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π-Conjugated Polymers Exhibiting a Novel Doping Based on Redox of Side Chains

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ABSTRACT: Novel polyphenylene and polythiophene derivatives that have *N,N′*-diphenyl-1,4-phenylenediamine (PDA) units were synthesized using the palladium-catalyzed Suzuki coupling or cross coupling. Each obtained polymer has good redox activity, and the polyphenylene derivatives have two redox couples in acetonitrile that contain 1 M trifluoroacetric acid, whereas the polythiophene derivatives show only one redox couple under the same conditions. The electronic conductivity of the polythiophene derivatives was dramatically enhanced (0.1 S/cm) by the one-electron oxidation of the PDA unit (0.4 V, vs Ag/Ag$^+$), because of the injection of a radical cation into the main chain from the PDA unit. Spectroelectrochemistry showed that the radical cation of the thiophene-substituted PDA was more delocalized than the phenylene-substituted unit. Electrochemical analysis of the model compounds revealed that the injection of radical monocation radical carriers into the main chain is based on electron communication between the intramolecular PDAs.

1. Introduction

The electrochemical properties of π-conjugated polymers are significantly influenced by electron communication between their redox-active[1−4] sites, through the π-conjugated backbone. The relationship between this electron communication and their electrochemical properties has not been sufficiently investigated, even though many π-conjugated polymers that have redox-active side groups, such as benzoquinone or ferrocene, have been studied. There have been no attempts to introduce two-electron-transfer redox-active molecules with a very stable radical cation as a mixed valence state with an intervalence charge-transfer (IV-CT) band,[5] because of the delocalization of electrons in which a rapid electron transfer occurs between the redox sites, to the π-conjugated polymers. The stable and delocalized electron that is formed at the side chains could act as a carrier in the π-conjugated chain through injection into the backbone of the polymer. *N,N′*-Diphenyl-1,4-phenylenediamine[6] (PDA) derivatives were employed as the stable two-electron redox moiety; these PDA derivatives possess a mixed valence state with an IV-CT band. PDA is the minimum redox unit of polyaniline,[7] which is a π-conjugated polymer with excellent redox properties that are due to proton doping, and is widely applied to materials that require a quick response, such as lightweight secondary batteries,[8] sensors,[9] catalysts,[10] and electrochromic displays.[11] We report herein the basic electrochemical properties of the π-conjugated polymers that have PDA units, focusing on the electron communication between the PDA units of their model compounds.[12] To investigate the electron communication between the redox-active units in the π-conjugated polymer, we synthesized novel π-conjugated polyphenylene and polythiophene derivatives that have PDA units via the palladium-catalyzed Suzuki coupling[13−15] or Stille coupling.[16−20] The poly-*p*-phenylene derivatives that have PDA units exhibit two reversible redox couples, such as PDA, but the polythiophene derivatives exhibit only a single redox couple, because of their electron communication between the PDA units through the π-conjugated backbone. The electronic conductivity of the polythiophene derivatives is dramatically enhanced by oxidation of the PDA unit, which is based on the injection of a radical cation into the main chain. The communication occurs through the electron transfer via a coupling group. Electrochemical analysis of the model compounds has revealed the existence of an electronic interaction between the intramolecular PDAs.

2. Experimental Section

2.1. Chemicals. Aniline was purchased from Aldrich Chemical Co., Inc., and 2,5-dibromo-1,4-benzoquinone was purchased from Tokyo Kasei Co., Ltd.; all other chemicals were purchased from Kantoh Kagaku Co., Inc. (reagent grade), and were used without further purification. The supporting electrolyte (TBABF$_4$) was recrystallized from a mixture of ethyl acetate and hexane before use. The following compounds were prepared according to literature procedures: benzene-1,4-diboronic acid,[15] 4,4′-biphenyldiboronic acid bis(neopentylglycol),[15] 2,5-bis(tributylstannyl)thiophene,[19] 5,5′-bis(tributylstannyl)-2,2′-bithiophene,[20] **2a**,[21] **3a**,[21] and **B**.[21]

2.2. Spectroscopic Measurements. UV−Vis spectra were obtained using a spectrometer (Shimadzu, model UV-2400PC) with an indium−tin oxide (ITO) electrode. Infrared (IR) spectra were obtained from a potassium bromide (KBr) pellet using another spectrometer (JASCO, model FT-IR-460Plus). NMR spectra were recorded using a JEOL model JMN400 FT-NMR spectrometer (400 MHz) in CDCl$_3$, THF-d_8, or a DMSO-d_6 + TMS internal standard solution. Matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) mass spectra were obtained using a Shimadzu/Kratos model KOMPACT MALDI mass spectrometer (positive mode, with a matrix of dithranol). EI mass

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spectra were obtained using a mass spectrometer (Hitachi, model M-80B). CHNS elemental analysis was performed using a Elementar Vario EL system. Elemental analysis for bromine was performed using the combustion flask method, with a Mettler model Metrohm 682 apparatus for the potentiometric titration. Gel permeation chromatography (GPC) was performed with a Shimadzu model CLASS-LC10 apparatus (with a Shodex model GPC-KD804 column (pore size, 200 Å; bead size, 7 μm; exclusion limit, 4×10^5; 8.0 mm inner diameter × 30 cm length) and a Shodex model GPC-KD802 column (pore size, 60 Å; bead size, 6 μm; exclusion limit, 5×10^3; 8.0 mm inner diameter × 30 cm length)) at 40 °C with a UV−Vis detector (Shimadzu, model SPD-M10AVP). Tetrahydrofuran (THF) was used as the eluent, at a flow rate of 1.0 mL/min. Molecular weights were calculated against polystyrene standards.

2.3. Electrochemical Measurements. Electrochemical analyses were performed using an electrochemical work station (BAS Co., Ltd., model ALS-660 or ALS-701a) under the following conditions. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed under a N_2 atmosphere after N_2 bubbling for 15 min. A glassy carbon (GC) disk electrode (0.071 cm^2) was used as the working electrode and was polished with 30-μm alumina before the experiments. The auxiliary electrode was a coiled platinum wire. The reference electrode was a commercial Ag/Ag^+ electrode, which was placed in the main cell compartment. The formal potential of the ferrocene/ferrocenium couple was 0.076 V, versus this reference electrode in acetonitrile. All potentials are quoted with respect to this Ag/Ag^+ reference electrode. The potential was normalized to the ferrocene/ferrocenium couple in acetonitrile. The scan rate was 100 mV/s. The amplitude for the DPV measurement was 50 mV. The in situ conductivity measurements were obtained as follows. The polymer films were prepared by casting onto an interdigitated platinum microelectrode (length, 2 mm; width, 10 μm; interval, 5 μm). The conductivity of the resulting polymers was measured between −0.1 V and 0.8 V in an acetonitrile−$TBABF_4$ electrolyte (0.2 M) that contained trifluoroacetic acid (TFA) (1 M) using CV (the counter electrode accounted for 0.1 V of the constant drain voltage).

