

High T_g , Ambipolar, and Near-Infrared Electrochromic Anthraquinone-Based Aramids with Intervalence Charge-Transfer Behavior

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ABSTRACT: Two novel series of ambipolar and near-infrared electrochromic aromatic polyamides with electroactive anthraquinone group were synthesized from new aromatic diamines, 2-(bis(4-aminophenyl)amino)anthracene-9,10-dione and 2-(4-(bis(4-aminophenyl)amino)phenoxy)anthracene-9,10-dione, respectively, via low-temperature solution polycondensation reaction. These polymers were readily soluble in many polar solvents and showed useful levels of thermal stability associated with high

glass-transition temperatures (T_g) (285–360 °C). Electrochemical studies of these electrochromic polyamides revealed ambipolar behavior with reversible redox couples and high contrast ratio both in the visible range and near-infrared region. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 50: 61–69, 2012

KEYWORDS: electrochemistry; functionalization of polymers; high performance polymers; polyamides

INTRODUCTION Electrochromic materials exhibit a reversible optical change in absorption or transmittance upon electrochemically oxidized or reduced, such as transition-metal oxides, inorganic coordination complexes, conjugated polymers, and organic molecules.¹ Despite the fact that the earliest electrochromic devices are mostly based on inorganic oxides, nevertheless, the organic compounds have several advantages over the former ones, such as processability, high coloration efficiency, fast switching ability, and multiple colors within the same material. Initially, investigation of electrochromic materials has been directed towards optical changes in the visible region (e.g., 400–800 nm), demonstrated useful and variable applications such as E-paper, optical switching devices, smart window, and camouflage materials.² Increasingly, attention of the optical changes has been focused extending from the near infrared (NIR; e.g., 800–2000 nm) to the microwave regions of the spectrum, which could be exploitable for optical communication, data storage, and thermal control (heat gain or loss) in buildings and spacecraft.³ Therefore, NIR electrochromic materials including organic metal complex (ruthenium dendrimer) and organic materials have been investigated in recent years.⁴ Wang and Wan^{4(c-i)} made efforts on the design of anthraquinone-containing cathodically electrochromic materials, which revealed high absorption in the NIR region upon electrochemical reduction. Reynolds^{5(ab)} and Wudl^{5(c,d)} reported different approach of color-to-transmissive NIR electrochromic conjugated polymers, and their devices exhibited colors in

neutral state and near transmissive in the visible-light region at the oxidized state.

Anthraquinone (AQ)-containing molecules were used in biochemical applications because of the anti-cancer behaviors and conjugated polymers as an electron acceptor unit due to the strong electron withdrawing characteristic.⁶ Recently, anthraquinone derivatives were studied to be cathodically electrochemical materials because of the anthraquinone moiety offers a high reversibility during electrochemical reduction.⁷ So far, the electrochromic properties of anthraquinone have not received much attention except a few researches about polyanthraquinones and anthraquinone imides.^{4(c-i),8}

Triarylamine derivatives are well known as its photo- and electroactive properties that have potentials for optoelectronic applications, such as photoconductors, hole-transporters, light-emitters, and memory devices.⁹ Electron-rich triaryl amines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a noticeable change of coloration. Thus, studies of the synthesis and electrochromism of triarylamine-based polymers have been reported in the literature.¹⁰ Since 2005, our groups have initiated some high-performance polymers (e.g., aromatic polyamides and polyimides) bearing the triarylamine unit as an electrochromic functional moiety.¹¹ It has also been reported in our previous publications¹² that the incorporation of electron-donating substituents at the *para*-position of phenyl groups on the electrochemically active

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sites of the triphenylamine (TPA) unit resulted in stable TPA cationic radicals and decreased oxidation potential, leading to a significantly enhanced redox and electrochromic stability of the prepared polymers.

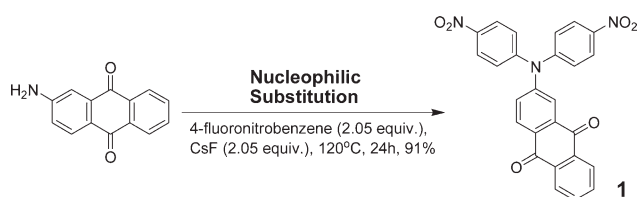
In this article, we therefore synthesized the novel AQ-based monomers, 2-(bis(4-aminophenyl)amino)anthracene-9,10-dione and 2-(4-(bis(4-aminophenyl)amino)phenoxy)anthracene-9,10-dione, and their derived polyamides containing electroactive TPA and AQ groups which could not only exhibit ambipolar character but also reveal high absorbance in visible and NIR regions during reduction procedure. It is well known that the aromatic polyamides as microelectronic materials have attracted great interests due to their outstanding thermal and mechanical resistance.¹³ Incorporation of packing-disruptive TPA and AQ units into polyamides not only preserves high thermal stability, glass transition temperature, and the solubility for enhancing the film-forming ability which is beneficial for their fabrication of large-area, thin-film electrochromic devices but also provides the electroactive center to facilitate both processing and electrochromic applications. We anticipated that the prepared polyamides should be stable for multiple electrochromic switching, improving optical response times, and enhancing CE with high NIR contrast.

