

A Novel Synthetic Route to Redox-Active Oligo(thio-1,4-phenylene) Derivatives via a Michael-Type Addition

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(Received March 6, 2002)

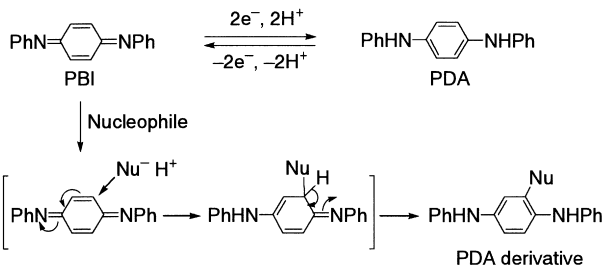
N,*N*′-Diphenyl-1,4-benzoquinone diimine (PBI), which is the minimum redox-active unit of polyaniline, was reduced to *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) derivatives through Michael-type additions of some nucleophiles. The addition of thiophenol to PBI proceeded very rapidly. The polyaddition of PBI-endcapped monomers (P-2PBI, B-2PBI, and TB-2PBI) with thiobisbenzenethiol (TB) produced the novel thermostable oligo(thio-1,4-phenylene)s (OTP) having PDA units as a redox-active site (OTP-P-PDA, OTP-B-PDA, and OTP-PDA). This polymerization proceeded at room temperature without catalysts. OTP-P-PDA, one of the oligomers obtained, was found to have a moderate molecular weight (M_w 8400) and to possess good thermostability ($Td_{10\%}$ 400 °C). The polymerization based on Michael-type additions was also confirmed by NMR measurements. The oligomers obtained behaved as good electro-responsive materials. The redox process was determined by the slope of the Nernst plot that involved two electrons and two protons per PDA unit.

Redox-active macromolecules such as π-conjugated polymers have received much attention as electrical materials,[1] especially as electrodes in batteries and in capacitors, sensors, and electronic displays. This is due to their properties of electrically quick response. Up to now, π-conjugated polymers[2] have been developed for this purpose due to their high electrical conductivity. However, they generally lack the chemical and thermal stability for these electrical applications. Thus, thermostable polymers possessing redox activity and good reliability for long term use have been strongly desired for use in electronic devices. One approach for obtaining the desired polymer involves the introduction of a redox active site into a thermostable aromatic polymer.[3] Poly(thio-1,4-phenylene) (PTP) is well known to exhibit good thermal stability, moldability and chemical resistance and is an excellent engineering plastic.[4] However, it is a difficult polymer to synthesize under mild conditions. Therefore, considerable effort has been exerted in developing new synthetic methods for its preparation.[5]

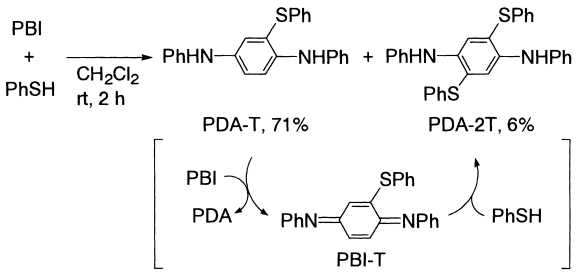
Recently, polyaniline has been shown to react with nucleophiles such as amines and thiols at room temperature.[6] This reaction is noteworthy for the arylsulfide bond formation via nucleophilic substitution of a thiol on the imine compounds. Herein, we describe a novel synthetic method of redox-active oligo(thio-1,4-phenylene)s (OTP) containing *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) units;[7] the yields, molecular weight, thermostability, and redox properties of the oligomers obtained were compared. The process involves a Michael-type addition on the compounds having a double bond with an electron-attractive group.[8]