2.4. Synthesis of Dibromo-Substituted PDA (A). Aniline (10.3 g, 111 mmol) was dissolved in chlorobenzene (40 mL) under nitrogen, and titanium(IV) tetrachloride (2.14 g, 11.3 mmol) was added dropwise at 90 °C. The addition funnel was then rinsed with chlorobenzene (10 mL). 2,5-Dibromo-1,4-benzoquinone (2.07 g, 7.79 mmol) that had been dissolved in chlorobenzene (100 mL) was added dropwise over 15 min to the mixture. The mixture was stirred in an oil bath at 135 °C for 12 h. The precipitate was removed by filtration and washed with chlorobenzene (20 mL). The filtrate was concentrated, and compound **A** (2.11 g, 65%, white powder) was isolated by silica gel chromatography (1:1 hexane:dichloromethane ratio). The analysis of **A** was as follows. ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.47 (s, 2H, $C_6\mathit{H}_2Br_2$), 7.30 (dd, $J = 7.8$, 7.2 Hz, 4H, m-C_6H_5), 7.04 (d, $J = 7.8$ Hz, 4H, o-C_6H_5), 7.00 (t, $J = 7.2$ Hz, 2H, p-C_6H_5), 5.76 (s, 2H, NH). ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C, TMS): δ 142.1 (NH−$\mathit{C}C_5H_5$), 135.4 (NH−$\mathit{C}[(CH)_2(CBr)_2]\mathit{C}$), 129.4 ($m$-$C_6H_5$), 121.9 ($p$-$C_6H_5$), 121.5 ($C(\mathit{C}H)_2(CBr)_2C$), 118.6 ($o$-$C_6H_5$), 113.1 (Br-$\mathit{C}$). IR (KBr, cm^{-1}): 3399 (N−H), 1598 (C−N), 1523 (C−N), 1469 (C═C), 1374, 1276, 1050, 887, 868 (C−H), 747 (C−H), 697 (C−H), 502. EI-MS: 416, 418, 420 $[M]^+$. Anal. Calcd for $C_{18}H_{18}Br_2N_2$: C, 51.71; H, 3.37; N, 6.70. Found: C, 51.80; H, 3.35; N, 6.73.

2.5. Synthesis of Compound A Substituted by an Octyl Group (C). 4-n-Octyl-aniline (10.8 g 52.6 mmol) was dissolved in chlorobenzene (20 mL) under nitrogen, and titanium(IV) tetrachloride (1.07 g, 5.64 mmol) was added dropwise at 90 °C. The addition funnel was then rinsed with chlorobenzene (5 mL). 2,5-Dibromo-1,4-benzoquinone (1.00 g, 3.76 mmol) that had been dissolved in chlorobenzene (50 mL) was added dropwise to the mixture over a period of 15 min. The mixture was stirred in an oil bath at 135 °C for 48 h. The precipitate was removed by filtration and washed with chlorobenzene (10 mL). The filtrate was concentrated, and compound **C** (1.98 g, 82%, pale yellow wax) was isolated by silica gel chromatography (1:1 hexane:dichloromethane ratio). The analysis of **C** was as follows. ^{1}H NMR (400 MHz, $CDCl_3$, TMS standard, ppm): δ 7.39 (s, 2H, $C_6\mathit{H}_2$-Br_2), 7.11 (d, $J = 8.3$ Hz, 4H, m-C_6H_5), 6.97 (d, $J = 8.3$ Hz, 4H, o-C_6H_5), 5.67 (s, 2H, NH), 2.56 (t, $J = 7.8$ Hz, 4H, Ph−$C\mathit{H}_2CH_2$−), 1.59 (p, $J = 4.8$, 2.4 Hz, 4H, Ph−$CH_2C\mathit{H}_2$−), 1.32−1.28 (m, 20H, −$(C\mathit{H}_2)_5$−CH_3), 0.88 (t, $J = 6.3$ Hz, 6H, −$C\mathit{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$ TMS standard, ppm): δ 139.8 (NH−$\mathit{C}C_5H_4$), 137.0 (NH−$\mathit{C}[(CH)_2(CBr)_2]\mathit{C}$), 135.7 ($C_8H_{17}$−$\mathit{C}C_5H_4$), 129.3 ($m$-$C_6H_4$), 120.9 ($C(\mathit{C}H)_2(CBr)_2C$), 119.3 ($o$-$C_6H_4$), 112.6 (Br−$\mathit{C}$), 35.4 (Ph−$\mathit{C}H_2$−), 32.0 ($\mathit{C}H_2$), 31.7 ($\mathit{C}H_2$), 29.6 ($\mathit{C}H_2$), 29.4 ($\mathit{C}H_2$), 29.4 ($\mathit{C}H_2$), 22.8 ($\mathit{C}H_2$), 14.2 ($\mathit{C}H_3$). IR (KBr, cm^{-1}): 3415 (N−H), 2956 (CH_2), 2920 (CH_2), 2846 (CH_2), 1614 (C−N), 1529 (C−N), 1459 (C═C), 1314, 1049, 892, 810 (C−H), 515. EI-MS: 644, 642, 640 $[M]^+$. Anal. Calcd for $C_{34}H_{46}Br_2N_2$: C, 63.55; H, 7.22; N, 4.36. Found: C, 63.81; H, 7.13; N, 4.35.

2.6. Synthesis of Diphenyl PDA (1a). A mixture that contained **A** (0.042 g, 0.10 mmol), benzeneboronic acid (73 mg, 0.6 mmol), and 5 mol % tetrakis(triphenylphosphine) palladium(0) (0.012 g, 0.01 mmol) that had been dissolved in dimethylether (DME) (2 mL) and 2 M aqueous sodium carbonate (1 mL) was stirred at 80 °C for 12 h under nitrogen. The mixture then was poured into water. The organic layer was washed with a saturated sodium hydrogen carbonate and separated off, and the aqueous layer was extracted with dichloromethane (3 times). The combined organic layers were dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated, and compound **1a** (36 mg, 87%, white powder) was isolated by silica gel chromatography (1:1 hexane:dichloromethane ratio). The analysis of **1a** was as follows. ^{1}H NMR (400 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 7.47 (d, $J = 7.4$ Hz, 4H, m-C_6H_5), 7.35 (s, 2H, $C_6\mathit{H}_2$), 7.33 (dd, $J = 7.4$, 7.4 Hz, 4H, m-C_6H_5), 7.24 (t, $J = 7.4$ Hz, 2H, p-C_6H_5), 7.09 (dd, $J = 7.3$, 8.3 Hz, 4H, m-C_6H_5NH), 6.91 (d, $J = 8.3$ Hz, 4H, o-C_6H_5NH), 6.68 (t, $J = 7.3$ Hz, 2H, p-C_6H_5NH), 6.36 (s, 2H, NH). ^{13}C NMR (100 MHz, THF-d_8): δ 145.9 (NH−$\mathit{C}C_5H_6$), 139.4 (C−$\mathit{C}C_5H_6$), 135.0 (NH−$\mathit{C}[(CH)_2$-$(C-Ph)_2]\mathit{C}$), 134.3, 128.9 (m-Ph), 128.8 (m-Ph), 128.2, 126.9, 124.4, 118.6 (p-C_6H_5NH), 115.5 (o-C_6H_5NH). IR (KBr, cm^{-1}): 3393 (N−H), 1601 (C−N), 1528 (C−N), 1497 (C═C), 1477, 1401, 1317, 1256, 768 (C−H), 746 (C−H), 704 (C−H), 694 (C−H). EI-MS: 412 $[M]^+$. Anal. Calcd for $C_{30}H_{24}N_2$: C, 87.35; H, 5.86; N, 6.79. Found: C, 87.27; H, 6.06; N, 6.89.

