# New Electroactive and Electrochromic Aromatic Polyamides with Ether-Linked Bis(triphenylamine) Units

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**ABSTRACT:** A new class of electroactive polyamides with etherlinked bis(triphenylamine)  $[O(TPA)_2]$  units were prepared through the direct phosphorylation polycondensation from *N*,*N*-di(4-aminophenyl)-*N*,*N*-diphenyl-4,4'-oxydianiline and aromatic dicarboxylic acids. These polyamides were amorphous with good solubility in many organic solvents, such as NMP and DMAc, and could be solution-cast into strong and flexible polymer films. Their decomposition temperatures (*T*<sub>d</sub>) at a 10% weight-loss in nitrogen and air were recorded at 556–568 °C and 537–555 °C, respectively. The glass-transition temperatures (*T*<sub>g</sub>) of all the polyamides were observed in the range of 218–253 °C by DSC. Cyclic voltammograms of the polyamide films cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.80–0.82 V

INTRODUCTION Electrochromic materials consist of redoxactive species that exhibit significant, lasting, and reversible changes in color upon electrochemical reduction or oxidation.<sup>1</sup> Research in electrochromic devices has received a great deal of attention due to the importance of this interesting phenomenon in applications such as electrochromic windows,<sup>2</sup> displays,<sup>3</sup> memory devices,<sup>4</sup> electronic papers,<sup>5</sup> and adaptive camouflages.<sup>6</sup> There is a vast amount of chemical species that exhibited electrochromic properties, including metal coordination complexes, metal oxide (especially tungsten oxide), viologens (4,4'-bipyridium salts), and conducting polymers (such as polyanilines, polypyrroles, polythiophenes, and polyselenophenes).<sup>7</sup> In recent years, the use of conjugated polymers as active layers in electrochromic devices became popular due to the advantageous properties such as fast switching time, ease of synthesis, and wide range of colors.<sup>8</sup> For efficient operation of an electrochromic device, it is necessary to take a number of properties into consideration: Electrochromic efficiency, optical contrast, response time, stability, and durability. The difficulty in achieving satisfactory values for all these parameters at the same time stimulates the development of new methods of preparation of and 0.96–0.98 V versus Ag/AgCl in an electrolyte containing acetonitrile solution. The polyamide films showed excellent electrochemical and electrochromic stability, with a color change from a colorless or pale yellowish neutral form to green and purple oxidized forms at applied potentials ranging from 0 to 1.2 V. These polymers can also be used to fabricate electrochromic devices, and they showed high coloration efficiency, high redox stability, and fast response time. © 2014 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *00*, 000–000

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electrochromic films, new materials, and components for the devices.  $^{9}$ 

Triarylamine derivatives are well known for photo- and electroactive properties that may find optoelectronic applications as photoconductors, hole-transporters, and light-emitters.<sup>10</sup> Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, many triarylaminebased electrochromic polymers have been reported in literature.<sup>11</sup> In recent years, Liou and coworkers<sup>12</sup> has performed extensive studies on the design and synthesis of triarylamine-based high-performance polymers such as aromatic polyamides and polyimides for potential electrochromic applications. In general, these polymers exhibit good solubility to organic solvents due to the introduction of bulky, packing-disruptive triarylamine moieties. In addition, by incorporating the triarylamine units of different electronic nature into the polymer backbone, different oxidation states of the polymers could be accessed, which make them to be a multi-electrochromic material. For example, it has been demonstrated that aromatic polyamides containing N,N,N',N'-tetraphenylphenylenediamine (TPPA) segments show attractive

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**SCHEME 1** Synthetic route to the target diamine monomer **6**. (a) 4-iodoanisole, Cu, K<sub>2</sub>CO<sub>3</sub>, TEGDME, 180 °C; (b) BBr<sub>3</sub>, CHCl<sub>3</sub>, rt, then quenched by MeOH; (c) *p*-fluoronitrobenzene, CsF, DMSO, 140 °C; (d) Pd/C, hydrazine, EtOH, reflux; (e) *p*-fluoronitrobenzene, CsF, DMSO, 140 °C; (f) Pd/C, hydrazine, EtOH, reflux.

electrochromic properties such as high coloration efficiency, high optical contrast, fast response time, long-term cycling stability, and multicolored electrochromism.<sup>13</sup> The radical cations of the TPPA-bearing polyamides generally showed rather strong bands in the near infrared (NIR) region due to a mixed-valence-type transition (charge transfer transition between pairs of chromophores in different oxidation states).14 Inserting the ether linkage between two triphenylamine (TPA) units has been shown to interrupt the electronic coupling between the amino centers as evidenced by electrochemical and spectroelectrochemical results.<sup>15</sup> Thus, the polyamides containing  $O(TPA)_2$  in the main chain showed significantly reduced intervalence charge-transfer (IV-CT) absorptions, which may lead to an enhanced optical contrast and color saturation in the visible region because the polaron absorption was constrained mainly in that region. Inspired by these interesting results, this work describes the synthesis and characterization of a new O(TPA)<sub>2</sub>-containing diamine, *N*,*N*-di(4-aminophenyl)-*N'*,*N'*-diphenyl-4,4'-oxydianiline (structure 6 as shown in Sch. 1), and its derived electroactive aromatic polyamides. The polyamides are expected to exhibit high thermal stability due to their aryl amide backbones, together with good solubility because of the laterally attached TPA groups. Due to the different electronic nature of the main-chain TPA unit and the pendent TPA unit, these O(TPA)<sub>2</sub>-containing polyamides are also expected to show a multi-colored electrochromic behavior.

#### **EXPERIMENTAL**

#### Materials

4-Hydroxytriphenylamine (2) (mp = 104-106 °C) was synthesized by demethylation of 4-methoxytriphenylamine (1)

resulting from the Ullmann reaction of diphenylamine with 4-iodoanisole by using copper powder according to a reported procedure.<sup>16</sup> Diphenylamine, iodobenzene, 4iodoanisole, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), triethylene glycol dimethyl ether (TEGDME), boron tribromide (BBr<sub>3</sub>), sodium hydrogen carbonate (NaHCO<sub>3</sub>), p-fluoronitrobenzene, cesium fluoride (CsF), 10% palladium on charcoal (Pd/C), hydrazine monohydrate, and triphenyl phosphite (TPP) were used as received from commercial sources. DMSO, DMF, N,N-dimethylacetamide (DMAc), pyridine, and NMP were dried over calcium hydride, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. The aromatic dicarboxylic acids such as terephthalic acid (7a, Wako), 4,4'dicarboxydiphenyl ether (7b, TCI), bis(4-carboxyphenyl) sulfone (7c, New Japan Chemicals), and 2,2-bis(4-carboxyphenyl)hexafluoropropane (7d, TCI) were used as received. Commercially obtained calcium chloride (CaCl<sub>2</sub>) was dried under vacuum at 180 °C for 8 h before use. Tetrabutylammonium perchlorate (TBAP), Bu<sub>4</sub>NClO<sub>4</sub>, was recrystallized from ethyl acetate under nitrogen atmosphere and then dried in vacuo before use.

