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

Sheng Wang,[†] Erin K. Todd,[‡] Maria Birau,[‡] Jidong Zhang,[‡] Xinhua Wan,*[,†] and
Zhi Yuan Wang*[,†,‡]

Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China, and Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

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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 ether)s 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 ether)s were studied by spectroelectrochemical analysis, which showed that the radical anions possess intense near-infrared absorption with λ_{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 1×10^{-6} and 3×10^{-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).[1] In addition to applications as smart windows, displays, and storage devices,[2] electrochromic (EC) materials have attracted a great deal of interest for use in devices that operate in the infrared and microwave regions,[3] as well in key components (i.e., variable optical attenuators)[4] in telecommunications that operate in the NIR region (e.g., around 1310 and 1550 nm).

Conjugated polymers such as polyanilines and polythiophenes,[5] mixed-valence metal complexes,[6] ruthenium−semiquinone complexes,[7] and conjugated aromatic diquinones[8] are known to be NIR electrochromic. These EC materials can become highly absorptive in the NIR region upon electrochemical oxidization or reduction. For making a flexible electrochemical device (e.g., electrochromic VOA), both anodically and cathodically NIR-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[5b] are less available and less studied than the p-type semiconductors and polymers for optoelectronic applications.[9] Cathodically NIR-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 pentacenediquinone).

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* To whom correspondence should be addressed. E-mail: wangw@ccs.carleton.ca.

[†] Peking University.

[‡] Carleton University.

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Pentacenediquinone (PDQ) is reported to undergo four concurrent reduction steps, although the third and fourth reduction steps are not completely reversible or even irreversible.[10] 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.[11] 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(aryl ether)s.

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_2O_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 (δ) 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 μ-Styragel columns (10^3, 10^4, and 10^5 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. 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 (Fc/Fc$^+$) 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.

2,9- and 2,10-Difluororopentacenediquinone (3a and 3b). Pyromellitic dianhydride (4.00 g, 0.018 mol), 30 mL of fluorobenzene, and AlCl$_3$ (2.40 g, 0.018 mol) were combined in a round-bottomed flask, and the suspension was heated to reflux for 4 h. The excess fluorobenzene was distilled off, and the residue was carefully decomposed by pouring onto ice/water (300 mL) containing 36% HCl (10 mL). The chunky solid was filtered, dissolved in a NaHCO$_3$ solution, and then filtered to remove insoluble solids. The clear filtrate was acidified with concentrated HCl to give a white precipitate that was collected by suction filtration. After drying in a vacuum oven at 100 °C overnight, a mixture of ketoacid (6.0 g) as white solids (**1a**, **1b**) was obtained in 81% yield. One gram of the ketoacid (**1a**, **1b**) was placed in a mortar and ground together with 7.0 g of AlCl$_3$ and 1.0 g of NaCl until a homogeneous fine powder was obtained. The powder was introduced into a flame-dried round-bottomed flask that was fitted with an air condenser. The mixture was heated at 200 °C for 4 h and then was allowed to cool to room temperature before a mixture of ice and aqueous HCl solution was carefully added into the flask. After standing overnight, 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^{-5} 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 $C_{22}H_8F_2O_4$ 374.0390, found 374.0379.

Difluoro Ketoesters (2a and 2b). Anhydrous ethanol (50 mL) and a mixture of isomeric ketoacids (**1a**, **1b**) (5.00 g, 0.011 mol) were added to a flame-dried flask equipped with a magnetic stirrer and a reflux condenser. To the suspension was then added 1 mL of concentrated H_2SO_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 (20%) and then acetone, recrystallization from toluene gave 3.6 g (65%) of ester **2a** as white prisms. The ethanolic solution containing the other isomer was concentrated under reduced pressure, and the yellow residue was taken in chloroform. The organic layer was washed with an aqueous K_2CO_3 solution (20%) until it was no longer acidic. The chloroform solution was dried over anhydrous MgSO$_4$, and the solvent was removed reduced pressure. Ester **2b** was obtained as an amorphous off-white solid (2.0 g, 35% yield).