2.7. Synthesis of Dithienyl-Substituted PDA (1b). A mixture that contained **A** (0.105 g, 0.25 mmol), 2-(tributylstannyl)thiophene (0.187 g, 0.5 mmol), and 2 mol % tetrakis(triphenylphosphine) palladium(0) (0.012 g, 0.01 mmol) that had been dissolved in dioxane (3 mL) was stirred at 100 °C for 24 h and cooled to room temperature, and a solution of KF (2 mL, 1.0 M) was added. The mixture was poured into water. The organic layer was washed using saturated sodium hydrogen carbonate and separated off, and the aqueous layer was extracted with dichloromethane (3 times). The combined organic layers were dried over anhydrous sodium sulfate, and compound **1b** (0.098 g, 92%, yellow powder) was isolated by silica gel chromatography (1:2 hexane: dichloromethane ratio). The analysis of **1b** was as follows. ^{1}H NMR (400 MHz, THF-d_8, TMS standard, 30 °C, ppm): δ 7.57 (s, 2H, $C_6H_2Th_2$), 7.32 (d, $J = 5.1$ Hz, 2H, α-Th), 7.31 (d, $J = 3.9$ Hz, 2H, β-Th), 7.12 (dd, $J = 7.3$, 7.3 Hz, 4H, m-C_6H_5), 6.99 (dd, $J = 3.9$, 5.1 Hz, 2H, β'-Th), 6.88 (d, $J = 7.3$ Hz, 4H, o-C_6H_5), 6.71 (t, $J = 7.3$ Hz, 2H, p-C_6H_5), 6.67 (s, 2H, NH). ^{13}C NMR (100 MHz, THF-d_8): δ 145.8 (NH$-$$CC_5H_5$), 140.0 ($C_6H_2-CC_3H_3S$), 135.3 (NH$-$$C$[(CH)$_2(CTh)_2$]$C$), 128.8 ($p$-$C_6H_5$), 128.4 ($\beta$-Th), 126.8 (NH$-$$C$[(CH)$_2(CTh)_2$]$C$), 125.7 ($\alpha$-Th), 125.6 ($\beta'$-Th), 124.5, 118.8, 115.5 (o-C_6H_5). IR (KBr, cm^{-1}): 3384 (N$-$H), 1601 (C$-$N), 1536 (C$-$N), 1518, 1497 (C$=$C), 1445, 1396, 1320, 1252, 845, 743 (C$-$H), 695 (C$-$H). EI-MS: 424 [M]$^+$. Anal. Calcd for $C_{26}H_{20}N_2S_2$: C, 73.55; H, 4.75; N, 6.60; S, 15.10. Found: C, 73.57; H, 4.84; N, 6.42.

2.8. Synthesis of PDAs Coupled through Thiophene (2b). Under nitrogen, a mixture that contained **B** (0.353 g, 0.50 mmol), 2,5-bis(tributylstannyl)thiophene (0.331 g, 1.00 mmol), and tetrakis(triphenylphosphine) palladium(0) (0.0231 g, 0.02 mmol) that had been dissolved in dioxane (7 mL) was stirred at 100 °C for 24 h and cooled to room temperature, and a solution of KF (5 mL, 1.0 M) was added to quench the reaction. The mixture was poured into water. The organic layer was washed using saturated sodium hydrogen carbonate and brine and then was separated off, and the aqueous layer was extracted with dichloromethane (3 times). The combined organic layers were dried over anhydrous sodium sulfate and filtered. Compound **2b** (0.245 g, 78%, yellow powder) was isolated by silica gel chromatography (1:2 hexane:dichloromethane ratio). The analysis of **2b** was as follows. ^{1}H NMR (400 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 7.40 (s, 2H, Th$-$C$H$$-$NH), 7.17 (s, 2H, Me$-CH$$-$NH), 7.13 (s, 2H, β-Th), 7.11 (dd, $J = 7.3$, 7.3 Hz, 4H, m-C_6H_5), 7.08 (dd, $J = 7.3$, 7.3 Hz, 4H, m-C_6H_5), 6.81 (d, $J = 7.3$ Hz, 4H, o-C_6H_5), 6.79 (d, $J = 7.3$ Hz, 4H, o-C_6H_5), 6.70 (t, $J = 7.3$ Hz, 2H, p-C_6H_5), 6.67 (t, $J = 7.3$ Hz, 2H, p-C_6H_5), 6.57 (s, 2H, NH), 6.48 (s, 2H, NH), 2.16 (s, 6H, CH_3). ^{13}C NMR (100 MHz, THF-d_8): δ 146.8 (NH$-$$CC_5H_5$), 146.6 (NH$-$$CC_5H_5$), 141.2, 138.0, 135.3, 132.0, 129.5, 127.6, 126.7, 126.0, 123.0, 119.3, 119.1, 116.4, 116.1, 17.9. IR (KBr, cm^{-1}): 3382 (N$-$H), 3044 (CH_3), 1598 (C$-$N), 1496 (C$=$C), 1398, 1304, 1243, 745, 692. TOF-MS: 628 [M]$^+$. Anal. Calcd for $C_{42}H_{36}N_4S$: C, 80.22; H, 5.77; N, 8.91; S, 5.10. Found: C, 79.95; H, 5.76; N, 8.79.

2.9. Synthesis of PDAs Coupled through Bithiophene (3b). A mixture that contained **B** (0.353 g, 0.50 mmol), 2,5-bis(tributylstannyl)thiophene (0.372 g, 1.00 mmol), and tetrakis(triphenylphosphine) palladium(0) (0.0231 g, 0.02 mmol) that had been dissolved in dioxane (7 mL) was stirred at 100 °C for 24 h under nitrogen and cooled to room temperature, and a solution of KF (5 mL, 1.0 M) was added to quench the reaction. The mixture was poured into water. The organic layer was washed using saturated sodium hydrogen carbonate and brine and then was separated off, and the aqueous layer was extracted with dichloromethane (3 times). Compound **3b** (0.315 g, 89%), a yellowish-brown powder, was isolated by silica gel chromatography (1:1 hexane: dichloromethane ratio). The analysis of **3b** was as follows. ^{1}H NMR (400 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 7.45 (s, 2H, Th$-$C$H$$-$NH), 7.19 (s, 2H, Me$-CH$$-$NH), 7.15 (d, $J = 3.9$ Hz, 2H, Th), 7.12 (dd, $J = 7.3$, 7.3 Hz, 4H, m-C_6H_5), 7.10 (dd, $J = 7.3$, 7.3 Hz, 4H, m-C_6H_5), 7.01 (d, $J = 3.9$ Hz, 2H, Th), 6.83 (d, $J = 7.3$ Hz, 4H, o-C_6H_5), 6.82 (d, $J = 7.3$ Hz, 4H, o-C_6H_5), 6.71 (t, $J = 7.3$ Hz, 2H, p-C_6H_5), 6.68 (t, $J = 7.3$ Hz, 2H, p-C_6H_5), 6.61 (s, 2H, NH), 6.58 (s, 2H, NH), 2.18 (s, 6H, CH_3). ^{13}C NMR (100 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 146.2 (NH$-$$CC_5H_5$), 145.9 (NH$-$$CC_5H_5$), 139.6, 137.5, 137.1, 134.5, 131.6, 128.7, 126.9, 126.5, 125.8, 123.1, 121.9, 118.6, 118.4, 115.6, 115.3, 17.1. IR (KBr, cm^{-1}): 3394 (N$-$H), 3368 (N$-$H), 3041 (CH_3), 1598 (C$-$N), 1517 (C$-$N), 1496, 1399, 1292, 802 (C$-$H), 745 (C$-$H), 692 (C$-$H). TOF-MS: 710 [M]$^+$. Anal. Calcd for $C_{46}H_{38}N_4S_2$: C, 77.71; H, 5.39; N, 7.88; S, 9.02. Found: C, 77.96; H, 5.36; N, 7.82.

