Synthesis, Photophysical and Electrochemical Properties of Novel Conjugated Donor-Acceptor Molecules Based on Phenothiazine and Benzimidazole

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Received June 4, 2007

Two series of new organic fluorophores such as asymmetrical 3-(benzimidazol-2-yl)-10-hexylphenothiazine derivatives **1** and symmetrical 3,7-bis(benzimidazol-2-yl)-10-hexylphenothiazine derivatives **2** have been synthesized. Electronic absorption, fluorescence, and electrochemistry measurements reveal that the electron withdrawing benzimidazole subunit directly connected to the phenothiazine core facilitates the charge transfer characters which were also verified by the theoretical calculations. Various substituents on the benzimidazole moieties can allow a fine-tuning of the LUMO energy levels of the molecules without significantly affecting the HOMO energy levels. The method provides a new route for designing ambipolar molecules whose energy levels are well-matched with the Fermi levels of the electrodes to facilitate the electron or hole injection/transfer in OLED devices.

Key Words : Phenothiazine, Benzimidazole, Charge transfer, Donor-acceptor, Fluorophore

Introduction

Architecture of π-conjugated donor-acceptor (D-A) molecules has been extensively studied because of their various applications in electronics and optoeletronics, such as organic light-emitting devices (OLEDs),[1] nonlinear optics,[2] electrogenerated chemiluminescence (ECL),[3] photovoltaic cells,[4] and fluorescent sensors.[5] The unique structure of D-A molecules has allowed their optical and electrochemical properties to be tuned delicately over a wide range by appropriate chemical modification to the donor and/or acceptor moieties, in which the structure-property relationship of those molecules could be understood.

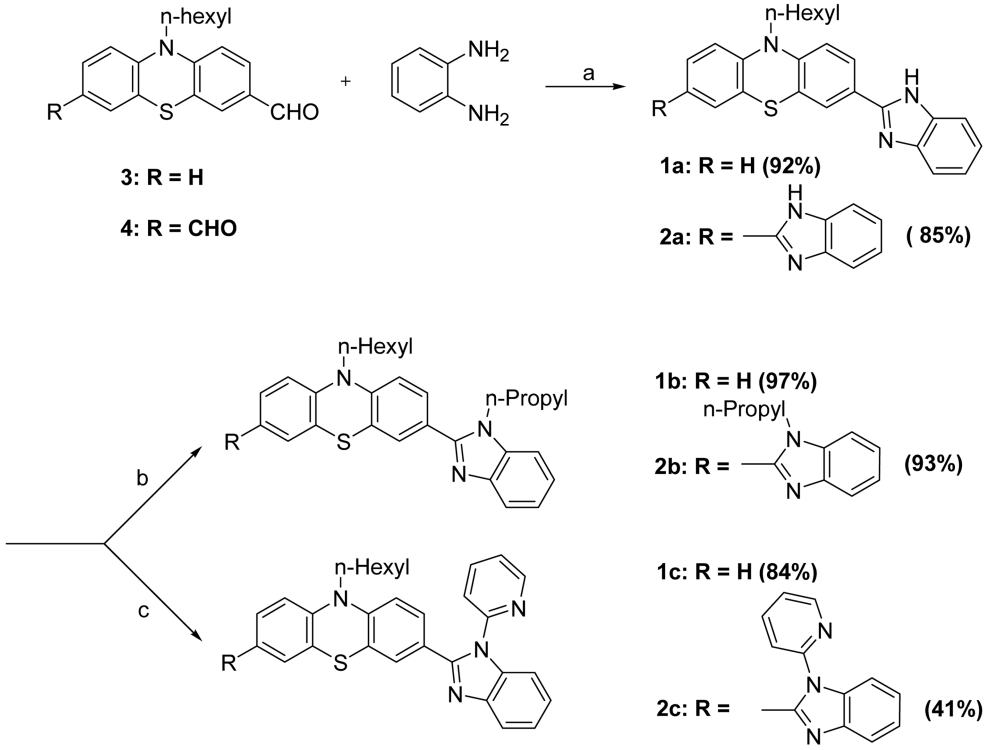
Heterocycles have often been incorporated into the organic materials to take advantage of their known chemical, thermal, thermooxidative, and photochemical stabilities, as well as high quantum yields. Among π-conjugated molecules, those containing electron-deficient benzene-fused five-membered heteroaromatic rings with nitrogen atom(s), *e.g.* benzothiazoles,[6] benzothiadiazoles,[1f,7] benzoxazoles,[6a,8] benzimidazoles,[6a,9] are widely employed as acceptor moieties in various optoelectronic materials[10] because of their high electron-accepting character. More importantly, the five-membered heteroaromatic rings directly bonded to a donor facilitate maximal coplanarity between the donor and the acceptor subunits, which might be critical for the efficient charge transfer in those molecules.