EXPERIMENTAL

Materials

4-(Bis(4-nitrophenyl)amino)phenol¹⁴ was prepared according to the reported literature. Commercially available diacid chlorides such as isophthaloyl dichloride (**5I**) and terephthaloyl dichloride (**5T**) were purchased from Tokyo Chemical Industry (TCI) Co. and used as received. Tetrabutylammonium perchlorate (TBAP) (ACROS) were recrystallized twice by ethyl acetate under nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Monomer Synthesis

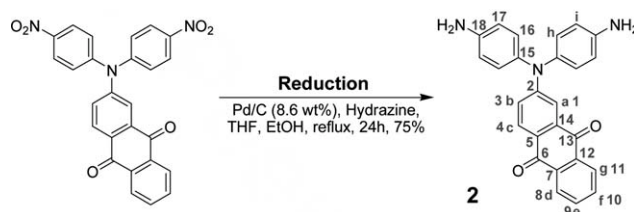


2-(bis(4-nitrophenyl)amino)anthracene-9,10-dione (**1**)

A mixture of 7.86 g (51.75 mmol) of cesium fluoride in 39 mL dimethyl sulfoxide (DMSO) was stirred at room temperature. To the mixture 5.63 g (25.24 mmol) of 2-aminoanthraquinone and 7.30 g (51.75 mmol) of 4-fluoronitrobenzene were added in sequence. The mixture was heated with stirring at 120 °C for 24 h and slowly poured into 150 mL of stirred methanol. The product was filtered to afford 10.69 g (91% in yield) of yellow powders with a mp of 247–248 °C (by Melting Point System at a scan rate of 1 °C/min). IR (KBr): 1,520, 1,340 cm⁻¹ (—NO₂ stretch).

¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 7.38 (m, 4H), 7.66 (m, 1H), 7.81 (d, *J* = 2.4 Hz, 1H), 7.93 (m, 2H), 8.15 (m, 1H),

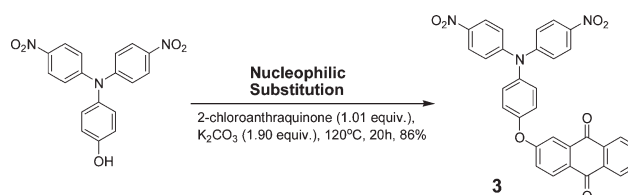
8.21 (m, 2H), 8.26 (m, 4H) ¹³C NMR (125 MHz, DMSO-*d*₆, δ , ppm): 121.4, 124.6, 125.7, 126.7, 129.2, 129.3, 129.7, 132.8, 132.9, 134.4, 134.7, 143.4, 150.0, 150.7, 181.1, 181.9. Anal. C₂₆H₁₅N₃O₆ (465.41): C, 67.10 %; H, 3.25 %; N, 9.03 %. Found: C, 67.11 %; H, 3.41 %; N, 8.94 %. ESI-MS: calcd for (C₂₆H₁₅N₃O₆)⁺: *m/z* 465.4 found: *m/z* 465.1.



2-(bis(4-aminophenyl)amino)anthracene-9,10-dione (**2**)

In a 100-mL three-neck round-bottomed flask equipped with a stirring bar under nitrogen atmosphere, 2.33 g (5.00 mmol) of dinitro compound **1** and 0.20 g of 10 % Pd/C were dispersed in 5 mL of ethanol and 20 mL THF. The suspension solution was heated to reflux, and 1.5 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 1.51 g (75 % in yield) of purple powder with a mp of 296–297 °C (by melting point system at a scan rate of 1 °C/min).

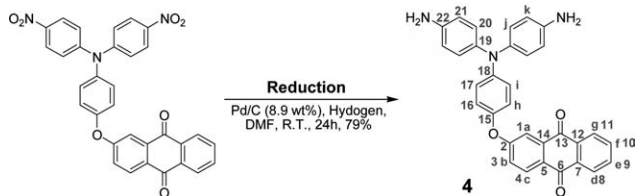
FTIR (KBr): 3470, 3380 cm⁻¹ (N—H stretch). ¹H NMR (500 MHz, DMSO-*d*₆, δ , ppm): 5.23 (s, 4H, —NH₂), 6.63 (d, *J* = 8.5 Hz, 4H, H_i), 6.88 (dd, 1H, H_b), 6.98 (d, *J* = 8.5 Hz, 4H, H_h), 7.21 (d, *J* = 2.5 Hz, 1H, H_a), 7.82 (t, 1H, H_e), 7.88 (t, 1H, H_f), 7.92 (d, *J* = 8.8 Hz, 1H, H_c), 8.07 (d, *J* = 7.5 Hz, 1H, H_d), 8.14 (d, *J* = 7.5 Hz, 1H, H_g). ¹³C NMR (125 MHz, DMSO-*d*₆, δ , ppm): 110.6, 114.9, 118.6, 122.0, 126.4, 126.5, 128.0, 129.1, 133.0, 133.3, 133.5, 133.6, 134.2, 134.5, 180.1, 183.1. Anal. Calcd (%) for C₂₆H₁₉N₃O₂ (405.45): C, 77.02; H, 4.72; N, 10.36. Found: C, 76.51; H, 4.76; N, 10.36. ESI-MS: calcd for (C₂₆H₁₉N₃O₂)⁺: *m/z* 405.4; found: *m/z* 405.1.



2-(4-(bis(4-nitrophenyl)amino)phenoxy)anthracene-9,10-dione (**3**)

A mixture of 5.07 g (36.7 mmol) of potassium carbonate in 40 mL dimethyl sulfoxide (DMSO) was stirred at room temperature. To the mixture 4.73 g (19.5 mmol) of 2-chloroanthracene-9,10-dione and 6.79 g (19.3 mmol) of 4-(bis(4-nitrophenyl)amino)phenol were added in sequence. The mixture was heated with stirring at 120 °C for 20 h and slowly poured into 300 mL methanol/water (2:1). The product was purified by THF to afford 9.33 g (86 % in yield) of yellow powders with a mp of 131–133 °C (by Melting Point System at a scan rate of 1 °C/min).