2.10. Polymerization of PP$-$PDA Complexes. A typical polymerization procedure is as follows. A mixture that contained **A** (0.105 g, 0.25 mmol), benzene-1,4-diboronic acid (0.0414 g, 0.25 mmol), and tetrakis(triphenylphosphine) palladium(0) (0.0058 g, 0.005 mmol) that had been dissolved in DME (2 mL) and aqueous sodium carbonate (2 M, 1 mL) was stirred at 80 °C for 48 h under nitrogen, The reaction mixture was reprecipitated in methanol.

2.10.1. PP$-$PDA. PP$-$PDA (89%, green powder) was obtained after collection via filtration and washing with water. The analysis of **PP$-$PDA** was as follows. GPC: $M_n = 1800$, $M_w/M_n = 1.2$. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C, TMS standard, ppm): δ 7.44 (4H, C_6H_4), 7.22 (2H, C_6H_2), 7.08 (6H, m-C_6H_5, NH), 6.84 (4H, o-C_6H_5), 6.66 (2H, p-C_6H_5). ^{13}C NMR (100 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 146.6 (NH$-$$CC_5H_5$), 137.9, 135.9, 134.7, 129.7, 128.6, 1255, 119.4, 116.3. IR (KBr, cm^{-1}): 3391 (N$-$H), 1600 (C$-$N), 1496 (C$=$C), 1386, 1307, 1257, 745 (C$-$H), 693 (C$-$H). TOF-MS: 1753 $[(C_{24}H_{18}N_2)_4C_{18}H_{14}Br_2N_2]^+$.

2.10.2. PP2$-$PDA. The analysis of **PP2$-$PDA** (100% yield, green powder) was as follows. GPC: $M_n = 2100$, $M_w/M_n = 2.0$. ^{1}H NMR (400 MHz, DMSO-d_6, 30 °C, TMS standard, ppm): δ 7.50 (4H, C_6H_4), 7.31 (4H, C_6H_4), 7.22 (2H, C_6H_2), 7.10 (6H, m-C_6H_5, NH), 6.88 (4H, o-C_6H_5), 6.65 (2H, p-C_6H_5). ^{13}C NMR (100 MHz, DMSO-d_6, 30 °C, TMS standard, ppm): δ 146.5 (NH$-$$CC_5H_5$), 137.8, 137.2, 133.6, 128.9, 128.8, 128.7, 126.1, 118.2, 115.3, 114.1. IR (KBr, cm^{-1}): 3395 (N$-$H), 1599 (C$-$N), 1495 (C$=$C), 1473, 1438, 1254, 880, 822 (C$-$H), 744 (C$-$H), 691 (C$-$H), 503. Anal. Calcd for $(C_{30}H_{22}N_2)_4C_{18}H_{14}Br_2N_2$: C, 80.45; H, 4.99; Br, 7.76; N, 6.80. Found: C, 79.97; H, 4.88; Br, 7.84; N, 6.04. TOF-MS: 1234 $[(C_{30}H_{22}N_2)_2C_{18}H_{14}Br_2N_2]^+$.

2.10.3. octPP$-$PDA. The analysis of **octPP$-$PDA** (98% yield, green powder) was as follows. GPC: $M_n = 4400$, $M_w/M_n = 1.8$. ^{1}H NMR (400 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 7.49 (4H, C_6H_4(backbone)), 7.30 (2H, C_6H_2), 6.98 (4H, m-C_6H_4), 6.87 (4H, o-C_6H_4), 6.45 (2H, NH), 2.49 (4H, CH_2(C_7H_{15})), 1.56 (4H, CH_2CH_2-(C_6H_{13})), 1.30 (20H, C_2H_4(CH_2)$_5$$CH_3$), 0.88, C$H_3$). ^{13}C NMR (100 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 144.3 (NH$-$$CC_5H_4$), 137.6, 136.0, 134.1, 129.6, 129.5, 124.1, 117.0, 36.0, 32.8, 32.7, 32.6, 30.4, 30.2, 23.5, 14.4. IR (KBr, cm^{-1}): 3392 (N−H), 2923 (CH_2), 2851 (CH_2), 1612 (C−N), 1513 (C=C), 1461, 1383, 1260, 824 (C−H). TOF-MS: 2870 $[(C_{40}H_{50}N_2)_4C_{34}H_{46}Br_2N_2]^+$.

2.10.4. octPP2−PDA. The analysis of **octPP2−PDA** (98% yield, green powder) was as follows. GPC: M_n = 7400, M_w/M_n = 2.7. ^{1}H NMR (400 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 7.62 (d, 4H, J = 8.3 Hz, C_6H_4(backbone)), 7.53 (d, 4H, J = 8.3 Hz, C_6H_4(backbone)), 7.35 (s, 2H, C_6H_2), 6.93 (d, 4H, J = 7.8 Hz, m-C_6H_4), 6.87 (d, 4H, J = 7.8 Hz, o-C_6H_4), 6.27 (s, 2H, NH), 2.45 (t, 4H, J = 7.8 Hz, $CH_2(C_7H_{15})$), 1.59 (m, 4H, J = 4.8, 2.4 Hz, $CH_2CH_2(C_6H_{13})$), 1.27−1.25 (m, 20H, $C_2H_4(CH_2)_5CH_3$), 0.84 (t, 6H, J = 6.7 Hz, CH_3). ^{13}C NMR (100 MHz, THF-d_8, 30 °C, TMS standard, ppm): δ 143.5 (NH−CC_5H_4), 139.4, 138.5, 135.2, 133.3, 133.2, 129.4, 128.7, 126.7, 123.5, 116.0, 35.2, 32.0, 31.9, 29.6, 29.5, 29.4. IR (KBr, cm^{-1}): 3407 (N−H), 2923 (CH_2), 2851 (CH_2), 1611 (C−N), 1511 (C=C), 1466, 1388, 1254. Anal. Calcd for $(C_{46}H_{54}N_2)_3C_{34}H_{46}Br_2N_2$: C, 81.10; H, 8.23; N, 4.40. Found: C, 80.72; H, 7.76; N, 3.94.

2.11. Polymerization of PT−PDA Complexes. A typical polymerization procedure is as follows. A mixture that contained **A** (0.105 g, 0.25 mmol), 2,5-bis(tributylstannyl)thiophene (0.166 g, 0.25 mmol), and tetrakis(triphenylphosphine) palladium(0 (0.0058 g, 0.005 mmol) that had been dissolved in dioxane (5 mL) was stirred at 100 °C for 48 h under nitrogen and cooled to room temperature, and a solution of KF (5 mL, 1.0 M) was added to quench the reaction. The reaction mixture was reprecipitated in methanol.

2.11.1. PT−PDA. PT−PDA (79% yield, orange powder) was obtained after collection via filtration and washing with water. The analysis of **PT−PDA** was as follows. GPC: M_n = 2100, M_w/M_n = 1.5. ^{1}H NMR (400 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 7.52 (2H, C_6H_2), 7.21 (2H, Th), 7.10 (4H, m-C_6H_5), 6.83 (4H, o-C_6H_5), 6.72 (2H, p-C_6H_5), 6.50 (2H, NH). ^{13}C NMR (100 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 145.5 (NH−CC_5H_5), 140.5, 135.4, 128.8, 128.3, 126.0, 124.0, 119.1, 115.9. IR (KBr, cm^{-1}): 3381 (N−H), 1599 (C−N), 1495 (C=C), 1394, 1303, 1248, 744 (C−H), 691 (C−H). TOF-MS: 1442 $[(C_{22}H_{16}N_2S)_3C_{18}H_{14}Br_2N_2]^+$.

