 with aromatic dicarboxylic acids 4a to 4d by using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). The polymerization proceeded homogeneously throughout the reaction and afforded a clear, highly viscous polymer solution. All the polymers precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured under stirring into methanol. The obtained polyamides had inherent viscosities in the range of 0.44 to 0.51 dL/g (Table 1), and the average molecular weights of these polymers are recorded in the range of 35500 to 45700 relative to polystyrene standards. All the polyamides can be solution-cast into flexible and strong films (see Supporting Information Fig. S8). The structures of the polyamides were confirmed by IR and NMR spectroscopy. Typical IR spectra for polyamides 5b and 5c are shown in Supporting Information Figure S9. The characteristic absorption bands at around 3307 or 3314 cm^{-1} (amide N-H stretch) and 1658 or 1670 cm^{-1} (amide carbonyl stretch) confirm the formation of main chain amide linkages of 5b and 5c. The ¹H NMR and COSY spectra of polyamides **5b** and **5c** in DMSO- d_6 are depicted in Supporting Information Figures S10 and S11, respectively. The spectra agree well with the proposed molecular structures of these two polyamides.



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					S	olubility in	Various Solve	ents ^c	
Polymer Code	$\eta_{\rm inh}~({\rm dL/g})^{\rm a}$	$M_{\rm w}{}^{\rm b}$	PDI ^b	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
5a	0.44	35,500	2.68	++	++	++	++	+	+-
5b	0.45	43,200	2.80	++	++	++	++	+	+
5c	0.44	39,300	2.78	++	++	++	++	+	+
5d	0.51	45,700	2.81	++	++	++	++	++	++

 $^{\rm a}$ Inherent viscosity measured at a concentration of 0.5 dL/g for polyamides **5a** to **5d** in DMAc-5 wt % LiCl at 30 °C.

 $^{\rm b}$ Measured by GPC calibrated with polystyrene standards, using NMP as eluent at a constant flow rate of 0.5 mL/min at 40 $^\circ\text{C}.$

^c The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. ++, soluble at room temperature; +, soluble on heating; +-, partially soluble on heating.

NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; PDI: polydispersity index (M_w/M_n).

Polymer Properties

Solubility

The qualitative solubility properties of the polymers in several organic solvents at 10% (w/v) are also summarized at Table 1. All of the polyamides were well dissolved in polar aprotic solvents such as NMP, DMAc, DMF, and DMSO at room temperature, and could be solution-cast into transparent, flexible, and strong films. Polyamide **5d** derived from 2,2-*bis*(4-carboxyphenyl)hexafluoropropane **(4d)** showed a high solubility; it could be readily soluble not only in polar aprotic organic solvents but also in less polar solvents such as *m*-cresol and THF at room temperature. Therefore, the excellent solubility makes these polymers potential candidates for practical applications by simple spin- or dipcoating processes.

Thermal Properties

Thermal properties of the polymers were investigated by DSC and TGA. The relevant data are summarized in Table 2. DSC measurements were conducted with a heating rate of



FIGURE 4 DSC curves (the second scans after quenching from 400 °C) of the polyamides with a heating rate of 20 °C/min in nitrogen. [Color figure can be viewed at wileyonlinelibrary. com]

20 °C /min under a nitrogen flow. Quenching from an elevated temperature of about 400 °C to 50 °C gave predominantly amorphous samples so that the glass transition temperature (T_g) of these polyamides could be easily measured in the second heating traces of DSC (see Fig. 4); they were observed in the range of 248 to 302 °C. Polyamide **5b** displayed the lowest T_g because of the presence of flexible ether linkage in its backbone. The highest T_g value associated with polymer **5a** could be attributed to the presence of rigid biphenylene that stiffens the polymer backbone.

The thermal stability of the polymers was evaluated by TGA in both air and nitrogen atmospheres. TGA curves of polyamides **5a** to **5d** measured in nitrogen and in air are illustrated in Figure 5. These polymers exhibited reasonable thermal stability without significant weight loss up to 450 °C under nitrogen or air atmosphere. The decomposition temperatures (T_d) at 5% and 10% weight losses in nitrogen and air atmospheres taken from the original TGA thermograms are given in Table 2. The decomposition temperatures at 5% weightloss of polyamides **5a** to **5d** in nitrogen and air were

TABLE 2 Thermal Properties of Polyamides

Polymer ^a		T _d a Weigh (°(t 5% nt Loss C) ^c	T _d at Weigh (°€	: 10% nt Loss C) ^c	Char Yield	
Code	T_{g}^{b} (°C)	$\text{In }N_2$	In Air	$In \ N_2$	In Air	(wt %) ^d	
5a	302	477	456	516	505	69	
5b	248	465	442	514	492	67	
5c	287	463	425	492	460	63	
5d	282	474	427	517	463	67	

 $^{\rm a}$ The polymer film samples were heated at 300 $^\circ\text{C}$ for 1 h before all the thermal analysis.