Results and Discussion

Michael-Type Additions of Nucleophiles to PBI. *N*,*N*′-Diphenyl-1,4-benzoquinone diimine (PBI), which is the minimum redox-active unit of polyaniline, is reversibly converted to *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) by chemical or electrochemical oxidation/reduction as shown in Scheme 1. PBI was reduced to PDA by a Michael-type addition of a nucleophile at room temperature. Since PBI has a absorption at 450 nm based on CT, the reduction process is confirmed as the decrease in the absorption of PBI in its UV-vis spectra. Initially, the Michael reaction of PBI with nucleophiles was investigated in *N*-methyl-2-pyrrolidone (NMP) as the solvent. The absorption at 450 nm gradually decreased with the addition of the nucleophile. Kinetic analysis of the UV-vis spectra revealed that thiols such as benzenethiol, hexadecanethiol, and methanethiol reacted quantitatively with PBI. The reactions were shown to obey pseudo-1st-order kinetics, where the rate constants for benzenethiol, hexadecanethiol, and sodium methoxide were found to be 3.4×10^{-3}, 2.8×10^{-4}, and 5.0×10^{-3} s^{-1}, respectively. In contrast, the addition of aniline or phenol to PBI was not observed due to its relatively low nucleophilicity. As a result, thiols were found to be good nucleophiles for PBI. During the addition of benzenethiol to PBI, a solvent effect was observed during the Michael reaction. The rate constants in NMP, *N*,*N*-dimethylformamide (DMF), acetone, and dichloromethane were determined to be 3.4×10^{-3}, 4.8×10^{-3}, 1.1×10^{-2}, and 1.3×10^{-2} sec^{-1}, respectively. The rate



Scheme 1.



Scheme 2.

constant in dichloromethane is 4 times greater than that in NMP. The reaction rapidly proceeds in a nonpolar solvent by preventing the stabilization of the nucleophile by the solvation.

Control Reaction of PBI with Benzenethiol. A control reaction of PBI with benzenethiol was carried out in dichloromethane for 2 h at room temperature (Scheme 2). The 2-phenylthio-PDA (PDA-T) and 2,5-bis(phenylthio)-PDA (PDA-2T) were isolated by silica gel column chromatography in 71 and 6% yields, respectively. The Michael-type addition of benzenethiol to the quinone of PBI gave PDA-T. On the other hand, PDA-2T was formed via the addition of benzenethiol to PBI-T, which was the oxidized form of PDA-T. Since PDA-T has a lower oxidation potential (0.23 V vs SCE at pH 1.3) than that of PDA (0.28 V), some of the PBI acts as an oxidant of PDA-T. As a result, PDA as the reduced form of PBI was detected in a 17% yield in this reaction. In other words, more than 94% of the PBI was converted to addition product in this reaction. Diphenyl disulfide as a side product was detected only in very small amounts based on HPLC. These results also suggest that the nucleophilic addition proceeded quantitatively. The ^{1}H-NMR spectrum of PDA-2T (Fig. 1b) supported the symmetry of PDA di-substituted with phenylthio groups at 2,5- or 2,3-positions; the positions were decided to be 2,5-ones by ^{1}H-COSY and NOESY measurements. Nuclear Overhauser effects (NOE) between the proton (a singlet peak at δ 6.98 ppm) on the central phenyl ring and the proton (δ 7.23 ppm) of the thiophenylene ring at the *o*-position were observed. These results provided support for the idea that the 2,3- and 2,6-bis(phenylthio)-PDAs were difficult to form via this reaction. Such results suggested that benzenethiol was preferentially substituted at the 5-position of the central 1,4-benzoquinone ring of PBI-T due to the steric hindrance and electron-donating effect of the phenylthio group. This means that a Michael-type addition should afford a linear thiophenylene polymer during polymerization conditions.

Synthesis of Oligo(thio-1,4-phenylene) Derivatives via a Michael-Type Addition. As a synthetic strategy for obtaining thermostable polymers having PDAs as a redox unit, we selected the Michael-type polyaddition of a dithiol to a PBI-endcapped compound (Scheme 3). Three kinds of PBI-endcapped monomers were obtained in 2 synthetic routes, as shown in Scheme 4. As PDA-endcapped monomers, 1,4-PDA-endcapped benzene (P-2PDA) and 4,4′-PDA-endcapped biphenyl (B-2PDA) were synthesized via route 1. P-2PDA and B-2PDA were synthesized in 80 and 77% yields, respectively, through Suzuki coupling of the *p*-phenylenebis(dihydroxyborane) or 4,4′-biphenyldiylbis(dihydroxyborane) with 2-bromo-5-methyl-*N*,*N*′-diphenyl-1,4-phenylenediamine (PDA-Br).