Difluoro Ketoester (2a). mp = 238 °C (DSC). IR (KBr, cm^{-1}): 1721, 1682, 1597, 1503, 1410, 1374, 1301, 1256, 1149, 1124, 1109, 1016, 949, 921, 845, 749. ^{1}H NMR (400 MHz, CDCl$_3$): 8.0 (s, 1H), 7.83 (dd, 2H, $J_1 = 5.3$ Hz, $J_2 = 3.2$ Hz), 7.18 (t, 2H, $J = 8$ Hz), 4.17 (q, 2H, $J = 8$ Hz), 1.12 (t, 3 H, $J = 8$ Hz). ^{13}C NMR (100 MHz, CDCl$_3$): 193.8, 167.3 ($^1J_{C-F} = 254$ Hz), 164.2, 142.4, 132.9 ($^4J_{C-F} = 3$ Hz), 132.5, 132.1 ($^3J_{C-F} = 9$ Hz), 129.6, 116.0

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($^2J_{C-F}$ = 22 Hz), 62.3, 13.6. HRMS calcd for $C_{22}H_{30}F_2O_6$ 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, 921, 853, 751. ^{1}H NMR (400 MHz, DMSO-d_6): δ 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 Hz), 1.05 (t, 3H, J = 8 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): 193.6, 166.4 ($^1J_{C-F}$ = 254 Hz), 163.9, 144.4, 132.7 ($^4J_{C-F}$ = 3 Hz), 132.0 ($^3J_{C-F}$ = 9.6 Hz), 131.2, 129.6, 126.9, 115.9 ($^2J_{C-F}$ = 22 Hz), 61.8, 13.3. HRMS calcd for $C_{22}H_{30}F_2O_6$ 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_2O 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 in a crucible and dried under vacuum at 100 °C for 24 h, affording 2 g (89%) of the corresponding acid. mp = 309 °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). ^{13}C NMR (100 MHz, DMSO-d_6): 193.6, 166.3 ($^1J_{C-F}$ = 252 Hz), 165.6, 141.8, 133.2, 133.0, 132.1 ($^3J_{C-F}$ = 9 Hz), 128.7, 115.9 ($^2J_{C-F}$ = 22 Hz). HRMS calcd for $C_{22}H_{12}F_2O_6$ 410.0612, found 410.0608.

Difluoro Ketoacid (1b). Compound **1b** was prepared using the same procedure as for **1a**. mp = 230 °C (DSC). IR (KBr, cm^{-1}): 1705, 1675, 1596, 1506, 1412, 1269, 1235, 1154, 1113, 922, 782. ^{1}H NMR (400 MHz, DMSO-d_6): 13.7 (s, 1H), 8.56 (s, 1H), 7.81 (dd, 2H, J_1 = 8 Hz, J_2 = 4 Hz,), 7.57 (s, 1H), 7.34 (t, 2H, J = 12 Hz). ^{13}C NMR (100 MHz, DMSO-d_6): 193.6, 166.2 ($^1J_{C-F}$ = 251 Hz), 165.7, 144.6, 133.0, 131.8 ($^3J_{C-F}$ = 10 Hz), 131.4, 130.6, 126.4, 115.8 ($^2J_{C-F}$ = 22 Hz). HRMS calcd for $C_{22}H_{12}F_2O_6$ 410.0612, found 410.0608.

2,9-Difluoropentacenediquinone (3a). Starting with the acid **1a** (2.00 g) and following the general procedure for cyclization in $AlCl_3$ melt, crude **3a** (1.4 g) was obtained in 77% yield. It was recrystallized from hot nitrobenzene to give 1.2 g of **3a** as golden prisms. mp > 400 °C. IR (KBr, cm^{-1}): 1678, 1587, 1468, 1265, 1216, 946, 851, 721. HRMS calcd for $C_{22}H_8F_2O_4$ 374.0390, found 374.0379.

2,10-Difluoropentacenediquinone (3b). Starting with the acid **1b** (1.5 g) and following the general procedure for cyclization in $AlCl_3$ melt, crude **3b** (0.8 g) was obtained in 60% yield. It was recrystallized from hot nitrobenzene to give 0.8 g of **3b** as golden prisms. mp > 400 °C. IR (KBr, cm^{-1}): 1674, 1581, 1468, 1275, 1126, 946, 851, 721. HRMS calcd for $C_{22}H_8F_2O_4$ 374.0390, found 374.0379.