# **Monomer Synthesis**

# 4-Methoxytriphenylamine (1)

A mixture of the diphenylamine (82.6 g, 0.3 mol), 4iodoanisole (70.2 g, 0.3 mol),  $K_2CO_3$  (82.9 g, 0.6 mol), Cu (19.2 g, 0.3 mol), and TEGDME (60 mL) was heated and stirred at 180 °C for 24 h. Then, the reaction mixture was poured into 1 L of water to precipitate the product. The crude product was collected by filtration and then recrystallized from methanol to give brown crystals (30.0 g, 60% yield) with a melting point of 104–106 °C. IR (KBr): 2830–2920 cm<sup>-1</sup> (methoxy C—H stretch).



**FIGURE 1** (a) <sup>1</sup>H NMR (b) <sup>13</sup>C NMR (c) H–H COSY and (d) C–H HMQC spectra of the target diamine monomer **6** in DMSO- $d_6$ . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

# 4-Hydroxytriphenylamine (2)

A solution of compound **1** (30.0 g; 0.11 mol) in 220 mL of chloroform was cooled to 0 °C, and BBr<sub>3</sub> (55.1 g; 0.22 mol, 220 mL 1*M* solution in CH<sub>2</sub>Cl<sub>2</sub>) was added slowly with stirring. After stirring for 1 h at 0 °C, the reaction mixture was allowed to warm to room temperature ( $\sim$ 25 °C) and stirred for 18 h. The reaction was carefully quenched with methanol

using an ice bath. The solvent was then removed under reduced pressure, and the residue was re-dissolved in ethyl acetate (440 mL). The resulting solution was washed with a saturated aqueous solution of NaHCO<sub>3</sub> (2  $\times$  220 mL) and water (2  $\times$  220 mL), dried over MgSO<sub>4</sub>, and evaporated to give green powder (22.8 g, 80% yield). IR (KBr): 3324 cm<sup>-1</sup> (broad absorption band; O—H stretch).



# 4-(4-Nitrophenoxy)triphenylamine (3)

In a 250 mL three-neck round-bottom flask equipped with a stirring bar, a mixture of 22.8 g (0.087 mol) of compound 2, 12.3 g (0.087 mol) of *p*-fluoronitrobenzene, and 13.2 g (0.087 mol) of CsF in 90 mL of dry DMSO was heated with stirring at 140 °C for 12 h under nitrogen atmosphere. After cooling, the reaction mixture was poured into 450 mL of stirred methanol slowly, and the precipitated yellow crystals (23.3 g, 70% yield; mp = 129-131 °C) were collected by filtration. IR (KBr): 1588, 1330 cm<sup>-1</sup> (-NO<sub>2</sub> stretch). <sup>1</sup>H NMR (500 MHz, DMSO $d_{6}$ ,  $\delta$ , ppm): 7.04 (d, J = 7.8 Hz, 4H, H<sub>c</sub>), 7.05 (t, J = 7.8 Hz, 2H,  $H_a$ ), 7.08 (d, J = 8.9 Hz, 2H,  $H_d$ ), 7.13 (d, J = 8.9 Hz, 2H,  $H_e$ ), 7.18 (d, J = 9.0 Hz, 2H, H<sub>f</sub>), 7.32 (t, J = 7.8 Hz, 4H, H<sub>b</sub>), 8.26 (d, J = 9.0 Hz, 2H. H<sub>g</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 117.09 (C<sup>10</sup>), 121.55 (C<sup>7</sup>), 122.97 (C<sup>1</sup>), 123.61 (C<sup>3</sup>), 125.30  $(C^{6})$ , 126.10  $(C^{11})$ , 129.51  $(C^{2})$ , 142.08  $(C^{12})$ , 144.50  $(C^{5})$ , 147.09 (C<sup>4</sup>), 149.26 (C<sup>8</sup>), 163.08 (C<sup>9</sup>).



#### 4-(4-Aminophenoxy)triphenylamine (4)

In a 500 mL three-neck round-bottom flask equipped with a stirring bar, 23.3 g (0.061 mol) of the nitro compound 3 and 0.15 g of 10% Pd/C were dissolved/suspended in 350 mL of ethanol under nitrogen atmosphere. The suspension solution was heated to reflux, and 8 mL of hydrazine monohydrate was added slowly to the mixture, then the solution was stirred at reflux temperature. After a further 24 h of reflux, the solution was filtered hot to remove Pd/C, and the filtrate was then cooled to precipitate white product. The product was collected by filtration and dried in vacuo at 80 °C to give 15.0 g (70% in yield) of white powders with an mp of 123-124 °C. IR (KBr): 3441, 3361 cm<sup>-1</sup> (-NH<sub>2</sub> stretch). <sup>1</sup>H NMR (500 MHz, DMSO $d_{6}$ ,  $\delta$ , ppm): 4.93 (s, 2H,  $-NH_2$ ), 6.58 (d, J = 8.7 Hz, 2H,  $H_g$ ),  $6.78 (d, J = 8.7 Hz, 2H, H_f), 6.83 (d, J = 8.9 Hz, 2H, H_d), 6.94 (d, J)$ J = 7.8 Hz, 4H, H<sub>c</sub>), 6.96 (t, J = 7.8 Hz, 2H, H<sub>a</sub>), 6.99 (d, J = 8.9Hz, 2H, H<sub>e</sub>), 7.25 (t, J = 7.8 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>, δ, ppm): 114.86 (C<sup>11</sup>), 117.61 (C<sup>6</sup>), 120.78 (C<sup>10</sup>), 122.10 (C<sup>1</sup>), 122.53 (C<sup>3</sup>), 126.91 (C<sup>7</sup>), 129.34 (C<sup>2</sup>), 141.05 (C<sup>12</sup>), 145.42 (C<sup>5</sup>), 145.67 (C<sup>9</sup>), 147.51 (C<sup>4</sup>), 155.32 (C<sup>8</sup>).