2.11.2. PT2−PDA. The analysis of **PT2−PDA** (100% yield, orange powder) was as follows. GPC: M_n = 2200, M_w/M_n = 1.4. ^{1}H NMR (400 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 7.58 (2H, C_6H_2), 7.24 (2H, Th), 7.14 (6H, m-C_6H_5, Th), 6.89 (4H, o-C_6H_5), 6.73 (2H, p-C_6H_5), 6.62 (2H, NH). ^{13}C NMR (100 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 146.8 (NH−CC_5H_4), 138.8, 136.7, 129.9, 129.7, 129.6, 127.6, 125.2, 124.6, 120.1, 116.8. IR (KBr, cm^{-1}): 3381 (N−H), 1598 (C−N), 1495 (C=C), 1394, 1303, 796 (C−H), 744 (C−H), 690 (C−H). TOF-MS: 1687 $[(C_{26}H_{18}N_2S_2)_3C_{18}H_{14}Br_2N_2]^+$.

2.11.3. octPT−PDA. The analysis of **octPT−PDA** (79% yield, orange powder) was as follows. GPC: M_n = 8200, M_w/M_n = 1.7. ^{1}H NMR (400 MHz, THF-d_8, 50 °C, TMS standard, ppm): δ 7.47 (2H, C_6H_2), 7.19 (2H, Th), 6.95 (4H, m-C_6H_4), 6.78 (4H, o-C_6H_4), 6.36 (2H, NH), 2.51 (4H, $CH_2(C_7H_{15})$), 1.57 (4H, $CH_2CH_2(C_6H_{13})$), 1.31 (20H, $C_2H_4(CH_2)_5CH_3$), 0.87 (6H, CH_3). ^{13}C NMR (100 MHz, THF-d_8, 50 °C, TMS standard, ppm): δ 143.9 (NH−CC_5H_4), 141.3, 136.2, 134.3, 129.5, 128.3, 126.6, 123.9, 117.2, 36.0, 32.8, 32.6, 30.4, 30.2, 30.1, 23.4, 14.3. IR (KBr, cm^{-1}): 3392 (N−H), 2923 (CH_2), 2851 (CH_2), 1612 (C−N), 1513 (C=C), 1461, 1383, 1260, 824 (C−H). TOF-MS: 3470 $[(C_{38}H_{48}N_2S)_5C_{34}H_{46}Br_2N_2]^+$. Anal. Calcd for $(C_{38}H_{48}N_2S)_6C_{34}H_{46}Br_2N_2$: C, 78.1; H, 8.35; Br, 3.96; N, 4.86. Found: C, 77.5; H, 7.92; Br, 3.66; N, 4.86.

2.11.4. octPT2−PDA. The analysis of **octPT2−PDA** (100% yield, orange powder) was as follows. GPC: M_n = 6300, M_w/M_n = 1.5. ^{1}H NMR (400 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 7.52 (2H, C_6H_2), 7.21 (2H, Th), 7.06 (2H, Th), 6.99 (4H, m-C_6H_4), 6.84 (4H, o-C_6H_4), 6.40 (2H, NH), 2.27 (4H, $CH_2(C_7H_{15})$), 1.59 (4H, $CH_2CH_2(C_6H_{13})$), 1.30 (20H, $C_2H_4(CH_2)_5CH_3$), 0.88 (6H, CH_3). ^{13}C NMR (100 MHz, THF-d_8, 60 °C, TMS standard, ppm): δ 144.0 (NH−CC_5H_4), 140.0, 138.4, 136.6, 134.6, 129.6, 128.6, 127.3, 124.3, 124.1, 117.2, 36.0, 32.8, 32.5, 30.4, 30.2, 30.1, 23.4, 14.3. IR (KBr, cm^{-1}): 3396 (N−H), 2921 (CH_2), 2850 (CH_2), 1598 (C−N), 1510 (C=C), 1435, 790 (C−H), 693 (C−H). TOF-MS: 3231 $[(C_{42}H_{50}N_2S_2)_4C_{34}H_{46}Br_2N_2]^+$.

3. Results and Discussion

3.1. Synthesis of Novel Polyphenylene and Polythiophene Derivatives That Have PDA Units and Model Compounds. The 2,5-dibromo- and 2-bromo-5-methyl-substituted PDA derivatives (**A**, **B**,[21] and **C**) were synthesized via dehydration of the 2,5-dibromo- or 2-bromo-5-methyl-benzoquinone with aniline or 4-n-octyl-aniline in the presence of $TiCl_4$ in yields of 65%, 56%, and 82%.[22] (See Scheme 1.) The simplest palladium-catalyzed cross-coupling reactions were used for the polymerization of the poly-p-phenylene or polythiophene derivatives.[23] Compounds **2a**,[21] **3a**,[21] **2b**, and **3b** were also synthesized through the coupling of 2 equimol of **B** with the difunctional phenylene[15] or thiophene[19,20] derivatives in yields of 80%, 77%, 78%, and 89%, respectively. The solubility of these compounds was sufficient in THF. Novel polyphenylene or polythiophene derivatives that had PDA units were obtained via the coupling of the oligo phenylene or oligo thiophene in good yields (79%−100%). The solubility of the non-octyl-substituted polymers (**PP−PDA**, **PP2−PDA**, **PT−PDA**, and **PT2−PDA**) was poor, the polymerizations proceeded nonuniformly, and the obtained THF-soluble portion of these polymers was precipitated into acetone to remove the oligomers. The octyl-substituted polymers (**octPP−PDA**, **octPP2−PDA**, **octPT−PDA**, and **octPT2−PDA**) were soluble in common organic solvents such as dichloromethane, chloroform, and THF. The results of the characterization of the polymers are listed in Table 1. The weight-average molecular weights (M_w) of the non-octyl-substituted polymers of the THF-soluble portionand of the octyl-substituted polymers were 2100−4100 and 7900−20000, with a polydispersity of 1.2−2.0 and 1.7−2.7, respectively, as determined by GPC (using THF as the eluent, based on polystyrene as the standard). The UV−Vis absorption spectra of the polymers in dilute solutions of THF were measured and classified into three categories, on the basis of the backbone arrangement. The UV−Vis absorption maxima of the poly-p-phenylene derivatives (**PP−PDA**, **PP2−PDA**, **octPP−PDA**, and **octPP2−PDA**), poly(thienylene) derivatives that include the mono-thiophenyl group (**PT−PDA** and **octPT−PDA**), and poly(thienylene) derivatives that include the dithienyl group (**PT2−PDA** and **octPT2−PDA**) appeared at 291−304, 306−310, and 442−460 nm, respectively. Because the absorption maxima are mainly determined by the backbone arrangement of the polymers, there are no effects of the substitute and molecular weight on the UV−Vis absorption maxima.

