1,4-Benzoxazino[2,3-*b*]phenoxazine and Its Sulfur Analogues: Synthesis, Properties, and Application to Organic Light-Emitting Diodes

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Several *N*,*N*′-dialkyl or -diaryl substituted 1,4-benzoxazino[2,3-*b*]phenoxazines (**1**) and sulfur analogues **2** were prepared. They had low oxidation potentials (+0.30 − +0.41 V vs SCE for **1** and +0.39 − +0.55 V vs SCE for **2**). *N*,*N*′-Dimethyl-1,4-benzoxazinophenoxazine (**1b**) gave stable radical cation salts by electrochemical oxidation or a charge-transfer complex with TCNQ. The derived salts and the charge-transfer complex showed moderate conductivities in the range of $2.0 \times 10^{-7} - 9.9 \times 10^{-4}$ S cm^{-1}. The *N*,*N*′-diaryl deivatives had high thermal stability. Their thermal behavior was clarified by means of DSC. The applicability of these diaryl compounds as hole injection meterials (HIMs) in organic light-emitting diodes was studied by fabrication of a simple Alq-emitting device of ITO/HIM (40 nm)/NPB (10 nm)/Alq (50 nm)/LiF (0.5 nm)/Al (100 nm). The device ability was tested by measuring the luminous efficiency and the device decay time at a high current density (50 mA/cm^2). The results were compared to a reference device of similar composition without HIM. Of compounds **1** and **2**, compound **2d** with the *N*,*N*′-bis-(1-naphthyl) substituent gave the best result; the insertion of a **2d** layer improved the device stability up to roughly 5 times with a high emitting efficiency.

Introduction

Because of their 8π-electronic structure in the central ring, phenothiazine and phenoxazine derivatives have attracted considerable interest not only in chemistry but also in materials science. Fundamental studies involving the structure[1] and electron-donating ability for the neutral molecules,[2] such as UV−vis[3] and EPR studies[4] of the radical cations, have been reported. In some cases, radical cation salts and/or charge-transfer complexes have been isolated,[5] and their structure and solid-state properties have been clarified.[6]

In contrast to the studies on the mononuclear phenothiazine or phenoxazine framework, relatively little information has been reported on their multinuclear phenothiazine derivatives. Assembling phenothiazine- or phenoxazine-8π-nuclei with a suitable conjugated linkage furnishes new redox active oligomer systems. Preparation of several functionalized oligophenothiaizines,[7] characterization and identification of phenylene-bridged di- or tri-(phenothiazine radical cation)s,[8] and intramolecular self-exchange interaction of similar diphenothiazine radical cations[9] have recently been reported.

Another approach condensing two phenoxazines or phenothiazines in a pentacene framework has also been carried out: depending on the position of the heteroatoms, there are two types each of benzoxazinophenoxazines and benzothiazinophenothiazines: 1,4-benzoxazino[2,3-*b*]phenoxazine (**1**), 1,4-benzothiazino[2,3-*b*]phenothiazine (**2**), 1,4-benzoxazino-[3,2-*b*]phenoxazine (**3**), and 1,4-benzothiazino[3,2-*b*]phenothiazine (**4**). Compound **4** has been synthesized via three methods, 1) direct sulfur-bridging using sulfur powder from *N*,*N*′-diphenyl-1,4-phenylenediamine,[10] 2) intramolecular nucleophilic thiol-cyclization of a diaminodihaloquinone derivative,[11] or 3) reductive acylation of known **6**.[12] The study of electric conductivity for **4** and the higher analogues has

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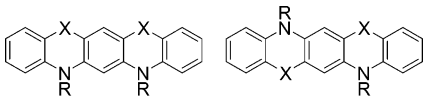
been reported by Case et al.[13] An oxygen analogue **3** has also been prepared by reductive acylation of **5**.[14] The meta-type sulfur compounds **2** have recently been prepared by two groups: Müllen's group through nitrene-induced cyclization (Cadogan cyclization)[15] and Sieberg's group through sulfur-bridging methods.[16] Although fundamental studies for **2** in both the neutral and the radical cation states have been reported, their solid-state properties have not been reported.[15,16] We have more recently prepared the oxygen and sulfur analogues **1** and **2** using an intramolecular Ullmann coupling reaction as a key step.[17] We have preliminarily shown that the benzoxazinophenoxazines **1a**,**b** (R = H, Me) have lower oxidation potentials than those of the benzothiazinophenothiazines **2a**,**b** (R = H, Me). The oxygen compound **1b** was easily converted into the radical cation salts and the TCNQ charge-transfer complex,[17] whereas the sulfur compound **2b** failed to give the radical ion salts or the charge-transfer complexes in pure form under the same conditions.



As shown later, *N*,*N*′-diaryl compounds **1c**,**d** and **2c**−**g** have higher oxidation potentials than the *N*,*N*′-dimethyl analogues **1b** and **2b**. However, the diaryl-derivatives could be converted into amorphous materials by introducing unsymmetric aryl groups. Such an amorphous compound might be used as a hole injection material (HIM) in organic light-emitting diodes (OLEDs). In this paper, we describe the synthesis and characterization of the neutral compounds **1a**−**d** and **2a**−**g**, the electronic conductivity for some **1b**-derived radical cation salts and the TCNQ complexes, and DSC analysis and application to HIMs in OLEDs for the diaryl derivatives **1c**,**d** and **2c**−**g**.

Experimental Procedures

4,6-Bis(2-bromophenyloxy)-1,3-dinitrobenzene (7). A 200 mL two-necked flask was charged with sodium hydride (2.3 g) and DMSO (60 mL). Then, *o*-bromophenol (10.1 g) was slowly added to the stirred mixture. After the evolution of hydrogen was ceased, 1,5-dichloro-2,4-dinitrobenzene (6.4 g) was added. The mixture was heated under a nitrogen atmosphere at 90 °C for 90 min. After cooling to room temperature, the reaction mixture was poured into cold water and extracted with ethyl acetate. The organic layer was dried over sodium sulfate and concentrated in vacuo. The resulting crude solid was recrystallized from ethanol to give **7** as a pale brownish powder (11.0 g, 80%). mp 153−154 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85 (s, 1H), 7.04 (dd, 2H, J = 8.0, 1.5 Hz), 7.09 (ddd, 2H, J = 7.7, 7.7, 1.5 Hz), 7.28 (ddd, 2H, J = 7.7, 7.7, 1.5 Hz), 7.55 (dd, 2H, J = 8.1, 1.7 Hz), 8.95 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.9, 115.4, 122.3, 126.0, 127.9, 129.3, 132.7, 134.3, 150.1, 155.5; MS(FAB) *m*/*z* 511 (MH^+); Anal. Calcd. for $C_{18}H_7Br_2N_2O_6$: C 42.38, H 1.98, N 5.49; found: C 42.58, H 1.80, N 5.40.