*N*,*N*-*Di*(4-*nitrophenyl*)-*N*',*N*'-*Diphenyl*-4,4'-*Oxydianiline* (5) In a 250 mL three-neck round-bottom flask equipped with a stirring bar, a mixture of 15.0 g (0.043 mol) of compound 4,

12.1 g (0.086 mol) of *p*-fluoronitrobenzene, 13.1 g (0.086 mol) of CsF, in 70 mL of dry DMSO was heated with stirring at 140 °C for 12 h under nitrogen atmosphere. After cooling, the reaction mixture was poured into 700 mL of stirred methanol slowly, and the crude product was collected by filtration and then re-crystallized from acetonitrile twice to give orange crystals (16.0 g, 70% yield) with a melting point of 164–167 °C. IR (KBr): 1573, 1344 cm<sup>-1</sup> (–NO<sub>2</sub> stretch). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 7.00 (d, J = 7.8 Hz, 4H, H<sub>c</sub>), 7.02 (t, J = 7.8 Hz, 2H, H<sub>a</sub>), 7.06 (s, 4H, H<sub>d</sub> + H<sub>e</sub>), 7.13 (d, J = 8.8 Hz, 2H, H<sub>g</sub>), 7.21 (d, J = 9.1 Hz, 4H, H<sub>h</sub>), 7.27 (d, J = 8.8 Hz, 2H, H<sub>f</sub>), 7.29 (t, J = 7.8 Hz, 4H, H<sub>b</sub>), 8.18 (d, J = 9.1 Hz, 4H, H<sub>i</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 119.75 (C<sup>11</sup>), 120.64 (C<sup>6</sup>), 122.12 (C<sup>14</sup>), 122.77 (C<sup>1</sup>), 123.31 (C<sup>3</sup>), 125.59 (C<sup>15</sup>), 125.98 (C<sup>7</sup>), 129.45 (C<sup>10</sup>), 129.54  $(C^2)$ , 139.18  $(C^{12})$ , 141.95  $(C^{16})$ , 143.42  $(C^5)$ , 147.34  $(C^4)$ , 151.45 (C<sup>9</sup>), 151.65 (C<sup>13</sup>), 156.15 (C<sup>8</sup>).



# N,N-Di(4-aminophenyl)-N',N'-Diphenyl-4,4'-Oxydianiline (6)

In 250 mL three-neck round-bottom flask equipped with a reflux condenser and a stirring bar were placed 16.0 g (0.027 mol) of the dinitro compound 5, 0.15 g of 10% Pd/C, 4 mL of hydrazine monohydrate, and 200 mL of ethanol. The reaction mixture was heated at a reflux temperature under nitrogen atmosphere for 24 h. After that, the solution was filtered hot to remove Pd/C, and the filtrate was then cooled to precipitate white product. The product was collected by filtration and dried in vacuo at 80 °C to give 10.1 g (70% in yield) of purple powders with a melting point of 198-199 °C. IR (KBr): 3423, 3348 cm<sup>-1</sup> (–NH<sub>2</sub> stretch). <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 4.94 (s, 2H,  $-NH_2$ ), 6.54 (d, I = 8.6 Hz, 4H, H<sub>i</sub>), 6.65 (d, I= 9.0 Hz, 2H, H<sub>g</sub>), 6.79 (d, J = 8.6 Hz, 4H, H<sub>h</sub>), 6.83 (d, J = 9.0Hz, 2H,  $H_f$ ), 6.88 (d, J = 8.9 Hz, 2H,  $H_d$ ), 6.95 (d, J = 7.8 Hz, 4H,  $H_c$ ), 6.97 (d, J = 7.8 Hz, 2H,  $H_a$ ), 7.01 (d, J = 8.9 Hz, 2H,  $H_e$ ), 7.26 (t, J = 7.8 Hz, 4H, H<sub>b</sub>). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ ,  $\delta$ , ppm): 114.79 (C<sup>15</sup>), 118.30 (C<sup>6</sup>), 118.49 (C<sup>11</sup>), 119.93 (C<sup>10</sup>), 122.16 (C<sup>1</sup>), 122.61 (C<sup>3</sup>), 126.62 (C<sup>7</sup>), 126.73 (C<sup>14</sup>), 129.30 (C<sup>2</sup>), 136.32 (C<sup>13</sup>), 141.53 (C<sup>12</sup>), 145.14 (C<sup>16</sup>), 145.93 (C<sup>5</sup>), 147.37 (C<sup>4</sup>), 147.79 (C<sup>9</sup>), 154.26 (C<sup>8</sup>). The assignments of all NMR signals are shown in Figure 1.

# Synthesis of Model Compounds 4-Phenoxytriphenylamine (M1)

A mixture of the compound **2** (6.00 g, 0.023 mol), iodobenzene (4.80 g, 0.023 mol),  $K_2CO_3$  (6.50 g, 0.047 mol), Cu (1.47 g, 0.023 mol), and TEGDME (10 mL) was heated and stirred at 180 °C for 24 h. Then, the reaction mixture was poured into methanol. The product was collected by



SCHEME 2 Synthesis of model compounds M1-M3.

filtration, washed by hexane, and dried to give brown powder (2.15 g, 28% yield) with a melting point of 116-119 °C.

#### 4,4'-Dibenzamido-4"-Phenoxytriphenylamine (M2)

A mixture of the 4,4'-diamino-4"-phenoxytriphenylamine (0.30 g, 0.82 mmol), benzoic acid (0.20 g, 1.65 mmol), 0.80 mL of TPP, 0.40 mL of pyridine, and 0.80 mL of NMP was heated and stirred at 120 °C for 3 h. Then, the reaction mixture was poured into methanol. The product was collected by filtration, washed by water, and dried to give pale green crystals (0.30 g, 60% yield) with a melting point of 113-115 °C.

# N,N-Di(4-benzamido)-N',N'-Diphenyl-4,4'-Oxydianiline (M3)

A mixture of the diamine compound **6** (0.34 g, 0.64 mmol), benzoic acid (0.16 g, 1.28 mmol), 0.65 mL of TPP, 0.30 mL of pyridine, and 0.65 mL of NMP was heated and stirred at 120 °C for 3 h. After that, the reaction mixture was poured into methanol. The product was collected by filtration, washed by water, and dried to give pale green powder (0.13 g, 28% yield) with a melting point of 108-111 °C.

#### **Polymer Synthesis**

The synthesis of polyamide 8a was used as an example to illustrate the general synthetic route used to produce the polyamides. A mixture of 0.45 g (0.85 mmol) of diamine monomer **6**, 0.14 g (0.85 mmol) of terephthalic acid **(7a)**, 0.15 g of anhydrous calcium chloride, 0.85 mL of TPP, 0.25

mL of pyridine, and 0.85 mL of NMP was heated with stirring at 120 °C for 3 h. 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 **8a**. The inherent viscosity of the polymer was 0.44 dL/g, measured in DMAc (containing 5 wt % LiCl) at a concentration of 0.5 g/dL at 30 °C. The IR spectrum of **8a** (film) exhibited characteristic amide absorption bands at 3300 cm<sup>-1</sup> (amide N—H stretch) and 1650 cm<sup>-1</sup> (amide carbonyl stretch).

