Near-Infrared Electrochromism in Electroactive Pentacenediquinone-Containing Poly(aryl ethers)

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The synthesis and near-infrared electrochromic properties of pentacenediquinone-containing monomers and polymers are reported. The electroactive pentacenediquinone units were incorporated into poly(aryl ethers) in varying degrees by copolymerization. The polymers possessed good thermal stabilities and high glass transition temperatures, and could undergo two reversible steps of electrochemical reduction. Near-infrared electrochromic properties of pentacenediquinone-containing poly(aryl ethers) were studied by spectroelectrochemical analysis, which showed that the radical anions possess intense near-infrared absorption with $\lambda_{\text{max}}$ values between 1331 and 1430 nm, while the dianions also exhibit absorption between 880 and 965 nm. The reduced polymer film displayed intense and broad near-infrared absorption, which was surprisingly stable in air over a long period. The neutral and reduced polymers had electrical conductivity of $1 \times 10^{-9}$ and $3 \times 10^{-3}$ S/cm, respectively.

Introduction

Electrochromism refers to the ability of a material to change its optical properties within the whole electromagnetic spectrum under an applied voltage, such as in the visible region (400–800 nm) and in the near-infrared (NIR) region (e.g., 1000–2000 nm). In addition to applications as smart windows, displays, and storage devices, electrochromic (EC) materials have attracted a great deal of interest for use in devices that operate in the infrared and microwave regions, as well as in various applications such as variable optical attenuators in telecommunications that operate in the NIR region (e.g., near infrared electrochromic; NIEC), as well as in key components (i.e., variable optical attenuators) in optoelectronic devices that operate in the NIR region (e.g., around 1310 and 1550 nm).

Conjugated polymers such as polyanilines and polythiophenes, mixed-valence metal complexes, ruthenium—semiquinone complexes, and conjugated aromatic diquinone mesomeric forms are known to be NIR electrochromic. These EC materials can become highly absorptive in the NIR region upon electrochemical oxidation or reduction. For making a flexible electrochemical device (e.g., electrochromic VOA), both anodically and cathodically NIEC-coloring organic materials are preferably needed. However, n-type organic semiconductors such as quinonones and imides and n-type polymers such as the polythiophenes containing low band gap electron-withdrawing units are less available and less studied than the p-type semiconductors and polymers for optoelectronic applications. Cathodically NIEC-coloring organic and polymeric materials are scarce and difficult to obtain, in part due to relatively poor stability of their charged states (e.g., radical anions of anthraquinone and pentacenedi-quinone).

Pentacenediquinone (PDQ) is reported to undergo four concurrent reduction steps, although the third and fourth reduction steps are not completely reversible or even irreversible. The formation of the radical anion and dianion in the first two reduction steps are generally reversible processes, and the radical anion and dianion species exhibit intense NIR absorptions due to $\pi^*-\pi^*$ excitations. Thus, if properly being functionalized, aromatic diquinones should be ideal candidates or precursors to cathodically NIR-coloring soluble polymers for use in optoelectronic devices for near-infrared applications. Herein we describe the NIR electrochromism and electrical conductivity of several functionalized pentacenediquinone derivatives and the corresponding poly(ary1 ether).

**Experimental Section**

**Materials.** Benzene and toluene were refluxed with sodium and then distilled prior to use. N,N-Dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were dried with P$_2$O$_5$ and distilled. 4,4’-Isopropylidenediphenol (BPA) was purchased from Acros and recrystallized from toluene. Other chemicals were purchased from Aldrich Canada Inc. and Beijing Chemical Reagents Company and were used as received.