IR (KBr): 1,575, 1,310 cm^{-1} ($-\text{NO}_2$ stretch). ^1H NMR ($\text{DMSO}-d_6$, δ , ppm): 7.26 (m, 4H), 7.33 (d, $J = 9.0$ Hz, 2H), 7.40 (d, $J = 9.0$ Hz, 2H), 7.58 (m, 1H), 7.68 (d, $J = 2.6$ Hz, 1H), 7.93 (m, 2H), 8.21 (m, 6H), 8.27 (d, $J = 8.5$ Hz, 1H). ESI-MS: calcd for $(\text{C}_{32}\text{H}_{19}\text{N}_3\text{O}_7)^+$: m/z 557.5 found: m/z 557.3.



2-(4-(bis(4-aminophenyl)amino)phenoxy)anthracene-9,10-dione (**4**)

In a 100-mL three-neck round-bottomed flask equipped with a stirring bar, 3.92 g (7.00 mmol) of dinitro compound **3** was dissolved in 43 mL DMF at room temperature, and 0.35 g of 10 % Pd/C were added in solution. The suspension solution was stirred under hydrogen atmosphere at room temperature. After a further 24 h of reaction, the solution was filtered to remove Pd/C, and the filtrate was slowly poured into 300 mL methanol/water (1:1). The product was collected by filtration and dried *in vacuo* at 80 $^{\circ}\text{C}$ to give 2.75 g (79 % in yield) of brown powder with mp of 243–244 $^{\circ}\text{C}$ (by Melting Point System at a scan rate of 1 $^{\circ}\text{C}/\text{min}$).

FT-IR (KBr): 3,400, 3,200 cm^{-1} (N-H stretch). ^1H NMR (500 MHz, $\text{DMSO}-d_6$, δ , ppm): 5.00 (s, 4H, $-\text{NH}_2$), 6.58 (d, $J = 8.5$ Hz, 4H, H_k), 6.69 (d, $J = 9.0$ Hz, 2H, H_i), 6.89 (d, $J = 8.5$ Hz, 4H, H_j), 6.95 (d, $J = 9.0$ Hz, 2H, H_h), 7.42 (dd, 1H, H_b), 7.46 (d, $J = 2.6$ Hz, 1H, H_a), 7.90 (m, 2H, H_{e+f}), 8.14 (dd, 1H, H_c), 8.17 (m, 2H, H_{g+d}). ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, δ , ppm): 112.1, 114.8, 117.3, 121.1, 122.1, 126.6, 126.7, 127.2, 127.3, 129.8, 132.9, 134.1, 134.5, 135.0, 135.7, 144.9, 145.7, 147.4, 181.1, 182.0. Anal. Calcd (%) for $\text{C}_{32}\text{H}_{23}\text{N}_3\text{O}_3$ (497.54): C, 77.25; H, 4.66; N, 8.45. Found: C, 77.08; H, 4.64; N, 8.35. ESI-MS: calcd for $(\text{C}_{26}\text{H}_{19}\text{N}_3\text{O}_2)^+$: m/z 497.5; found: m/z 497.2.

Polymer Synthesis

The synthesis of polyamide **AQ-T** was used as an example to illustrate the general synthetic route used to produce the polyamides. A solution of 0.20 g (0.5 mmol) of **2** in 1.5 mL of NMP was cooled to -25 to -30 $^{\circ}\text{C}$ on a ice/acetone bath. After 0.16 mL of propylene oxide was added to the mixture, 0.10 g (0.5 mmol) of **5T** was added in to the mixture. The mixture was then stirred at -10 $^{\circ}\text{C}$ for 1 h then room temperature for 2 h. The solution was poured slowly into 200 mL of methanol. The precipitated polymer was collected by filtration, and dried at 100 $^{\circ}\text{C}$. Reprecipitations of the polymer by *N,N*-dimethylacetamide (DMAc)/methanol were carried out twice for further purification. The yield of the polymer was 0.28 g (98%). The inherent viscosity and weight-average molecular weights (M_w) of the obtained polyamide **AQ-T** were 0.62 dL/g (measured at a concentration of 0.5 g/dL in DMAc at 30 $^{\circ}\text{C}$) and 117,700 daltons, respectively. The FT-IR spectrum of **AQ-T** (film) exhibited characteristic amide absorption bands at 3,315 cm^{-1} (N-H stretch), 3,065 cm^{-1} (aromatic C-H stretch), 1,670 cm^{-1} (amide carbonyl).