2,9-and 2,10-Bis(4-*tert*-butylphenoxy)pentacenediquinone (4a and 4b). In a dry three-necked, round-bottomed flask equipped with a magnetic stirrer, argon inlet, Dean−Stark trap, and reflux condenser were added 4-*tert*-butylphenol (0.30 g, 2.00 mmol), K_2CO_3 (0.83 g, 6.0 mmol), 25 mL of toluene, and 5 mL of anhydrous DMF. The mixture was heated at 120 °C for 2 h until most of the K_2CO_3 was consumed and a yellowish color appeared. The temperature was raised to 150 °C, and the toluene was collected in the Dean−Stark trap. When all the toluene had been removed, the mixture of **3a** and **3b** (0.43 g, 0.001 mol) and another 5 mL of anhydrous DMF were added to the flask. Upon the addition, the solution turned green, and the reaction was allowed to proceed overnight. The mixture was cooled to room temperature and poured onto ice. The solid was filtered by suction and dried in a vacuum oven at 150 °C for 24 h, giving 0.692 g (90%) of the desired product. mp > 400 °C. IR (KBr, cm^{-1}): 1677, 1589, 1507, 1405, 1274, 1239, 1170. HRMS calcd for $C_{42}H_{34}O_6$ 634.2355, found 634.2360.

Repeating the same reaction using **3a** and **3b** separately, **4a** and **4b** were obtained, respectively.

4a: mp > 400 °C. IR (KBr, cm^{-1}): 1677, 1589, 1507, 1405, 1274, 1239, 1170. ^{1}H NMR (400 MHz, $CDCl_3$): 9.09 (s, 1H), 8.27 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2 Hz), 7.73 (s, 1H), 7.39 (d, 2H, J = 10 Hz), 7.33 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 6.98 (d, 2H, J = 10 Hz), 1.3 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 180.5, 179.5, 163.0, 151.0, 147.5, 136.9, 135.8, 134.5, 139.5, 126.9, 126.2, 125.1, 123.3, 120.0, 114.3, 34.7, 31.4. HRMS calcd for $C_{42}H_{34}O_6$ 634.2355, found 634.2360.

4b: mp > 400 °C. IR (KBr, cm^{-1}): 1678, 1590, 1505, 1410, 1364, 1261, 1092, 1019, 799. ^{1}H NMR (400 MHz, $CDCl_3$): 9.09 (s, 1H), 8.26 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2 Hz), 7.39 (d, 2H, J = 8.8 Hz), 7.34 (d, 1H, J = 2.8 Hz), 7.31 (d, 1H, J = 2.4 Hz), 6.97 (d, 2H, J = 8.8 Hz), 1.3 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): 181.5, 180.5, 164.0, 152.0, 148.5, 136.9, 136.8, 135.5, 130.5, 127.9, 127.2, 127.1, 123.3, 120.0, 114.3, 34.7, 31.4. HRMS calcd for $C_{42}H_{34}O_6$ 634.2355, found 634.2360.

Pentacenediquinone (5). Pyromellitic dianhydride (1.00 g, 4.50 mmol) was placed into a flame-dried flask equipped with a magnetic stirrer and a reflux condenser. To the flask were added 20 mL of anhydrous benzene and $AlCl_3$ (2.40 g, 0.018 mol). Upon heating, the mixture turned a bright yellow color, and the suspension was heated to reflux for 4 h. The excess benzene was distilled off, and the residue was carefully decomposed on ice and HCl. The solid was filtered and dissolved in a $NaHCO_3$ solution. The resulting solution was filtered to remove insoluble inorganic solids, and the clear liquid was acidified with concentrated HCl. The resulting white precipitate was isolated through suction filtration, and dried in a vacuum oven overnight at 100 °C to yield 0.98 g (57%) of a white solid. The product (0.98 g, 2.60 mmol) and 8 mL of concentrated sulfuric acid were placed in a flame-dried flask equipped with a magnetic stirrer and fitted with an air condenser. The resulting brown-yellow solution was heated in an oil bath at 120 °C for 5 h. Upon cooling, a large mass of fine yellow needles precipitated. The suspension was carefully poured onto ice, and the needlelike precipitate was collected by filtration. The precipitate was then stirred in a $NaHCO_3$ solution to remove the remaining acid, filtered, and then stirred again in acetic acid. Finally, the compound was filtered, dried in a vacuum oven at 120 °C, and recrystallized from nitrobenzene. After recrystallization and drying in a vacuum oven at 220 °C for 24 h, 0.84 g (95%) of golden needles was obtained. mp > 400 °C. IR (KBr, cm^{-1}): 1673, 1592, 1310, 1266, 1128, 969, 704. ^{1}H NMR (400 MHz, DMSO-d_6): 8.89 (1H, s), 8.30 (dd, 1H, J_1 = 5.6 Hz, J_2 = 2 Hz), 8.0 (dd, 1H, J_1 = 5.6 Hz, J_2 = 2.8 Hz). HRMS calcd for $C_{22}H_{10}O_4$ 338.0579, found 338.0598.