**Measurements.** The UV/vis/NIR absorption spectra were recorded on a Lambda 900 Perkin-Elmer spectrophotometer. Infrared spectra of the samples in pressed KBr pellets were recorded on a Bio-Rad FTS 165 FT-IR spectrometer. The $^1$H NMR and $^{13}$C NMR spectra were measured using Bruker-400 ARX-400 or Varian 300 FT-NMR spectrometers. Chemical shifts ($\delta$) are reported in parts per million (ppm) downfield from tetramethylsilane. Melting points were determined on a Fisher-Johns melting point apparatus or by differential scanning calorimetry. Gel permeation chromatography (GPC) measurements were performed on a Waters 2410 instrument equipped with three Waters $\mu$-Styrage columns (10$^5$, 10$^4$, and 10$^3$ Å), using tetrahydrofuran (THF) at a flow rate of 1.0 mL/min at 35 °C. The molecular weights and polydispersities (PDI) were calculated relative to monodisperse polystyrene standards. Thermogravimetric analyses (TGA) of polymer powders were conducted on a TA Instruments SDT 2960 with a heating rate of 10 °C/min and an air flow of 75 cm$^3$/min at 35 °C. The glass transition temperatures of the polymers were measured by differential scanning calorimetry (DSC) on a TA Instruments Q100 using a temperature range from 30 to 280 °C at a heating rate of 10 °C/min under a continuous nitrogen flow.

Cyclic voltammograms were recorded on a BAS 100 electrochemical workstation. The solutions were made in DMF or dimethyl sulfoxide (DMSO) containing 0.1 M tetra-$n$-butylammonium perchlorate (TBAP), tetrabutylammonium hexafluorophosphate (TBAPF$_6$), or lithium perchlorate (LiClO$_4$) and were degassed with nitrogen prior to electrochemical work. Platinum working and counter electrodes were used together with a silver pseudoreference electrode. All the electrochemical measurements were referenced to either the silver/silver ion or ferrocene/ferrocenium (Fe/Ce$^{4+}$) potential, and the potentials were reported relative to NHE. The spectroelectrochemical measurements were performed in an optical transparent thin layer (OTTLE) cell.

To measure the conductivity, thin film was cast from the polymer solution onto an ITO glass (typically 2 × 2 cm$^2$) and dried under nitrogen overnight. To obtain the reduced state, the film was electrochemically reduced in a three-electrode system using a BAS 100 electrochemical workstation and then washed and dried. Four circle gold electrodes of 2 mm diameter were deposited onto the polymer film (in either neutral or reduced state) under a dynamic vacuum of 10$^{-6}$ Torr using a BOC Edwards 500 evaporator. The current—voltage characteristics of the resistance were measured in a probing dark box using a Keithley 236 source meter. The measurements were done at each of the four contacts for each sample, and the data were averaged.

**Difluoro Ketoster (2a and 2b).** Anhydrous ethanol (50 mL) and a mixture of isomeric ketocoids (1a, 1b) (5.00 g, 0.011 mol) were added to a flame-dried flask equipped with a magnetic stirrer and a reflux condenser. The suspension was then added 1 mL of concentrated H$_2$SO$_4$. The reaction mixture was heated to reflux for 48 h. The suspension was allowed to cool to room temperature, and a white crystalline solid precipitated from solution and was collected by suction filtration. After stirring in aqueous NaHCO$_3$ solution, the solids were collected by suction filtration and then stirred in a solution of NaHCO$_3$ for 4 h. The solids were filtered and finally stirred in acetic acid at room temperature for 1 h. After filtration, the product was collected and dried in a vacuum oven at 200 °C for 24 h. Recrystallization from hot nitrobenzene and subsequent sublimation at 450 °C under 10$^{-2}$ Torr afforded 0.430 g (47%) of a yellow precipitate. mp > 400 °C. IR (KBr, cm$^{-1}$): 1682, 1587, 1472, 1401, 1277, 1090, 994, 943, 849, 714, 690, 639. HRMS calcd for C$_2$H$_7$F$_2$O$_4$: 374.0390, found 374.0379.

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(1) mp = 22 Hz), 62.3, 13.6. HRMS calcd for C$_{22}$H$_{30}$F$_{2}$O$_{6}$ 466.1273, found 466.1233.