4,6-Bis(2-bromophenyloxy)-1,3-diaminobenzene (9). A 500 mL flask was charged with tin (II) chloride dihydrate (47.4 g) and ethanol (200 mL). Compound **7** (10.5 g) was slowly added to the solution, and the mixture was heated at 70 °C for 40 min under nitrogen. After cooling to room temperature, the mixture was poured into water and neutralized by the addition of a sodium hydroxide solution (1 M). The mixture was extracted with ether. After drying and evaporating the solvent, the diamine **9** was obtained as a dark brown oil (7.4 g, 80%), which was unstable under aerated conditions and used for the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 4H), 6.31 (s, 1H), 6.59 (s, 1H), 6.82 (dd, 2H, J = 8.2, 1.3 Hz), 6.90 (ddd, 2H, J = 7.7, 7.6, 1.4 Hz), 7.18 (ddd, 2H, J = 7.7, 7.3, 1.6 Hz), 7.56 (dd, 2H, J = 8.1, 1.5 Hz), ^{13}C NMR (100 MHz, C_6D_6) δ 103.2, 112.2, 115.5, 116.2, 123.4, 128.7, 133.3, 133.7, 137.6, 155.3; IR (KBr, cm^{-1}), 3450 (m), 3364 (m); HRMS (FAB) *m*/*z* Calcd. for $C_{18}H_{14}Br_2N_2O_2$: 447.9422; found: 447.9420.

4,6-Bis(2-bromophenyloxy)-1,3-(diacetylamino)benzene (10). The diamine **9** (7.4 g) was treated with acetic anhydride (120 mL) at 0 °C for 15 min under nitrogen. The reaction mixture was poured into water and alkalized by the addition of a sodium hydroxide solution (1 M). The resulting precipitates were filtered, washed with water, and dried over P_2O_5 in vacuo. The crude product was recrystallized from ethanol to give **10** as a colorless powder (7.4 g, 84%). mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 6H), 6.35 (s, 1H), 6.88 (d, 2H, J = 7.8 Hz), 7.00 (t, 2H, J = 7.8 Hz), 7.23 (t, 2H, J = 7.8 Hz), 7.45 (brs, 1H), 7.59 (d, 2H, J = 7.8 Hz), 9.12 (brs, 2H); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.04 (s, 6H), 6.06 (s, 1H), 6.95 (d, 2H, J = 7.8 Hz), 7.06 (t, 2H, J = 7.8 Hz), 7,32 (d, 2H, J = 7.8 Hz), 7.64 (d, 2H, J = 7.8 Hz), 8.39 (s, 1H), 9.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 108.4, 113.7, 116.9, 119.2, 125.5, 125.7, 129.0, 133.9, 142.0, 152.9, 168.2; IR (KBr, cm^{-1}) 3288 (m), 1670 (s), 1541 (s), 1261 (m); MS(FAB) *m*/*z* 535 (MH^+); Anal. Calcd. for $C_{22}H_{18}Br_2N_2O_4$: C 49.47, H 3.40, N 5.24; found: C 49.46, H 3.38, N 5.34.

5,7,12,14-Tetrahydro-5,7-diacetyl-5,7-diaza-12,14-dioxapentacene (13). A 100 mL two-necked flask was charged with a copper powder (240 mg), potassium carbonate (2.7 g), **10** (5.0 g), and *o*-dichlorobenzene (50 mL). The mixture was heated at 185−190 °C for 2 h under nitrogen. After cooling to room temperature, the reaction mixture was filtered to remove insoluble solids. The filtrate was concentrated in vacuo. The crude product was purified by a silica gel column eluted with a hexanes−ethyl acetate mixed solvent (1:1 v/v) to give almost pure **13** (2.5 g, 73%). The compound was recrystallized from ethanol (colorless powder). mp 211−212 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.37 (s, 6H), 6.89 (s, 1H), 7.10−7.25 (m, 6H), 7.43 (d, 2H, J = 7.1 Hz), 7.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.9, 105.0, 116.9, 121.9, 123.7, 124.3, 125.1,

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127.1, 129.2, 149.4, 150.7, 169.4; IR (KBr, cm^{-1}) 1682 (s), 1670 (s), 1508 (m), 1250 (s); MS (FAB) *m*/*z* 373 (MH^+); Anal. Calcd. for $C_{22}H_{16}N_2O_4$: C 70.96, H 4.33, N 7.52; found: C 70.73, H 4.27, N 7.47.

5,7,12,14-Tetrahydro-5,7-diaza-12,14-dioxapentacene (1a). To a 100 mL two-necked flask containing **13** (1.0 g) was added an ethanol solution (38 mL) of potassium hydroxide (2.6 g). The mixture was stirred at room temperature for 25 min under nitrogen atmosphere. Then, the reaction mixture was poured into water (200 mL). The produced yellow brown precipitates were filtered, washed with ethanol, and dried under P_2O_5 to give **1a** as a yellow brown powder (628 mg, 81%). mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 5.74 (s, 1H (H5)), 6.08 (s, 1H (H6)), 6.41 (d, 2H, J = 7.6 Hz), 6.54−6.56 (m, 4H), 6.68−6.73 (m, 2H), 7.94 (brs, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 98.8, 103.7, 113.2, 115.0, 120.1, 123.7, 127.6, 132.3, 135.4, 142.4; IR (KBr, cm^{-1}) 3389 (m); HRMS (EI) *m*/*z* Calcd. for $C_{18}H_{12}N_2O_2$: 288.0899; found: 288.0904.

5,7,12,14-Tetrahydro-5,7-dimethyl-5,7-diaza-12,14-dioxapentacene (1b). To a 20 mL two-necked flask containing **1a** (200 mg), dry THF (2 mL) and dry toluene (4 mL) were added dropwise a hexane solution of *n*-butyllithium (0.88 mL, 1.58 M) via a syringe at −35 °C under nitrogen. After stirring for 30 min, dimethyl sulfate (0.1 mL) was added via a syringe at −35 °C. The solution was warmed to room temperature and stirred overnight. The reaction mixture was poured into water and alkalized by the addition of a solution of sodium carbonate (10%) and stirred for 1 h. Then, the mixture was extracted with ethyl acetate. The organic layer was dried over sodium sulfate and concentrated in vacuo. The product was purified by a silica gel column eluted by a hexanes−ethyl acetate system (7:3 v/v) to give **1b** (171 mg, 78%), which was recrystallized from ethanol as pale brown plates. mp 197−198 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.06 (s, 6H), 6.11 (s, 1H (H5)), 6.29 (s, 1H (H6)), 6.67−6.79 (m, 6H), 6.83−6.89 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 31.2, 97.5, 103.6, 112.0, 114.8, 120.8, 124.1, 130.4, 134.7, 137.8, 144.5; MS (CI) *m*/*z* 316; Anal. Calcd. for $C_{20}H_{16}N_2O_2$: C 75.93, H 5.10, N 8.86; found: C 75.98, H 5.00, N 8.83.

5,7,12,14-Tetrahydro-5,7-diphenyl-5,7-diaza-12,14-dioxapentacene (1c). A 50 mL two-necked flask was charged with **1a** (300 mg), iodobenzene (467 mg), sodium *t*-butoxide (300 mg), palladium diacetate (9.4 mg), toluene (20 mL), and a toluene solution (1.1 mL, 0.0296 mol/L) of tri-*t*-butylphosphine. The mixture was refluxed under nitrogen. After 4 h, ca. 20 mL of toluene was further added into the hot suspension to dissolve the product. The hot mixture was filtered, and the filtrate was dried and concentrated in vacuo. The pure **1c** was obtained by recrystallization from toluene as white needles (60%). mp >300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.57 (s, 1H (H5)), 5.77−5.80 (m, 2H), 6.33 (s, 1H (H6)), 6.58−6.71 (m, 6H), 7.14 (d-like, 4H, J = 7.1 Hz), 7.30−7.44 (m, 6H); ^{13}C NMR (150 MHz, DMSO-d_6, at 80 °C) δ 116.2, 118.6, 119.5, 122.6, 126.5, 126.7, 127.0, 127.9, 128.8, 129.4, 129.9, 130.6; MS (EI) *m*/*z* 440; Anal. Calcd. for $C_{30}H_{20}N_2O_2$: C 81.80, H 4.58, N 6.36; found: C 81.83, H 4.45, N 6.28.