#### **Preparation of the Polyamide Films**

A solution of the polymer was made by dissolving about 0.6 g of the polyamide sample in 8 mL of DMAc. The homogeneous solution was poured into a 7-cm glass Petri dish, which was placed in a 90 °C oven overnight to remove most of the solvent. The cast film was then released from the glass substrate and was further dried *in vacuo* at 160 °C for 8 h. The obtained films were about 50–60  $\mu$ m in thick and were used for XRD measurements and thermal analyses.

# Fabrication of the Electrochromic Devices

Electrochromic polymer films were prepared by dropping solution of the polyamides (3 mg/mL in DMAc) onto the ITO-coated glass substrate ( $20 \times 30 \times 0.7$  mm,  $50-100 \Omega/$  cm<sup>2</sup>). A gel electrolyte based on PMMA ( $M_w = 120,000$ ) and





SCHEME 3 Synthesis of polyamides 8a-8d.

LiClO<sub>4</sub> was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (1 g) was dissolved in dry acetonitrile (4 mL), and LiClO<sub>4</sub> (0.1 g) was added to the polymer solution as supporting electrolyte. Then propylene carbonate (1.5 g) was added as plasticizer. The mixture was then gently heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

#### **Instrumentation and Measurements**

IR spectra were recorded on a Horiba FT-720 FT-IR spectrometer. <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. WAXD measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a

**TABLE 1** Inherent Viscosity and Solubility Behavior of

 Polyamides

		Solubility in Various Solvents <sup>b</sup>					
Polymer Code	η <sub>inh</sub> <sup>a</sup> (dL/g)	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF
8a	0.44	++	++	++	++	+h	
8b	0.33	++	++	++	+h	+-	+-
8c	0.38	++	++	++	++	+h	+-
8d	0.31	++	++	++	++	+h	++

 $^a$  Inherent viscosity measured at a concentration of 0.5 dL/g in DMAc–5 wt % LiCl at 30  $^\circ\text{C}.$ 

Solvents: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

graphite monochromator (operating at 40 kV and 30 mA), using nickel-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54$  Å). The scanning rate was 2°/min over a range of  $2\theta = 10-40^{\circ}$ . TGA was performed with a PerkinElmer Pyris 1 TGA. Experiments were performed on approximately 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 PerkinElmer Pyris 1 DSC at a scan rate of 20 °C/min in flowing nitrogen. Electrochemistry was performed with a CHI 750A electrochemical analyzer. Cyclic voltammetry was conducted with the use of a three-electrode cell, in which ITO (polymer films area about 0.8 imes 1.25 cm) 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 calibration (+0.48 V vs. Ag/AgCl). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards.



**FIGURE 2** TGA curves of polyamide **8d** with a heating rate of 20 °C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

<sup>&</sup>lt;sup>b</sup> The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent. Notation of solubility behavior: ++, soluble at room temperature; +h, soluble on heating; --, insoluble even on heating; +-, partially soluble.

TABLE 2 Thermal Properties o	· Pol	vamides
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Polymer Code	7 <sub>g</sub> (°C) <sup>a</sup>	T <sub>d</sub> at 5% Weight Loss (°C) <sup>b</sup>		T <sub>d</sub> at Weigh (°C	10% t Loss :) <sup>b</sup>	Char Yield (wt %) <sup>c</sup>	
		$\text{In }N_2$	In Air	$ln \ N_2$	In Air		
8a	241	510	472	565	555	76	
8b	218	511	466	567	538	65	
8c	253	500	485	556	537	66	
8d	233	519	475	568	545	69	

<sup>a</sup> Midpoint temperature of the baseline shift on the second DSC heating trace (heating rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (cooling rate = 200 °C/min) in nitrogen.

 $^{\rm b}$  Decomposition temperature at which a 5 or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 cm<sup>3</sup>/min.

<sup>c</sup> Residual weight % at 800 °C at a scan rate 20 °C/min in nitrogen.

Spectroelectrochemistry analyses were performed 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 target aromatic diamine monomer, N,N-di(4-aminophenyl)-N',N'-diphenyl- 4,4'-oxydianiline (6), was synthesized starting from diphenylamine by a six-step reaction sequence as depicted in Scheme 1. In first step, the intermediate compound 4-methoxytriphenylamine (1) was synthesized through Ullmann reaction between diphenylamine and 4iodoanisole by using copper powder. Demethylation of compound **1** with boron tribromide gave the 4hydroxytriphenylamine (2).<sup>16</sup> Then, 4-(4-nitrophenoxy)triphenylamine (3) was prepared by the nucleophilic aromatic fluoro-displacement reaction of p-fluoronitrobenzene with compound 2 in the presence of cesium fluoride (CsF). Reduction of the nitro group of compound 3 by means of hydrazine and Pd/C gave 4-(4-aminophenoxy)triphenylamine (4). The target diamine monomer 6 was prepared by hydrazine Pd/C-catalyzed reduction of dinitro compound 5, which was prepared from the CsF-assisted N,N-diarylation reaction of compound **4** with two equivalent amount of *p*fluoronitrobenzene.

The chemical structures of all the intermediate compounds and the target compound **6** were verified by FTIR and NMR spectroscopies. The FT-IR spectra of intermediate compounds **1–5** and diamine monomer **6** are compiled in Figure S1 of Supporting Information. The methoxy groups of compound **1** shows characteristic peaks ( $-OCH_3$ , C-H stretching) at 2831 and 2910 cm<sup>-1</sup>. After demethylation, the characteristic absorptions of the phenol group (-OH stretching) appeared in the region of 3100-3500 cm<sup>-1</sup>. The nitro groups (-NO<sub>2</sub> asymmetric and symmetric stretching) of compound 3 and 5 gave two characteristic bands at around 1573–1588 and 1330–1344 cm<sup>-1</sup>. After reduction, the characteristic absorptions of the nitro group disappeared and the amino group showed the typical N-H stretching absorption pair in the region of  $3300-3500 \text{ cm}^{-1}$  as shown in the IR spectra of compounds 4 and 6. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the intermediate compounds 3-5 are included in Supporting Information Figures S2-S4. The NMR spectra of the target diamine monomer 6 are shown in Figure 1. The assignments of all proton and carbon signals were assisted by the 2D NMR spectra. These spectra are in good agreement with the proposed molecular structures of these synthesized compounds. The model compounds M1-M3 were also prepared according to Scheme 2. The FT-IR spectra of these model compounds are shown in Supporting Information Figure S5. The characteristic absorptions are in good agreement with their molecular structures.