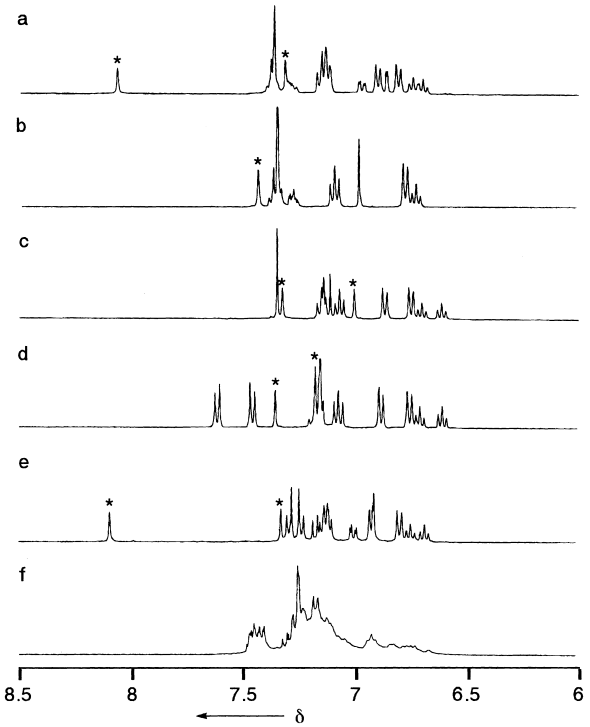
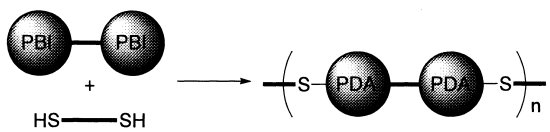
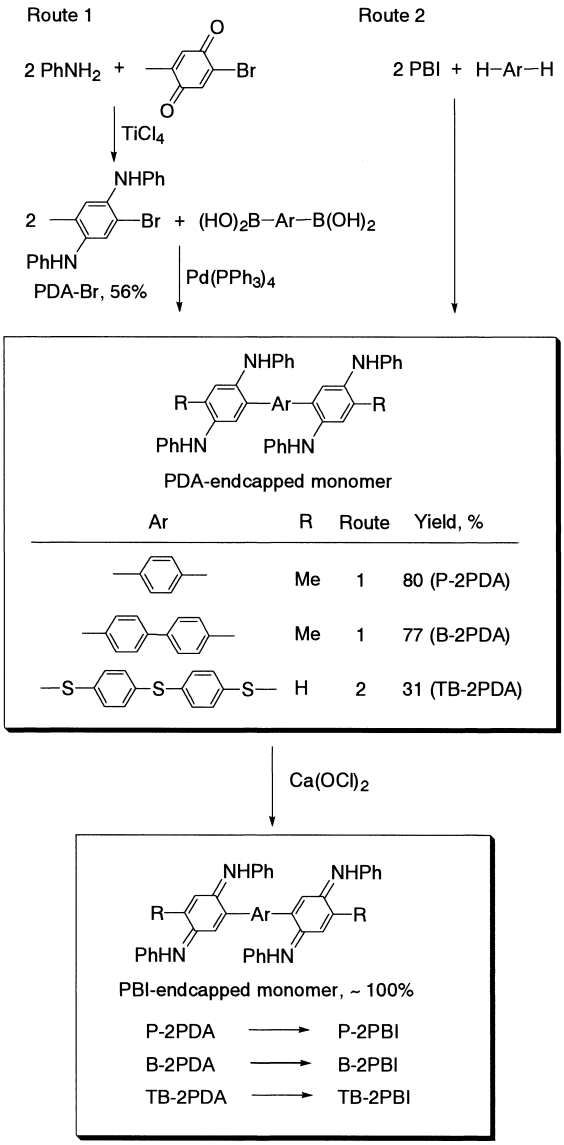


Fig. 1. The ^{1}H NMR spectra (400 MHz, DMSO−d_6) of (a) PDA-T, (b) PDA-2T, (c) P-2PDA, (d) B-2PDA, (e) TB-2PDA, and (f) OTP-PDA. The marked peaks (*) are assigned to amine protons.