5,7,12,14-Tetrahydro-5,7-di(1-naphthyl)-5,7-diaza-12,14-dioxopentacene (1d). A 50 mL two-necked flask was charged with **1a** (300 mg), 1-iodonaphthalene (581 mg), sodium *t*-butoxide (300 mg), palladium diacetate (9.4 mg), *o*-xylene (20 mL), and a toluene solution (20 mL, 0.0296 mol/L) of tri-*t*-butylphosphine. The mixture was refluxed under nitrogen. After 4 h, toluene (ca. 20 mL) was further added, and the hot reaction mixture was filtered. The filtrate was concentrated in vacuo. The crude product was purified by a short silica gel column eluted by toluene. Recrystallization from toluene gave **1d** as a yellow powder (80%). mp >300 °C; ^{1}H NMR (400 MHz, pyridine-d_5, at 25 °C) δ 4.20 (s, 0.5H (H5)), 4.36 (s, 0.5 H (H5)), 5.76 (d, 2H, J = 8.1 Hz), 6.49 (t, 2H, J = 6.6 Hz), 6.65−6.70 (m, 3H including a broad singlet for H6 (0.5 + 0.5 H) at 6.65), 6.90 (d, 2H, J = 6.6 Hz), 7.00−7.07 (m, 2H), 7.16−7.33 (m, 4H), 7.40−7.52 (m, 2H), 7.65 (d, 1H, J = 8.5 Hz), 7.70−7.74 (m, 3H), 7.90 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 8.0 Hz); MS (EI) *m*/*z* 540; Anal. Calcd. for $C_{38}H_{24}N_2O_2$: C 84.42, H 4.47, N 5.18; found: C 84.30, H 4.30, N 5.13.

4,6-Bis(2-bromophenylthio)-1,3-dinitrobenzene (8). To a 300 mL two-necked flask containing sodium hydride (2.1 g) and DMSO (80 mL) was added dropwise *o*-bromothiophenol (6.0 mL). After the evolution of hydrogen was ceased, 1,5-dibromo-2,4-dinitrobenzene (7.9 g) was added, and the reaction mixture was stirred at room temperature for 10 min under nitrogen. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was dried over magnesium sulfate and evaporated in vacuo. The crude product was recrystallized from ethanol to give **8** as yellow needles (8.7 g, 66%). mp 219−220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.08 (s, 1H), 7.21−7.28 (m, 4H), 7.45−7.49 (m, 4H), 9.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.0, 125.3, 128.9, 129.6, 131.1, 132.4, 134.5, 137.8, 140.4, 144.2: HRMS (EI) *m*/*z* Calcd. for $C_{18}H_{10}Br_2N_2O_4S_2$: 541.8428; found: 541.8450.

4,6-Bis(2-bromophenylthio)-1,3-diaminobenzene (11). To a 200 mL flask containing tin (II) chloride dihydrate (9.8 g) and ethanol (50 mL) was added slowly compound **8** (2.0 g). The mixture was heated at 70 °C for 15 min under nitrogen atmosphere. The reaction mixture was poured into water and neutralized by the addition of a sodium hydroxide solution (1 M). The aqueous mixture was extracted with ethyl acetate. The organic phase was dried over sodium sulfate and concentrated in vacuo to give **11** as a brown powder in a quantitative yield. Compound **11** was unstable under aerated conditions and immediately used for the next step without further purification. mp ∼163 °C (dec.) ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.45 (s, 4H), 6.23 (s, 1H), 6.73 (dd, 2H, J = 8.1, 1.5 Hz), 6.97 (td, 2H, J = 7.3, 1.4 Hz), 7.13 (td, 2H, J = 7.3, 1.5 Hz), 7.50 (dd, 2H, J = 8.0, 1.2 Hz), 7.60 (s, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 99.2, 102.7, 120.6, 126.1, 126.3, 127.8, 133.0, 139.8, 148.4, 152.7; IR (KBr, cm^{-1}) 3474 (m), 3371 (m): HRMS (FAB) *m*/*z* Calcd. for $C_{18}H_{10}Br_2N_2S_2$: 479.8965; found: 479.8969.

4,6-Bis(2-bromophenylthio)-1,3-(diacetylamino)benzene (12). To a 500 mL flask containing **11** (4.2 g) was added acetic anhydride (180 mL) at room temperature. The solution was heated at 60 °C for 40 min under nitrogen. The reaction mixture was poured into cold water, and the mixture was neutralized by the addition of sodium hydroxide solution (3 M). The pale red precipitates obtained were filtered, washed with water, and dried over P_2O_5 in vacuo. The crude product was recrystallized from ethanol to give **12** as a colorless powder (4.3 g, 86%). mp 239−240 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.11 (s, 6H), 6.68 (dd, 2H, J = 7.9, 1.7 Hz), 7.04 (td, 2H, J = 7.5, 1.7 Hz), 7.14 (td, 2H, J = 7.5, 1.4 Hz), 7.55 (dd, 2H, J = 7.8, 1.5 Hz), 7.83 (s, 1H), 8.18 (brs, 1H), 9.58 (brs, 2H); ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.04 (s, 6H), 6.78 (s, 2H, J = 7.8 Hz), 7.13 (s, 2H, J = 7.8 Hz), 7.22 (s, 1H), 7.26 (t, 2H, J = 7.8 Hz), 7.61 (d, 2H, J = 7.8 Hz), 8.20 (s, 1H), 9.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.8, 112.6, 114.4, 121.7, 127.6, 127.8, 128.2, 133.1, 136.7, 143.0, 144.7, 168.3; IR (KBr, cm^{-1}) 3369 (s), 1711 (s), 1514 (s), 1242 (s); MS (FAB) *m*/*z* 567 (MH^+); Anal. Calcd. for $C_{22}H_{18}Br_2N_2O_2S_2$: C 46.66, H 3.20, N 4.95; found: C 46.68, H 3.22, N 4.92.

5,7,12,14-Tetrahydro-5,7-diacetyl-5,7-diaza-12,14-dithiopentacene (14). A 200 mL two-necked flask was charged with a copper powder (330 mg), potassium carbonate (1.8 g), **12** (3.0 g), and nitrobenzene (60 mL). The suspension was heated at 180−185 °C for 60 min under nitrogen. After cooling to room temperature, the reaction mixture was filtered to remove insoluble solids. The filtrate

was concentrated in vacuo. The crude products were purified by a silica gel column eluted with a hexanes−ethyl acetate system (1:3 v/v). The product was recrystallized from ethanol to give **14** as a colorless powder (1.5 g, 72%). mp 235−236 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (brs, 6H), 6.93 (br, 2H), 7.18−7.35 (m, 4H), 7.41 (ddd, 4H, J = 7.5, 7.5, 1.3 Hz). This compound showed broad peaks for acetyl methyl protons and aromatic protons in the central ring, probably because of rotamers of the amide C−N bonds. IR (KBr, cm^{-1}) 1672 (s); MS (FAB) *m*/*z* 405 (MH^+); Anal. Calcd. for $C_{22}H_{16}N_2O_2S_2$: C 65.32, H 3.99, N 6.93; found: C 65.04, H 3.99, N 6.69.