# **Polymer Synthesis**

According to the phosphorylation technique described by Yamazaki et al.,<sup>17</sup> a series of novel aromatic polyamides **(8a–** 



**FIGURE 3** (a) Cyclic voltammograms and (b) differential pulse voltammograms of the cast films of polyamides **8a–8d** on the ITO-coated glass slide in  $0.1M \text{ Bu}_4\text{NCIO}_4/\text{CH}_3\text{CN}$  at scan rate of 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymer	Absor Wave of 1 Films	rption length Thin (nm)	Oxidation Potential (V) <sup>a</sup>						E <sub>g</sub> (eV) <sup>b</sup>	Energy Level (eV)			
	$\lambda_{\max}^{abs}$	$\lambda_{\max}^{abs}$	Eo	nset	E	ox1 1/2	$E_1^{\circ}$	ox2 1/2		НО	MO <sup>c</sup>	LUI	MOd
			CV	DPV	CV	DPV	CV	DPV		CV	DPV	CV	DPV
8a	305	458	0.60	0.61	0.81	0.79	0.94	0.96	2.70	5.17	5.15	2.47	2.45
8b	309	411	0.61	0.61	0.82	0.82	0.94	0.97	3.02	5.18	5.18	2.16	2.16
8c	305	500	0.70	0.58	0.81	0.80	0.96	0.95	2.48	5.17	5.16	2.69	2.68
8d	303	409	0.63	0.62	0.82	0.80	0.95	0.96	3.03	5.18	5.16	2.15	2.13
8'a	306	419	0.45	0.30	0.57	0.60	0.95	0.97	2.96	4.95	4.96	1.99	2.00

<sup>a</sup> From cyclic voltammograms versus Ag/AgCl in CH<sub>3</sub>CN.  $E_{1/2}$ : Average potential of the redox couple peaks. <sup>b</sup> The data were calculated from polymer films by the equation:  $E_{q}$  =

<sup>o</sup> The data were calculated from polymer films by the equation:  $E_{g} = 1240/\lambda_{onset}$  (energy gap between HOMO and LUMO).

8d) with  $O(TPA)_2$  units were synthesized from diamine monomer 6 and aromatic dicarboxylic acids 7a - 7d using TPP and pyridine as condensing agents (Sch. 3). All the polymerizations proceeded homogeneously throughout the reaction and afforded clear and highly viscous polymer solutions. The products precipitated in a tough, fiber-like form when the resulting polymer solutions were slowly poured into methanol. As shown in Table 1, the obtained polyamides had inherent viscosities in the range of 0.31-0.44 dL/g and could be solution-cast into flexible and strong films (Supporting Information Fig. S6), indicating the formation of high molecular weight polymers. This mechanical property is important for the further development of flexible optoelectronic devices. The formation of polyamides was also confirmed by IR and NMR spectroscopy. The representative IR spectrum for polyamide 8a is included in Supporting Information Figure S7, which shows the characteristic absorption

 $^{\rm c}$  The HOMO energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (4.8 eV).

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

bands of the amide group at around 1650 cm<sup>-1</sup> (amide carbonyl) and 3300 cm<sup>-1</sup> (N—H stretching). Supporting Information Figure S8 shows the <sup>1</sup>H NMR and COSY spectra of polyamide **8a** in DMSO- $d_6$ . All the peaks could be readily assigned to the hydrogen atoms in the repeating unit. The resonance peak appearing at 10.35 ppm in the <sup>1</sup>H NMR spectrum also supports the formation of amide linkages.

#### **Solubility of Polyamides**

The WAXD patterns of the polyamide films are shown in Supporting Information Figure S9. These polymers exhibited an amorphous nature because of the bulky, packing-disruptive  $O(TPA)_2$  unit along the polymer backbone, which does not favor their close chain packing. The solubility behavior of polyamides **8a**-**8d** was tested qualitatively, and the results are summarized in Table 1. All the polyamides were highly soluble in polar solvents such as NMP, DMAc, and DMF, and the



**FIGURE 4** Cyclic voltammetric diagrams of model compounds M1, M2, and M3 ( $10^{-3}M$ ) in 0.1*M* Bu<sub>4</sub>NCIO<sub>4</sub>/CH<sub>3</sub>CN solution at a scan rate of 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 4 Anodic oxidation pathways of polyamides (a) 8a and (b) 8'a. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

good solubility could be attributed in part to the introduction of propeller-shaped TPA moiety in the repeat unit, which decreases interchain interactions and increases the free volume. The polyamide **8d** showed a better solubility as compared with the other polymers due to the effect of the large volume of  $CF_3$  groups. Thus, the excellent solubility makes these polymers potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices.

#### **Thermal Properties**

The thermal properties of all the polyamides were investigated by TGA and DSC techniques, and their thermal behavior data are summarized in Table 2. Typical TGA curves of a representative polyamide 8d in both air and nitrogen atmospheres are illustrated in Figure 2. All the polymers exhibited good thermal stability with insignificant weight loss up to 450 °C in both air and nitrogen atmospheres. The decomposition temperatures  $(T_d)$  at a 10% weight-loss of the polyamides in nitrogen and air were recorded in the range of 556-568 and 537-555 °C, respectively. The mount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 65% at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The  $T_{g}$  of all the polymers were measured to be in the range of 218-253 °C by DSC as shown in Supporting Information Figure S10. All the polymers indicated no clear melting endotherms up to the  $T_{\rm d}$  on the DSC thermograms. The thermal analysis results showed that these polyamides exhibited excellent thermal stability, which in turn is beneficial to increase the service time in device application and enhance the morphological stability to the spin-coated film.

#### **Electrochemical Properties**

The electrochemical behavior of the polyamides was investigated by CV and differential pulse voltammetry (DPV) conducted for the cast films on an ITO-coated glass substrate as working electrode immersed in dry acetonitrile (CH<sub>3</sub>CN) containing 0.1M of Bu<sub>4</sub>NClO<sub>4</sub> as an electrolyte under nitrogen atmosphere. In comparison to CV, DPV offers a higher sensitivity and sharper redox onsets throughout the

**TABLE 4** Electrochemical Properties of Model Compounds and

 Polyamide 8a

Code	Oxidation Potentials (V) v AgCl in CH <sub>3</sub> CN	s. Ag/
	$E_{1/2}^{ox1}$	$E_{1/2}^{ox2}$
M1	0.93	-
M2	0.73	-
M3	0.74	0.96
8a	0.81	0.94