Scheme 1

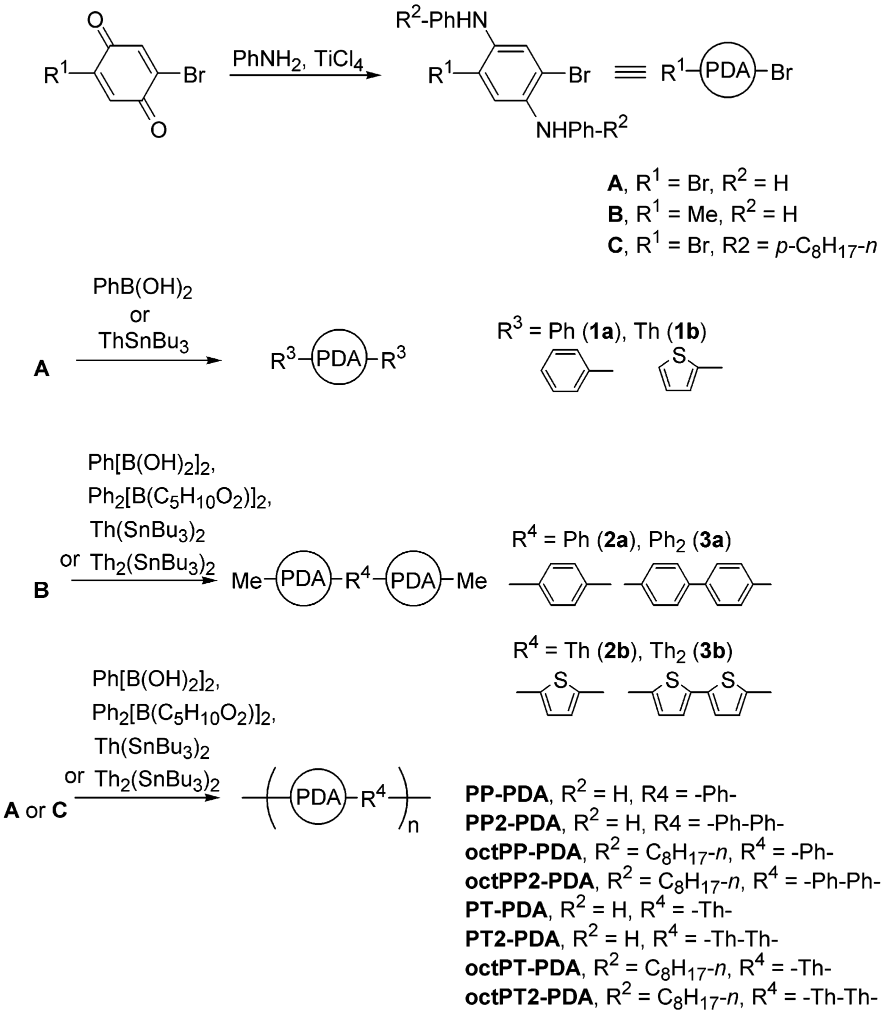


Table 1. Palladium-Catalyzed Polymerization[a]

polymer	yield[b] (%)	solvent	M_w[c] (g/mol)	M_w/M_n[c] (g/mol)	λ_{max}[d] (nm)	E^{o}[e] (V)
PP−PDA	89	DME, H_2O[f]	2100	1.2	291	0.28, 0.48
octPP−PDA	98	DME, H_2O[f]	7900	1.8	294	0.29, 0.44
PP2−PDA	100	DME, H_2O[f]	4100	2.0	302	0.29, 0.46
octPP2−PDA	100	DME, H_2O[f]	20000	2.7	304	0.27, 0.41
PT−PDA	79	dioxane[g]	3100	1.5	306, 436	0.40
octPT−PDA	93	dioxane[g]	14000	1.7	310, 437	0.36
PT2−PDA	100	dioxane[g]	3100	1.4	442, 303	0.40
octPT2−PDA	100	dioxane[g]	9500	1.5	460, 311	0.33

[a] All polymerizations were conducted for 48 h with 1 mol % palladium(0) catalysts. [b] Methanol-insoluble part. [c] Soluble portion, estimated by GPC (THF, PS). [d] In THF. [e] Redox potential of the polymer films on a GC electrode. Conditions: acetonitrile solution that contained $TBABF_4$ (0.2 M) and TFA (1 M). [f] A 2:1 mixture, with a concentration of 0.08 M at a temperature of 80 °C. [g] Concentration of 0.05 M at a temperature of 100 °C.

The IR spectra of all polymers showed absorptions at $\sim$3400 cm^{-1}, which indicate a N−H stretching vibration. Typical examples of the ^1H NMR spectra of **octPP2−PDA** and **octPT−PDA** are shown in Figure 1. The ^1H NMR spectra of **octPP2−PDA** and **octPT-PDA** in THF-d_8 each showed a sharp singlet, centered at 6.22 and 6.36 ppm, respectively, that was derived from the amine of the PDA units. No separated signals of the leaving group (such as the boronic acid, boronic acid, dimethylpropyl ester, or tributyltin groups as an end group) were identified, and the ^1H NMR chemical shift of the end groups, which have a bromine leaving group, had almost the same value as that of the backbone, and almost no end groups in these polymers were observed in the NMR. All signals were clearly detected, and the ratios of the integrated intensity of the amine were consistent with the expected polymers. These polymers are quite stable in air at room temperature.

3.2. Electrochemistry and Spectroelectrochemistry. The redox properties of the model compounds (PDA, **1a**, and **1b**) were confirmed by cyclic voltammetry (CV) (see Figure 2). These compounds underwent a two-step oxidation, from the amine to the radical cation to the imine forms. In the absence of TFA, the second redox couple was not reversible, because the oxidative half-reaction of the second couple involves the loss of one electron and two protons, whereas the cathodic half-reaction entails the gain of one electron and two

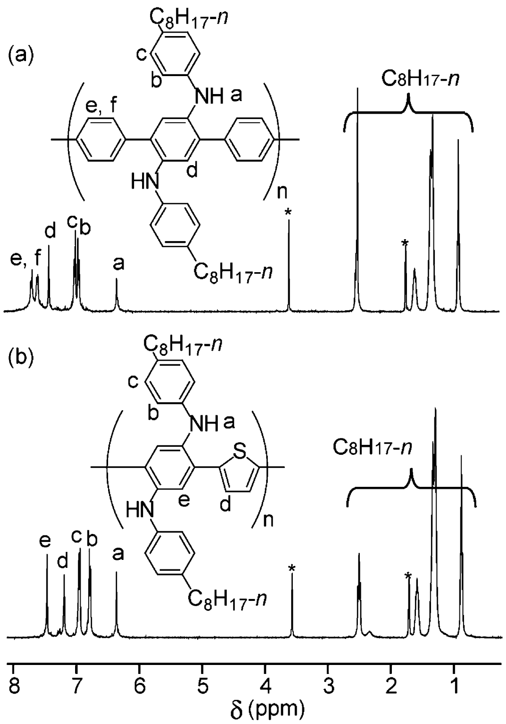


Figure 1. ^1H NMR spectra of (a) **octPP2−PDA** and (b) **octPT−PDA** in THF-d_8. Peaks marked with an asterisk (*) are assigned to the solvent (THF).