**Difluoro Ketoester (2b).** mp = 90 °C (DSC). IR (KBr, cm$^{-1}$): 1727, 1680, 1597, 1506, 1410, 1301, 1239, 1154, 1111, 1042, 853, 751. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.55 (s, 1H), 7.81 (dd, $J_1 = 5.6$ Hz, 2H, $J_2 = 3.2$ Hz), 7.72 (s, 1H), 7.36 (t, 2H, $J = 8.8$ Hz), 4.13 (q, 2H, $J = 8.8$ Hz), 1.05 (t, 3H, $J = 7.8$ Hz). $^1$C NMR (100 MHz, DMSO-$d_6$): 193.6, 166.4 ($\delta_{_{_{_{C-F}}} = 254$ Hz), 163.9, 144.4, 132.7 ($\delta_{_{_{_{C-F}}} = 3$ Hz), 132.0 ($\delta_{_{_{_{C-F}}} = 9.6$ Hz), 131.2, 129.6, 126.9, 115.9 ($\delta_{_{_{_{C-F}}} = 22$ Hz). 61.8, 13.3. HRMS calcd for C$_{22}$H$_{30}$F$_{2}$O$_{6}$ 466.1273, found 466.1233.

**Difluoro Ketoacid (1a).** Ester 2a (3.00 g, 0.005 mol), 50 mL of glacial acetic acid, and 5 mL of 48% aqueous HBr solution were added to a 100 mL round-bottomed flask equipped with a magnetic stirrer. The flask was then fitted with a reflux condenser, and the mixture was heated at 120 °C for 48 h. The suspension was allowed to cool to room temperature, and then 10 mL of cold distilled H$_2$O was added to the mixture. The flask was kept on ice for 2 h. The white solid was filtered by suction and then dissolved in aqueous NaHCO$_3$ solution. The resulting solution was filtered to remove any unreacted ester, and the clear filtrate was acidified with HCl until pH 1. The white precipitate was collected and dried under vacuum. The resulting white solid was filtered by suction and then dissolved in aqueous NaHCO$_3$ solution. The resulting solution was filtered to remove any unreacted ester, and the clear filtrate was acidified with HCl until pH 1. The white precipitate was collected and dried under vacuum.

**Difluoro Ketoacid (1b).** Compound 1b was prepared using the same procedure as for 1a. mp = 230 °C (DSC). IR (KBr, cm$^{-1}$): 1701, 1678, 1596, 1526, 1412, 1269, 1253, 1154, 1013, 922, 782. $^1$H NMR (400 MHz, DMSO-$d_6$): 13.7 (s, 1H), 7.95 (s, 1H), 7.84 (dd, 2H, $J_1 = 5.6$ Hz, $J_2 = 3.2$ Hz), 7.37 (t, 2H, $J = 8.8$ Hz). $^1$C NMR (100 MHz, DMSO-$d_6$): 193.6, 166.3 ($\delta_{_{_{_{C-F}}} = 252$ Hz), 165.6, 141.8, 133.2, 133.0, 132.1 ($\delta_{_{_{_{C-F}}} = 9$ Hz), 128.7, 115.9 ($\delta_{_{_{_{C-F}}} = 22$ Hz). HRMS calcd for C$_{22}$H$_{30}$F$_{2}$O$_{6}$ 466.1273, found 460.0612, 410.0612, 466.1233.