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**FIGURE 5** Cyclic voltammograms of the cast films of polyamides (a) **8a** and (b) **8'a** on the ITO-coated glass slide in 0.1MBu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at a scan rate of 50 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrochemical process owing to a reduced contribution of the charging background currents. Figure 3 shows the CV and DPV curves for all polyamides, and the relevant oxidation potential data are summarized in Table 3. There are two reversible oxidation redox couples with half-wave potentials  $(E_{1/2})$  of 0.80-0.82 V and 0.96-0.98 V at scan rate of 50 mV/s. In comparison with those found in TPPA-based polyamides,<sup>13</sup> the present polyamides showed a closer redox potential splitting  $\Delta E$  of the two waves. This implies a weak electronic coupling between the two TPA amino redox centers mediated by the ether connector and is consistent with the observation made by the Liou and coworkers.<sup>15</sup> During the CV scanning we also found these polyamides showed interesting multi-colored electrochromic behaviors with coloration changing from colorless through green to purple. The HOMO energy levels of the investigated polyamides were calculated from the oxidation onset potentials ( $E_{\text{onset}}$ ) and by comparison with ferrocene (4.8 eV). These data together with absorption spectra were then used to obtain the LUMO energy levels (Table 3). According to the HOMO and LUMO

energy levels obtained, the polyamides in this study appear to be appropriate as hole injection and transport materials.

For a clear understanding the order of the oxidation processes occurring in these polyamides, we studied the CV behaviors of the model compounds **M1–M3**. The results are shown in Figure 4, and the relevant oxidation potential data are summarized in Table 4. Judging from the CV curves of these model compounds, we believe that the first oxidation peak appears to involve one electron loss from the mainchain TPA unit of the polyamides **8a–8d** [see Sch. 4(a)]. This can be rationalized because this TPA segment is more electron-rich and becomes more easily oxidized. The second oxidation peak is related to the electron losses from the side-chain TPA unit.

Furthermore, the CV curves of polyamides **8a** and **8'a** are shown in Figure 5 for comparison. The oxidation peaks in the CV curve of the referenced polyamide **8'a** are well separated ( $\Delta E_{pa} = 0.40$  V), indicating a strong electronic coupling between the amino centers. The radical cation species of **8'a** belongs to the Robin/Day class III [delocalized redox centers, see Sch. 4(b)]<sup>14(b)</sup> where both TPA centers share a common phenylene spacer. In contrast, the radical cation species of **8a** displayed a class I like transition (localized redox centers) with a smaller redox potential splitting  $\Delta E_{pa}$ of the two redox waves. This implies that the separated redox centers in the O(TPA)<sub>2</sub> unit exhibited an independent electrochemical behavior, and two electrons within the O(TPA)<sub>2</sub> segment are removed in sequence to form a dicationic structure without intramolecular electron transfer.

#### Spectroelectrochemistry and Electrochromic Properties

Spectroelectrochemical measurements were performed on films of polymers drop-coated onto ITO-coated glass slides immerged in electrolyte solution. The electrode preparations and solution conditions were identical to those used in the CV experiments. The change in absorption of polyamide 8d film at various applied potentials is shown in Figure 6, which was representative for the other 8a-8c counterparts. In the neutral form, at 0 V, polyamide 8d exhibited strong absorption at wavelength around 303 nm, but it almost transparent in the visible region. When the applied voltage was stepped from 0 to 0.8-1.0 V, the intensity of the absorption band around 303 nm decreased gradually, and new peaks at 400 and 790 nm gradually increased in intensity [Fig. 6(a,b)]. We attribute these spectral changes to the formation of a stable cation radical of the mainchain TPA moiety. Upon further oxidation at applied voltages to 1.2 V, corresponding to the second step oxidation, the peaks of characteristic absorbance of the radical cation decreased gradually and one new band grew up at 558 nm [Fig. 6(c)]. The new spectrum arises from the dication formation in the  $O(TPA)_2$  segment of polyamide **8d**. From the photos shown in inset Figure 6(a,c) it can be seen that the film changed from a transmissive neutral state (nearly colorless) to a highly absorbing semi-oxidized state (light green, green) and a fully oxidized state (purple). When the



FIGURE 6 Spectroelectrochemistry of the polyamide 8d thin film on the ITO-coated glass substrate in 0.1M Bu<sub>4</sub>NCIO<sub>4</sub>/CH<sub>3</sub>CN at (a) 0.8 V, (b) 1.0 V, and (c) 1.2 V. The photos (d) show the transmittance change ( $\Delta T$ %) of the film on an ITO electrode at indicated potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

applied voltage was stepped 0-1.0 V, the polymer 8d exhibited high contrast of optical transmittance change ( $\Delta T\%$ ) up to 48% at 400 nm and 87% at 790 nm for green coloring and when the applied voltage was stepped 0-1.2 V, the polymer **8d** exhibited  $\Delta T$ % up to 58% at 558 nm for purple coloring [see Fig. 6(d)].



FIGURE 7 Spectroelectrochemistry of the polyamides (a) 8a and (b) 8'a thin film on the ITO-coated glass substrate in 0.1M Bu<sub>4</sub>N-CIO<sub>4</sub>/CH<sub>3</sub>CN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 8** Potential step absorptometry of the cast film of polyamide **8d** on the ITO-glass slide (coated area: 1 cm<sup>2</sup>)(in CH<sub>3</sub>CN with 0.1*M* TBAP as the supporting electrolyte) by applying a potential step (a) 0.0 V0.8 V and (b) 0.0 V1.2 V with a cycle time of 16 s. Optical switching for polyamide **8d** at (c)  $\lambda_{max} = 790$  nm as the applied voltage was stepped between 0 and 0.8 V (vs. Ag/Ag/Cl) and (d) at  $\lambda_{max} = 558$  nm as the applied voltage was stepped between 0 and 1.2 V (vs. Ag/Ag/Cl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For a comparative purpose, the spectral changes of polyamides 8a and 8'a upon electro-oxidation are illustrated in Figure 7. Upon electro-oxidation of the 8'a film (increasing applied voltage from 0 to 0.7 V), the absorption of  $\pi$ - $\pi$ \* transition at 306 nm gradually decreased, whereas a new absorption peak at 425 nm and a broadband having its maximum around 990 nm in the NIR region grew up. We attribute this spectral change to the formation of a stable monocation radical from the TPPA moiety. The absorption band in the NIR region is assigned to an IV-CT between states in which the positive charge is centered at different amino centers.<sup>13</sup> Upon further oxidation at applied voltages to 1.1 V, the IV-CT band gradually decreased, with a formation of a new strong absorption band centered at about 725 nm. From the photos shown in Figure 7(b) inset, it can be seen that the film changed from a transmissive neutral state (nearly colorless) to a highly absorbing semi-oxidized state (yellowish green) and a fully oxidized state (blue). Figure 7(a) presents the UV-vis-NIR absorption spectra of polyamide 8a film at various applied potentials. No IV-CT band could be detected for the 8a film upon oxidation. The two amino centers in the O(TPA)<sub>2</sub> segment were oxidized in sequence with a color switches from near colorless (neutral state) to green, blue, and purple (oxidized states) of the electrochromic film. The result suggests that the introduction of ether-linkage between the TPA units can tune the UV-vis-NIR absorption profile of the polarons of polyamides.