5,7,12,14-Tetrahydro-5,7-diaza-12,14-dithiopentacene (2a).[16] To a 200 mL two-necked flask containing an ethanolic potassium hydroxide (56 mL containing 3.8 g of KOH) was added an ethanol solution (56 mL) of **14** (700 mg) at room temperature under a nitrogen atmosphere. After 5 h, the solution was poured into water (200 mL). The yellow brown precipitates were filtered, washed with ethanol, and dried under P_2O_5 to give **2a** as a pale brown powder (524 mg, 95%). mp >300 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.15 (s, 1H (H5)), 6.49 (s, 1H (H6)), 6.75−6.97 (m, 4H), 6.88 (dd, 2H, J = 6.9, 2.0 Hz), 6.97 (td, 2H, J = 8.0, 1.5 Hz), 8.56 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 101.0, 108.1, 114.5, 116.7, 121.6, 123.2, 126.1, 127.3, 141.7, 168.3; IR (KBr, cm^{-1}) 3387 (w), 3319 (w); MS (EI) *m*/*z* 320.

5,7,12,14-Tetrahydro-5,7-dimethyl-5,7-diaza-12,14-dithiopentacene (2b). To a 50 mL two-necked flask was taken sodium hydride (183 mg) and DMSO (20 mL). To this suspension was added dropwise a DMSO solution (5 mL) of **2a** (200 mg) via a syringe. After the evolution of hydrogen was ceased, dimethyl sulfate (0.4 mL) was added into the solution. The mixture was stirred at 60 °C for 60 min under nitrogen. The reaction mixture was poured into cold water and extracted with ethyl acetate. The organic layer was dried over magnesium sulfate and concentrated in vacuo. The crude products were purified by a silica gel column eluted with a hexanes−ethyl acetate system (3:1 v/v). The crude product was recrystallized from ethanol to give **2b** as pale brown plates (97 mg, 45%). mp ∼262 °C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.37 (s, 6H), 6.49 (s, 1H (H5), 5% NOE at 3.37 ppm irradiation), 6.92−6.98 (m, 5H including a singlet at 6.93 (1H (H6)), a doublet 6.96 (2H (H1), J = 7.6 Hz, 10% NOE at 3.37 ppm irradiation), and a triplet (2H, J = 7.6 Hz)), 7.14 (d, 2H (H1), J = 7.6 Hz), 7.21 (t, 2H, J = 7.6 Hz); ^{1}H NMR (400 MHz, pyridine-d_5) δ 3.22 (s, 6H), 6.24 (1H (H5), 7% NOE at 3.22 ppm irradiation, 6.85 (2H (H1), J = 7.6 Hz, 11% NOE at 3.22 ppm), 6.97 (t, 2H, J = 7.6 Hz), 7.02 (s, 1H (H6)), 7.20 (t, 2H, J = 7.6 Hz), 7.26 (d, 2H (H1), J = 7.6 Hz), ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.2, 102.4, 114.74 (2C), 122.3, 122.6, 124.2, 126.7, 127.7, 145.3, 145.6; MS (EI) *m*/*z* 348; Anal. Calcd. for $C_{20}H_{16}N_2S_2$: C 68.93, H 4.63, N 8.04; found: C 68.76, H 4.56, N 7.97.

5,7,12,14-Tetrahydro-5,7-diphenyl-5,7-diaza-12,14-dithiopentacene (2c). A 10 mL two-necked flask was charged with **2a** (200 mg), a copper powder (40 mg), potassium carbonate (172 mg), and iodobenzene (1.0 mL). The mixture was heated at 190 °C for 13 h under nitrogen. The reaction mixture was filtered to remove insoluble solids. The filtrate was concentrated in vacuo. The crude products were recrystallized from a dichloromethane−ethanol mixed solvent to give **2c** as yellow prisms (72%). mp 258−259 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.09 (s, 1H (H5)), 6.02 (d, 2H, J = 7.5 Hz), 6.78 (s, 1H (H6)), 6.79−6.89 (m, 4H), 7.01−7.10 (m, 6H), 7.36−7.44 (m, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 105.5, 111.6, 115.8, 118.9, 122.6, 123.4, 126.6, 127.2, 128.1, 129.7, 130.7, 139.7, 142.9, 143.0; HRMS (EI) *m*/*z* Calcd. for $C_{30}H_{20}N_2S_2$: 472.1068; found: 472.1061.

5,7,12,14-Tetrahydro-5,7-bis(1-naphthyl)-5,7-diaza-12,14-dithiopentacene (2d). Compound **2d** was prepared in a similar manner as described for **1d** in 74% yield as yellow prisms from toluene−heptane, mp 218−219 °C; ^{1}H NMR (400 MHz, pyridine-d_5 at −35 °C) δ 4.66 (s, 0.5H (H5)), 4.82 (s, 0.5H (H5)), 5.95 (d, 2H, J = 8.4 Hz), 6.63−6.71 (m, 2H), 6.81−6.88 (m, 3H), 6.96−7.09 (m, 3H including two singlets at 7.02 (0.5H (H6) and 7.05 (0.5H (H6)), 7.23−7.26 (m, 3H), 7.33−7.42 (m, 3H), 7.49−7.58 (m, 2H), 7.80−7.87 (m, 4H), 8.02 (d, 1H, J = 2.0 Hz); ^{1}H NMR (400 MHz, pyridine-d_5 at 85 °C) δ 4.77 (s, 1H (H5)), 5.94 (d, 2H (H1), J = 8.0 Hz), 6.58 (td, 2H (H2), J = 8.0, 1.6 Hz), 6.69 (td, 2H (H3), J = 7.5, 1.6 Hz), 6.78 (s, 1H (H6)), 6.98 (d, 2H (H13), J = 7.5 Hz), 7.01 (dd, 2H (H4), J = 7.5, 1.6 Hz), 7.09−7.15 (t-like, 4H (H8, H12), J ∼8.0 Hz), 7.35 (d, 2H (H11), J = 7.5 Hz), 7.68 (d, 2H (H9), J = 8.0 Hz), 7.71 (d, 2H (H7), J = 8.0 Hz), 7.79 (s, 2H (H10), J = 8.0 Hz); MS (EI) *m*/*z* 572; Anal. Calcd. for $C_{38}H_{24}N_2S_2$: C 79.69, H 4.22, N 4.89; found: C 79.67, H 4.11, N 4.86.

5,7,12,14-Tetrahydro-5,7-bis(3-tolyl)-5,7-diaza-12,14-dithiopentacene (2e). Compound **2e** was prepared in a similar manner as described for **1d** in 60% yield as yellow prisms from toluene−heptane, mp 198−199 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 1.88 (s, 6H), 5.01 (s, 1H (H5)), 6.13−6.17 (m, 2H), 6.44 (s, 2H), 6.53−6.61 (m, 6H), 6.69 (s, 1H (H6)), 6.72 (d, 2H, J = 7.5 Hz), 6.85 (t, 2H, J = 7.7 Hz), 6.92−6.95 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6) δ 21.0, 106.3, 113.1, 116.2, 120.6, 122.6, 124.0, 126.8, 127.0, 127.6, 130.0, 131.4, 140.1, 141.0, 143.9, 144.5; MS (EI) *m*/*z* 500; Anal. Calcd. for $C_{32}H_{24}N_2S_2$: C 76.76, H 4.83, N 5.60; found: C 76.73, H 4.73, N 5.57.