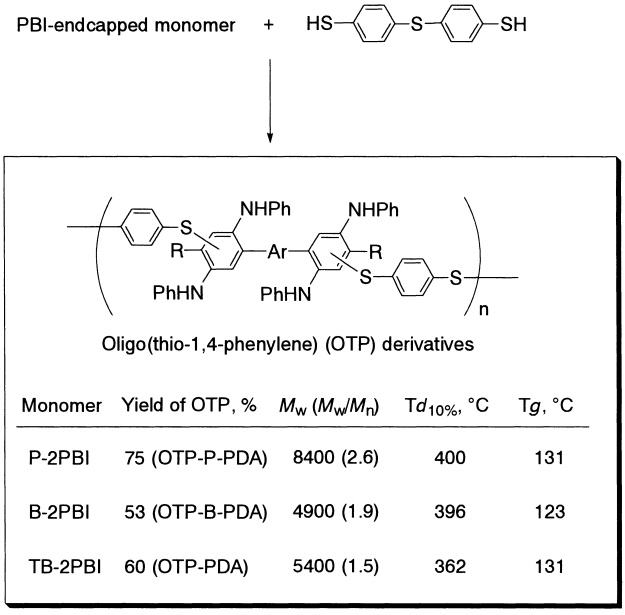


Scheme 3.

The PDA-Br was obtained in 56% yield by the dehydration of 2-bromo-5-methyl-1,4-benzoquinone with aniline in the presence of titanium(IV) tetrachloride. 1,1′-PDA-endcapped 4,4′-thiobis(benzenethiol) (TB-2PDA) was synthesized using route 2. TB-2PDA was synthesized in a 31% yield by the Michael-type reaction of PBI (1.0 mmol) with TB (0.5 mmol). The three kinds of PDA-endcapped monomers obtained, using both routes, were quantitatively converted to the PBI-endcapped monomers by oxidation with $Ca(OCl)_2$. As shown in Scheme 5, the polymerization of the PBI-endcapped monomers with TB proceeded in dichloromethane at room temperature for 24 h to give the corresponding oligomers (OTP-P-PDA, OTP-B-PDA, and OTP-PDA). The orange color of the mixture disappeared during the polymerization due to the reduction of the imine to the amine structure. The mixture was poured into methanol to precipitate the oligomer. The oligomers were isolated in 53–75% yields as white powders that were soluble in dichloromethane, DMSO, THF and NMP. The yields, molecular weight (M_w and M_w/M_n), and thermostability ($Td_{10\%}$ and T_g) are summarized in Scheme 5.[9] The oligomer obtained in a higher yield (PTP-P-PDA, a 75% yield) showed higher molecular weight (M_w 8400) based on the general rule of polyaddition. The thermostability ($Td_{10\%}$) was enhanced up to 400 °C



Scheme 4.



Monomer	Yield of OTP, %	M_w (M_w/M_n)	$Td_{10\%}$, °C	Tg, °C
P-2PBI	75 (OTP-P-PDA)	8400 (2.6)	400	131
B-2PBI	53 (OTP-B-PDA)	4900 (1.9)	396	123
TB-2PBI	60 (OTP-PDA)	5400 (1.5)	362	131

Scheme 5.

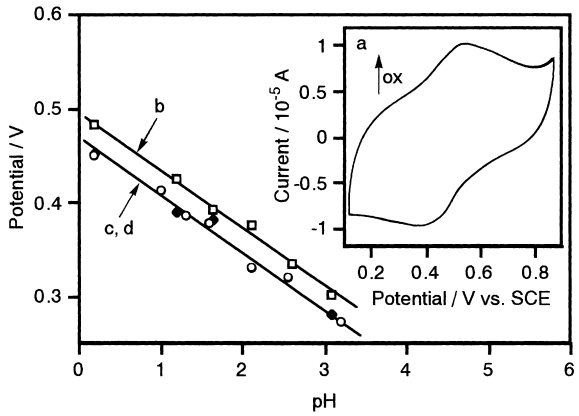
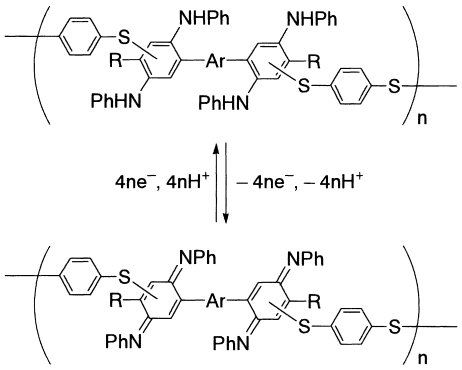


Fig. 2. (a) Cyclic voltammograms of OTP-PDA coated on a glassy carbon electrode in 0.2 M Na_2SO_4/H_2SO_4 aqueous solution (pH 0.19) and the Nernst plots of (b) OTP-P-PDA, (c) OTP-P-PDA, and (d) OTP-B-PDA.

by introduction of the *p*-terphenyl moiety into the main chain of the oligomer without decrease in the solubility.