**Difluoro Ketoester (2b).** mp = 90 °C (DSC). IR (KBr, cm$^{-1}$): 1727, 1680, 1597, 1506, 1410, 1301, 1239, 1154, 1111, 1042, 853, 751. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 8.55 (s, 1H), 7.81 (dd, $J_1 = 5.6$ Hz, 2H, $J_2 = 3.2$ Hz), 7.72 (s, 1H), 7.36 (t, 2H, $J = 8.8$ Hz), 4.13 (q, 2H, $J = 8.8$ Hz), 1.05 (t, 3H, $J = 7.8$ Hz). $^1$C NMR (100 MHz, DMSO-$d_6$): 193.6, 166.4 ($\delta_{_{_{_{C-F}}} = 254$ Hz), 163.9, 144.4, 132.7 ($\delta_{_{_{_{C-F}}} = 3$ Hz), 132.0 ($\delta_{_{_{_{C-F}}} = 9.6$ Hz), 131.2, 129.6, 126.9, 115.9 ($\delta_{_{_{_{C-F}}} = 22$ Hz). 61.8, 13.3. HRMS calcd for C$_{22}$H$_{30}$F$_{2}$O$_{6}$ 466.1273, found 466.1233.

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oven at 120 °C, compound 6 was obtained as a yellow crystalline solid: 1.10 g (89%), mp > 400 °C with decomposition. IR (KBr, cm⁻¹): 1683, 1592, 1538, 1375, 1316, 1177, 1069, 1006, 887, 851, 710. HRMS calcd for C₂₃H₁₈N₂O₈ 428.0281, found 428.0298. Anal. calcd for C₂₃H₁₈N₂O₈ C 61.69, H 1.88, N 6.54; found C 61.44, H 2.04, N 6.50.

1,8-Bis(4-tert-butylphenoxy)pentacenediquinone (7). Compound 6 (1.07 g, 2.25 mmol), 4-tert-butylphenol (0.75 g, 5.00 mmol), K₂CO₃ (1.38 g, 10.0 mmol), 5 mL of toluene, and 15 mL of DMF were placed together in a 100 mL three-necked flask equipped with a Dean–Stark trap, nitrogen inlet and outlet, and condenser. The mixture was heated to about 120 °C, and the water was removed together with toluene over 2 h. After removal of toluene, the reaction continued at 140 °C overnight. The reaction solution was then cooled to room temperature and poured into water. The desired product (1.25 g, ~100% yield) as crystalline solids was collected by centrifugation and dried in an oven at 85 °C. Analytical sample (1.15 g, 91%) was obtained after further purification by column chromatography (chloroform). mp = 328 °C (DSC). IR (KBr, cm⁻¹): 2961 (υC-H), 1677 (υC=O), 1270 (υC-O). ¹H NMR (400 MHz, CDCl₃): 9.18 (2H, s), 8.18 (2H, dd, J₁ = 7.0 Hz, J₂ = 1.0 Hz), 7.72 (2H, t, J = 7.0 Hz), 7.34 (2H, dd, J₂ = 1.0 Hz, J₃ = 8.3 Hz), 7.42 (4H, d), 7.34 (2H, dd, J₂ = 1.0 Hz, J₃ = 8.3 Hz), 7.04 (4H, d), 1.34 (18H, s). MS (EI, m/z): 634 (M⁺). ¹³C NMR (100 MHz, CDCl₃): 181.6, 180.1, 158.4, 153.5, 147.2, 137.4, 135.9, 135.4, 135.1, 127.0, 126.8, 125.7, 122.6, 118.7, 34.3, 31.3. HRMS calcd for C₂₂H₁₄O₈ C 61.69, H 1.88, N 6.54; found C 61.44, H 2.04, N 6.50.

General Procedure for Polymerization. Compound 6 (0.193 g, 0.450 mmol), bis(4-fluorophenyl)sulfone (0.457 g, 1.80 mmol), BPA (0.514 g, 2.25 mmol), K₂CO₃ (0.742 g, 37.0 mmol), 14 mL of toluene, the reaction continued at 140 °C overnight. The desired product (1.25 g, 91%) was obtained after further purification by column chromatography (chloroform). mp = 328 °C. After 3 h, the polymer product was obtained in quantitative yield after precipitation with methanol.