Preparation of the Films

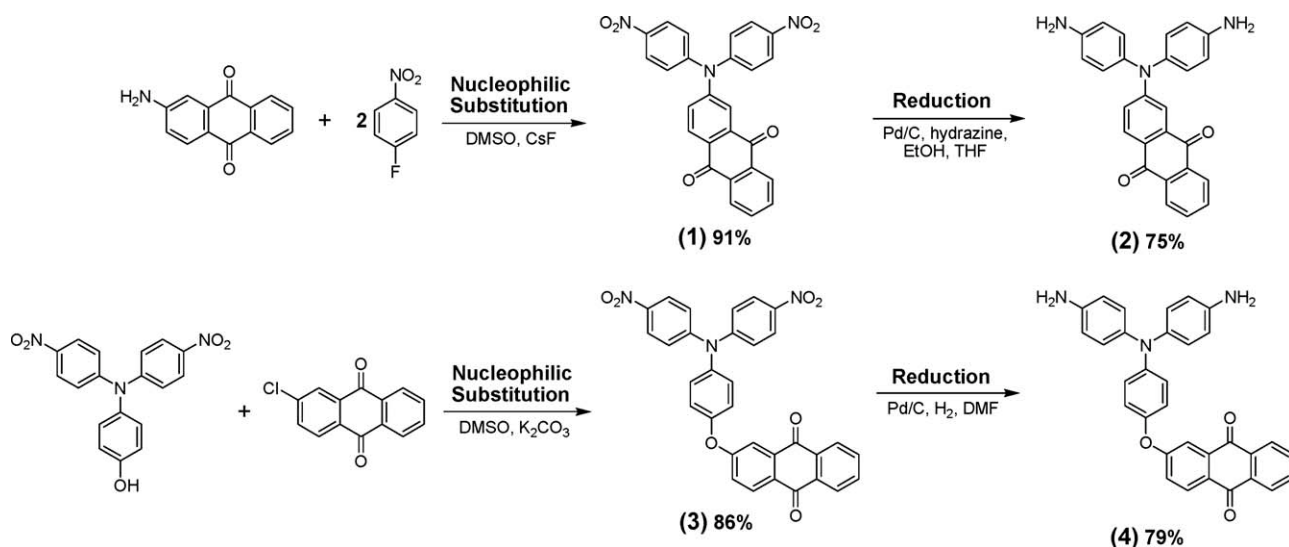
A solution of the polymer was made by dissolving about 0.3 g of the polyamide sample in 9 mL of DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 $^{\circ}\text{C}$ oven for 5 h to remove most of the solvent; then the semi-dried film was further dried *in vacuo* at 170 $^{\circ}\text{C}$ for 8 h. The obtained films were about 40–60 μm thick and were used for solubility tests, and thermal analyses.

Fabrication of the Electrochromic Device

Electrochromic polymer films were prepared by dropping solutions of the polyamide **OAQ-T** (4 mg/mL in DMAc) onto a ITO coated glass substrate (20 $\times$ 30 $\times$ 0.7 mm, 50–100 Ω/square). The polymers were drop-coated onto an active area (about 20 mm $\times$ 20 mm) then dried in vacuum. A gel electrolyte based on PMMA (M_w : 350000) and LiClO_4 was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (3 g) was dissolved in dry acetonitrile (15 g), and LiClO_4 (0.3 g) was added to the polymer solution as supporting electrolyte. Then, propylene carbonate (5 g) was added as plasticizer. 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.

Measurements

Infrared spectra were recorded on a PerkinElmer RXI FT-IR spectrometer. Elemental analyses were run in an Elementar Vario EL-III. ^1H and ^{13}C NMR spectra were measured on a Bruker AVANCE-500 FT-NMR using tetramethylsilane as the internal standard, and peak multiplicity was reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The inherent viscosities were determined at 0.5 g/dL concentration using Tamson TV-2000 viscometer at 30 $^{\circ}\text{C}$. Gel permeation chromatographic (GPC) analysis was performed on a Lab Alliance RI2000 instrument (one column, MIXED-D from Polymer Laboratories) connected with one refractive index detector from Schambeck SFD GmbH. All GPC analyses were performed using a polymer/DMAc solution at a flow rate of 1 mL/min at 70 $^{\circ}\text{C}$ and calibrated with polystyrene standards. Thermogravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6–8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 $^{\circ}\text{C}/\text{min}$. DSC analyses were performed on a Perkin-Elmer Pyris 1 DSC at a scan rate of 20 $^{\circ}\text{C}/\text{min}$ in flowing nitrogen (20 cm^3/min). Electrochemistry was performed with a CH Instruments 612C 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 ITO (polymer films area about 0.5 cm $\times$ 1.2 cm) was used as a working electrode and a platinum wire as an auxiliary electrode at a scan rate of 50 mV/s against a Ag/AgCl reference electrode in anhydrous acetonitrile (CH_3CN) and dimethylformamide (DMF), using 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte under a nitrogen atmosphere. All cell



SCHEME 1 Synthesis route to diamine monomers **2** and **4**.

potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-visible cuvette using Hewlett-Packard 8453 UV-Visible diode array spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. CE (η) determines the amount of optical density change (δOD) at a specific absorption wavelength induced as a function of the injected/ejected charge (Q) which is determined from the *in situ* experiments. CE is given by the equation: $\eta = \delta OD/Q = \log[T_b/T_c]/Q$, where η (cm^2/C) is the coloration efficiency at a given wavelength, and T_b and T_c are the bleached and colored transmittance values, respectively. The thickness of the polyamide thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcoorder ET3000, Japan). Colorimetric measurements were obtained using JASCO V-650 spectrophotometer and the results are expressed in terms of lightness (L^*) and color coordinates (a^* , b^*).