The NMR Measurements of the PDA-Endcapped Monomers and Oligomers.[10] In each oligomer, the presence of an amino group (3386–3399 cm^{-1}) was confirmed by its IR spectrum. Polymerization via the Michael-type addition was also indicated from the ^1H NMR measurements. PDA units, mono-substituted at the 2-position, and PDA units di-substituted at the 2,5-position, showed large differences in the chemical shifts of the peaks assigned to the amine protons by exchange with D_2O. In the spectrum of mono-substituted PDA-T, two peaks attributed to the two amine protons appeared at δ 8.06 and δ 7.32 ppm (Fig. 1a). Similar to the NMR of PDA-T, the two peaks assigned to the 4 amine protons at δ 8.08 and δ 7.32 ppm were confirmed in the spectra of TB-2PDA (Fig. 1e). In contrast, one peak assigned to the two amine protons appeared at δ 7.43 ppm in the spectrum of di-substituted PDA-2T (Fig. 1b). These spectra show that a peak around 8.0 ppm in the mono-substituted PDA unit is shifted to around 7.4 ppm in a di-substituted one. This shift was also confirmed in the spectra of P-2PDA and B-2PDA, that is, two peaks between 7.5–7.0 ppm appeared in each spectrum since P-2PDA and B-2PDA have PDA units di-substituted by a methyl group and a phenyl one at the 2,5-position (Figs. 1c and 1d). Therefore, the absence of peaks around 8.0 ppm in the spectrum of OTP-PDA support the conclusion that the PDA units in TB-2PDA were converted to di-substituted ones by polymerization based on the Michael-type addition (Fig. 1f).

Electrochemical Property of Oligomers. The electrochemical response of the oligomers was examined using the electrode modified by the oligomer film (1.6×10^{-8} unit mol/cm^2) as shown in Fig. 2a. Three types of oligomers showed a similar redox activity in an acidic medium (pH 0–4). The redox potentials of OTP-P-PDA, OTP-B-PDA, and OTP-PDA were observed at 0.45, 0.45, and 0.48 V vs SCE at pH 0.19, respectively. The potentials are slightly different due to the dif-



Scheme 6.

ferent substitutent groups on the PDA units. The redox cycles were stable for more than one hundred scans. The oxidation and reduction peak currents are proportional to the scan rate during cyclic voltammetry. These results mean that excellent redox activity was maintained even in the thiophenylene polymers. The redox potentials depend on the pH of the mixture, which means that the electron transfer process is associated with proton transfer. On the basis of the Nernst plots, the slope for the redox reaction of each oligomer was determined to be ca. −60 mV/pH (Figs. 2b, 2c, and 2d). These results indicate that the redox process involves two electron and two proton transfers per PDA unit (Scheme 6). The oligomers promote a two-electron transfer accompanied with a two-proton transfer, thereby functioning as good electro-responsive materials.

Conclusion

Based on the rapid Michael-type addition of thiophenol to *N*,*N*′-diphenyl-1,4-benzoquinone diimine (PBI), we established a novel synthetic method for preparing oligo(thio-1,4-phenylene) derivatives having redox-active *N*,*N*′-diphenyl-1,4-phenylenediamine (PDA) units. This polyaddition proceeded at room temperature without catalysts to give the oligomers with moderate molecular weight and thermostability. The oligomers obtained behaved as good electro-responsive materials, and the redox process which involved two electrons and two protons per PDA unit was determined by the slope of the Nernst plot.

