# Highly Redox-Stable and Electrochromic Aramids with Morpholinyl-Substituted Triphenylamine Units

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ABSTRACT: A novel morpholinyl-substituted, triphenylaminebased diamine monomer, namely 4,4'-diamino-4"-(4-morpholinyl)triphenylamine, was synthesized and polymerized with various aromatic dicarboxylic acids via the phosphorylation polyamidation reaction leading to a series of electroactive aromatic polyamides (aramids). All aramids were readily soluble in polar organic solvents and could be solution cast into tough and flexible films with high thermal stability. Cyclic voltammograms of the aramid films on the indium-tin oxide-coated glass substrate exhibited a pair of reversible oxidation waves with very low onset potentials of 0.36 – 0.41 V (vs. Ag/AgCl) in ace-

**INTRODUCTION** Wholly aromatic polyamides are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.<sup>1</sup> Fibers obtained from anisotropic solutions of these high-performance materials have been used in applications where high thermal stability and mechanical strength are required. However, rigidity of the backbone and strong hydrogen bonding results in high melting or glass-transition temperatures  $(T_g s)$  and limited solubility in most organic solvents. These properties make them generally intractable or difficult to process, thus restricting their applications. To overcome such a difficulty, polymer structure modification becomes necessary. One approach to solving this problem has been the incorporation of bulky groups in the main chain or as the pendent groups.<sup>2-7</sup> It has also been reported that aromatic polyamides bearing the propeller-shaped triphenylamine (TPA) unit in the main chain were amorphous and easily soluble in organic solvents and they could be solution-cast into flexible films with good mechanical property and high thermal stability.8-10 Moreover, polyamides can be endowed with new functions by changing the chemical structure and composition. There is continuously a huge effort directed toward tonitrile solution. The polymer films showed reversible electrochemical oxidation accompanied by strong color changes with high coloration efficiency, high contrast ratio, and rapid switching time. The optical transmittance change ( $\Delta\%T$ ) at 650 nm between the neutral state and the fully oxidized state is up to 90%. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 1289–1298

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expanding the application of the aromatic polyamides as optically active materials, luminescent, and electroactive films, gas or ion-exchange membranes, etc. by incorporating new chemical functionalities in the polyamide backbone or lateral structure.<sup>11-13</sup>

TPA derivatives and polymers are well-known for their electroactive and photoactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.<sup>14,15</sup> TPAs can be easily oxidized to form stable radical cations as long as the para-position of the phenyl rings is protected, and the oxidation process is always associated with a strong change of coloration. In the past decade, a lot of high-performance polymers (typically, aromatic polyamides and polyimides) carrying the redox-active TPA unit have been prepared and evaluated for electrochromic applications.<sup>16-24</sup> As reported in the pioneering works by Nelson and Adams et al.,<sup>25,26</sup> unsubstituted TPA undergoes dimerization to tetraphenylbenzidine (TPB) after the formation of an unstable monocation radical. This is accompanied by the loss of two protons per dimer and the dimer is more easily oxidized than TPA and also can undergo further oxidations in two discrete one-electron steps to give

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TPB<sup>+•</sup> and finally the quinoidal TPB<sup>+2</sup>. Quantitative data have been obtained for several 4-substituted TPAs in the form of second-order coupling rate constants, and it was generally found that electron-donating substituents such as methoxy group tended to stabilize the cation radicals while electron-withdrawing groups such as nitro group had the opposite effect.<sup>27</sup> Thus, several highly redox-stable, electrochromic polyamides and polyimides with methoxysubstituted TPA units have been reported in literature.<sup>28–35</sup>

On the other hand, dialkylamino substituents are even better electron pair donors than the corresponding alkoxy substituents and stabilize a radical cation to which they are attached. In a previous publication,<sup>36</sup> we have demonstrated that polyamides with extremely electron-donating dimethylamino-TPA moieties exhibit greatly lowered oxidation potentials and enhanced electrochemical and electrochromic stability. As a continuation of our efforts in developing electrochromic materials with long-term stability, rapid redox switching, and high optical contrast between their bleached and colored states, herein we synthesize a new diamine monomer, 4,4'diamino-4"-(4-morpholinyl)triphenylamine, and its derived aramids containing the electroactive TPA unit with electrondonating 4-morpholinyl group para substituted on the pendent phenyl ring. The effect of incorporating the heterocyclic morpholinyl substituent on the electrochemical and electrochromic properties of the aramids will be investigated.