RESULTS AND DISCUSSION

Monomer and Polymer Synthesis

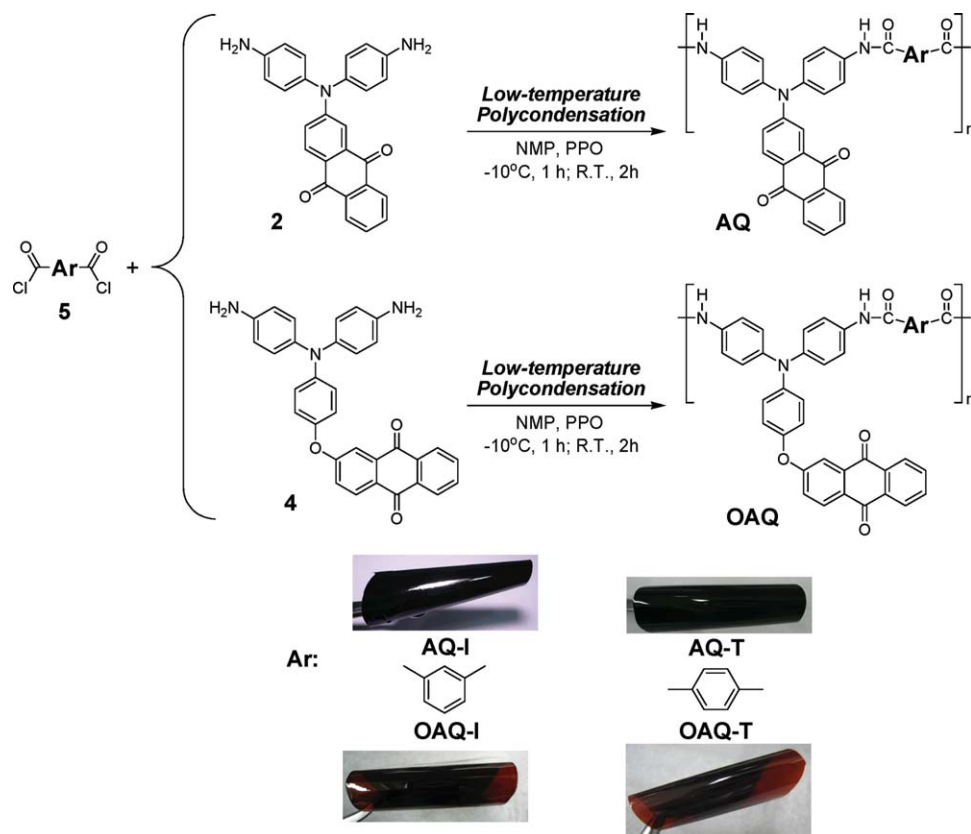
The new AQ-based diamine monomer 2-(bis(4-aminophenyl)amino)anthracene-9,10-dione (**2**) was prepared by the CsF-mediated nucleophilic displacement reaction of 2-aminoanthraquinone with 4-fluoronitrobenzene followed by hydrazine Pd/C-catalytic reduction (Scheme 1). The diamine 2-(4-(bis(4-aminophenyl)amino)phenoxy)anthracene-9,10-dione (**4**) with a bulky pendent anthraquinone unit was successfully synthesized by Pd/C-catalyzed reduction of the aromatic dinitro compound 2-(4-(bis(4-nitrophenyl)amino)phenoxy)anthracene-9,10-dione (**3**) as shown in Scheme 1. Elemental analysis, FT-IR, and NMR spectroscopy were used to identify structures of the intermediate dinitro compound **1** and the target diamine monomer **2**. The FT-IR spectra of these two synthesized compounds are illustrated in Supporting Information Figure S1. The nitro groups of compounds

showed characteristic bands at around 1520 and 1340 cm^{-1} due to NO_2 asymmetric and symmetric stretching. After reduction to diamine monomers, the characteristic absorption bands of the nitro group disappeared and the primary amino group revealed the typical absorption pair at 3470 and 3380 cm^{-1} (N-H stretching). The ^1H , ^{13}C , and two-dimensional (2D) HMQC NMR spectra of the diamine monomers **2** and **4** are illustrated in Supporting Information (Figs. S1–S3) and agree well with the proposed molecular structures. Thus, the results of all the spectroscopic and elemental analyses suggest the successful preparation of the target diamine monomer.

Two series of novel polyamides were obtained by the low-temperature solution polycondensation¹⁵ from the diamines and commercial diacid chlorides in NMP in the presence of propylene oxide as an acid acceptor as shown in Scheme 2. All polymerization reactions proceeded homogeneously and gave highly viscous polymer solutions. The obtained polyamides had inherent viscosities in the range of 0.57 – 0.64 dL/g with weight-average molecular weights (M_w) and polydispersity (PDI) of $79,800$ – $117,800$ daltons and 1.25 – 2.17 , respectively, relative to polystyrene standards (Supporting Information Table S1). All the high molecular weights polymers could be cast into transparent and tough films via solution casting. The appearance and quality of these films are also shown in Scheme 2. The structure of the polyamides was confirmed by IR spectroscopy. A typical IR spectrum for polyamide **AQ-T** shown in Supporting Information Figure S4 exhibits characteristic IR absorption bands of the amide group at around 3315 (N-H stretching) and 1670 cm^{-1} (amide carbonyl).

Solubility and Film Property

The solubility behavior of polymers was investigated qualitatively, and the results are listed in Supporting Information Table S2. Most of the polyamides were readily soluble in polar aprotic organic solvents such as *N*-methyl-2-pyrrolidinone



SCHEME 2 Synthesis of polyamides by low-temperature solution polycondensation.

(NMP), *N,N*-dimethylacetamide (DMAc), and *m*-cresol. The polyamides **OAQ** had higher solubility than **AQ** can be attributed to the introduction of the soft segment of ether linkage with bulky pendent anthraquinone-substituted TPA moiety into the repeat unit. The excellent solubility in polar organic solvents makes these polymers as potential candidates for practical applications by spin-coating or inkjet-printing processes to afford high performance thin films for optoelectronic devices.

