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Synthesis and characterization of *p*-phenylenediamine derivatives bearing a thiadiazole unit

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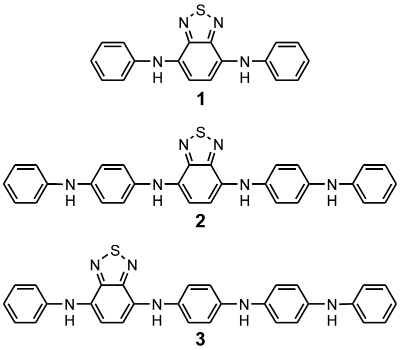
Abstract—New *p*-phenylenediamine derivatives bearing a thiadiazole unit were synthesized by palladium-catalyzed amination. Cyclic voltammetry revealed that the electrochemical properties depend on the position of the benzothiadiazole ring. © 2002 Elsevier Science Ltd. All rights reserved.

The π-conjugated polymers have attracted much attention in the application to electrical materials depending on their electrical properties.[1] The oxidation states of the π-conjugated polymers and oligomers interconvert each other.[2] For example, polyanilines exist in three different discrete redox forms, which include a fully reduced leucoemeraldine base form, a semioxidized emeraldine one, and a fully oxidized pernigraniline one.[3] These properties are considered to permit the construction of a catalytic system for oxidation reaction. Polyanilines and polypyrroles serve as synthetic metal catalysts under an oxygen atmosphere in the dehydrogenative oxidation of benzylamines, 2-phenylglycine, and 2,6-di-*t*-butylphenol.[4] Similar catalysis is also achieved with the quinonediimine derivatives.[5] Two nitrogens of the quinonediimine moiety have been revealed to be capable of participating in the complexation with transition metals.[6]

Furthermore, control of the band gap of π-conjugated polymers and oligomers is a research issue of ongoing interest. Such control is essential for the desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford a conducting polymer.[7] One of the most successful approaches to the low band gap polymers depends on an alternating sequence of donor–acceptor units in the π-conjugated polymer chain.[8,9] 2,1,3-Benzothiadiazole, which bears two electron-withdrawing imine (C=N) nitrogens, is known as a typical electron-accepting unit. When this unit is combined with an electron-donating unit, the donor–acceptor polymer or oligomer may exhibit a narrow band gap. However, most of these donor–acceptor polymers comprise pyrrole, thiophene, or phenylene as a donor unit. Introduction of acceptor units like benzothiadiazole into an aniline oligomer chain is expected to give a novel π-conjugated compound, which exhibits different redox properties as compared with those of aniline oligomers themselves.[5] In this paper, we report the synthesis and characterization of *p*-phenylenediamine derivatives bearing a thiadiazole unit. Not only the aniline analogue **1**, but also **2** and **3** bearing the thiadiazole unit in a different position were used in order to study the effect of the position on an aniline oligomer chain (Scheme 1).

Synthetic routes to **1**, **2** and **3** are shown in Scheme 2. Amination of 4,7-dibromo-2,1,3-benzothiadiazole (**4**)[10] was carried out by modifying a method reported for the preparation of aniline oligomers by Buchwald et al.,[11]



Scheme 1. *p*-Phenylenediamine derivatives bearing a thiadiazole unit investigated in this study.

Keywords: *p*-phenylenediamine; thiadiazole; redox; donor/acceptor.

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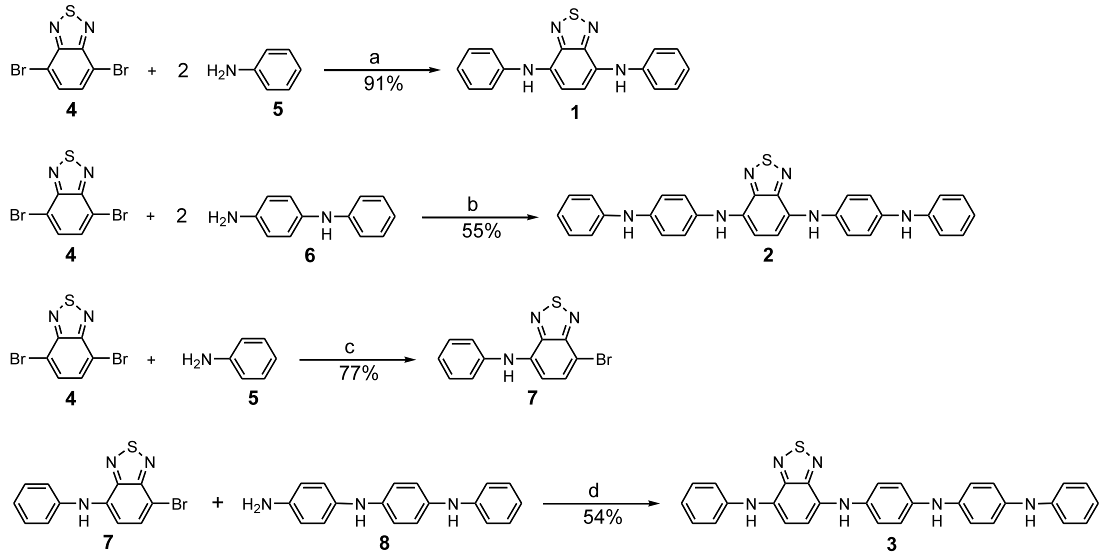