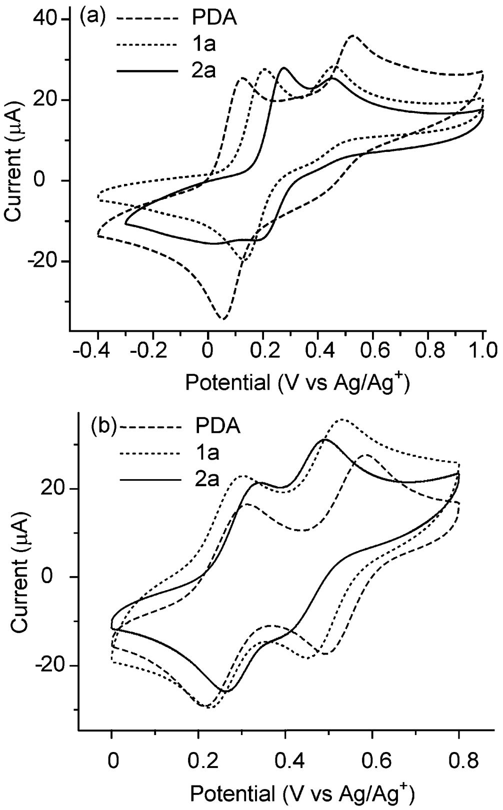


Figure 2. Cyclic voltammograms of model PDA compounds, **1a**, and **1b** (1 mM) for (a) an aprotic solution and (b) a solution that contained trifluoroacetic acid (1 M) in an acetonitrile. The electrolyte is TBABF$_4$ (0.2 M), and the scan rate is 100 mV/s.

protons.[6] In the presence of 1 M TFA, the cyclic voltammograms of PDA, **1a**, and **1b** each show two reversible redox waves at E°_1 and E°_2 (see Table 2). The potential splitting, ΔE ($E^\circ_2 - E^\circ_1$), of **1b** showed the smallest magnitude, because of the radical monocation delocalization into the thienyl group. These results were supported by the spectroelectrochemical measurement. The λ_{max} values of 698, 717, and 751 nm of the radical monocation were found for **PDA**, **1a**, and **1b**, respectively, meaning that the enhancement of the radical cation delocalization is expected to vary in the following order: **PDA** < **1a** < **1b**. The most broadened absorption band was exhibited by **1b**. These results show that the delocalization of the radical monocation expanded into the thiophene group via π-conjugation.

Table 2. $E_{1/2}$ Potentials (V, vs Ag/Ag$^+$) of Model Compounds (PDA, 1a, 1b) in Acetonitrile That Contained TBABF$_4$ (0.2 M) and Trifluoroacetic Acid (0.2 M)

	Potential (V)			Wavelength (nm)	
compound	E°_1[a]	E°_2[b]	ΔE[c]	λ_{max1}[d]	λ_{max2}[e]
PDA	0.27	0.55	0.28	698	518
1a	0.27	0.50	0.23	717	545
1b	0.30	0.45	0.15	751	551

[a] For a 0/1+ couple. [b] For a 1+/2+ couple. [c] $\Delta E = E^\circ_2 - E^\circ_1$. [d] For the radical monocation. [e] For the dication.

Table 3. Electrochemical Parameters of Model Compounds (1a−3a and 1b−3b)

compound	$\Delta E_{i/4}$[a] (mV)	ΔE[b] (mV)	$\Delta E_{(amine)}$[c] (mV)
1a	67	42	228
2a	72	48	220
3a	74	50	221
1b	67	42	170
2b	89	63	155
3b	87	61	132

[a] $\Delta E_{i/4}$ is the full width at three-fourths-maximum current of DPV. [b] Potential splitting based on the interaction between PDA units via the linking group. [c] Potential splitting based on the interaction between amines within a single PDA unit.

3.3. Electron Communication via a Backbone. To determine the potential difference between the PDA units exactly, the first redox waves of the compounds that have two PDA units (**2a**, **3a**, **2b**, and **3b**) were compared to the compounds that have one PDA unit, using the differential pulse voltammetry[24] (DPV) measurement (see Table 3 and Figure 3). Two oxidation peaks were observed in the case of the dimeric compounds of **2a**, **3a**, **2b**, and **3b**, despite them having four redox sites. Some electrochemical interactions, such as the coulombic repulsion, results in more splitting or broadening of the DPV oxidation waves, according to the electron communication intensity. Both the first and second oxidation waves of **2a** and **3a** or **2b** and **3b** show broadened peaks, compared to that of **1a** or **1b**. The full width at three-fourths maximum current ($\Delta E_{i/4}$) of DPV values of **2a** and **3a** were 72 and 74 mV, respectively, which are similar to that of **1a**. On the other hand, the $\Delta E_{i/4}$ values of **2b** and **3b** are 89 and 87 mV, respectively, which are 15 mV higher than that of **1b** (63 mV, which possesses nonelectron communication). These results support the existence of the intramolecular interaction between the two PDA units through the linking group in **2b** and **3b**. In addition, the potential difference between the two redox waves ($\Delta E_{(amine)}$) in **2b** and **3b** is smaller than that in **1b**, because the electronic communication between two PDA units reduces the coulombic repulsion within each PDA unit. The overlapping on the oxidation potential of the thiophene group (~0.6 V, vs Ag/Ag$^+$) and the PDA units is considered to allow the electronic communication

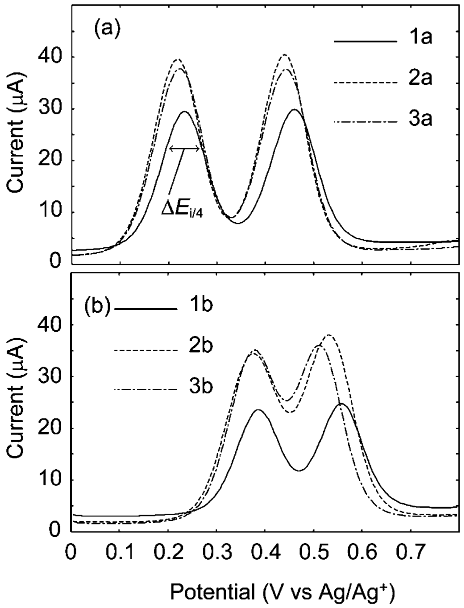


Figure 3. Differential pulse voltammograms of (a) **1a**, **2a**, and **3a** (1 mM) in an acetonitrile solution that contained TBABF$_4$ (0.2 M) and TFA (1 M), and (b) **1b**, **2b**, and **3b** in an acetonitrile solution that contained TBABF$_4$ (0.2 M) and TFA (5 M). Amplitude of DPV measurement is 50 mV.

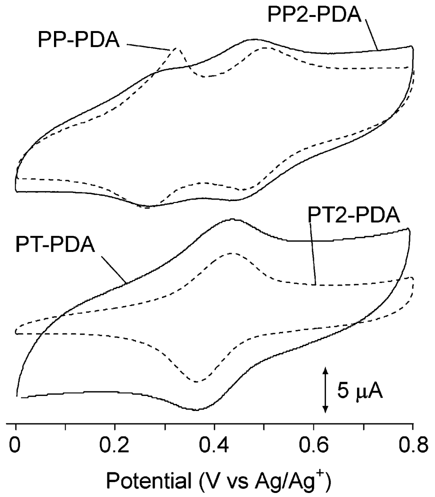


Figure 4. Cyclic voltammograms of cast films of **PP−PDA**, **PP2−PDA**, **PT−PDA**, and **PT2−PDA** on a GC electrode (0.071 cm^2) in an acetonitrile solution that contained TBABF$_4$ (0.2 M) and TFA (1 M) with a sweep range of 0.0−0.8 V, vs Ag/Ag$^+$. Scan rate is 100 mV/s.