## EXPERIMENTAL

## Materials

Morpholine (TCI), 4-fluoronitrobenzene (Acros), 10% palladium on charcoal (Pd/C) (Fluka), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) (Showa), cesium fluoride (CsF) (Acros), triphenyl phosphite (TPP) (Acros), dimethyl sulfoxide (DMSO), and hydrazine monohydrate (TCI) were used as received from commercial sources. N,N-Dimethylacetamide (DMAc) (Tedia), N.N-dimethylformamide (DMF) (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 a sealed bottle. The commercially available aromatic dicarboxylic acids such as terephthalic acid (5a) (Wako), isophthalic acid (5b) (Wako), 4,4'-biphenydicarboxylic acid (5c) (TCI), 4,4'-dicarboxydiphenyl ether (5d) (TCI), bis(4-carboxyphenyl) sulfone (5e) (New Japan Chemicals Co.), 2,2-bis(4-carboxyphenyl)hexafluoropropane (5f) (TCI), 1,4-naphthalenedicarboxylic acid (5g) (Wako), and 2,6-naphthalenedicarboxylic acid (5h) (TCI) were used as received. Commercially obtained calcium chloride (CaCl<sub>2</sub>) (Wako) was dried under vacuum at 180 °C for 8 h prior to use. Tetra-n-butylammonium perchlorate (TBAP) was obtained from Acros and recrystallized twice from ethyl acetate and then dried vacuo before use.

## **Monomer Synthesis**

## 4-(4-Nitrophenyl)morpholine (1)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 13.1 g (0.15 mol) of morpholine, 21.2 g (0.15 mol) of

4-fluoronitrobenzene, and 20.7 g (0.15 mol) of  $K_2CO_3$  in 100 mL of DMSO was heated with stirring at 120 °C for 20 h. After cooling, the mixture was poured into 400 mL mixed solution of ethanol/water (1:1), and the formed yellow crystals were collected by filtration with an yield of 30.4 g (97%) and a melting point of 149 – 151 °C. IR (KBr): 1583, 1319 cm<sup>-1</sup> (-NO<sub>2</sub> str.). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 8.07 (d, J = 9.5 Hz, 2H, H<sub>d</sub>), 7.03 (d, J = 9.5 Hz, 2H, H<sub>c</sub>), 3.74 (t, J = 4.9 Hz, 4H, H<sub>a</sub>), 3.41 (t, J = 4.9 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 154.94 (C<sup>3</sup>), 137.29 (C<sup>6</sup>), 125.56 (C<sup>5</sup>), 112.53 (C<sup>4</sup>), 65.66 (C<sup>1</sup>), 46.39 (C<sup>2</sup>).



#### 4-(4-Morpholinyl)aniline (2)

In a 500 mL round-bottom flask, 14.6 g (0.07 mol) of 4-(4nitrophenyl)morpholine (**1**), 0.15 g of 10 wt % Pd/C, 10 mL hydrazine monohydrate and 140 mL of ethanol was stirred at a reflux temperature for 10 h. The solution was filtered hot to remove Pd/C and then allowed to cool to room temperature, and the filtrate was concentrated by rotary evaporation. The precipitate was collected and dried in vacuum to give 8.9 g (yield 71%) of amine **2** as purplish red crystals with a melting point of 132 - 134 °C. IR (KBr): 3330,  $3225 \text{ cm}^{-1}$  (—NH<sub>2</sub> str.). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 6.68 (d, J = 8.8 Hz, 2H, H<sub>d</sub>), 6.51 (d, J = 8.8 Hz, 2H, H<sub>c</sub>), 4.55 (s, 2H, —NH<sub>2</sub>), 3.69 (t, J = 4.7 Hz, 4H, H<sub>a</sub>), 2.87 (t, J = 4.7 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 142.30 (C<sup>3</sup>), 142.17 (C<sup>6</sup>), 117.49 (C<sup>5</sup>), 114.70 (C<sup>4</sup>), 66.24 (C<sup>1</sup>), 50.55 (C<sup>2</sup>).