Optical switching studies were examined for probing changes in transmittance with time while repeatedly stepping the potential between neutral and oxidized states. The polymer film was cast onto an ITO-coated glass slide in the same manner as described earlier and each film was potential stepped between its neutral (0 V), oxidized (+0.8 V), and fully oxidized (+1.2 V) state. While the films were switched, the absorbance at 790 and 558 nm was monitored as a function of time with UV-vis-NIR spectroscopy. Switching data for the cast film of polyamide **8d** are given in Figure 8. The switching time was calculated at 90% of the full switch

TABLE 5 Electrochromic Properties of Polyamide 8d

λ <sub>max</sub> ª (nm)	$\Delta\%T$	Response Time <sup>b</sup>		$\Delta OD^{c}$	$Q_d^{d}$ (mC/cm <sup>2</sup> )	CE <sup>e</sup> (cm <sup>2</sup> /C)	
		$t_{\rm c}~({\rm s})$	$t_{\rm b}$ (s)				
790	72	2.4	1.3	0.589	3.69	160	
558	50	4.3	2.0	0.301	3.42	88	

<sup>a</sup> Wavelength of absorption maximum.

<sup>b</sup> Time for 90% of the full-transmittance change.

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

 $^{\rm d}$   ${\it Q}_{\rm d}$  is ejected charge, determined from the *in situ* experiments.

<sup>e</sup> Coloration efficiency (CE) =  $\Delta OD/Q_d$ .



**FIGURE 9** (a) Cyclic voltammograms of the cast film in the electrochromic device based on polyamide **8d**, (b) schematic illustration of the structure of the electrochromic cell, (c) photos of sandwich-type ITO-coated glass electrochromic cell, and (d) spectroelectrochemistry of the device. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**FIGURE 10** Potential step absorptometry of the cast film of device **8d** on the ITO-glass slide (in CH<sub>3</sub>CN with 0.1*M* TBAP as the supporting electrolyte) by applying a potential step (a) 0.0 V2.2 V and (b) 0.0 V2.6 V with a cycle time of 16 s. Optical switching for device **8d** at (c)  $\lambda_{max} = 800$  nm as the applied voltage was stepped between 0 and 2.2 V (vs. Ag/Ag/Cl), and (d) at  $\lambda_{max} = 558$  nm as the applied voltage was stepped between 0 and 2.6 V (vs. Ag/Ag/Cl). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



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because it is difficult to perceive any further color change with naked eye beyond this point. As shown in Figure 8(a,b) after over 100 cyclic scans between 0 and 0.8 V and over 50 cyclic scans between 0 and 1.2 V, the polymer films still exhibited good reversibility of electrochromic characteristics. As shown in Figure 8(c,d) the polyamides switch rapidly between the highly transmissive neutral state and the colored oxidized state. Thin film from polyamide 8d required 2.4 s at 0.8 V for switching absorbance at 790 nm and 1.3 s for bleaching. When the potential was set at 1.2 V, the thin film from polyamide 8d would require 4.3 s for the coloring process at 558 nm and 2 s for the bleaching process. The electrochromic coloring efficiency (CE) of green ( $\eta$  =  $\Delta OD_{790}/Q$  and purple coloring ( $\eta = \Delta OD_{558}/Q$ ) of the polyamide 8d were calculated to be 160 and 88 cm<sup>2</sup>/C, respectively (Table 5).

On the basis of the foregoing results, it can be concluded that these polyamides can be used in the construction of electrochromic devices and optical display due to the fast response time and the robustness of the polymers. Therefore, we fabricated as preliminary investigations single layer electrochromic cells [Fig. 9(b)]. The polymer films were drop-coated onto ITOcoated glass and then dried. Afterwards, the gel electrolyte was spread on the polymer-coated side of the electrode and the electrodes were sandwiched under atmospheric condition. To prevent leakage, an epoxy resin was applied to seal the device. As a typical example, an electrochromic cell based on polyamide  ${\bf 8d}$  was fabricated. When the voltage applied was increased (to a maximum of 2.6 V), the color changed from colorless (neutral) to green (semi-oxidized) and purple (fully oxidized), the same as was already observed for the solution spectroelectrochemistry experiments. The color and spectral changes of the electrochromic device can be seen in Figure 9(c,d), which are similar to those observed in the electrochemical cell. Switching data for the electrochromic layer in the device based on polyamide 8d are given in Figure 10. Although the response time is slightly slower than that observed in the electrochemical cell (Table 5), the device showed stable absorbance change in the first 40 cyclic scans between 0 and 2.2 V at 800 nm, and in the first 10 cyclic scans between 0 and 2.6 V at 558 nm.

#### CONCLUSIONS

The new TPA-based aromatic diamine monomer, N,N-di(4aminophenyl)-N',N'-diphenyl-4,4'-oxydianiline (**6**) was successfully synthesized in high purity and good yield from readily available reagents. Aromatic polyamides bearing ether-linked bis(triphenylamine)  $[O(TPA)_2]$  units were readily prepared from the newly synthesized diamine monomer and various aromatic dicarboxylic acids by the phosphorylation polyamidation technique. Because of the introduction of 3D TPA units in polymer backbone, all the polymers were amorphous, had good solubility in many polar aprotic solvents, and exhibited excellent film-forming ability. In addition to high  $T_g$  values and good thermal stability, all the obtained polyamides also showed good electrochemical and electrochromic stability along with multielectrochromic behavior. The color changes from the colorless or pale yellowish neutral form to the green, blue, and purple oxidized forms when scanning potentials positively from 0.0 to 1.2 V. These polyamides did not show IV-CT absorption during oxidation because of the presence of ether linkage between the TPA units. The electrochemical, electrochromic, and device performance suggest that the present polyamides have great potential for use in optoelectronic applications.

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#### **REFERENCES AND NOTES**

**1** P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky, Electrochromism and Electrochromic Devices; Cambridge University Press: Cambridge, **2007**.

**2** (a) R. D. Rauch, *Electrochim. Acta* **1999**, *44*, 3165–3176; (b) A. Michaelis, H. Berneth, D. Haarer, S. Kostromine, R. Neigl, R. Schmidt, *Adv. Mater.* **2001**, *13*, 1825-1828; (c) H. W. Heuer, R. Wehrmann, S. Kirchmeyer, *Adv. Funct. Mater.* **2002**, *12*, 89-94; (d) G. A. Niklasson, C. G. Granqvist, *J. Mater. Chem.* **2007**, *17*, 127-156; (e) R. Baetens, B. P. Jelle, A. Gustavsen, *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 87-105.