The thermal properties of polyamides were examined by TGA and DSC, and the thermal behavior data are also summarized in Supporting Information Table S3. Typical TGA curves of representative polyamides **AQ-T** and **OAQ-T** in both air and nitrogen atmospheres are shown in Supporting Information Figure S5. All the prepared polyamides had good thermal stability with insignificant weight loss up to 440 °C under nitrogen or air atmosphere. The 10 % weight loss temperatures of these polymers in nitrogen and air were recorded in the range of 470–495 and 440–490 °C, respectively. The carbonized residue (char yield) of these polymers in a nitrogen atmosphere was more than 60 % at 800 °C. The high char yields of these polymers can be ascribed to their high aromatic content. The glass-transition temperatures (T_g) of polyamides were measured in the DSC thermograms; they were observed in the range of 283–360 °C (as shown in Supporting Information Fig. S6), depending upon the stiffness of the polymer chain. Higher glass transition temperature of these polymers com-

pared to the TPA-based polyamides^{11(b)} can be ascribed to their planar molecular structure and intra-/inter-molecular hydrogen bonding even with the introduction of pendant AQ groups. The lower T_g value of polymers **OAQ** in this series polymers can be explained in terms of the flexible ether linkage in its pendent group.

Electrochemical Properties

The redox behavior of the polyamides were investigated by cyclic voltammetry (CV) conducted for the cast film on an

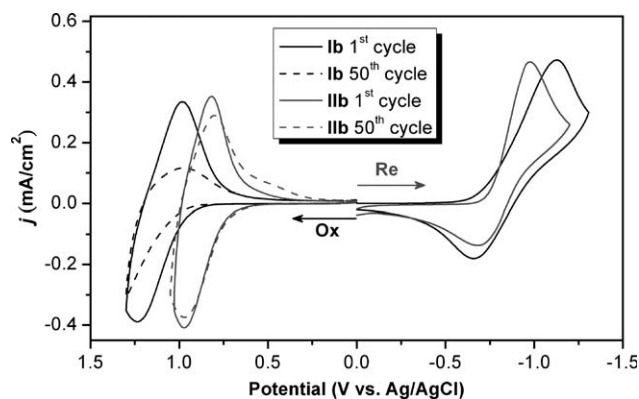


FIGURE 1 Cyclic voltammetric diagrams of polyamide **AQ-T** and **OAQ-T** films on an ITO-coated glass substrate over cyclic scans in 0.1 M TBAP/CH₃CN at a scan rate of 50 mV/s.

TABLE 1 Redox Potentials and Energy Levels of Polyamides

Code	Thin films (nm)		Oxidation ^a		Reduction ^b		E_g^{EC} (eV)	E_g^{Opt} (eV)	$HOMO^{EC}$ (eV) ^c	$LUMO^{Opt}$ (eV)	$LUMO^{EC}$ (eV) ^c
	λ_{max}	λ_{onset}	$E_{1/2}$ (V)	$E_{1/2}$ (V)	E_{re} p,ca						
AQ-I	325	613	1.11	-0.87	-1.79		1.98	2.02	-5.47	-3.45	-3.49
AQ-T	323	610	1.11	-0.82	-1.75		1.93	2.03	-5.47	-3.44	-3.54
OAQ-I	335	438	0.84	-0.84	-1.73		1.68	2.83	-5.20	-2.37	-3.52
OAQ-T	340	447	0.89	-0.78	-1.69		1.67	2.77	-5.25	-2.43	-3.58

E_g^{EC} (Electrochemical band gap): Difference between $HOMO^{EC}$ and $LUMO^{EC}$.

E_g^{Opt} (Optical band gap): Calculated from polymer films ($E_g = 1240/\lambda_{onset}$).

$LUMO^{Opt}$ (LUMO energy levels calculated from optical method): Difference between $HOMO^{EC}$ and E_g^{Opt} .

^a Versus Ag/AgCl in CH_3CN .

^b Versus Ag/AgCl in DMF.

^c The $HOMO^{EC}$ and $LUMO^{EC}$ energy levels were calculated from cyclic voltammetry and were referenced to ferrocene (-4.8 eV; $E_{1/2} = 0.44$ V) and ($E_{1/2} = 0.52$ V), respectively.^{12(h)}

indium-tin oxide (ITO)-coated glass slide as working electrode in anhydrous CH_3CN and DMF, using 0.1 M of TBAP as a supporting electrolyte under a nitrogen atmosphere. The typical CV for polyamides **AQ-T** and **OAQ-T** are shown in Figure 1 and Supporting Information Figure S7 for comparison. The half-wave potentials ($E_{1/2}$) of the reduction process were recorded in the range from -0.78 to -0.87 V due to the reduction of anthraquinone unit. The color of the polyamide **OAQ-T** film changed from pale yellow to red upon electrochemical reduction. The half-wave potentials ($E_{1/2}$) of the oxidation process were found to be around 0.84–1.11 V resulted from the electroactive triarylamine group. The color of the polyamide **OAQ-T** film turned from pale yellow to green upon oxidation. After 50 continuous cyclic scans, the polyamide **AQ-T** (without the ether linkage in pendent group) gradually lost its redox reversibility. This result shows that the introduction of AQ unit on the electron-rich nitrogen atom not only increased the oxidation potential but also decreased electrochemical stability. The other polyamides showed similar CV curves to Figure 1. The redox potentials of the polyamides as well as their respective highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the corresponding polymers can be determined from the oxidation and reduction half-wave potentials ($E_{1/2}$) and the onset absorption wavelength, and the results were listed in Table 1.