#### 4,4'-Dinitro-4"-(4-morpholinyl)triphenylamine (3)

In a 250 mL round-bottom flask equipped with a stirring bar, a mixture of 12.5 g (0.07 mol) of 4-morpholinoaniline (2), 19.8 g (0.14 mol) of 4-fluoronitrobenzene, and 21.3 g (0.14 mol) of CsF in 60 mL of DMSO was heated with stirring at 120 °C for 20 h. After cooling, the mixture was poured into 400 mL mixed solution of ethanol/water (1:1), and the dark red precipitate was collected by filtration. Recrystallization from DMF/H<sub>2</sub>O yielded 24.7 g of the desired dinitro compound (3) as red crystals in 84% yield with a melting point of 186-188 °C. IR (KBr): 1579, 1338 cm<sup>-1</sup> ( $-NO_2$  str.). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 8.16 (d, J = 9.2 Hz, 4H, H<sub>f</sub>), 7.18 (d, J = 9.2 Hz, 4H,  $H_{e}$ ), 7.13 (d, J = 9.0 Hz, 2H,  $H_{d}$ ), 7.05 (d, J = 9.0 Hz, 2H,  $H_{c}$ ), 3.75 (t, J = 4.7 Hz, 4H, H<sub>a</sub>), 3.17 (t, J = 4.7 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 151.69 (C<sup>7</sup>), 149.84 (C<sup>3</sup>), 141.53 (C<sup>10</sup>), 135.03 (C<sup>6</sup>), 128.46 (C<sup>5</sup>), 125.41 (C<sup>9</sup>), 121.60 (C<sup>8</sup>), 116.24 (C<sup>4</sup>), 65.99 (C<sup>1</sup>), 47.79 (C<sup>2</sup>).



**SCHEME 1** Synthetic route to the target diamine monomer 4: (a) *p*-fluoronitrobenzene, K<sub>2</sub>CO<sub>3</sub>, DMSO, 120 °C, 20 h; (b) hydrazine, Pd/C, EtOH, reflux, 10 h; (c) *p*-fluoronitrobenzene, CsF, DMSO, 120 °C, 20 h; (d) hydrazine, Pd/C, EtOH, reflux, 20 h.



## 4,4'-Diamino-4"-(4-morpholinyl)triphenylamine (4)

In a 500 mL round-bottom flask, 12.6 g (0.03 mol) of dinitro compound 3, 0.15 g of 10 wt % Pd/C, 9 mL hydrazine monohydrate and 200 mL of ethanol was stirred at a reflux temperature for 20 h. The solution was filtered hot to remove Pd/C and then allowed to cool to room temperature, and the filtrate was concentrated by rotary evaporation. The precipitate was collected and dried in vacuum to give 10.0 g (yield 93%) of diamine 4 as white needles with a melting point of 213-215 °C. IR (KBr): 3356, 3209 cm<sup>-1</sup> (-NH<sub>2</sub> str.). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 6.75 (d, J = 9.1 Hz, 2H, H<sub>c</sub>), 6.68 (two overlapped doublets, 6H,  $H_d + H_e$ ), 6.49 (d, J = 8.7 Hz, 4H,  $H_f$ ), 4.79 (s, 4H, -NH<sub>2</sub>), 3.69 (t, J = 4.5 Hz, 4H, H<sub>a</sub>), 2.95 (t, J = 4.5 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, *δ*, ppm): 144.50 (C<sup>10</sup>), 144.07 (C<sup>7</sup>), 142.24 (C<sup>3</sup>), 137.44 (C<sup>6</sup>), 125.46 (C<sup>8</sup>), 120.69 (C<sup>5</sup>), 116.35 (C<sup>4</sup>), 114.73 (C<sup>9</sup>), 66.12 (C<sup>1</sup>), 49.46 (C<sup>2</sup>). ANAL. Calcd for  $C_{22}H_{24}N_4O$  (360.45) : C, 73.31%; H, 6.71%; N, 15.54%. Found : C, 73.17%; H, 6.65%; N, 15.31%.



#### Synthesis of Polyamides

The synthesis of polyamide **6a** is used as an example to illustrate the general synthetic route used to produce the polyamides. A 50 mL round-bottom flask equipped with a magnetic stirrer was charged with 0.5046 g (1.40 mmol) of diamine

monomer 4, 0.2326 g (1.40 mmol) of terephthalic acid (5a), 1.4 mL of TPP, 1.4 mL of NMP, 0.4 mL of pyridine, and 0.2 g of calcium chloride (CaCl<sub>2</sub>). The reaction mixture was heated with stirring at 120 °C for 3 h. The resulting viscous polymer solution was poured slowly into 200 mL of stirring methanol giving rise to a stringy, fiber-like precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. The polyamide exhibited inherent viscosity of 0.86 dL/g, measured on 0.5 g/dL in DMAc. IR (film): 3298 (amide N—H str.), 1653 cm<sup>-1</sup> (amide C=O str.). The other polyamides were prepared by an analogous procedure.