Scheme 2. Synthesis of aniline oligomers bearing a thiadiazole unit. *Reagents and conditions*: (a) 10 mol% $Pd(OAc)_2$, 11 mol% DPEphos, 2.8 equiv. *t*-BuONa, toluene, reflux, 27 h; (b) 10 mol% $Pd(OAc)_2$, 11 mol% DPEphos, 2.8 equiv. *t*-BuONa, toluene, reflux, 72 h; (c) 5 mol% $Pd(OAc)_2$, 5.5 mol% DPEphos, 1.4 equiv. *t*-BuONa, toluene, 80°C, 20 h; (d) 5 mol% $Pd(OAc)_2$, 5.5 mol% DPEphos, 1.4 equiv. *t*-BuONa, toluene, reflux, 72 h.[12]

using bis(2-(diphenylphosphino)phenyl) ether (DPEphos)[13] as a ligand. The reaction of **4** with aniline (**5**) or 4-anilinoaniline (**6**) in refluxing toluene afforded **1** or **2** in 91% or 55% yield, respectively. For the preparation of unsymmetrical pentamer **3**, the amination of **4** with an equimolar amount of aniline was performed at 80°C to give the mono-coupling product **7** selectively, followed by the coupling with **8**.

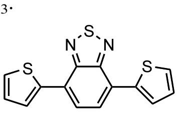
Table 1 lists the absorption maxima of **1**–**3** and the related compounds **9** and **10**. The absorption maximum of **1** in $CHCl_3$ was 522 nm, indicating that **1** has a small HOMO–LUMO gap as compared with the thiophene derivative **9**, and has almost the same absorption maximum as observed with the pyrrole derivative **10**, which is known as the smallest HOMO–LUMO gap system in these series.[9e] Furthermore, **2** showed a more red-shifted absorption maximum at 550 nm. The absorption maximum of **3** was 546 nm between the values of **1** and **2**. The red shift is considered to be related to the donor–acceptor interaction and expanded conjugation.

Table 1. The absorption maxima of **1**–**3** and related compounds

Compound	**1**	**2**	**3**	**9**[a]	**10**[a]
λ_{max} (nm)[b]	522	550	546	447	532

[a] Ref. 9e.

[b] In $CHCl_3$.



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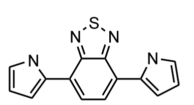

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The redox chemistry of **1**, **2** and **3** was investigated by cyclic voltammography. A scan from −2.2 to +1.2 V for **1** revealed two reversible one-electron oxidation processes at +0.10 and +0.44 V ($E_{1/2}$). The one-electron reduction process was observed at −1.91 V ($E_{1/2}$, Fig. 1). The electrochemical behavior of **1** in acetonitrile is likely to be explained by A→B→C→D (E) shown in Scheme 3.

The redox potentials from −2.2 to +1.4 V of **2** and **3** are listed in Table 2. These electrochemical processes might be accounted for as shown in Scheme 4. Reversible two one-electron oxidation waves (B→C and C→D) and one two-electron oxidation wave (D→E) were observed with both compounds. The redox potentials were almost the same for the oxidation processes, B→C and C→D, of **2** and **3**. On the other hand, the two-electron oxidation wave of **3** appeared at +0.35 V ($E_{1/2}$), which is much lower than that of **2** (+0.62 V). This oxidation corresponds to the formation of the fully oxidized form E. Such lower potential E^4 may be due to the structure of the half-oxidized form D bearing the phenylenediamine moiety, where the next-HOMO lies.