5,7,12,14-Tetrahydro-5,7-bis(4-tolyl)-5,7-diaza-12,14-dithiopentacene (2f). Compound **2f** was prepared in a similar manner as described for **1d** in 63% yield as yellow prisms from toluene−heptane, mp 2410−241 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 2.04 (s, 6H), 5.05 (s, 1H (H5)), 6.17 (dd, 2H, J = 7.7, 1.6 Hz), 6.52−6.71 (m, 13H including a singlet at 6.66 ppm (1H (H6))), 6.93 (dd, 2H, J = 6.9, 2.0 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 21.0, 106.1, 112.8, 116.0, 120.5, 122.5, 124.1, 126.8, 127.1, 130.6, 130.9, 137.1, 138.3, 144.0, 144.5; MS (EI) *m*/*z* 500; Anal. Calcd. for $C_{32}H_{24}N_2S_2$: C 76.76, H 4.83, N 5.60; found: C 76.72, H 4.72, N 5.56.

5,7,12,14-Tetrahydro-5,7-bis(4-methoxyphenyl)-5,7-diaza-12,14-dithiopentacene (2g). Compound **2g** was prepared in a similar manner as described for **1d** in 65% yield as yellow prisms from toluene−heptane, mp 242−243 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 3.31 (s, 6H), 5.00 (s, 1H (H5)), 6.21 (dd, 2H, J = 8.1, 1.3 Hz), 6.48−6.66 (m, 13H including a singlet of H6 proton at 6.66 ppm overlapping with AA′BB′ signals of *N*-anisyl ring), 6.93 (dd, 2H, J = 7.3, 1.7 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ 54.9, 106.0, 112.5, 115.6, 115.9, 120.3, 122.5, 122.6, 126.9, 127.1, 132.1, 133.3, 144.3, 144.8, 159.2; MS (EI) *m*/*z* 532; Anal. Calcd. for $C_{32}H_{24}N_2O_2S_2$: C 72.15, H 4.54, N 5.26; found: C 72.22, H 4.43, N 5.23.

Preparation of the Charge-Transfer Complex, 1a-TCNQ. Compound **1a** (20 mg) and TCNQ (14.2 mg) were separately dissolved in a minimum amount (ca 100 mL for **1a**, ca. 6 mL for TCNQ) of dry acetonitrile. The TCNQ solution was slowly added to the **1a** solution at room temperature, and the solution was concentrated to ca. 5 mL. The green precipitates were filtered and recrystallized from dry acetonitrile to give **1a**-TCNQ as dark green needles (23%). mp >300 °C.

Preparation of the Charge-Transfer Complex, 1b-TCNQ. Compound **1b** (50 mg) and TCNQ (33 mg) were separately dissolved in a minimum amount (1.3 mL for **1b**, ca. 10 mL for TCNQ) of dry dichloromethane. The **1b** solution was added to the TCNQ solution at room temperature to give dark green precipitates. The precipitates were filtered and recrystallized from dry acetonitrile to give **1b** TCNQ as dark green needles (80%). mp 210−211 °C.

Preparation of the Charge-Transfer Complex, 1b-I_5. A dry dichloromethane solution of **1b** (5 mg in 3 mL) and a dry dichloromethane solution of iodine (10 mg in 3 mL) were slowly mixed in a H-type tube. The produced dark precipitates were filtered to give **1b**-I_5 (44%). mp >300 °C.

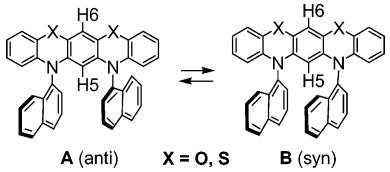
Preparation of the Charge-Transfer Complex $2b_2$-DDQ_3-$2H_2O$. Compound **2b** and DDQ were dissolved in a minimum amount of dichloromethane, respectively. Both solutions were mixed at room temperature to give $2b_2$-DDQ_3-$2H_2O$ as a dark brown solid (81%). mp >300 °C.

General Procedure for the Synthesis of Radical Cation Salts by Electrochemical Oxidation. The electrochemical oxidation was carried out in an electrochemical cell. The cell has two rooms separated by a glass filter: the larger room (for the anodic oxidation in this case) with ca. 50 mL volume and the smaller room (for the cathodic reduction) with ca. 10 mL volume. A suitable electrolyte solution (typically 50 mg of electrolyte ($TBAClO_4$, $TBAI_3$, $TBAPF_6$) in ca. 40 mL of solvent listed in Table 3) was prepared. The electrolyte solution (ca. 32 and 8 mL) was added into the two rooms of the cell. Benzoxazinophenoxazine **1a** (~10 mg) was added to the electrolyte solution in the larger room and dissolved. The cell was purged by nitrogen gas for about 20 min and electrolyzed at constant current of 1.0 − 2.0 μA using Pt-electrodes in both anode and cathode. After about 1 week, dark green materials were deposited (typically 1 − 5 mg) on the surface of the anode electrode.

Fabrication of OLED Devices. HIMs and NPB were thermally evaporation onto an ITO-coated glass substrate with monitoring film thickness by an oscillating quartz thickness monitor. The emitting area was defined by using a shadow mask with a size of 0.5 × 0.5 cm^2. The power supply was controlled using a personal computer and GP-IB. The light−current curve was measured with an ADVANTEST R6450 digital multimeter. The luminance was measured with a TOPCOM BM-7 luminance meter. The EL spectra were measured with a HITACHI U-4010 fluorescence spectrophotometer. All measurements were carried out under atmosphere.

Results and Discussion

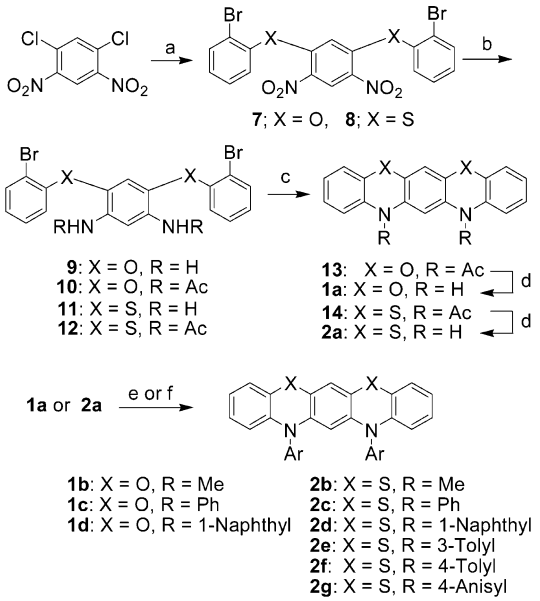
Synthesis and Oxidation Potentials of Neutral Compounds 1a−d and 2a−g. The oxygen compound **1a** was synthesized in a stepwise manner through an intramolecular Ullmann coupling reaction as illustrated in Scheme 1. Nucleophilic substitution reaction of 1,5-dichloro-2,4-dinitrobenzene with *o*-bromophenolate gave **7** in 80% yield. Reduction of the nitro groups, followed by acylation, afforded **10**. Intramolecular Ullmann coupling in *o*-dichlorobenzene afforded **13**, which gave the desired **1a** after hydrolysis. *N*-Lithiation of **1a** in THF-toluene (1:2 v/v), followed by treatment of dimethyl sulfate, gave **1b** in 78% yield. The Pd(0)-mediated cross-coupling reaction of **1a** with phenyl or 1-naphthyl iodide afforded *N*-arylated **1c** or **1d** in 60 or 80% yield, respectively. The sulfur derivatives **2a** could be prepared in a similar manner or through sulfur bridging of *N*,*N*′-diphenyl-1,3-phenylenediamine.[16]