## Measurements

Infrared (IR) spectra were recorded on a Horiba FT-720 FT-IR spectrometer. Elemental analyses were run in a Heraeus Vario EL III CHNS elemental analyzer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker AVANCE 500 FT-NMR system with tetramethylsilane as an internal standard. The inherent viscosities were determined with a Cannon-Fenske viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator (operating at 40 kV and 30 mA), using nickel-filtered Cu-Kα radiation ( $\lambda = 1.5418$  Å). The scanning rate was 2°/min over a range of  $2\theta = 10 - 40^{\circ}$ . Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA. Experiments were carried out on  $\sim 4-6$  mg of samples heated in flowing nitrogen or air (flow rate =  $40 \text{ cm}^3/\text{min}$ ) at a heating rate of 20 °C/min. DSC analyses were performed on a Perkin-Elmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen. Thermomechanical analysis (TMA) was determined with a Perkin-Elmer TMA 7 instrument. The TMA experiments were carried out from 50 to 350 °C at a scan rate of 10 °C/min with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures  $(T_s)$  were taken as the onset temperatures of probe displacement on the TMA traces. Electrochemistry was performed with a CH Instruments 600c electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which indium-tin oxide (ITO) was used as a working electrode. A platinum wire was used as an auxiliary 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



SCHEME 2 Synthesis of polyamides 6a-6h.

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 Ag/AgCl reference electrode. Absorption spectra in the spectroelectrochemical experiments were measured with an Agilent 8453 UV-Visible diode array spectrophotometer.

## **RESULTS AND DISCUSSION**

## **Monomer Synthesis**

The new TPA-based diamine monomer, 4,4'-diamino-4"-(4morpholinyl)triphenylamine (4), was prepared by a four-step reaction sequence outlined in Scheme 1. In the first step, 4-(4-nitrophenyl)morpholine (1) was obtained by the nucleophilic aromatic displacement of 4-fluoronitrobenzene with morpholine using potassium carbonate as the base. Then, the nitro compound 1 was reduced to 4-(4-morpholinyl)aniline (2) by hydrazine monohydrate and Pd/C catalyst in refluxing ethanol. In the third step, 4,4'-dinitro-4"-(4-morpholino)triphenylamine (3) was synthesized by the cesium fluoride (CsF)-promoted N,N-diarylation reaction of the amino compound 2 with two equivalent 4fluoronitrobenzene. Finally, the nitro groups of compound 3 were reduced by the same technique used in the second step to give the targeted diamine monomer 4. FT-IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques were used to confirm the structures of all the synthesized compounds 1-4. The FT-IR spectra of compounds 1-4 are included in the Supporting Information Figure S1. The nitro groups of compounds 1 and 3 gave two characteristic bands at around 1580 and 1330 cm<sup>-1</sup> (-NO<sub>2</sub> asymmetric and symmetric stretching). After reduction, the characteristic absorptions of the nitro group disappeared and the primary amino group showed the typical N—H stretching absorptions in the region of  $3200 - 3500 \text{ cm}^{-1}$ . The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds **1** to **4** are collected in Supporting Information Figures S2 and S3, respectively. Assignments of each hydrogen and carbon in the diamine monomer **4** are assisted by the twodimensional (2-D) NMR spectra (see Supporting Information Figs. S4 and S5), and these spectra agree well with the proposed molecular structure of the targeted diamine monomer.

TABLE 1	Inherent	Viscosity	and	Solubility	Behavior	of
Polyamic	les					

		Solubility in Various Solvents <sup>b</sup>					
Polymer Code	η <sub>inh</sub> a (dL/g)	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
6a	0.86	+	+	+	+	+	_
6b	0.45	+	+	+	+	+	-
6c	0.92	+	+	+	+	+	-
6d	0.68	+	+	+	+	+	-
6e	0.40	+	+	+	+	+	+-
6f	0.68	+	+	+	+	+	+-
6g	0.80	+	+	+	+	+	-
6h	0.78	+	+	+	+	+	-

 $^{\rm a}$  Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc at 30 °C.