Spectroelectrochemistry

Spectroelectrochemical experiments were used to evaluate the optical properties of the electrochromic films. For the investigations, the polyamide films were cast on an ITO-coated glass slide, and a homemade electrochemical cell was built from a commercial ultraviolet (UV)-visible cuvette. The cell was placed in the optical path of the sample light beam in a UV-vis-NIR spectrophotometer, which allowed us to acquire electronic absorption spectra under potential control in a 0.1 M TBAP/ CH_3CN solution for oxidation and 0.1 M TBAP/DMF solution for reduction, respectively.

The result of polyamide **AQ-T** film is presented in Figure 2(a) as a series of UV-vis-NIR absorbance curves correlated to electrode potentials. In the neutral form (0 V), the film

exhibited strong absorption at 317 nm (triarylamine) and 500 nm (charge-transfer complex formation). Upon oxidation, the intensity of the absorption peak at 317 nm gradually decreased while a new peak at 875 nm gradually increased in intensity. We attribute the spectral change in visible range to the formation of a stable monocation radical of the triarylamine moiety. The polyamide **AQ-T** film

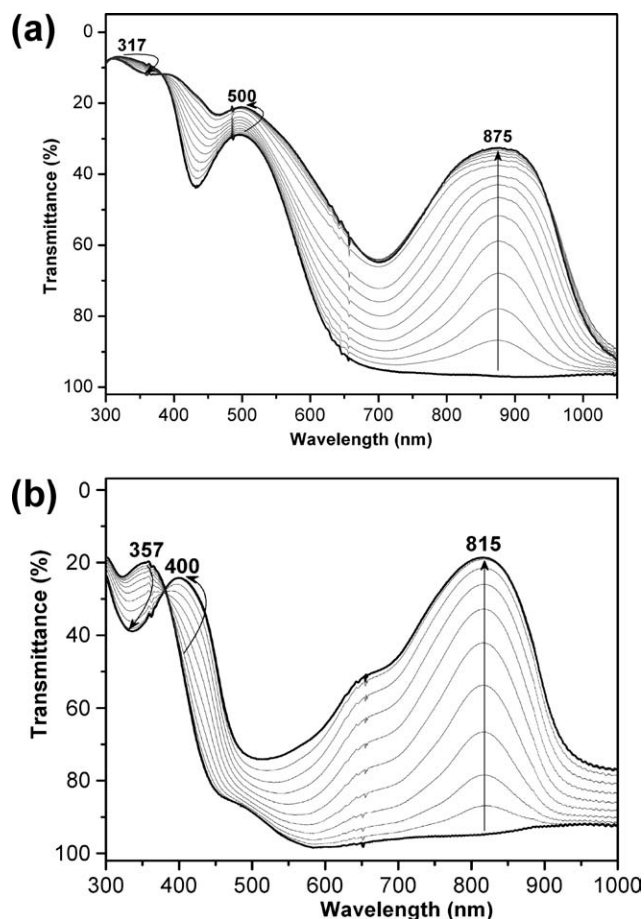


FIGURE 2 Electrochromic behavior of polyamide **AQ-T** (~170 nm) and **OAQ-T** (~80 nm) thin film on the ITO-coated glass substrate (coated area: 1.6 cm × 0.6 cm) in 0.1 M TBAP/ CH_3CN .

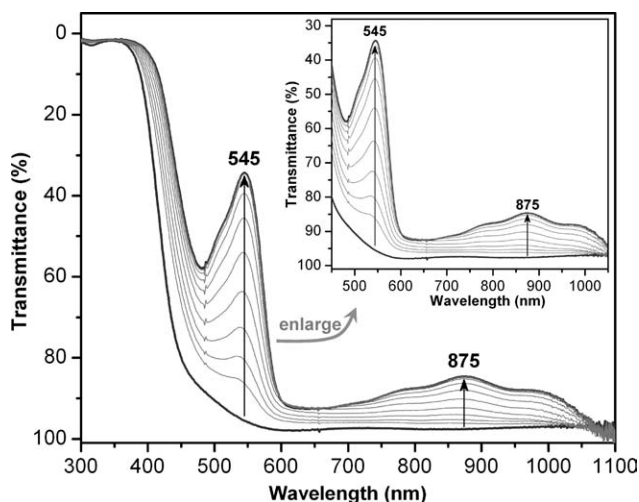


FIGURE 3 UV-vis-NIR spectra of polyamide **OAQ-T** thin film (~ 180 nm in thickness) on the ITO-coated glass substrate (coated area: $1.6\text{ cm} \times 0.6\text{ cm}$) in 0.1 M TBAP/DMF.

switched from a transmissive neutral state (pale-red; L^* , 80.9; a^* , 29.7; b^* , 22.0) to a highly absorbing oxidized state (brown; L^* , 50.5; a^* , 2.9; b^* , 22.0) with a high optical transmittance change ($\Delta\%T$) of 64% at 875 nm.

On the other hand, the spectroelectrochemical behavior of polyamide **OAQ-T** film shown in Figure 2(b) also exhibited strong absorption at around 357 nm in the neutral form (0 V). Upon oxidation (increasing applied voltage from 0 to 1.10 V), the intensity of the absorption peak at 357 nm decreased while a new peak at 400 and 815 nm gradually increased in intensity due to the formation of a stable mono-cation radical of the TPA unit. The polyamide **OAQ-T** film switches from a transmissive neutral state (pale-yellow; L^* , 91.9; a^* , -3.2; b^* , 50.6) to a highly absorbing oxidized state (green; L^* , 51.3; a^* , -23.2; b^* , 23.2) with a high optical transmittance change ($\Delta\%T$) of 76% at 815 nm. Besides, the distribution of coloration across these polymer films was very homogeneous with high electrochemical stability.