In the ^{1}H NMR spectra of the condensed diphenoxazines **1a**−**d** and diphenothiazines **2a**−**g**, we observed that the H5-proton of the *N*,*N*′-diaryl derivatives received a large shielding effect (see formula A and B). Distinction between the two singlets (H5 and H6) was achieved by the NOE experiments for **2b** (positive NOE (5%) between H5 and *N*,*N*′-dimethyl groups) and **2d** (positive NOE between H5 and H7 (7%), H13 (3%), Figure 1), showing that the H5-proton appears in the higher field than the H6-proton. Although the H5-proton of the unsubstituted (**1a**, **2a**) and *N*,*N*′-dimethyl substituted derivatives (**1b**, **2b**) appeared in slightly high field (5.75−6.49 ppm, Table 1), the proton of the *N*,*N*′-diaryl substituted derivatives (**1c**,**d** and **2c**−**g**) appeared in a much higher field (4.20−5.09 ppm, Table 1). The observed large upfield shift in the *N*,*N*′-diaryl derivatives is ascribed to the double anisotropic effect of the two *N*,*N*′-substituted aryl rings, whose orientation is expected to be almost perpendicular toward the diphenoxa(thia)zine ring. Furthermore, *N*,*N*′-bis(1-naphthyl) derivatives **1d** and **2d** showed a hindered rotation around the naphthyl C1−N bond. The presence of two rotamers, A and B (1:1 ratio in both **1d** and **2d**), was observed at 25 °C for **1d** and at −35 °C for **2d** in pyridine-d_5 solvent. Compound **1d** showed a broad spectrum even at 85 °C, whereas compound **2d** gave a sharp spectrum with rapid exchange of the rotamers at 85 °C through a coalescence temperature of T_c ~15 °C. Some temperature-dependent spectra for **2d** are shown in Figure 1 with an assignment at 85 °C. Activation barriers of the rotation of the naphthyl group around the C1−N bond were estimated to be $\Delta H^{\ddagger} = 11.2 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -16.6 \pm 2.9$ e.u. for **1d** and $\Delta H^{\ddagger} = 17.6 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = 13.0 \pm 3.6$ e.u. for **2d** using the line shape analysis of the H5-protons of the rotamers.

The redox potentials of these oxygen (**1a**−**d**) and sulfur compounds (**2a**−**g**) are summarized in Table 2. Although there have been some electrochemical studies for simple

Scheme 1[a]



[a] Reagents and conditions: (a) *o*-bromophenol (2 equiv), NaH/DMSO, rt, 10 min; (b) 1: $SnCl_2 \cdot 2H_2O$/EtOH and 2: Ac_2O; (c) Cu-powder-K_2CO_3/*o*-dichlorobenzene, 185−190 °C for 2 h; (d) KOH/ethanol: (e) for **1b** and **2b**: *n*-BuLi/THF-toluene (1:2)-Me_2SO_4; (f) for **1c**,**d** and **2c**-**g**: ArI, $Pd(OAc)_2$-NaO^{t}Bu-P^tBu_3/toluene or Cu-powder-K_2CO_3/nitrobenzene. [c]At 80 °C.

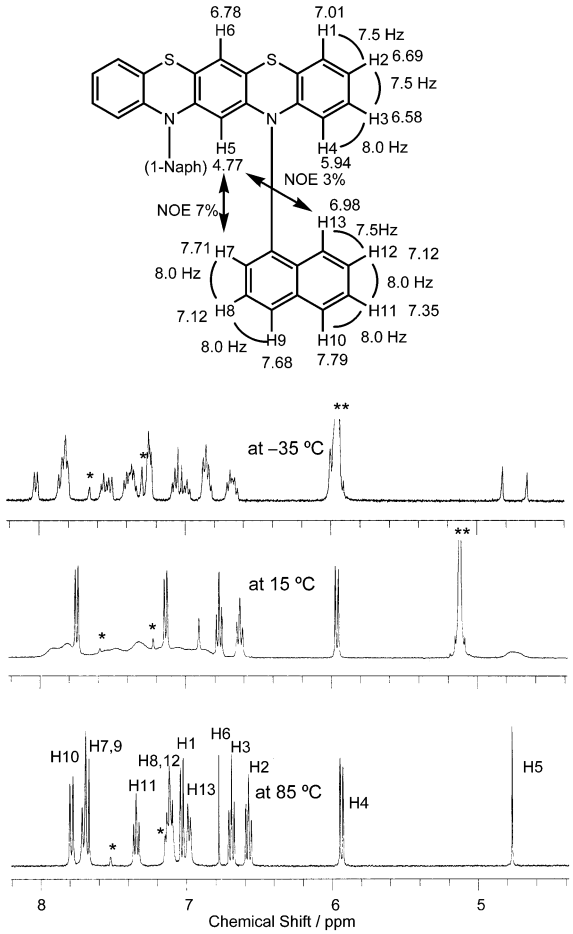


Figure 1. ^{1}H NMR assignment of **2d** at 85 °C (upper panel) and temperature-dependent ^{1}H NMR spectra at some selected temperatures in pyridine-d_5 (lower panel; *, pyridine and **, water).

Table 1. Chemical Shift Values of H5- and H6-Protons of the Condensed Diphenoxazines 1a−d and Diphenothiazines 2a−g

	H5[a]	H6[a]	solvent
1a	5.75	6.08	DMSO-d_6
1b	6.11	6.29	DMSO-d_6
1c	4.57	6.33	DMSO-d_6
1d	4.20, 4.36	6.65	pyridine-d_5
2a	6.15	6.49	DMSO-d_6
2b	6.49	6.93	DMSO-d_6
	6.24	7.02	pyridine-d_5
2c	5.09	6.78	DMSO-d_6
2d	4.66,[b] 4.82[b]	7.02,[b] 7.05[b]	pyridine-d_5
	4.77[c]	6.78[c]	pyridine-d_5
2e	5.01	6.69	C_6D_6
2f	5.05	6.66	C_6D_6
2g	5.00	6.66	C_6D_6

[a] At 25 °C, unless otherwise noted. [b] At −35 °C.

phenoxazines and phenothiazines,[18] the reported values are not consistent. We have measured the oxidation potentials of **1**, **2**, and the simple mononuclear derivatives under identical conditions. The values are corrected using $FeCp_2$/$FeCp_2^+$ as a standard (+0.48 V vs SCE in DMF). All the condensed compounds had lower oxidation potentials than the mononuclear phenoxazine or phenothiazine by 0.3 − 0.4 V. Furthermore, the oxygen derivatives had lower oxidation potentials than the sulfur derivatives in most cases. The higher oxidation potentials for the sulfur compounds can be ascribed to the longer C(sp^2)−S bonds as compared to the C(sp^2)−O bonds, which cause larger steric repulsion in the sulfur derivative radical cations between the substituent on the nitrogen atom and the peri-hydrogen atom attached on the C1 carbon atom. *N*,*N*′-Dimethyldiphenoxazine **1b** had a lower oxidation potential than the diaryl diphenoxazines (**1c**,**d**). However, *N*,*N*′-dimethyldiphenothiazine (**2b**) had a similar oxidation potential to those of *N*,*N*′-diaryldiphenothiazines (**2c**−**g**). The oxygen compounds, **1a** to **1c**, and the sulfur compound **2a** had lower oxidation potentials than TTF (+0.41 V vs SCE under the same conditions).