<sup>b</sup> The solubility was determined with a 10 mg sample in 1 mL of a solvent. Solubility: +: soluble at room temperature; +-: partially soluble; -: insoluble even on heating. Solvent: NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran. TABLE 2 Thermal Properties of Polyamides<sup>a</sup>

			7 <sub>d</sub> at 10 wt % loss <sup>d</sup> (°C)		
Polymer Code	<i>T</i> g <sup>b</sup> (°C)	T₅ <sup>c</sup> (°C)	In $N_2$	In Air	Char Yield <sup>e</sup> (%)
6a	288 (295)	285	545	545	74
6b	284 (290)	280	500	511	75
6c	295 (302)	_f	550	577	68
6d	287 (283)	284	543	570	75
6e	293 (296)	292	506	531	70
6f	278 (288)	270	584	578	68
6g	293 (295)	291	520	539	72
6h	295 (307)	-	560	563	77

 $^{\rm a}$  The polymer film samples were heated at 300  $^\circ {\rm C}$  for 30 min prior to all the thermal analyses.

<sup>b</sup> The sample were heated from 50 to 400 °C at a scan rate 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 to 400 °C at heating rate 20 °C/min) was defined as  $T_g$ . Values indicated in parentheses are data of analogous **6**' series polyamides with the corresponding diacid residue as in the **6** series polymers.

 $^{\rm c}$  Softening temperature measured by TMA using a penetration method.  $^{\rm d}$  Decomposition temperature at which a 10% weight loss was recorded

by TGA at a heating rate of 20 °C/min.

<sup>e</sup> Residual weight percentages at 800 °C under nitrogen flow.

<sup>f</sup> No discernible  $T_s$  was observed.

#### **Polymer Synthesis**

According to the phosphorylation technique described by Yamazaki et al.<sup>37</sup> a series of novel TPA-based aromatic polyamides, 6a-6h, with morpholinyl para-substituted on the pendent phenyl ring were prepared from the diamine 4 and various aromatic dicarboxylic acids (5a-5h) by the direct polycondensation reaction with TPP and pyridine as condensing agents (Scheme 2). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear, highly viscous polymer solutions. The polymers precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured with stirring into methanol. These polyamides were obtained in almost quantitative yields, with inherent viscosity values in the range of 0.40 - 0.92 dL/g, as summarized in Table 1. All the polymers can be solution-cast into flexible and tough films, and this is indicative of the formation of high molecular weight polymers. Structural features of these polyamides were verified by FTIR spectra based on characteristic absorption bands observed around 3298 (amide N-H stretching), 1653 (carbonyl C–O stretching), and 1279 cm<sup>-1</sup> (amine C–N stretching). Figure S6 (Supporting Information) illustrates a typical FTIR spectrum of the representative polyamide **6a**.



## Properties of Polyamides Organo-Solubility and X-Ray Diffraction Data

The solubility properties of polyamides 6a-6h in several organic solvents at 10% (w/v) are summarized in Table 1. All the polyamides exhibited excellent solubility in a variety of solvents such as NMP, DMAc, DMF, DMSO, and *m*-cresol. The high solubility of these aramids can be attributed in part to the incorporation of bulky, three-dimensional (4-morpholinyl)TPA groups, which retard dense chain packing and lead to a decreased chain-chain interaction. Therefore, the good solubility makes these polymers potential candidates for practical applications in solution processing. All of the polyamides 6a-6h could afford flexible and tough films, and they were amorphous in nature as evidenced by wide-angle X-ray diffraction (WAXD) patterns (see Supporting Information Fig. S7)

## **Thermal Properties**

The thermal properties of polyamides were examined by DSC, TMA, and TGA techniques. The relevant thermal behavior data are summarized in Table 2. The glass-transition temperatures  $(T_{\sigma})$  of polyamides **6a-6h** were in the range of 278 - 295 °C by DSC. The lower  $T_{\rm g}$  values of **6b** and **6f** can be explained in terms of the flexibility and low rotation barrier of its diacid moiety. As compared to the corresponding parent  $\mathbf{6}'$  series polyamides, the  $\mathbf{6}$  series polyamides revealed a slightly lower  $T_{g}$  possibly due to the internal plasticization effect of the 4-morpholinyl substituents. The softening temperatures  $(T_s)$  of the polymer films were determined with TMA by the penetration method. The  $T_s$ value was read from the onset temperature of the probe displacement on the TMA curve. A typical TMA thermogram for polyamide 6b is illustrated in Supporting Information Figure S8. The  $T_{\rm s}$  values of the polyamides are in the range from 278 - 292 °C. In most cases, the  $T_{\rm s}$  values of the polyamides obtained by TMA are comparable to the  $T_{\rm g}$  values measured by the DSC experiments. The thermal stability of polyamides was evaluated by TGA in both air and nitrogen atmospheres. Typical TGA thermograms for polyamide 6f are illustrated in



**FIGURE 1** TGA curve of polyamide **6f** with a heating rate 20 °C/ min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a dication quinonediimine)

SCHEME 3 Proposed oxidation pathways of the (4-morpholinyI)TPA segment in the 6 series polyamides.