### Results and Discussion

#### Model Compounds and Monomers

Pentacenediquinone has two positions on its terminal benzo units for substitution. The substitutions at the 1- and 2-positions may potentially lead to PDQ derivatives possessing quite different physical and optical properties. Incorporation of PDQ into a polymer such as poly(aryl ether) can be done via either the α- or β-positions, depending on the availability of the required PDQ monomers. Thus, derivatization of PDQ initially focused on the introduction of functional groups that are good leaving groups (e.g., fluoro and nitro) in aromatic nucleophilic displacement polymerization, at 1,8-, 2,9-, and 2,10-positions of PDQ. To functionalize PDQ with fluoro groups, it was also of interest to synthesize PDQ derivatives with the functional groups at the 1,8-positions. Thus, the dinitro derivative ⁶ existed as a mixture of isomers when a mixture of 3a and 3b was employed in the reaction. It is certainly conceivable that PDQ can be introduced into a variety of poly(aryl ether)s using either 3a or 3b or a mixture of both by direct polycondensation with bisphenols. Alternatively, the polymer product was obtained in quantitative yield after precipitation with methanol.

- **Results and Discussion**

  **Monomers and Model Compounds**

  Pentacenediquinone (PDQ) is a well-known class of molecules with a variety of potential applications. However, the synthesis of PDQ derivatives with functional groups at the 1,8-positions has been limited due to the complexity of the reaction. One approach to overcome this challenge is to use poly(aryl ether) monomers, which can be readily prepared using the ketoesters as a better candidate to prepare polymers, since it was more remained in solution and was obtained after removal of ethanol. Each of the two esters was subsequently hydrolyzed to the corresponding acid (1a or 1b) using a solution of 48% HBr in acetic acid and then cyclized to give 2,9-difluoropentacenediquinone (3a) or 2,10-difluoropentacenediquinone (3b). As a model reaction for polymerization, displacement of the fluoro groups with 4-tert-butylphenol was carried out, resulting in the formation of the corresponding ethers 4a and 4b. These ether derivatives were obtained as solid products by reaction of 3a or 3b, or as a mixture of isomers when a mixture of 3a and 3b was employed in the reaction. It is certainly conceivable that PDQ can be introduced into a variety of poly(aryl ether)s using either 3a or 3b or a mixture of both by direct polycondensation with bisphenols. Alternatively, the same poly(aryl ether) could also be prepared via their precursor monomers, which should be easily prepared using the ketoesters as a better candidate to prepare polymers, since it was more...
correlation curve calibrated using the model compound content in the polymers was readily determined from the incorporated into the polymers (Table 1). The actual PDQ merizations in amounts ranging from 5 to 25%, and there fluorophenyl)sulfone were adjusted in order to incorporate standards by GPC analysis (see Supporting Information) were.

The weight-average molecular weights relative to polystyrene and further indirectly confirmed by elemental analysis of the sulfur content in the polymers (see Supporting Information). The thermal stability of the polymers was determined using thermogravimetric analysis, and it was found that the polymers were all stable to temperatures in excess of 300 °C in air. The glass transition temperatures \( T_g \) of the polymers were determined by DSC, and there was a strong correlation between the \( T_g \) values and the amount of monomer 6 incorporated into the polymers. The \( T_g \) increased from 196 to 246 °C linearly according to an increase of the PDQ content in the polymers from 6.9 to 26% (see Supporting Information).

**Electrochemical and Electrochromic Studies in Solution.** The electrochemical properties of the monomers and PDQ-containing polymers were examined using cyclic voltammetry (CV) in THF containing polystyrene standards. \( ^1 \) From GPC measurements in THF using polystyrene standards. \( ^2 \) The onset temperature for 5% weight loss in air. \( ^3 \) Intrinsic viscosity of the polymers in THF for polymers 8a–8c and DMF for polymer 8d.

readily available as one isomer than the former in large quantity and its 1,8-linkage may lead to more soluble polymers due to a larger kink. Compound 6 was repeatedly recrystallized, and its purity was confirmed by elemental analysis.