Table 2. Oxidation Potentials of 1a−d and 2a−g and Related Compounds[a,b]

compound	E_1	E_2
1a	+0.30	+0.52
1b	+0.32	+0.83[c]
1c	+0.40	+0.80[c]
1d	+0.41	+0.83[c]
Phenoxazine	+0.61	
N-methylphenoxazine	+0.68	
N-phenylphenoxazine	+0.80	
2a	+0.39	+0.60
2b	+0.55	+0.84
2c	+0.54	+0.89
2d	+0.52	+0.87
2e	+0.49	+0.85
2f	+0.49	+0.85
2g	+0.47	+0.84
Phenothiazine	+0.68	
N-methylpheothiazine	+0.80	+1.36
N-phenylphenothiazine	+0.77	

[a] V vs SCE measured in DMF in the presence of *n*-Bu_4NClO_4 (0.1 M) with a sweep rate of 50 mV/s; the value was corrected with a reference of $E(FeCp_2/FeCp_2^+)$ = +0.48 V vs SCE. [b] Half-wave potentials. [c] Peak potentials.

Preparation of Charge-Transfer Salts and Radical Cation Salts Derived from 1a, 1b, and 2b. The condensed phenoxazines and phenothiazines, **1a**, **1b**, **2a**, and **2b**, were expected to form charge-transfer (CT) complexes or radical ion salts. Experiments for their preparation either by mixing with suitable acceptors or oxidizing under electrochemical (EC) conditions have been examined. The diphenoxazines **1a**,**b** gave CT complexes with TCNQ. However, the other compounds did not form CT complexes. The electrochemical oxidation was achieved in the presence of suitable electrolytes ($TBAClO_4$, $TBAI_3$, $TBAPF_6$) with a constant current (1.0 − 2.0 μA). Solid deposition on the anodic electrode (Pt) was observed after several days for the oxidation of **1b**. In some cases, the NH derivative **1a**, **2a**, and the *N*-methyl derivative **2b** also provided the colored solid on the electrode. However, they were not pure enough to identify their elemental composition. Table 3 summarizes the results of the products whose composition was in accord with the elemental analysis within ±0.5%. The complexes and radical ion salts were dark green except for blue for **1a**-TCNQ and dark brown for **2b**$_2$-DDQ_3-$2H_2O$. The conductivity measured as a compressed powder is also listed in Table 3. The conductivity was in the range of semiconductor for all the CT complexes and the salts. The highest value was observed for the **1b**-TCNQ CT complex. The X-ray structure, the degree of charge transfer of the **1b**-TCNQ complex, and the EPR and electronic spectrum of the radical cation salts have already been described in our preliminary paper.[17]

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Table 3. Formula and Conductivities of CT Complexes and Radical Cation Salts Prepared from Condensed Phenoxazines and Phenothiazines

compound	solvent (method)	formula	elementary analysis (obsd calcd)	conductivity σ (S cm^{-1})
1a-TCNQ	CH_3CN (mixing)	$C_{30}H_{16}N_6O_2$	C 72.62, H 3.14, N 16.67 C 73.12, H 3.27, N 17.06	7.8×10^{-6}
1b-TCNQ	CH_3CN (mixing)	$C_{32}H_{20}N_6O_2$	C 73.79, H3.74, N 15.98 C 73.84, H3.87, N 16.14	9.9×10^{-4}
1b-I_5	CH_2Cl_2 (mixing)	$C_{20}H_{16}N_2O_2I_5$	C 25.26, H 1.70, N 2.95 C 25.37, H 1.59, N 2.85	2.0×10^{-7}
1b-ClO_4	THF (EC-ox)	$C_{20}H_{16}ClN_2O_6$	C 57.72, H 3.88, N 6.68 C 57.77, H 3.88, N 6.74	5.6×10^{-7}
$\mathbf{1b}_2$-I_3	PhCl (EC-ox)	$C_{40}H_{32}N_4O_4I_3$	C 47.38, H 2.95, N 5.24 C 47.41, H 3.18, N 5.53	3.0×10^{-5}
1b-PF_6	THF (EC-ox)	$C_{20}H_{16}N_2O_2PF_6$	C 52.41, H 3.41, N 6.14 C 52.07, H 3.50, N 6.07	9.8×10^{-6}
$\mathbf{2b}_2$-DDQ_3-$2H_2O$	CH_2Cl_2 (mixing)	$C_{64}H_{36}N_{10}Cl_6S_4O_8$	C 54.63, H 2.43, N 9.43 C 54.36, H 2.57, N 9.91	1.5×10^{-4}

DSC Studies for *N*,*N*′-Diary Derivatives 1c,d and 2c−g. Although *N*,*N*′-diaryl-diphenoxazines **1c**,**d** and -diphenothiazines **2c**−**g** had higher oxidation potentials (+0.40 − +0.54 V) than *N*,*N*′-dimethyldiphenoxazine **1b**, they might be converted into amorphous materials when the aryl-substituents were suitably designed. We have examined DSC (differential scanning calorimetry) experiments for all the *N*,*N*′-diaryl compounds. We have found that the sulfur derivatives **2d**, **2e**, and **2f** have clear glass transitions in their DSC curves (Figure 2). For compound **2d**, the first heating scan (10 °C/min) showed the melting point (212 °C). After heating, the sample was cooled (20 °C/min) to 0 °C using liquid nitrogen, giving a supercooled glass without crystallization. The second heating scan (10 °C/min) of supercooled glass showed a glass transition temperature (T_g ~109 °C). Similar behavior was observed for **2e** (T_g ~59 °C). For **2f**, the second heating gave a glass transition temperature (T_g ~72 °C) and crystallization at T_c = 119 °C to a new crystalline phase that melted at 217 °C. The observation of the glass transition clearly indicates that these diphenothiazine compounds **2d**, **2e**, and **2f** have an amorphous nature. The other diphenothiazines and all the diphenoxazines were reversibly crystallized under cooling. Of these, compound **1d** showed two endothermic melting peaks at 315 and 325 °C (ca. 1:2 intensity ratio) at the first scan. After cooling, the second heating scan showed a major peak at 325 °C with only a minor peak at 315 °C. The peak at 315 °C completely disappeared in the third heating scan. These observations would be related to the rotamer transformation in the solid state for **1d**. Both the unsymmetrical nature of the aryl groups and the diphenothiazine structure rather than the diphenoxazine structure seem to be essential for the observation of glass transition phenomena. When applying these materials as a HIM inserted between ITO and a hole-transporting layer, the amorphous nature has an advantage in morphological stability of the devices. Although these DSC experiments suggest potential applicability of **2d**, **2e**, and **2f** as HIMs in OLEDs, the deposition of these materials on the ITO surface under high vacuum does not necessarily mean that their morphology is identical with that in the DSC experiments. For this reason, applicability to HIMs in OLEDs was examined for all *N*,*N*′-diaryl derivatives.