Figure 1. The decomposition temperatures  $(T_d)$  at 10% weight losses in nitrogen and air atmosphere read from the original TGA thermograms are also summarized in Table 2. All of the polymers exhibited good thermal stability; the  $T_d$  values at a 10% weight loss were recorded in the range of 500 - 584 °C in nitrogen and 511 - 578 °C in air, respectively. The amount of carbonized residues (char yield) at 800 °C in nitrogen for all polyamides was in the range from 68 to 77 wt %. The high char yields of these polyamides can be attributed to their high aromatic content.

#### **Electrochemical Properties**

The electrochemical properties of the polyamides were investigated by CV conducted for the cast films on an ITO-coated glass slide as working electrode in anhydrous acetonitrile (MeCN), using 0.1 M of TBAP as a supporting electro-lyte. For comparison, referenced polyamides 6a'-6h' were prepared from dicarboxylic acids 5a-5h and 4,4'-diaminotriphenylamine in a similar synthetic procedure used for the **6** series polyamides. The typical cyclic voltammograms for polyamides **6d** and **6d'** are compared in Figure 2. There are two reversible oxidation redox couples at half-wave potentials ( $E_{1/2}$ ) of 0.52 and 0.88 V, respectively, for polyamide **6d** and only one reversible oxidation redox couple at  $E_{1/2} = 0.86$  V for polyamide **6d**' in the oxidative scan. Polyamide **6d** revealed a lower onset oxidation potential  $(E_{\text{onset}} = 0.40 \text{ V})$  in comparison with its parent analog **6d**' ( $E_{\text{onset}} = 0.72$  V). This indicates that the first oxidation wave in the CV diagram of polyamide 6d is associated with its morpholinyl groups. It was also found that the film changed color from colorless to green and then to deep blue because of electrochemical oxidation of polymer 6d. The oxidative and electrochromic reversibility of 6d is maintained on repeated scanning between 0.0 and 1.2 V (vs. Ag/AgCl). This result confirms that para-substitution of the morpholinyl group on the TPA unit lends considerable stability to both the cation radical and dication guinonediimine species, as shown in Scheme 3. The other polyamides showed similar CV diagrams to that of 6d. As shown in Figure 3, after 500 consecutive cyclic scans between 0 and 0.67 V polyamide 6d still retained a high electrochemical stability. The redox potentials of the various polyamides as well as their respective HOMO and LUMO potentials (vs. vacuum) are included in Table 3. The  $E_{1/2}$  and  $E_{onset}$  values of the external ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox standard in MeCN were recorded at 0.44 and 0.37 V (vs. Ag/AgCl), respectively. Under the assumption that the HOMO energy level for the ferrocene standard was 4.80 eV with respect to the zero JOURNAL OF POLYMER SCIENCE Chemistry

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**FIGURE 2** Cyclic voltammograms of (a) ferrocene and the films of polyamides (b) **6d** and (c) **6d**' on an ITO-coated glass substrate in MeCN containing 0.1 M TBAP with a scanning rate of 100 mV/s. Polyamide **6d** was determined in two different potential ranges: 0 - 0.8 and 0 - 1.2 V. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