**3** (a) D. R. Rosseinsky, R. J. Mortimer, *Adv. Mater.* **2001**, *13*, 783-793; (b) G. Sonmez, F. Wudl, *J. Mater. Chem.* **2005**, *15*, 20-22; (c) R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays* **2006**, *27*, 2-18; (d) P. Andersson, R. Forchheimer, P. Tehrani, M. Berggren, *Adv. Funct. Mater.* **2007**, *17*, 3074–3082.

**4** G. Sonmez, H. B. Sonmez, *J. Mater. Chem.* **2006**, *16*, 2473-2477.

**5** (a) U. Bach, D. Corr, D. Lupo, F. Pichot, M. Ryan, *Adv. Mater.* **2002**, *14*, 845-848; (b) N. Kobayashi, S. Miura, M. Nishimura, H. Urano, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 136-139; (c) P. Tehrani, L. O. Hennerdal, A. L. Dyer, J. R. Reynolds, M. Berggren, *J. Mater. Chem.* **2009**, *19*, 1799-1802.

6 S. Beaupre, A. C. Breton, J. Dumas, M. Leclerc, *Chem. Mater.* 2009, *21*, 1504-1513.

**7** (a) W. C. Dautremont-Smith, *Displays* **1982**, *3*, 3-32; (b) W. C. Dautremont-Smith, *Displays* **1982**, *3*, 67-80; (c) R. J. Mortimer, *Chem. Soc. Rev.* **1997**, *26*, 147-156; (d) R. J. Mortimer, *Electrochim. Acta* **1999**, *44*, 2971-2981; (e) P. S. Somani, S. Radhakrishnan, *Mater. Chem. Phys.* **2002**, *77*, 117-133.

8 (a) G. Sonmez, *Chem. Commun.* 2005, *42*, 5251-5259; (b) A. Patra, M. Bendikov, *J. Mater. Chem.* 2010, *20*, 422-433; (c) P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* 2010, *110*, 268-320; (d) G. Gunbas, L. Toppare, *Chem. Commun.* 2012, *48*, 1083-1101.

9 (a) M. A. Invernale, Y. Ding, D. M. D. Mamangun, M. S. Yavus, G. A. Sotzing, *Adv. Mater.* 2010, *22*, 1379-1382; (b) M. Icli, M. Pamuk, F. Algi, A. M. Onal, A. Cihaner, *Chem. Mater.* 2010, *22*, 4034-4044; (c) S. Koyuncu, O. Usluer, M. Can, S. Demic, S. Icli, N. Serdar, *J. Mater. Chem.* 2011, *21*, 2684-2693; (d) F. Baycan Koyuncu, E. Sefer, S. Koyuncu, E. Ozdemir, *Macromolecules* 2011, *44*, 8407-8414; (e) T. Dey, M. Invernale, Y. Ding, Z. Buyukmumcu, G. A. Sotzing, *Macromolecules* 2011, *44*, 2415-2417; (f) D. M. Chao, X. T. Jia, H. T. Liu, L. B. He, L. L. Cui, C. Wang, E. B. Berda, *J. Polym. Sci. Part A: Polym. Chem.* 2011, *49*, 1605-1614; (g) X. T. Jia, D. M. Chao, H. T. Liu, L. B. He, T. Zhang, X. J. Bian, C. Wang, *Polym. Chem.* 2011, *2*, 1300-

1306; (h) C. J. Yao, Y. W. Zhong, J. N. Yao, *Inorg. Chem.* **2013**, *52*, 10000-10008; (i) M. Li, Y. X. Wei, J. M. Zhang, D. Zhu, C. Y. Xu, *Org. Electron.* **2014**, *15*, 428-434.

**10** (a) M. Thelallat, *Macromol. Mater. Eng.* **2002**, *287*, 442-461; (b) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953-1010.

**11** (a) M.-Y. Chou, M.-K. Leung, Y. O. Su, C.-L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo, C.-Y. Mou, *Chem. Mater.* **2004**, *16*, 654-661; (b) S. Beaupre, J. Dumas, M. Leclerc, *Chem. Mater.* **2006**, *18*, 4011-4018; (c) J. Natera, L. Otero, F. D'Eramo, L. Sereno, F. Fungo, N.-S. Wang, Y.-M. Tsai, K.-T. Wong, *Macromolecules* **2009**, *42*, 626-635.

12 (a) H.-J. Yen, H.-Y. Lin, G.-S. Liou, *Chem. Mater.* 2011, *23*, 1874-1882; (b) H.-J. Yen, K.-Y. Lin, G.-S. Liou, *J. Mater. Chem.* 2011, *21*, 6230-6237; (c) H.-J. Yen, G.-S. Liou, *Polym. Chem.* 2012, *3*, 255-264; (d) H.-J. Yen, G.-S. Liou, *Chem. Commun.* 2013, *49*, 9797-9799; (e) H.-J. Yen, C.-J. Chen, G.-S. Liou, *Adv. Funct. Mater.* 2013, *23*, 5307-5316.

**13** (a) G.-S. Liou, C.-W. Chang, *Macromolecules* **2008**, *41*, 1667-1674; (b) C.-W. Chang, C.-H. Chung, G.-S. Liou, *Macromolecules* **2008**, *41*, 8441-8451; (c) C.-W. Chang, G.-S. Liou, *J. Mater. Chem.* **2008**, *18*, 5638-5646; (d) H.-J. Yen, G.-S. Liou, *Chem. Mater.* **2009**, *21*, 4062-4070.

**14** (a) C. Lambert, G. Noll, *Angew. Chem. Int. Ed.* **1998**, *37*, 2107-2110; (b) C. Lambert, G. Noll, *J. Am. Chem. Soc.* **1999**, *121*, 8434-8442; (c) C. Lambert, G. Noll, *Synth. Met.* **2003**, *139*, 57-;62.

**15** H.-J. Yen, S.-M. Guo, G.-S. Liou, J.-C. Chung, Y.-C. Liu, Y.-F. Lu, Y.-Z. Zeng, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3805-3816.

**16** (a) M. Faccini, M. Balakrishnan, M. B. J. Diemeer, R. Torosantucci, A. Driessen, D. N. Reinhoudt, W. Verboom, *J. Mater. Chem.* **2008**, *18*, 5293-5300; (b) Y.-H. Liu, C. Chen, L.-M. Yang, *Tetrahedron Lett.* **2006**, *47*, 9275–9278.

**17** N. Yamazaki, M. Matsumoto, F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 1373-1380.