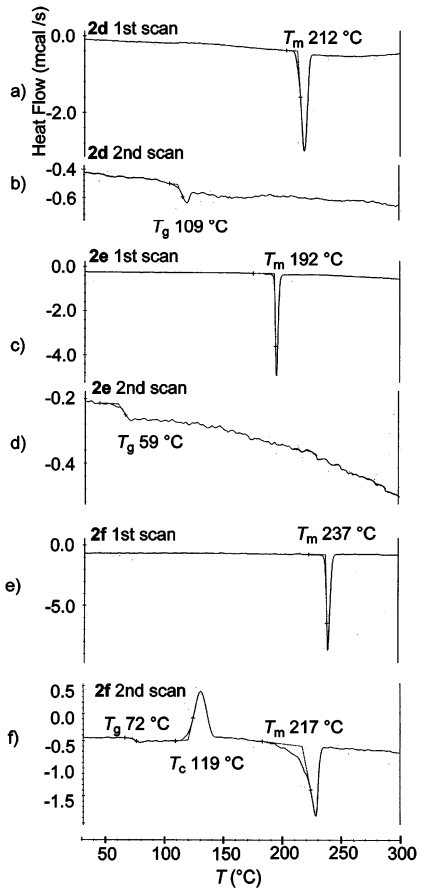

Figure 2. DSC curves for first heating (rapid cooling) and second heating processes of *N*,*N*′-diaryldiphenothiazines **2d**,**e**,**f**.

Application to OLEDs for the *N*,*N*′-Diaryl Derivatives. The electron-rich amorphous compounds are expected to be useful as hole-transport (HTMs) or hole-injection materials (HIMs) in OLEDs.[19,20] *N*,*N*′-Bis(1-naphthyl)-*N*,*N*′-diphenyl-4,4-biphenyl (NPB, $E^1_{1/2}$ = +0.85 vs SCE) has long been known as a superior hole-transfer as well as hole-injection material.[19] As shown later, a disadvantage of this material is in a rather fast degradation under OLED operating conditions. We have shown that the present diphenothiazines **2** and diphenoxazines **1** are stable toward the oxidation and that some of their radical cations can be isolated. The multilayered structure covering the NPB layer with com-

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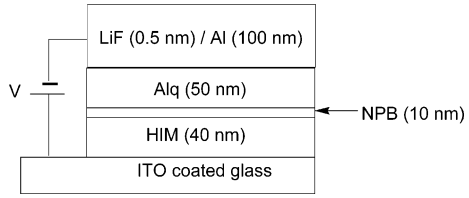
Table 4. Characterization of the Device of ITO/HIM (40 nm)/NPB (10 nm)/Alq (50 nm)/LiF (0.5 nm)/Al (100 nm) Using 1c,d or 2c−g as a HIM Layer



	characteristics at 100 cd/m^2				
compound	*V*	mA/cm^2	cd/A	lm/W	half-life[a] (h)
1c	4.4	4.3	2.3	1.7	*b*
1d	5.0	3.1	3.2	2.1	97
2c	4.3	2.2	4.5	3.3	23
2d	4.3	2.8	3.6	2.6	90
2e	4.3	3.1	3.2	2.3	73
2f	4.7	2.4	4.2	2.8	13
2g	4.3	2.8	3.5	2.6	47
c	3.9	3.9	2.5	2.1	10−28

[a] Measured at high current density (50 mA/cm^2) without sealing technique under aerated conditions. [b] Not determined. [c] In the absence of HIM-layer with 50 nm NPB.

pounds **1** or **2** as a HIM may improve the device stability hopefully with higher luminous efficiency.

We have fabricated the simple device ITO/HIM (**1** or **2**, 40 nm)/NPB (10 nm)/Alq (50 nm)/LiF (0.5 nm)/Al (100 nm), where Alq is tris(8-hydroxyquinolino)aluminum. The device emits green light (550 nm) from the Alq layer.[21] The characteristics of these devices measured in an aerobic environment with **1** or **2** as a HIM are summarized in Table 4 and can be compared to the reference device without HIM, ITO/NPB (50 nm)/Alq (50 nm)/LiF (0.5 nm)/Al (100 nm). The half-life in Table 4 is the decay time to half of the initial luminance without any sealing technique in an aerobic environment at a high current density (50 mA/cm^2), which corresponds to the initial luminance of 1600 (**1d**), 2520 (**2c**), 2212 (**2d**), 1900 (**2e**), 2350 (**2f**), and 2033 cd/m^2 (**2g**). The condensed diphenoxazine **1c** showed lower luminous efficiencies (lm/W) than the reference devices. The 1-naphthyl derived **1d** improved half-life time but still is in low efficiency. In contrast to these condensed diphenoxazine derivatives, the diphenothiazine derivatives showed higher luminous efficiency (lm/W) than the reference device. Compounds **2c** showed the highest luminous efficiency, but the half-life time was not improved. Compounds **2d**, **2e**, and **2g** showed good properties in both luminous efficiency and the half-life time. Although there is no precise correlation between the first oxidation potentials of the HIMs and the luminous efficiencies of the devices, it seems that the HIMs with higher oxidation potentials give the higher luminous efficiencies (**2c** > **2f**, **2d**, **2g**, **2e** > **1d**, **1c**). The poor efficiencies for **1c** and **1d** may reflect the highly endothermic electron-transfer process from NPB ($E^1 = +0.85$) to HIM radical cations. On the other hand, the device lifetime is independent of the oxidation potentials of HIMs. The lifetime seems to be related to the structure of aryl-substitutents on the nitrogen atoms; the longer lifetime is observed when the aryl substituents have an unsymmetrical structure (**1d**, **2d**, **2e**), suggesting the importance of the morphological feature in the electron-transfer process at the HIM−NPB interface.

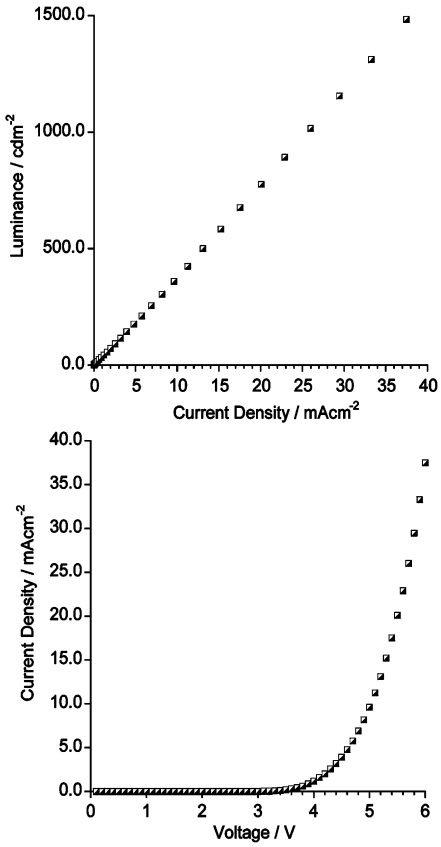


Figure 3. Luminance vs current density plots and current density vs voltage plots for the device ITO/**2d** (40 nm)/NPB (10 nm)/Alq (50 nm)/LiF(0.5 nm)/Al (100 nm).

Especially, compound **2d** showed the best HIM property in this series. The luminance (cd/m^2) versus current density (mA/cm^2) and current density versus applied voltage (V) plots for **2d** are shown in Figure 3. These data (Table 4 and Figure 3) can be directly compared to the recently developed Alq-emitting devices modified by dihydrophenazine HIMs[22] (typically ∼2.2 lm/W with the half-life of ∼100 h) or by electron-transporting silole-derived materials (typically ∼2.2 lm/W with the half-life of ∼50 h).[23] Thus, the present study clearly demonstrates that the insertion of a **2d** layer in this simple Alq-emitting device improves the device stability up to roughly 5 times with high emitting efficiency, suggesting the utility of **2d** as a superior HIM covering the HTM (NPB).

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Supporting Information Available: General experimental methods, IR data, and temperature-dependent NMR spectra of **1d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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