Experimental

Synthesis of PDA-T and PDA-2T. *N*,*N*′-Diphenyl-1,4-benzoquinone diimine (PBI, 129 mg, 0.500 mmol) dissolved in dichloromethane (50 mL) was added to the dichloromethane solution (50 mL) of benzenethiol (55.1 mg, 0.500 mmol) using a dropping funnel. The reaction mixture was stirred at room temperature for 2 h. The orange color of the solution changed to yellow. The solution was concentrated, and PDA-T (131 mg, 71%, brown viscous liquid) and PDA-2T (11.3 mg, 6%, yellow crystals) were isolated by silica gel column chromatography (hexane:dichloromethane = 3:1–1:1). PDA-T: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 8.06 (s, 1H), 7.32 (s, 1H), 7.34 (m, 5H), 7.18 (d, 1H, J = 8.79 Hz), 7.14 (m, 4H), 6.97 (dd, 2H, J = 2.44, 8.79 Hz), 6.90 (d, 2H, J = 8.31 Hz), 6.86 (d, 1H, J = 2.44 Hz), 6.81 (d, 2H, J = 8.30 Hz), 6.74 (t, 1H, J = 7.81 Hz), 6.70 (t, 1H, J = 7.32 Hz); ^{13}C NMR (100 MHz, DMSO−d_6, TMS standard, 30 °C) δ 145.92, 143.47, 139.53, 134.25, 133.92, 131.26, 130.42, 129.51, 129.01, 128.89, 128.38, 124.25, 119.42, 119.27, 118.24, 117.55, 116.04, 114.98; IR (KBr) 3389 (NH), 1496 cm^{-1}(phenyl); EI-MS *m*/*z* 368 [M]$^+$; Anal. Calcd for $C_{24}H_{20}N_2S$: C, 78.22; H, 5.47; N, 7.60%. Found: C, 77.84; H, 5.11; N, 7.35%. PDA-2T: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 7.43 (s, 2H), 7.33 (m, 8H), 7.23 (m, 2H), 7.09 (t, 4H, J = 7.81 Hz), 6.98 (s, 2H), 6.77 (d, 4H, J = 7.82 Hz), 6.72 (t, 2H, J = 7.32 Hz); ^{13}C NMR (100 MHz, DMSO−d_6, TMS standard, 30 °C) δ 144.28, 136.91, 133.90, 130.85, 129.56, 128.87, 127.61, 127.44, 123.79, 119.32, 116.15; IR (KBr) 3366 (NH), 1507 cm^{-1} (phenyl); EI-MS *m*/*z* 476 [M]$^+$; Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.59; H, 5.08; N, 5.88%. Found: C, 75.57; H, 4.71; N, 5.89%.

Synthesis of PDA-Br. Titanium tetrachloride (2.14 g, 11.3 mmol) was added in the chlorobenzene solution (40 mL) of aniline (9.35 g, 0.100 mol) at 90 °C. 2-Bromo-5-methyl-*p*-benzoquinone (1.51 g, 5.68 mmol) dissolved in chlorobenzene (20 mL) were added in the solution, and the mixture was stirred at 135 °C for 24 h. The solution was filtrated and concentrated, and PDA-Br (1.12 g, 3.18 mmol, 56%) was isolated by silica gel column chromatography (hexane:dichloromethane = 1:1, R_f = 0.52). PDA-Br: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C,) δ 7.40 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.19 (dd, J = 8.4, 8.4 Hz, 2H), 7.18 (dd, J = 8.4, 8.4 Hz, 2H), 7.15 (s, 1H), 6.88 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 6.76 (t, J = 8.4 Hz, 1H), 6.76 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO−d_6, TMS standard, 30 °C) δ 144.87, 144.76, 137.45, 135.09, 130.74, 128.89, 128.77, 124.72, 124.35, 118.77, 118.73, 115.73, 115.62, 114.00, 17.65; IR (KBr) 3404 (NH), 1597 cm^{-1} (phenyl); EI-MS *m*/*z* 352 [M]$^+$, 354 [M + 2]$^+$; Anal. Calcd for $C_{19}H_{17}N_2Br$: C, 64.60; H, 4.85; N, 7.93%. Found: C, 64.78; H, 4.71; N, 7.81%.

Synthesis of P-2PDA. PDA-Br (353 mg, 1.00 mmol), 1,4-phenylenebis(dihydroxyborane) (82.9 mg, 0.50 mmol), and $Pd(PPh_3)_4$ (55.6 mg, 0.048 mmol) were dissolved in DMF (9 mL). Sodium carbonate (2 M aq, 4.5 mL) was added in the solution, and the solution was stirred at 70 °C for 16 h. Dichloromethane was added in the reaction mixture; the dichloromethane solution was washed with aqueous ammonium and brine, and dried over anhydrous sodium sulfate. P-2PDA (249 mg, 0.40 mmol, 80%) was isolated by silica gel column chromatography (hexane : dichloromethane = 2:1, R_f = 0.47 in the solution of hexane:dichloromethane 1:1). P-2PDA: ^{1}H NMR (400 MHz, THF−d_8, TMS standard, 30 °C) δ 7.38 (s, 4H), 7.22 (s, 2H), 7.17 (s, 2H), 7.09 (dd, J = 7.3, 7.3 Hz, 4H), 7.08 (dd, J = 7.3, 7.3 Hz, 4H), 6.85 (d, J = 7.3 Hz, 4H), 6.81 (d, J = 7.3 Hz, 4H), 6.67 (t, J = 7.3 Hz, 2H), 6.66 (t, J = 7.3 Hz, 2H), 6.51 (s, 2H), 6.29 (s, 2H), 2.20 (s, 2H); ^{13}C NMR (100 MHz, THF−d_8, TMS standard, 30 °C) δ 146.98, 146.85, 138.91, 137.35, 135.77, 133.34, 131.92, 129.61, 129.46, 129.42, 125.31, 124.86, 119.18, 119.00, 116.20, 116.11, 17.88; IR (KBr) 3396 (NH), 1599 cm^{-1} (phenyl); EI-MS *m*/*z* 622 [M]$^+$; Anal. Calcd for $C_{44}H_{38}N_4$: C, 84.85; H, 6.15; N, 9.00%. Found: C, 84.40; H, 6.44; N, 8.74%.