1,8-Dinitropentacenediquinone (6). The procedures reported in the literature were modified as follows:[12] Pentacenediquinone (1.00 g, 0.003 mol) was added to a round-bottomed flask and dissolved in 5 mL of concentrated H_2SO_4. The flask was then placed on ice and to the solution was added dropwise 7 mL of a mixture of HNO_3 and H_2SO_4 (1:1 v/v). After the addition was complete, the flask was heated to 90 °C for 35 min. The solution was then poured onto ice and the yellowish precipitate was collected by filtration. After recrystallization from nitrobenzene and drying in a vacuum

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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 $C_{22}H_8N_2O_8$ 428.0281, found 428.0298. Anal. calcd for $C_{22}H_8N_2O_8$ C 61.69, H 1.88, N 6.54; found C 61.44, H 2.04, N 6.50.

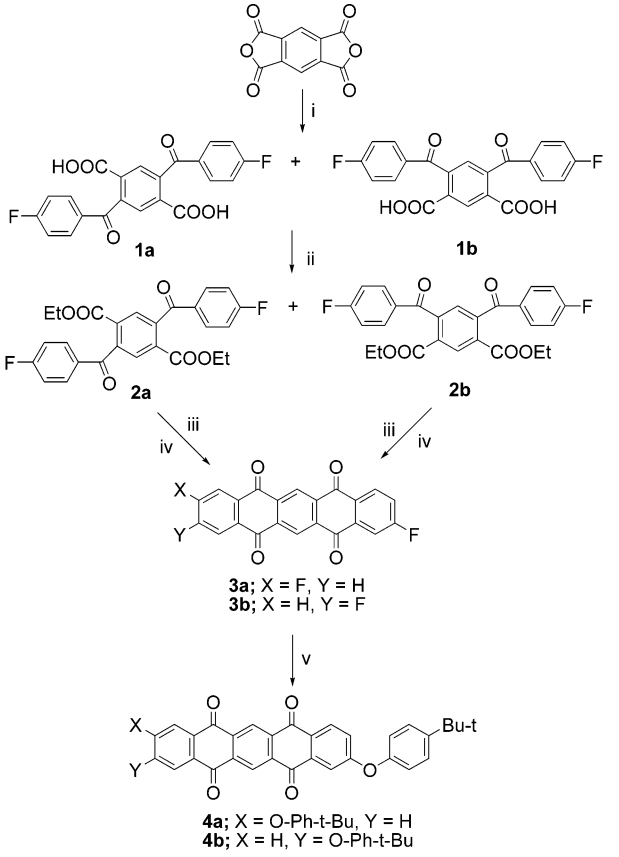
1,8-Bis(4-*tert*-butylphenoxy)pentacenediquinone (7). Compound **6** (1.07 g, 2.00 mmol), 4-*tert*-butylphenol (0.75 g, 5.00 mmol), K_2CO_3 (1.38 g, 10.0 mmol), 5 mL of toluene, and 15 mL of DMF were placed together in a 100 mL, three-necked flask equipped with a Dean–Stark trap, nitrogen inlet and outlet, 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 (ν_{CH_3}), 1677 ($\nu_{C=O}$), 1270 (ν_{C-O-C}). ^{1}H NMR (400 MHz, $CDCl_3$): 9.18 (2H, s), 8.18 (2H, dd, $J_1 = 7.0$ Hz, $J_2 = 1.0$ Hz), 7.72 (2H, t, $J_1 = 7.0$ Hz, $J_3 = 8.3$ Hz), 7.42 (4H, d), 7.34 (2H, dd, $J_2 = 1.0$ Hz, $J_3 = 8.3$ Hz), 7.04 (4H, d), 1.34 (18H, s). MS (EI, m/z): 634 (M$^+$). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{42}H_{34}O_6$ 634.2355, found 634.2354.