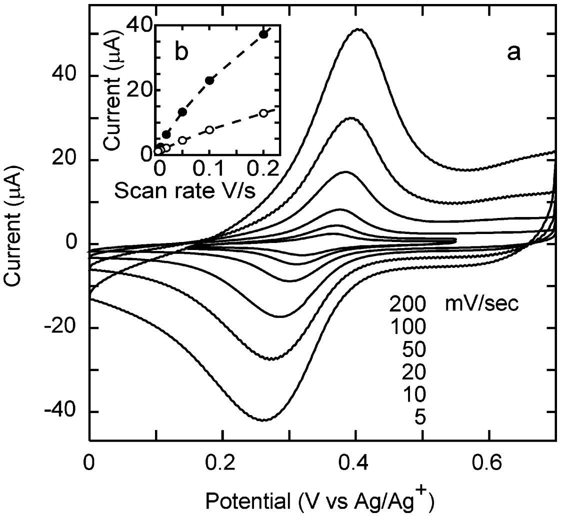


Figure 5. (a) Cyclic voltammograms of a cast film of **octPT2-PDA** on a GC electrode (0.071 cm^2) in an acetonitrile solution that contained TBABF$_4$ (0.2 M) and TFA (1 M) with a sweep range of 0.0−0.7 V, vs Ag/Ag$^+$. Scan rates of 5, 10, 20, 50, 100, and 200 mV/s were used. Inset (labeled b) shows the redox activity of (○) **octPT−PDA** and (●) **octPT2−PDA** polymers on a GC electrode (0.071 cm^2) in an acetonitrile solution that contained TBABF$_4$ (0.2 M) and TFA (1 M). This inset figure shows the relationship between the oxidation peak current (i_{pa}) and the scan rate in the cyclic voltammogram.

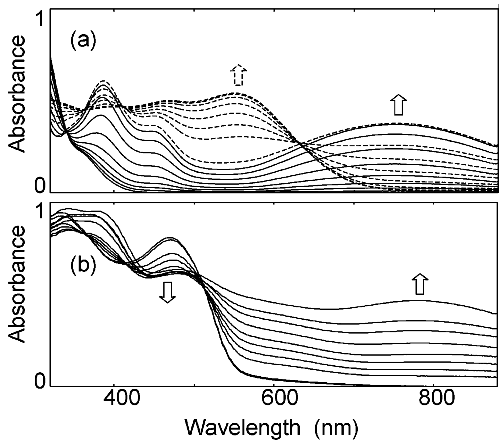


Figure 6. (a) UV−Vis spectra of the oxidation of **1b** (—) to the radical cation at a potential of 0−0.35 V, vs Ag/Ag$^+$, and (---) to the dication at a potential of 0.4−0.9 V, vs Ag/Ag$^+$. (b) UV−Vis spectra of **PT−PDA** film on an ITO electrode (0.2−0.6 V, vs Ag/Ag$^+$).

between the PDA units in **2b** and **3b**. In contrast, the higher oxidation potential of the phenyl group than that of the PDA units makes it difficult to have an interaction between the two PDA units.

3.4. Electrochemical Property of the Polymers. The redox properties of the resulting polymer films were confirmed by CV. The results of the redox waves were different between the poly-*p*-phenylene derivatives and the polythiophene derivatives. The typical results of the obtained polymer (**PP−PDA**, **PP2−PDA**, **PT−PDA**, and **PT2−PDA**) are shown in Figure 4, and the redox potentials are listed in Table 1. The polymer films of the poly-*p*-phenylene derivatives show two reversible redox couples, similar to the model compounds. However, that of the polythiophene derivatives showed only one reversible redox couple, at the center potential of the poly-*p*-phenylene derivatives. The octyl-substituted polymer films have redox potentials that are lower than those of the others. The octyl-substituted thiophene backbone polymers showed a good redox activity, and the plot of the oxidation peak current (i_{pa}) versus the scan rate (v) of the **octPT−PDA** and **octPT2−PDA** followed a straight line, with correlation coefficients of 0.993 and 0.991, respectively (see Figure 5).

From the spectroelectrochemical analysis of **1b**, two types of spectral changes that are based on two one-electron oxidations were confirmed at a potential of 0.0−0.8 V (see Figure 6, a). The absorption at ~751 nm and a potential of 0.35 V is assigned to the radical cation, which was formed by the one-electron oxidation per PDA unit, and that at ~551 nm and a potential of 0.6 V is assigned to the dication. These results show the character of the radical cation of only one PDA unit and the

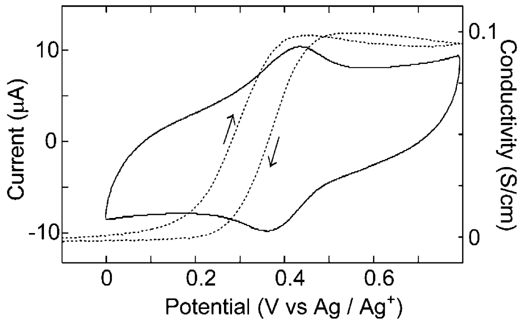
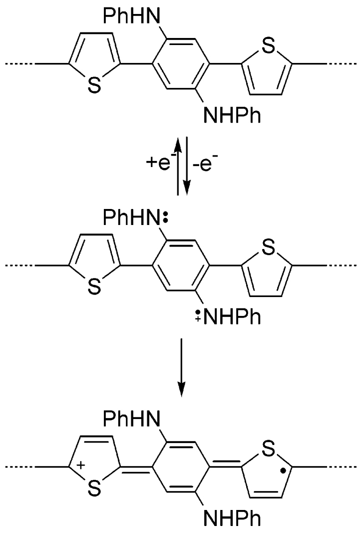


Figure 7. (—) Cyclic voltammogram and (···) in situ conductivity measurement) of **PT−PDA** films. Conditions: acetonitrile solution that contained $TBABF_4$ (0.2 M) and TFA (1 M), with a sweep range of 0.0−0.8 V, vs Ag/Ag^+, scan rate of 100 mV/s; cast film on a GC electrode (0.071 cm^2), scan rate of 100 mV/s for CV; cast film on platinum interdigitated array electrode, scan rate of 10 mV/s for conductivity measurement.

Scheme 2



example of no interaction between the two PDA units, similar to the model compounds **2a** and **3a** and the poly-*p*-phenylene derivatives. Only one redox wave was observed in the cyclic voltammograms of the films that contained the polythiophene derivatives. In the spectroelectrochemical analysis of the **PT−PDA** film, a broad absorption at ~750 nm and potentials of 0.5 V or higher is assigned to the radical cation, and the absorption did not disappear at a potential higher than 0.6 V (see Figure 6b). These results show that the radical cation formed in the polythiophene derivatives is stabilized by π-conjugation, expanded through the polythiophene backbone.

The conductivities of **PT−PDA** and **PT2−PDA** were measured using an interdigitated array electrode that was modified with a polymer by casting.[25−27] **PT−PDA** and **PT2−PDA** exhibited conductivities of 0.10 and 0.067 S/cm, respectively, by the one-electron oxidation of the PDA unit at 0.4 V, because of the formation of polarons in the main chain (see Figure 7 and Scheme 2).

4. Conclusion

Novel π-conjugated polymers and model compounds that have *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) units which act as two-electron redox units were synthesized and their redox properties were investigated. The polythiophene derivatives that have a PDA show a strong interaction between the intramolecular PDAs, and the radical cation that was formed at the amine of the PDA was delocalized. The electron transfer between the PDAs through the backbone of the thiophene was investigated.

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(22) It should be noted that compounds **A**, **B**, and **C** were obtained in a reduced state, because an excess amount of aniline worked as a reductant and their yields were dependent on their reductive efficiency to the products.
(23) As a coupling reaction for the introduction of a phenyl group, we employed one of the typical $Pd(0)(PPh_3)_4$ cross-coupling conditions. The cross coupling of PDA with a thiophene group was performed using a Stille coupling agent without CuI. The PDA unit would be oxidized in the palladium-catalyzed cycle, but model compounds of the polymers, 2,5-diphenyl- (**1a**) or 2,5-dithienyl- (**1b**) PDAs, were obtained in a reduced state through palladium-catalyzed Suzuki coupling or cross coupling of **A** with benzeneboronic acid or 2-(tributylstannyl)-thiophene in yields of 87% and 92%, respectively.
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