## **TABLE 3** Electrochemical Properties of the Polyamides

		$E_{1/2}$ (V) <sup>b</sup> (vs. Ag/AgCl)			HOMO (eV) <sup>d</sup>		LUMO (eV) <sup>e</sup>	
Code	E <sub>onset</sub> (V) <sup>a</sup>	First	Second	$E_{\rm g}~({\rm eV})^{\rm c}$	Eonset	E <sub>1/2</sub>	E <sub>onset</sub>	E <sub>1/2</sub>
6a	0.37	0.50 (0.87) <sup>f</sup>	0.88	2.66	4.80	4.86	2.14	2.20
6b	0.39	0.55 (0.85)	0.90	2.82	4.82	4.91	2.00	2.09
6c	0.38	0.54 (0.86)	0.91	2.71	4.81	4.90	2.10	2.19
6d	0.40	0.52 (0.86)	0.88	2.97	4.83	4.88	1.86	1.91
6e	0.40	0.55 (0.88)	0.93	2.58	4.83	4.91	2.25	2.33
6f	0.41	0.56 (0.88)	0.92	2.82	4.84	4.92	2.02	2.10
6g	0.41	0.56 (0.85)	0.91	2.83	4.84	4.92	2.01	2.09
6h	0.36	0.53 (0.85)	0.91	2.65	4.79	4.89	2.14	2.24

<sup>a</sup> Onset oxidation potentials from cyclic voltammograms.

<sup>b</sup> Oxidation half-wave potentials from cyclic voltammograms.

<sup>c</sup> Energy band gap calculated from absorption edge of the polymer film <sup>e</sup>

according to the following equation:  $E_g = 1240/\lambda_{abs,onset}$ .

 $^{\rm d}$  The HOMO energy levels were calculated from  $E_{\rm onset}$  or  $E_{\rm 1/2}$  values and were referenced to ferrocene (4.8 eV).

<sup>e</sup> LUMO = HOMO -  $E_{g}$ .

<sup>f</sup> Values in parentheses are data of the parent polyamides **6**' having the corresponding diacid residue as in the **6** series.





**FIGURE 3** Cyclic voltammograms of the cast films of (a) polyamide **6d** film on an ITO-coated glass substrate over 500 cyclic scans and (b) ferrocene in MeCN containing 0.1 M TBAP at a scan rate of 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vacuum level, the HOMO energy levels for polyamides **6a**–**6h** were estimated to be 4.86–4.92 eV and 4.79–4.84 eV calculated from  $E_{1/2}$  and  $E_{\text{onseb}}$  respectively. The lower ionization potential could suggest an easier hole injection into films from ITO electrodes in electronic device applications.

## Spectroelectrochemical and Electrochromic Properties

Following the electrochemical tests, the optical properties of the electrochromic films were evaluated by using spectroe-



**FIGURE 4** Spectral change of **6d** thin film on the ITO-coated glass substrate (in MeCN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage: 0 (**I**), 0.50 (•), 0.60 (**A**), 0.65 (**V**), 0.80 (•), 0.95 (**C**), 1.00 ( $\bigcirc$ ), 1.05 ( $\triangle$ ), 1.10 ( $\bigtriangledown$ ), and 1.20 V ( $\diamondsuit$ ) vs. Ag/AgCl couple as reference. The inset shows the photographic images of the film at indicated applied voltages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 5** Optical switching for polyamide **6d** at  $\lambda_{max} = 906$  nm as the applied voltage was stepped between 0 and 0.55 V (vs. Ag/AgCl).

lectrochemistry. For these investigations, the polyamide film was cast on an ITO-coated glass slide (a piece that fit in the commercial UV-visible cuvette), and a homemade electrochemical cell was built from a commercial UV-visible cuvette. The cell was placed in the optical path of the sample light beam in a commercial diode array spectrophotometer. This procedure allowed us to obtain electronic absorption spectra under potential control in a 0.1 M TBAP/MeCN solution. The result of the polyamide 6d film is presented in Figure 4 as a series of UV-vis absorbance curves correlated to electrode potentials. In the neutral form, at 0 V, the film exhibited strong absorption at wavelength around 342 nm, characteristic for  $\pi - \pi^*$  transitions of TPA and other aromatic components, but it was almost transparent in the visible region. Upon oxidation of the polyamide **6d** film (increasing applied voltage from 0 to 0.80 V), the intensity of the absorption



**FIGURE 6** (a) Potential step absorptometry and (b) current consumption of the polyamide **6d** film on to the ITO-coated glass substrate (coated area:  $1 \text{ cm}^2$ ) during the continuous cycling test by switching potentials between 0 and 0.55 V (vs. Ag/AgCl) with a pulse width of 6 s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

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TABLE 4 Coloration Efficiency of Polyamide 6d