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), K_2CO_3 (0.742 g, 37.0 mmol), 14 mL of DMAc, and 12 mL of toluene were placed in a three-necked flask equipped with a Dean–Stark trap, nitrogen inlet and outlet, and condenser. After 2 h, toluene was removed and the reaction temperature was increased to 170 °C. After 3–5 h, the polymer solution was cooled to room temperature and poured into water. The polymer product was obtained in quantitative yield after washing with methanol and drying at 100 °C under vacuum. To remove any oligomers or cyclics, the polymer was dissolved in chloroform (about 1 g per 20 mL) and then isolated by reverse 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, the Friedel–Crafts acylation of fluorobenzene with pyromellitic dianhydride in the presence of $AlCl_3$ was first carried out (Scheme 1). The resulting fluoro ketoacids (**1a** and **1b**) were cyclized in $AlCl_3$ melt to form the corresponding pentacenediquinones **3a** and **3b** as a mixture. Compounds **1a** and **1b** could also be separated prior to cyclization through formation of ketoesters **2a** and **2b**. Ester **2a** was insoluble in ethanol and precipitated out of solution, while isomer **2b** 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 individual isomers 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)s could also be prepared via their precursor polymers, which should be readily prepared using the ketoesters **2a** and **2b**.

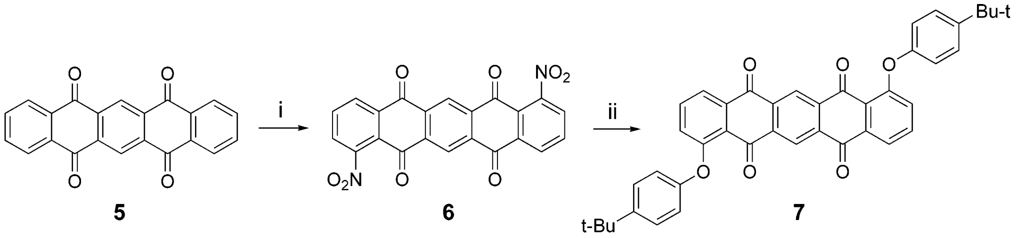
Scheme 1. Syntheses of Difluoropentacenediquinone Monomers and Model Compounds[a]



[a] (i) PhF, $AlCl_3$, reflux, 4 h. (ii) EtOH, H$^+$, reflux, 48 h. (iii) 48% aq HBr, AcOH. (iv) $AlCl_3$/NaCl melt, 4 h. (v) 4-*tert*-butylphenol, DMF, K_2CO_3, 120 °C.

It was also of interest to synthesize PDQ derivatives with the functional groups at the 1,8-positions. Thus, the dinitro derivative **6**[12] was synthesized by nitration of pentacenediquinone (**5**) as shown in Scheme 2. The nitro groups in **6** are activated by the strong electron-withdrawing keto groups at its ortho positions, as evident by the facile, high-yield formation of the ether derivative **7** with 4-*tert*-butylphenol in the presence of potassium carbonate. Among the two potential monomers **3** and **6**, the latter was identified as a better candidate to prepare polymers, since it was more

Scheme 2. Synthesis of Dinitro Monomer and Model Compound[a]



[a] (i) HNO_3, H_2SO_4, 90 °C. (ii) 4-*tert*-butylphenol, K_2CO_3, DMF, 120 °C.