Chemical oxidation was also carried out. When **1** was treated with 1.2 molar amounts of Ag_2O in THF, the

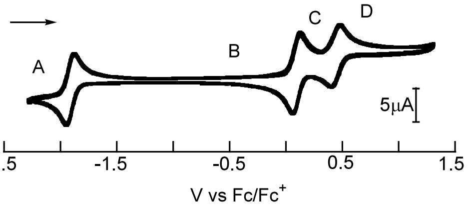
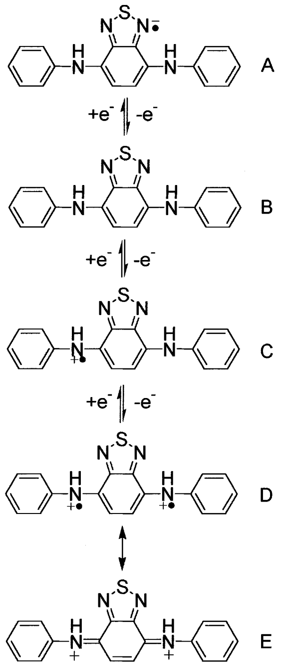


Figure 1. Cyclic voltammogram of **1** (1.0×10^{-3} M) in MeCN (0.10 M Bu_4NClO_4) at a platinum working electrode with scan rate = 100 mV s^{-1} under an argon atmosphere.



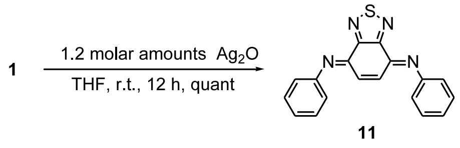
Scheme 3. Plausible redox processes of **1**.

Table 2. $E_{1/2}$ values for the electrode processes of **1**–**3**[a]

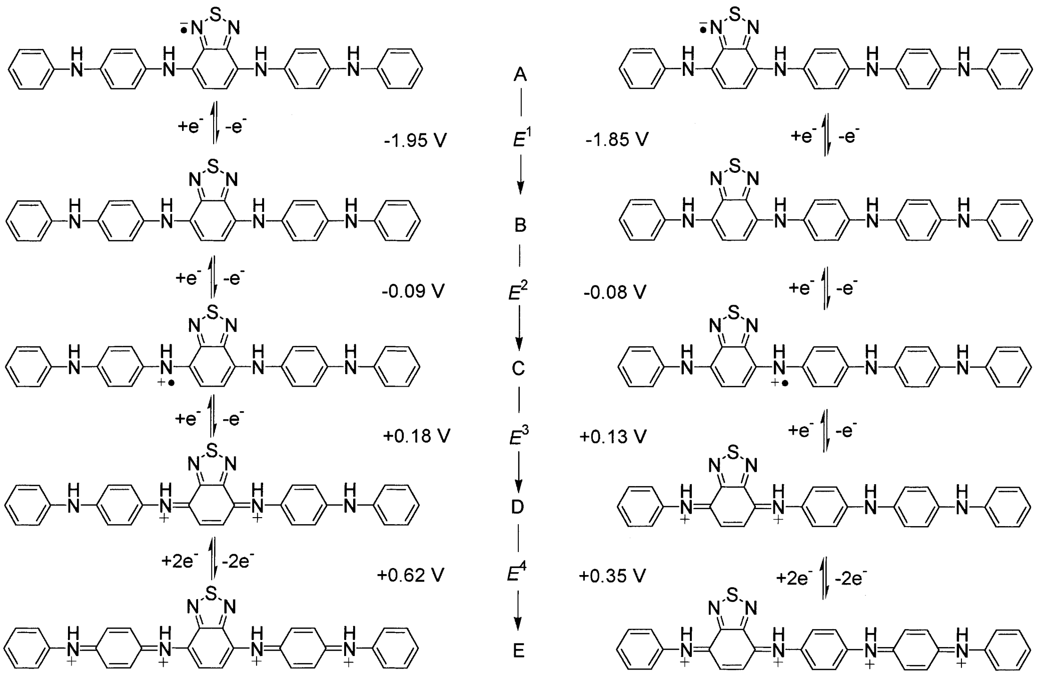
Compound	E^1 (V)	E^2 (V)	E^3 (V)	E^4 (V)
1	−1.91	+0.10	+0.44	–
2	−1.95	−0.09	+0.18	+0.62
3	−1.85	−0.08	+0.13	+0.35

[a] 1.0×10^{-3} M in MeCN (0.10 M Bu_4NClO_4) at a platinum working electrode with scan rate = 100 mV s^{-1} (V versus Fc/Fc^+) under an argon atmosphere.