Synthesis of OTP-P-PDA. Calcium hypochlorite (0.215 g, 1.50 mmol) was added to the dichloromethane solution (4 mL) of P-2PDA (0.153 g, 0.245 mmol), and the solution was stirred at room temperature for 4 h. The yellow color of the solution changed to orange. P-2PBI (0.149 g, 98%, orange powder) was isolated by filtration and concentration of the reaction mixture. TB (50 mg, 0.2 mmol) dissolved in dichloromethane (25 mL) was added to the dichloromethane solution (25 mL) of P-2PDI (0.124 g, 0.20 mmol) using a dropping funnel, and stirred at room tem-

perature for 24 h. The orange color of the solution changed to white. The reaction mixture was reprecipitated in methanol; OTP-P-PDA (0.130 g, 75%, yellow powder) was isolated by filtration. OTP-P-PDA: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 7.40–6.29 (m), 2.39–2.14 (m); IR (KBr) 3399 (NH), 1491 cm^{-1} (phenyl).

Synthesis of B-2PDA. PDA-Br (353 mg, 1.00 mmol), 4,4′-biphenyldiylbis(dihydroxyborane) (121 mg, 0.50 mmol), and $Pd(PPh_3)_4$ (55.6 mg, 0.048 mmol) were dissolved in 1,2-dimethoxyethane (9 mL). Sodium carbonate (2 M aq, 4.5 mL) was added in the solution, and the solution was stirred at 70 °C for 16 h. Dichloromethane was added in the reaction mixture; the dichloromethane solution was washed with aqueous ammonia and brine, and dried over anhydrous sodium sulfate. B-2PDA (0.269 g, 77%) was isolated by silica gel column chromatography (hexane:dichloromethane = 2:1, R_f = 0.26 in the solution of hexane:dichloromethane = 1:1). B-2PDA: ^{1}H NMR (400 MHz, THF−d_8, TMS standard, 30 °C) δ 7.60 (d, J = 8.0 Hz, 4H), 7.47 (d, J = 8.0 Hz, 4H), 7.25 (s, 2H), 7.22 (s, 2H), 7.10 (dd, J = 8.0, 8.0 Hz, 4H), 7.10 (dd, J = 8.0, 8.0 Hz, 4H), 6.90 (d, J = 8.0 Hz, 4H), 6.82 (d, J = 8.0 Hz, 4H), 6.69 (t, J = 8.0 Hz, 2H), 6.67 (t, J = 8.0 Hz, 2H), 6.55 (s, 2H), 6.36 (s, 2H), 2.21 (s, 2H); ^{13}C NMR (100 MHz, THF−d_8, TMS standard, 30 °C) δ 146.23, 139.11, 138.62, 136.65, 135.07, 132.52, 131.34, 129.33, 128.75, 128.68, 126.95, 126.51, 124.69, 124.23, 118.40, 118.23, 115.37, 115.30, 17.16; IR (KBr) 3389 (NH), 1599 cm^{-1} (phenyl); MALDI-TOF-MS m/z 698 $[M]^+$; Anal. Calcd for $C_{50}H_{42}N_4$: C, 85.93; H, 6.06; N, 8.02%. Found: C, 85.77; H, 6.00; N, 7.74%.