^b The samples were heated from 50 to 400 °C at scan rete of 20 °C/min followed by rapid cooling to 50 °C at –200 °C/min in nitrogen. The midpoint temperature of baseline shift on the subsequent DSC trace (from 50 °C to 400 °C at a heating rate 20 °C/min) was defined as $T_{\rm q}$.

 $^{\rm c}$ Decomposition temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20 °C/min.

^d Residual weight percentage when heated to 800 °C in nitrogen.



FIGURE 5 TGA curves of the polyamides: (a) in nitrogen and (b) in air, with a heating rate of 20 °C/min. [Color figure can be viewed at wileyonlinelibrary.com]

recorded in the range of 463 to 477 °C and 425 to 456 °C, respectively. The decomposition temperatures at 10% weight-loss of polyamides **5a** to **5d** in nitrogen and air were recorded in the range of 492 to 516 °C and 460 to 505 °C, respectively. The amount of carbonized residues (char yield) at 800 °C in nitrogen for all polymers was in the range of 63 to 69 wt %. The high char yields of these polyamides can be attributed to their high aromatic content.

Electrochemistry

The cyclic voltammetry (CV) diagram of the diamine monomer **3** is shown in Figure 6. As shown in Figure 6, there are three electrochemically reversible redox waves with oxidation peaks at around 0.46, 0.58, and 1.01 V. The first oxidation process is associated with the primary amino groups, and the second and third oxidation processes are related to the 2,7-*bis*(diphenylamino)naphthalene unit. CV oxidation of diamide model compound **M** shows two electrochemically reversible waves (Fig. 7), with closely separate oxidation peaks at 0.75 and 0.90 V. The shift of the first oxidation peak of the 2,7-*bis*(diphenylamino)naphthalene unit to a higher potential can be attributed to an electronwithdrawing nature of the benzamido group. The electron-



FIGURE 6 Cyclic voltammogramof 5×10^{-4} M diamine **3** in 0.1 M Bu₄NClO₄/MeCN solution at a scan rate of 50 mV/s. [Color figure can be viewed at wileyonlinelibrary.com]

withdrawing nature of the benzamido group can be evidenced by comparing the proton NMR spectra of diamine monomer **3** and the model compound **M** shown in Figure 2 and Supporting Information Figure S5, respectively. As shown in Figure 2, protons Hg *ortho* to the amino group appear at a higher field region of 6.55 ppm due to the resonance effect caused by the amino group. After condensation reaction with benzoic acid, the resonance signal of protons Hg of model compound **M** downfield shifts to 7.69 ppm (Supporting Information Fig. S5).

The electrochemical behavior of the polymer was investigated by CV conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (MeCN) containing 0.1 M of Bu_4NClO_4 as the supporting electrolyte and saturated Ag/AgCl as the reference electrode under nitrogen atmosphere. The derived oxidation potentials are



FIGURE 7 Cyclic voltammogram of 5×10^{-4} M model compound **M** in 0.1 M Bu₄NClO₄/MeCN solution at a scan rate of 50 mV/s. [Color figure can be viewed at wileyonlinelibrary. com]



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FIGURE 8 Comparison of CV diagrams of polyamides (a) **5b** and (b) **5b'** on an ITO-glass slide in MeCN (0.1 M Bu₄NCIO₄) at a scan rate of 50 mV/s. [Color figure can be viewed at wileyonlinelibrary.com]