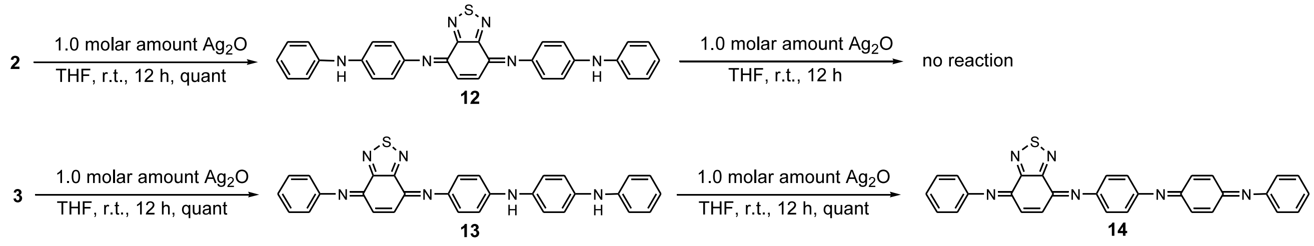
(*E*,*E*)-quinonediimine derivative **11** was obtained quantitatively and no other isomers were detected (Scheme 5).[14] Judging from Table 2, the behavior of **2** and **3** in chemical oxidation are expected to be different. Oxidation of **2** with an equimolar amount of Ag_2O afforded a half-oxidized form **12**, which corresponds to D in the redox cycle shown in Scheme 4. Because of the high oxidation potential of **12**, no further oxidation proceeded even though an excess amount of Ag_2O was added. On the other hand, the fully oxidized form **14** could be prepared with ease due to the low oxidation potential. Actually, **3** was oxidized with an equimolar amount of Ag_2O to give **13**, which was further transferred to **14** quantitatively by treatment of another equimolar amount of Ag_2O (Scheme 6).



Scheme 5. Chemical oxidation of **1**.[12]



Scheme 4. Plausible redox processes of **2** (left) and **3** (right).



Scheme 6. Chemical oxidation of **2** and **3**.[12]

In summary, we have established the synthesis of *p*-phenylenediamine derivatives bearing a thiadiazole unit, in which a small HOMO–LUMO gap system was achieved. Cyclic voltammography indicates that the electrochemical properties were related to the length of the chain and the position of the benzothiadiazole ring.

Acknowledgements

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12. New compounds gave satisfactory spectroscopic data. **1**: mp 148–149°C; ^{1}H NMR (CDCl$_3$, 600 MHz) δ 7.34 (dd, $J=8.4$, 7.2 Hz, 4H), 7.24 (d, $J=8.4$ Hz, 4H), 7.21 (s, 2H), 6.99 (t, $J=7.2$ Hz, 2H), 6.68 (s, 2H); ^{13}C NMR (CDCl$_3$, 150 MHz) 109.2, 109.8, 118.2, 121.5, 128.0, 129.3, 142.1 ppm; IR (KBr, cm^{-1}) 3394, 1599, 1523, 1475, 1428, 1385, 1300, 889, 756, 699, 431. Anal. calcd for $C_{18}H_{14}N_4S$: C,