**PDQ-Containing Poly(aryl ether)s.** Polymerizations of monomer 6, bis(4-fluorophenyl)sulfone, and BPA were carried out in DMAC in the presence of potassium carbonate as a base to yield the corresponding PDQ-containing poly-(aryl ethers) 8a–8d. The ratios of monomers 6 and bis(4-

fluorophenyl)sulfone were adjusted in order to incorporate varying amounts of the electroactive PDQ groups in the resulting polymers. Monomer 6 was added into the polymerizations in amounts ranging from 5 to 25%, and there was a good correlation with the amounts that were actually incorporated into the polymers (Table 1). The actual PDQ content in the polymers was readily determined from the correlation curve calibrated using the model compound 7 and further indirectly confirmed by elemental analysis of the sulfur content in the polymers (see Supporting Information).

The weight-average molecular weights relative to polystyrene standards by GPC analysis (see Supporting Information) were in a range of \( 1.0 \times 10^4 \) to \( 2.0 \times 10^4 \) with the polydispersity indices ranging from 1.7 to 3.4 for the polymer samples that were reverse precipitated several times. The GPC results, together with the viscosity data (0.18–0.22 dL/g), indicated that the PDQ-containing polymers had moderate molecular weights. As expected, these polymers exhibited good solubility in THF and chloroform, presumably due to a large kink in the polymer main chain. The thermal stability of the polymers was determined using thermogravimetric analysis, and it was found that the polymers were all stable to temperatures in excess of 300 °C in air. The glass transition temperatures \( T_g \) of the polymers were determined by DSC, and there was a strong correlation between the \( T_g \) values and the amount of monomer 6 incorporated into the polymers. The \( T_g \) increased from 196 to 246 °C linearly according to an increase of the PDQ content in the polymers from 6.9 to 26% (see Supporting Information).

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DMF solutions, which typically showed the maximum peak around 265 nm with a small shoulder around 380 nm. Electrochemical reduction of these pentacenediquinones produced radical anions that exhibited intense absorptions in the NIR region. Upon reduction, the radical anion of pentacenediquinone (5) shows a maximum peak (λ\text{max}) at 1335 nm, while 3 and 4 have their λ\text{max}'s at 1360 and 1331 nm, respectively. In the case of the two isomers of 3, the λ\text{max} position for the semiquinone changes only by 2–5 nm compared with that for the isomeric mixture. For example, the semiquinone from 2,9-difluoropentacenediquinone possesses a maximum at 1355 nm, while for the mixture λ\text{max} is present at 1360 nm. Thus, a mixture of isomeric 3 can be used without separation for the purpose of NIR activity investigations. Compounds 6 and 7, which are substituted at the 1,8-positions, are more red shifted with λ\text{max} values at 1430 and 1396 nm, respectively.

The electrochromic properties of model compound 7 and polymers 8a–8d were compared. Compound 7 was reduced electrochemically to the radical anionic state by applying a potential of −800 mV. The UV/vis/NIR absorption spectrum of the reduced species showed two overlapping peaks in the NIR region of the spectrum centered at 1170 and 1396 nm. The radical anion also possessed two absorption peaks at 273 and 304 nm. Further reduction to the dianionic state was achieved by applying a voltage of −1200 mV to the system. This species also had absorptions in the NIR region. However, they were blue shifted relative to the radical anion to 880 and 965 nm, respectively, while the UV absorptions shifted to 255 and 317 nm, respectively. Application of a more negative bias (−1800 mV) resulted in small peaks around 500 and 600 nm and precipitation of the compound in the OTTLE cell, which did not allow for full characterization of this reduced form. The polymer solutions were also characterized by cyclic voltammetry and the onsets of their absorptions in their NIR spectra. From cyclic voltammetry of the model compound 7, the LUMO for the neutral state is 4.0 eV, while the band gaps for the radical anion and dianion are 0.38 and 0.76 eV, respectively. For the polymers, the LUMO levels for the neutral states were about 4.0 eV and the band gaps for the radical anions were about 0.29 eV. The band gaps based on the absorbance spectra for these compounds were all very similar and were around 0.77 and 1.02 eV for the radical anion and dianion states, respectively.