summarized in Table 3. As illustrated in Supporting Information Figure S12, all the polyamides show two electrochemically reversible oxidation waves, with the first oxidation peak potentials at about 0.86 to 0.89 V and the second oxidation peak potentials at about 1.02 to 1.08 V. The small potential differences (ΔE_p) between these two oxidation peaks could indicate a weak interaction between redox centers in the 2,7-bis(diphenylamino)naphthalene unit. For comparison, the CV diagrams for polyamides 5b (with 2,7bis(diphenylamino)naphthalene unit) and 5b' (with 1,4-bis(diphenylamino)benzene unit) are shown in Figure 8. The larger $\Delta E_{\rm p}$ for polymers **5b'** than for **5b** could be ascribed to a stronger electronic interaction between redox centers in the former. Supporting Information Figures S13 and S14 display the CV curves of the polyamides 5a to 5d at different scanning rates between 50 and 300 mV/s in 0.1 M Bu₄N-ClO₄/MeCN solution. In the scan rate dependence experiments for polyamide films, both anodic and cathodic peak current values increase linearly with an increasing scan rate, indicating that the electrochemical processes are reversible and not diffusion limited, and the electroactive polymer is well adhered to the working electrode (ITO glass) surface.

Spectroelectrochemistry

Spectroelectrochemical measurements were performed on polymer films drop-coated onto ITO-coated glass slides immerged in an electrolyte solution. The electrode preparations and solution conditions were identical to those used in the CV experiments. During the test, a three-electrode configuration was used for applying potential to the polymer films in a 0.1 M Bu₄NClO₄/acetonitrile electrolyte solution. When the films were electrochemically oxidized, an obvious color change of them was observed. The results of all the polyamides upon electro-oxidation are presented in Supporting Information Figures S15 to S18, respectively, as a series of UV-Vis absorption curves correlated to electrode potentials. The films of all polyamides exhibited strong absorption at wavelength around 300 to 310 nm in the neutral form, but they were almost transmissive in the visible region. Upon oxidation, two main bands located at around 400 and 800 nm are growing, while the main band of the neutral species around 300 nm gradually decreases in intensity. The long wavelength absorption band which appears upon oxidation is characteristic of the cation-radical form. In the same time, the films turned from colorless into pale green and

	UV-Vis tion	UV-Vis Absorp- tion (nm) ^a		Oxidation Potential (V) ^b				
Polymer Code	λ_{\max}	λ_{onset}	E _{onset}	$E_{1/2}^{Ox1}$	$E_{1/2}^{Ox2}$	$E_{g} (eV)^{c}$	HOMO (eV) ^d	LUMO (eV) ^d
5a	300	435	0.62	0.77	0.91	2.85	5.13	2.28
5b	305	421	0.63	0.75	0.92	2.94	5.11	2.17
5c	308	445	0.64	0.77	0.93	2.78	5.13	2.35
5d	311	427	0.65	0.78	0.93	2.90	5.14	2.24

TABL	.E 3	Optical	and	EI	ectroc	hemical	Ρ	roperties	of	the	Pol	yami	des
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^a UV-Vis absorption maximum and onset wavelengths for the polymer films.

 $^{\rm b}$ Read from the first CV scans, in acetonitrile at a scan rate of 50 mV/s (vs. Ag/AgCl).

 $^{\rm c}$ Optical bandgap calculated from absorption edge of the polymer film: $E_{\rm g}=1240/\lambda_{\rm onset}.$

^d The HOMO and LUMO energy levels were calculated from $E_{1/2}^{Ox1}$ values of CV diagrams and were referenced to ferrocene (4.8 eV relative to vacuum energy level; $E_{onset} = 0.37$ V; $E_{1/2} = 0.44$ V in acetonitrile). $E_{HOMO} = E_{1/2}^{Ox1} + 4.8 - 0.44$ (eV); $E_{LUMO} = E_{HOMO} - E_{g}$.



FIGURE 9 Spectral and color changes of the cast films of polyamides (a) **5b** and (b) **5b'** on ITO-coated glass in 0.1 M $Bu_4NCIO_4/MeCN$ at various applied voltages. [Color figure can be viewed at wileyonlinelibrary.com]

then deeper green color with increasing applied voltages. Because the oxidation occurred on the same 2,7-*bis*(dipheny-lamino)naphthalene unit, all the polyamide films displayed similar spectral and color changes upon oxidation.