Synthesis of OTP-B-PDA. Calcium hypochlorite (0.215 g, 1.50 mmol) was added to the dichloromethane solution (4 mL) of B-2PDA (0.175 g, 0.250 mmol), and the solution was stirred at room temperature for 4 h. The yellow color of the solution changed to orange. B-2PBI (0.170 g, 98%, orange powder) was isolated by filtration and concentration of the reaction mixture. TB (50 mg, 0.2 mmol) dissolved in dichloromethane (25 mL) was added to the dichloromethane solution (25 mL) of B-2PDI (0.140 g, 0.20 mmol) using a dropping funnel. The solution was stirred at room temperature for 24 h. The orange color of the solution changed to white. The reaction mixture was reprecipitated in methanol; OTP-B-PDA (0.113 g, 53%, yellow powder) was isolated by filtration. OTP-B-PDA: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 7.75–6.32 (m), 2.25–2.07 (m); IR (KBr) 3388 (NH), 1490 cm^{-1} (phenyl).

Synthesis of TB-2PDA. PDI (0.260 g, 1.00 mmol) dissolved in dichloromethane (100 mL) was added to the dichloromethane solution (50 mL) of TB (0.123 g, 0.50 mmol) using an additional funnel. The reaction mixture was stirred at room temperature for 2 h. The orange color of the solution changed to yellow. The solution was concentrated, and TB-2PDA (112 mg, 31%, brown yellow solid) was isolated by silica gel column chromatography (hexane:dichloromethane = 3:1–1:1). TB-2PDA: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 8.08 (s, 2H), 7.32 (s, 2H), 7.28 (d, 4H, J = 8.31 Hz), 7.23 (d, 4H, J = 8.31 Hz), 7.17 (d, 2H, J = 8.30 Hz), 7.13 (t, 4H, J = 7.32 Hz), 7.11 (t, 4H, J = 7.32 Hz), 7.00 (dd, 2H, J = 2.45, 8.79 Hz), 6.92 (d, 4H, J = 7.32 Hz), 6.91 (d, 2H, J = 2.45 Hz), 6.79 (d, 4H, J = 7.81 Hz), 6.74 (t, 2H, J = 7.32 Hz), 6.68 (t, 2H, J = 7.32 Hz); ^{13}C NMR (100 MHz, DMSO−d_6, TMS standard, 30 °C) δ 145.76, 143.39, 139.53, 134.33, 134.25, 133.28, 131.54, 131.44, 129.19, 129.00, 128.84, 124.27, 119.87, 119.35, 118.27, 117.94, 116.17, 115.00; IR (KBr) 3390 (NH), 1499 cm^{-1} (phenyl); FAB-MS m/z 767 $[M+1]^+$; Anal. Calcd for $C_{48}H_{38}N_4S_3$: C, 75.16; H, 4.99; N, 7.31%. Found: C, 75.11; H, 4.69; N, 7.06%.

Synthesis of OTP-PDA. Calcium hypochlorite (0.172 g, 1.20 mmol) was added to the dichloromethane solution (4 mL) of TB-2PDA (0.153 g, 0.20 mmol), and the solution was stirred at room temperature for 4 h. The yellow color of the solution changed to orange. The reaction mixture was reprecipitated in water; TB-2PBI (99%, orange powder) was isolated by filtration and concentration of the reaction mixture. TB (50 mg, 0.2 mmol) dissolved in dichloromethane (25 mL) was added to the dichloromethane solution (25 mL) of the TB-2PBI using a dropping funnel. The solution was stirred at room temperature for 24 h. The orange color of the solution changed to white. The reaction mixture was reprecipitated in methanol; OTP-PDA (60%, yellow powder) was isolated by filtration. OTP-PDA: ^{1}H NMR (400 MHz, DMSO−d_6, TMS standard, 30 °C) δ 7.45–6.62 (m); IR (KBr) 3386 (NH), 1495 cm^{-1} (phenyl).

This work was partially supported by Grants-in-Aid for Scientific Research (Nos. 11555253, 11136245, and 11167273) from the Ministry of Education, Science, Sports and Culture, ; by a Kanagawa Academy of Science and Technology research Grant (Project No. 23); by the Kawakami foundation; and by a Grant-in-Aid for Unique Development for Technology from the Science and Technology Agency.

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9 High molecular weight polymers were not obtained in the reaction, because a part of the PBI-type monomers were reduced to PDA-type by the reaction with PDA units of the oligomers, similar to the case of the control reaction of PBI with benzenethiol. Therefore, both ends of the obtained oligomers are considered to be thiol groups.

10 The PDA units of the compounds obtained are gradually oxidized to PBI in the air with moisture, but they are stable over 6 months in a refrigerator.