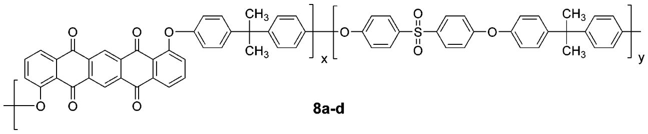
Table 1. Characterization of PDQ-Containing Poly(aryl ether)s

polymer	PDQ in feed (*x*:*y*)[a]	PDQ in polymer (*x*:*y*)[b]	M_w ($\times 10^{-4}$)[c]	M_w/M_n	T_d[d] (°C)	T_g (°C)	η[e]
8a	5% (1:9)	6.9% (1:7)	1.3	3.4	441	196	0.22
8b	10% (1:4)	9.9% (1:4)	2.0	1.9	406	212	0.19
8c	17% (1:2)	17% (1:2)	1.8	1.9	387	227	0.18
8d	25% (1:1)	26% (1:1)	1.0	1.7	375	246	0.20

[a] The mole ratio of PDQ in feed of polymerization. [b] The mole ratio of PDQ in polymer as calculated from the UV−vis absorption of each polymer in chloroform. [c] From GPC measurements in THF using polystyrene standards. [d] The onset temperature for 5% weight loss in air. [e] 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 ether)s **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 1.0×10^4−2.0×10^4 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).



Electrochemical and Electrochromic Studies in Solution. The electrochemical properties of the monomers and PDQ-containing polymers were examined using cyclic voltammetry (CV) in DMF solutions containing 0.1 M TBAP or $TBAPF_6$. Compounds **3** and **4** (either isomers or mixture) possessed two reversible reduction steps at $E_{1/2} = -0.36$ and -0.80 V and $E_{1/2} = -0.41$ and -0.86 V, respectively. In contrast, CV of model compound **7** showed three redox waves corresponding to three different reduced states related to the PDQ moiety, namely, the radical anion, dianion, and trianion. While the first two reductions were reversible at $E_{1/2} = -0.44$ and -0.93 V, the third redox wave ($E_{1/2} = -1.79$ V) did not exhibit good reversibility. When the electrochemical experiments of compounds **3** and **4** were conducted in DMF containing $TBAPF_6$, their voltammograms showed two reversible couples with a 70−90 mV cathodic−anodic peak separation. When the experiments were repeated in DMF or DMSO solutions containing 0.1 M $LiClO_4$, the difference between the cathodic and anodic peaks broadened, varying from 30 to 140 mV in both solvents. For polymers **8** containing the pentacenediquinone moiety, only two reduction steps corresponding to the formation of the radical anions and dianions were observed during CV scanning up to −2.2 V. The half-wave potentials corresponding to the first two redox waves occurred at approximately −0.40 and −0.85 V, respectively. Figure 1 shows the CV traces of model compound **7** and polymer **8b** obtained in DMF solutions containing TBAP.

The electrochromic properties of the functionalized pentacenediquinones (**3a,b**, **4a,b**, **6**, and **7**) and polymers (**8a**−**8d**) were analyzed in solution using an OTTLE cell.[13] The UV/vis properties of these compounds were analyzed in

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(13) Kejecik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179.

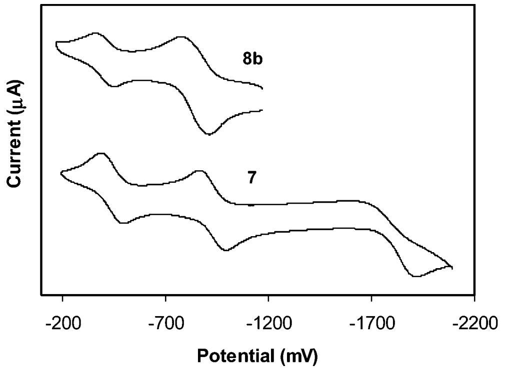

Figure 1. Cyclic voltammograms of model compound **7** and polymer **8b** in DMF (10^{-3} M) containing TBAP (0.1 M).

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_{max}) at 1335 nm, while **3** and **4** have their λ_{max}'s at 1360 and 1331 nm, respectively. In the case of the two isomers of **3**, the λ_{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_{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_{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 spectroelectrochemical analysis. The electrochemical behavior of the polymers was similar to that of the model compound **7**. Figure 2 shows the UV/vis/NIR spectra of polymer **8c** in its neutral, radical anionic, and dianionic states, which were obtained by applying negative potentials to the polymer solutions containing TBAP.