Moreover, coloration changes were also observed in these polyamides during reduction procedure as shown in Figure 3. Upon reduction (decreasing applied voltage from 0 to -1.20 V), the absorption of **OAQ-T** film at 545 nm and a broad IV-CT band centered around 875 nm gradually increased in intensity. We attribute the broad absorption around 875 nm was the characteristic result due to IV-CT excitation between states in which the negative charge is located at different oxygen atoms, which was consistent with the phenomenon reported by Wang and Wan.^{4(c-i)} The color of film changed from pale yellow neutral state to a red reduced form (L^* , 45.0; a^* , 27.4; b^* , 19.0), which also exhibited good contrast in the visible region with a high optical transmittance change ($\Delta\%T$) of 61% at 545 nm for red coloring at the reduction stage. This result demonstrated that the incorporation of anthraquinone groups into TPA-based polymers is a new approach for preparing ambipolar and NIR electrochromic materials.

Electrochromic Switching Studies

For electrochromic switching studies, polymer films were cast on ITO-coated glass slides in the same manner as described above, and chronoamperometric and absorbance measurements were performed. While the films were switched, the absorbance at the given wavelength was monitored as a function of time with UV-vis-NIR spectroscopy. Switching data for the representative cast film of polyamide **AQ-T** were shown in Supporting Information Figure S8. 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. As depicted in Supporting Information Figure S8a, polyamide **AQ-T** thin film revealed switching time of 5.5 s at 1.13 V for coloring process at 885 nm and 1.2 s for bleaching, polyamide **OAQ-T** required 5.7 s for coloration at 820 nm at 0.95 V and 1.7 s for bleaching (Supporting Information Fig. S8b). The polyamides switched between the highly transmissive neutral state and the colored oxidized state.

As shown in Supporting Information Figures S9 and S10, the electrochromic stability of the polyamide **AQ-T** and **OAQ-T** was determined by measuring the optical change as a function of the number of switching cycles. The better electrochromic stability of **OAQ-T** could be due to the lower oxidation potential and the isolated ether bond between TPA and AQ groups. The electrochromic CE ($\eta = \delta OD/Q$) and injected charge (electroactivity) after various switching steps were monitored and summarized in Supporting Information Tables S4 and S5. The modern result of these electrochromic films was due to the strong electron withdrawing AQ group decreasing the reversibility and stability of the monocation radical form.

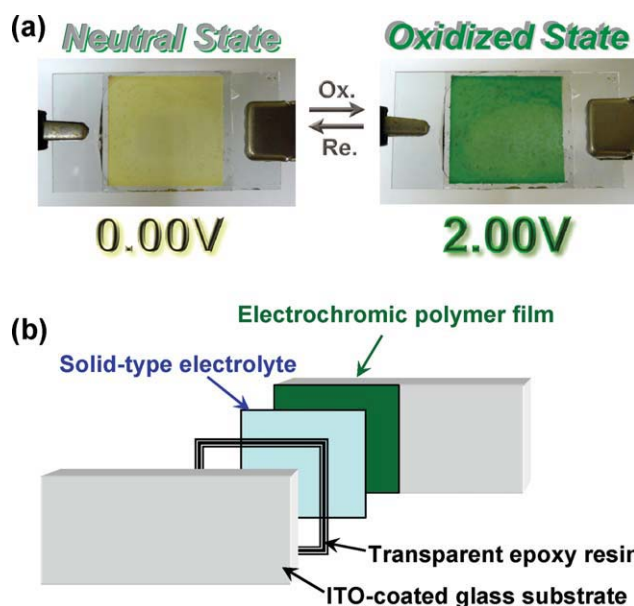


FIGURE 4 (a) Photographs of single-layer ITO-coated glass electrochromic device, using polyamide **OAQ-T** (~ 100 nm in thickness) as active layer. (b) Schematic diagram of polyamide electrochromic device sandwich cell.

Furthermore, a single layer electrochromic cell was fabricated as preliminary investigation (Fig. 4). The polyamide films were spray-coated onto ITO-glass and then dried. Afterwards, the gel electrolyte was spread on the polymer-coated side of the electrode and the electrodes were sandwiched. To prevent leakage, an epoxy resin was applied to seal the device. As a typical example, an electrochromic cell based on polyamide **OAQ-T** was fabricated. The polymer film is pale yellow in neutral form. When the voltage was increased (to a maximum of 2.0 V), the color changed to green due to electro-oxidation, the same as that was already observed in the solution type electrolyte system. When the potential was subsequently set back at 0 V, the polymer film turned back to original pale yellow. We believe that optimization could further improve the device performance and fully explore the potential of these electrochromic polyamides.

CONCLUSIONS

A novel series of electrochromic aromatic polyamides with TPA and AQ units were readily prepared *via* the low-temperature solution polycondensation. In addition to high T_g , thermal stability, and good solubility, all the obtained polymers reveal valuable electrochromic characteristics such as high contrast ratio and low switching times. Thus, these characteristics suggest that the introduction of reduction active anthraquinone group into the polymer side chain could provide the prepared polyamide as potential anodically and cathodically coloring materials.

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