67.90; H, 4.43; N, 17.60; S, 10.07. Found: C, 67.89; H, 4.71; N, 17.49; S, 10.11. HRMS (EI) calcd for $C_{18}H_{14}N_4S$: 318.0940. Found: 318.0941. **2**: mp 140–141°C; ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.23 (dd, $J=8.4$, 7.2 Hz, 4H), 7.21 (d, $J=8.7$ Hz, 4H), 7.11 (d, $J=8.7$ Hz, 4H), 7.05 (s, 2H), 7.00 (d, $J=8.4$ Hz, 4H), 6.86 (t, $J=7.2$ Hz, 2H), 6.59 (s, 2H), 5.71 (s, 2H); ^{13}C NMR (CD_2Cl_2, 150 MHz) 117.2, 118.6, 121.8, 123.9, 125.4, 125.6, 128.1, 129.3, 135.7, 142.1, 142.3, 150.0, 151.2, 155.8 ppm; IR (KBr, cm^{-1}) 3392, 3042, 2360, 1597, 1511, 1494, 1384, 1293, 1229, 1175, 1051, 889, 813, 748, 696, 511. Anal. calcd for $C_{30}H_{24}N_6S$: C, 71.98; H, 4.83; N, 16.79; S, 6.41. Found: C, 71.70; H, 4.82; N, 16.64; S, 6.44. HRMS (EI) calcd for $C_{30}H_{24}N_6S$: 500.1783. Found: 500.1782. **3**: mp 150–151°C; ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.32–7.29 (m, 2H), 7.23–7.18 (m, 7H), 7.07–6.93 (m, 10H), 6.83 (t, $J=7.2$ Hz, 1H), 6.61 (br, 2H), 5.65 (br, 2H); ^{13}C NMR (CD_2Cl_2, 150 MHz) 149.6, 148.8, 144.5, 142.6, 139.1, 138.1, 136.1, 134.6, 130.1, 129.0, 128.9, 126.4, 121.3, 120.9, 120.6, 119.3, 119.0, 118.2, 117.2, 115.5, 111.5, 106.6 ppm; IR (KBr, cm^{-1}) 3388, 3027, 2362, 1737, 1596, 1513, 1294, 818, 748, 695, 485, 422. HRMS (EI) calcd for $C_{30}H_{24}N_6S$: 500.1783. Found: 500.1784. **11**: mp 179–180°C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.41 (dd, $J=8.4$, 7.2 Hz, 4H), 7.23 (t, $J=7.2$ Hz, 2H), 7.04 (s, 2H), 7.00 (d, $J=8.4$ Hz, 4H); ^{13}C NMR ($CDCl_3$, 150 MHz) 120.6, 125.8, 126.2, 129.0, 148.8, 151.4, 155.4 ppm; IR (KBr, cm^{-1}) 3046, 2957, 1591, 1483, 1337, 1225, 1094, 825, 781, 724, 695, 498, 432. HRMS (EI) calcd for $C_{18}H_{12}N_4S$: 316.0783. Found: 316.0784. **12**: mp 193–194°C; ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.30 (dd, $J=8.4$, 7.2 Hz, 4H), 7.21 (s, 2H), 7.15 (d, $J=8.7$ Hz, 4H), 7.14 (d, $J=8.4$ Hz, 4H), 7.05 (d, $J=8.7$ Hz, 4H), 6.97 (t, $J=7.2$ Hz, 2H), 5.99 (s, 2H); ^{13}C NMR (CD_2Cl_2, 150 MHz) 108.3, 115.8, 119.5, 120.1, 120.2, 128.3, 128.8, 136.1, 136.9, 144.1, 148.9 ppm; IR (KBr, cm^{-1}) 3380, 3053, 2957, 2320, 1594, 1557, 1500, 1384, 1319, 1230, 1167, 1100, 1042, 833, 748, 696, 502, 420. HRMS (EI) calcd for $C_{30}H_{22}N_6S$: 498.1626. Found: 498.1618. **13**: mp 191–193°C; ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.43 (dd, $J=8.4$, 7.2 Hz, 2H), 7.37–6.95 (m, 17H), 6.87 (t, $J=7.2$ Hz, 1H), 5.90 (br, 1H), 5.73 (br, 1H); ^{13}C NMR (CD_2Cl_2, 150 MHz) 156.8, 155.9, 152.4, 149.8, 144.5, 141.6, 138.5, 136.1, 135.5, 129.6, 129.4, 127.0, 125.7, 125.3, 124.5, 122.0, 120.9, 120.5, 118.5, 116.8, 116.0, 104.0 ppm; IR (KBr, cm^{-1}) 3379, 3025, 1599, 1507, 1294, 891, 819, 747, 695, 626, 503. HRMS (EI) calcd for $C_{30}H_{22}N_6S$: 498.1626. Found: 498.1612. **14**: mp 179–180°C; ^{1}H NMR (CD_2Cl_2, 600 MHz) δ 7.46–7.35 (m, 4H), 7.26–6.94 (m, 12H), 6.91–6.75 (m, 4H); IR (KBr, cm^{-1}) 2924, 1653, 1602, 1559, 1507, 1302, 1163, 830, 745, 697. HRMS (EI) calcd for $C_{30}H_{20}N_6S$: 496.1596. Found: 496.1580.

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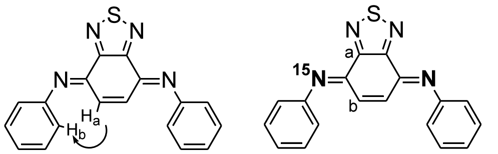
14. The geometry of **11** was determined by the nuclear Overhauser effect (NOE) between H_a and H_b, and the $^2J(^{13}C,^{15}N)$ values[15] of C_a and C_b (7.46 and 2.71 Hz, respectively).



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