Cycles <sup>a</sup>	$\delta \text{OD}_{906}{}^{\text{b}}$	<i>Q</i> (mC/cm <sup>2</sup> ) <sup>c</sup>	$\eta \ (\text{cm}^2/\text{C})^{\text{d}}$	Decay (%) <sup>e</sup>
1	0.182	0.614	296	0
100	0.195	0.679	287	3.0
200	0.192	0.671	286	3.4
300	0.194	0.686	284	4.1
400	0.186	0.654	284	4.1
500	0.179	0.633	283	4.4
600	0.177	0.627	282	4.7
700	0.171	0.611	280	5.4
800	0.168	0.599	280	5.4
900	0.167	0.601	278	6.1
1000	0.161	0.582	277	6.4

 $^a$  Times of cyclic scan by applying potential steps: 0.00  $\leftrightarrow$  0.55 V (vs. Ag/AgCl) with a pulse width of 6 s.

<sup>b</sup> Optical density change at 906 nm.

<sup>c</sup> Ejected charge, determined from the *in situ* experiments.

<sup>d</sup> Coloration efficiency is derived from the equation:  $\eta = \delta OD_{906}/Q$ .

<sup>e</sup> Decay of coloration efficiency after cyclic scans.

peak at 342 nm gradually decreased while a new peak at 402 nm and a broad band having its maximum absorption wavelength at 906 nm gradually increased in intensity. We attribute this spectral change to the formation of a stable monocation radical of the morpholinyl-TPA moiety. The absorption band in the near infrared (NIR) region can be attributed to an intervalence charge-transfer (IV-CT) between states in which the positive charge is centered at different amino centers (morpholine and TPA units).38,39 As the applied potential became more anodic to 1.20 V, the absorption bands of the cation radical decreased gradually in intensity, with the formation of a new strong absorption band centered at around 650 nm. This spectral change can be attributable to the formation of a dication in the morpholino-TPA segment of the polyamide (see Scheme 3). The observed UV-vis absorption changes in the film of **6d** at various potentials are fully reversible and are associated with strong color changes; indeed, they even can be seen readily by the naked eye. From the inset shown in Figure 4, it can be seen that the film of 6d switches from a transmissive neutral state (colorless) to a highly absorbing semioxidized state (green) and a fully oxidized state (deep blue). The film colorations are distributed homogeneously across the polymer film and survive for more than hundreds of redox cycles. The polyamide 6d shows a good optical contrast in the visible region, with an extremely high optical transmittance change ( $\Delta$ %*T*) of 90% at  $\lambda_{max} = 650$  nm.

For optical switching studies, the polymer film was cast on ITO-coated glass slides in the same manner as described above, and the film was potential stepped between its neutral (0 V) and oxidized (+0.55 V) state. While the films were switched, the absorbance at 906 nm was monitored as a function of time with UV-vis-NIR spectroscopy. Switching data for the cast film of polyamide **6d** are given 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. The polyamide switched rapidly (within three seconds) between the highly transmissive neutral state and the colored oxidized states. Thin film of polyamide 6d required only 2.7 s at 0.55 V for coloring and 1.4 s for bleaching, reflecting the different reaction rates between the neutral and oxidized forms of the film of 6d. As shown in Figure 6, the absorbance changes at 906 nm reflect the switch in current, and the kinetics of the charge transport process can be referenced to the coloration response time. The electrochromic coloration efficiencies ( $\eta = \delta OD_{906}/$ Q) after various switching steps of the film of polyamide 6d are summarized in Table 4. The electrochromic film of 6d was found to exhibit high coloration efficiencies up to 296 cm<sup>2</sup>/C at 906 nm, and to retain near 94% of its optical response after 1000 coloring/bleaching cycles. Therefore, the electrochromic switching behavior appears to be a highly reversible process.

#### CONCLUSIONS

A new TPA-based aromatic diamine monomer, 4,4'-diamino-4"-(4-morpholinyl)triphenylamine, was successfully synthesized in high purity and good yield. A new family of 4morpholinyITPA-functionalized aromatic polyamides were readily prepared form the newly synthesized diamine monomer with various aromatic dicarboxylic acids by the phosphorylation polyamidation reaction. All the polymers were amorphous with good solubility in many polar aprotic solvents and could afford flexible and strong films with high thermal stability by solution casting. Incorporating the morpholinyl substituent on the TPA unit greatly lowered the oxidation potentials of the polyamides. In addition, these polymers also revealed multi-colored electrochromic properties, high coloration efficiency, good electrochemical, and electrochromic stability, and rapid switching times. Thus, these characteristics suggest that the present polyamides have great potential for optoelectronics applications.

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