The absorption and color changes of the cast films of polyamides **5b** and **5b'** are compared in Figure 9. As shown in Figure 9(b), the film of **5b'** exhibited absorption at wavelength around 350 nm in the neutral form. As the applied voltage was stepped from 0 to 0.61 V, the absorbance at 350 nm decreased, and new peak at 440 nm and a broadband having its maximum around 1034 nm in the near infrared (NIR) region. The absorption band in the NIR region is assigned to an intervalence charge-transfer (IV-CT) between states in which positive charge is centered at different amino centers.^{24,25} As the applied voltage was raised to 0.97 V, the absorption bands at 440 and 1034 nm decreased in intensity and strong absorption bands at 674 and 859 nm appeared. As shown in the inset of Figure 9(b), polyamide **5b'** changed



FIGURE 10 Potential step absorptiometry of the cast films of **5b** on the ITO-glass slide (coated area ~1 cm²) (in MeCN with 0.1 M Bu₄NClO₄as the supporting electrolyte) by applying a potential step: (a) optical switching at potential 0.00 V \Rightarrow 0.89 V (20 cycles) with a pulse width of 15 s, monitored at $\lambda_{max} = 807$ nm; (b) the first cycle transmittance change for the **5b** thin film. [Color figure can be viewed at wileyonlinelibrary.com]



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TABLE 4 Electrochrom	ιic Pro	perties of	f the	Poly	amide	Films
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			Respon	Response Time ^b			
Polymer Code	λ_{\max}^{a} (nm)	$\Delta\%T$	$t_{\rm c}~({\rm s})$	$t_{\rm b}$ (s)	ΔOD^c	$Q_{\rm d}^{\rm d}$ (mC/cm ²)	CE ^e (cm ² /C)
5a	807	70	7.4	1.4	0.57	3.69	153
5b	807	82	8.0	1.8	0.89	6.38	140
5c	788	54	7.7	1.3	0.36	3.81	95
5d	791	76	6.2	1.4	0.68	6.12	111

^a Wavelength at absorption maximum.

^b Time for 90% of the full-transmittance change.

^c Optical density (Δ OD) = log[$T_{bleached}/T_{colored}$], where $T_{colored}$ and $T_{bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

color to green in the semi-oxidized state and to deep blue in the fully oxidized state. In contrast, no significant NIR absorption due to IV-CT effect was observed during the electro-oxidation processes of polyamide **5b** [Fig. 9(a)]. Therefore, the electron communication between the amino centers in the 2,7-bis(diphenylamino)naphthalene segment is weakened by the 2,7-naphthalene bridge.

Electrochromic Switching and Stability

Electrochromic switching studies for the polymers were performed to monitor the % transmittance (% T) as a function of time at their absorption maximum (λ_{max}) and to determine the response time by stepping potential repeatedly between the neutral and oxidized states. The active area of the polymer film on ITO-glass is approximately 1 cm². As a typical example, Figure 10 depicts the %*T* and current density changes of polyamide 5b as a function of time at its longwavelength absorption maximum (at 807 nm) by applying square wave potential steps (between 0 and 0.89 V) with a residence time of 15 s. The response time was calculated at 90% of the full-transmittance change because it is difficult to perceive any further color change with naked eye beyond this point. The optical contrast measured as $\Delta \% T$ between neutral and oxidized state was found to be 82% for polyamide 5b. The results for the other polyamides are included in the Supporting Information (Supporting Information Figs. S19–S21). The optical contrast measured as Δ %T of these polymers between neutral and oxidized state was found to be 70% for 5a, 54% for 5c, and 76% for 5d, respectively. As can be seen from the switching test, all the polyamides exhibited good electrochromic stability in the first twenty switching cycles. The electrochromic properties of all polymer films during electro-oxidation processes are summarized in Table 4.

CONCLUSIONS

A new *bis*(diphenylamino)naphthalene-based diamine monomer, *N,N'-bis*(4-aminophenyl)-*N,N'-bis*(4-methoxyphenyl)-2,7naphthalenediamine (**3**) has been synthesized and characterized. New aromatic polyamides containing 2,7-*bis*(diphenylamino)naphthalene moieties was readily prepared from ^d Q_d is ejected charge, determined from the *in situ* experiments. ^e Coloration efficiency (CE) = $\Delta OD/Q_d$.

diamine monomer **3** with various dicarboxylic acids via the phosphorylation polyamidation reaction. Because of the presence of 2,7-*bis*(diphenylamino)naphthalene unit in the main chain, all polymers exhibited high solubility in many polar aprotic solvents, good film-forming ability, and high thermal stability. The polyamides also showed stable electrochemical stability and anodically green coloring when oxidized. The two arylamino centers showed a weak electronic interaction via the 2,7-naphthalene bridge, and thus they started to oxidize almost at the same time. No IVCT phenomenon was observed during the oxidation processes of these polyamides.

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