To investigate the solvent and electrolyte dependence on the NIR activity of the PDQ derivatives, spectroelectrochemical studies of **3** and **4** were carried out in DMSO and DMF using $LiClO_4$ and Bu_4NClO_4 as electrolytes. For both solvent and electrolyte studies, the positions of λ_{max} for the semiquinones shifted only by 5−10 nm, which indicates that the NIR spectra are independent of solvent and electrolyte. When the large, noncoordinating counterion Bu_4N^+ was used, the spectroelectrochemical experiments were fully reversible and no residual NIR absorptions were observed in either DMSO or DMF upon reoxidation. However, when $LiClO_4$ was utilized, the reoxidation was incomplete and residual NIR absorptions were present, which is probably related to the low solubility of the resulting complex formed between the radical anion and the strongly coordinating Li^+ counterion.

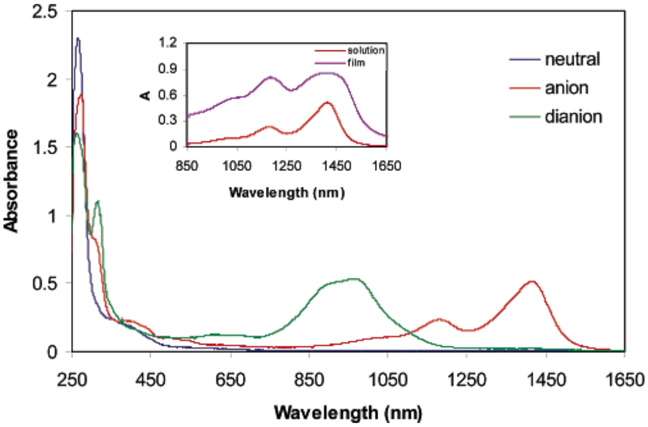

Figure 2. UV/vis/NIR spectra of polymer **8c** in DMF containing TBAP in its neutral, anionic, and dianionic states. The inset shows the NIR absorptions in solution and in the solid state.

The band gaps of compound **7** and polymers **8a**−**8d** were measured based on their onsets for reduction and oxidation as determined 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 nonconjugated nature of polymer backbone (Figure 3). Considering the film thickness, the attenuation

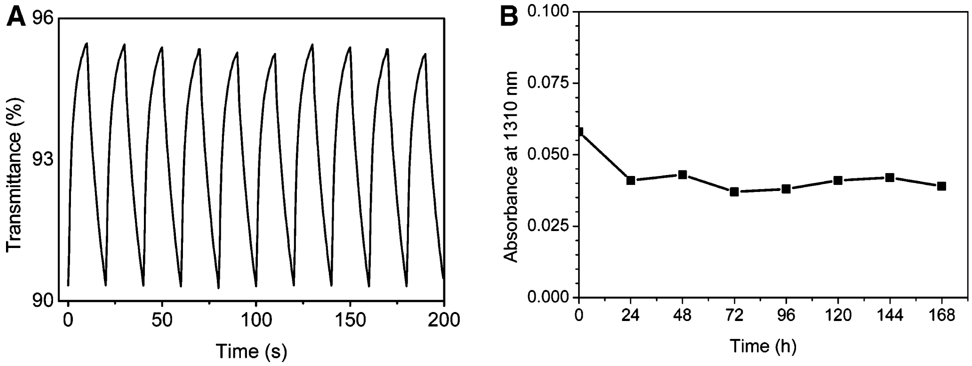

Figure 3. (A) Changes in optical transmission of film (400 nm) of polymer **8c** at 1310 nm over time with stepping potentials between −1.5 and +1.5 V. (B) Stability of electrochemically reduced thin film of polymer **8c** as measured by changes in absorbance at 1310 nm over time at ambient temperatures in air (in the dark).

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 1×10^{-6} S/cm, while the conductivity of the reduced film was significantly increased to 3×10^{-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 polythiophenes[5a] 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.

Acknowledgment. This work was supported by the National Science Foundation of China (Project Nos. 20228407, 20325415), the Natural Sciences and Engineering Research Council of Canada, and the National Capital Institute of Telecommunications.

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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