**Electrochemical and Electrochromic Studies of Polymer Films.** Thin films of the polymers on ITO glass were prepared by casting from the polymer solution (5–10 wt %) in DMF and were subjected to electrochemical and spectroelectrochemical studies. Upon electrochemical reduction, the NIR-absorbing radical anionic state was readily reached. The inset in Figure 2 shows that the solution and solid-state NIR absorptions for polymer 8c are virtually the same, although the peaks in the film are broader. Studies on dynamic attenuation or optical switching were performed using a glass cuvette cell, which contained an ITO glass plate coated with a layer of polymer 8c with a thickness of 400 nm, a solution of TBAP in acetonitrile, a silver reference electrode, and a platinum counter electrode. The optical attenuation was recorded at one of the telecommunication wavelengths (1310 nm) with stepping potentials between −1.5 and +1.5 V. The film displayed a 5.4% change in light transmission or optical attenuation of 0.24 dB with a long switching time of about 25 s due to the noncojugated nature of polymer backbone (Figure 3). Considering the film thickness, the attenuation
power of polymer 8c containing only 17% NIR-active PDQ chromophore is 0.6 dB/μm. For a full response, it needs ~180 s to reach an optical attenuation of 1.1 dB or 2.8 dB/μm at 1310 nm.

It is interesting to find that the electrochemically reduced film of polymer 8c on ITO was surprisingly stable, when left standing in air at ambient temperatures over a long period of time. After an initial loss in the intensity of its NIR absorption at 1310 nm, its optical intensity remained virtually constant over a monitoring period of 7 days (Figure 3). This exceptionally good stability of the radical anions in the solid polymer might be due to the unconfirmed barrier property of this poly(ether ketone/sulfone) toward oxygen, which prevents the oxygen from permeating or diffusing into the polymer film.

Finally, the conductivity of polymer 8c in the neutral and reduced (semiquinone) states was measured. A gold electrode was sputtered onto the polymer film coated on ITO glass. The cross-film conductivity for the neutral film was found to be $1 \times 10^{-6}$ S/cm, while the conductivity of the reduced film was significantly increased to $3 \times 10^{-3}$ S/cm and even higher than that ($10^{-5}$ S/cm) of the sodium-doped conjugated polyquinones derived from the functionalized anthraquinone.14

Conclusions

A new class of electroactive PDQ-containing poly(aryl ether)s are shown to be uniquely NIR electrochromic in the spectral region of interest to telecommunications. The reduced polymer in its radical anionic state shows an exceptional stability in air, strongly absorbs in the near-infrared region, and is also electrically conductive. These PDQ-containing polymers are also interesting and useful candidates for further exploration in optical attenuation and photovoltaics in the NIR region. The results suggest that an electrochromic VOA thin-film device could in principle be constructed using PDQ-containing polymers as an anodically NIR-coloring layer and a cathodically NIR-coloring polymer such as some p-type polythiophenes5a and mixed-valence ruthenium complex materials.6,7 To achieve a large dynamic range, one needs a polymer having a high content of PDQ; to ensure faster switching time, ideally a conjugated polythiophene having the pendent PDQ or a copolymer derived from the functionalized PDQ and a suitable thiophene monomer is required.

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Supporting Information Available: NMR and IR spectra for compound 7 and polymer 8a, DSC, TGA, and GPC traces of polymers 8a–8d, UV–vis calibration curve for determining the PDQ content in polymers, correlation curve of $T_g$ and PDQ content, and sulfur analysis results. This material is available free of charge via the Internet at http://pubs.acs.org.

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