Phenothiazines, a pharmaceutically important class of heterocycles, have been extensively investigated as a donor in ECL systems[3,12] and optoelectronic devices,[13] such as organic and polymeric light-emitting diodes, field effect transistors, photovoltaic cells and molecular wires because of their unique nonplanar geometry and low reversible oxidation potentials.[11,14]

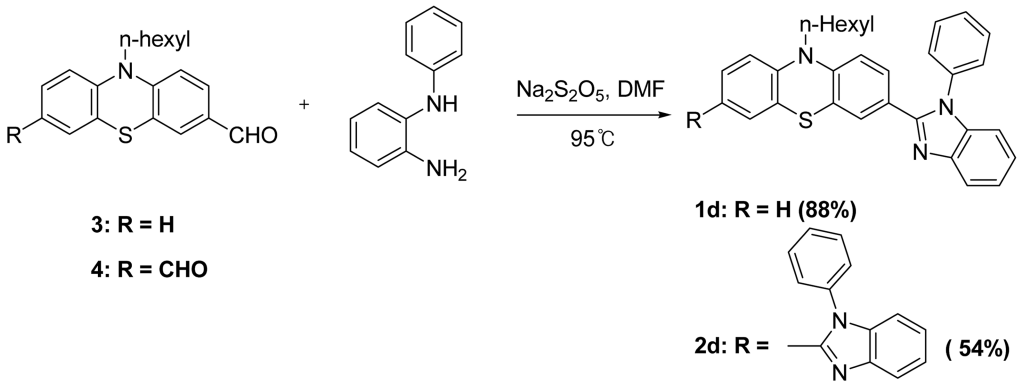
Recently, we have been interested in using the phenothiazine derivatives as the key material for electronic applications such as OLED.[15] Thus, we have synthesized various derivatives of the phenothiazine and studied the molecular structure-property relationship. Herein, we report the syntheses of two series molecules whose structures are in donor-acceptor (D-A) shape based on phenothiazine as the donor and benzimidazole as the acceptor, and discuss their photophysics as well as electrochemistry.

Results and Discussion

Syntheses. The asymmetrical 3-(benzimidazol-2'-yl)-10-hexylphenothiazine **1a** and symmetrical 3,7-bis(benzimidazol-2'-yl)-10-hexylphenothiazine **2a** were obtained by the oxidative coupling of *o*-phenylenediamine with 10-*n*-hexylphenothiazine-3-carbaldehyde, and 10-*n*-hexylphenothiazine-3,7-dicarbaldehyde under the treatment of sodium metabisulfite, respectively. The *N*-alkylation at 1'-position of the benzimidazole subunit gave the 3-(1'-propylbenzimidazol-2'-yl)-10-hexylphenothiazine **1b** and 3,7-bis(1'-propylbenzimidazol-2'-yl)-10-hexylphenothiazine **2b** in excellent yields. The 3-(1'-pyrid-2''-ylbenzimidazol-2'-yl)-10-hexylphenothiazine **1c** and 3,7-bis(1'-pyrid-2''-ylbenzimidazol-2'-yl)-10-hexylphenothiazine **2c** were obtained by the CuI-catalyzed coupling reaction of 2-bromopyridine with **1a** and **2a**, respectively (Scheme 1). Although CuI-catalyzed[16] coupling reaction of iodobenzene with **1a** can give **1d** in a moderate yield (51%), this method was verified to be inefficient to the synthesis of **2d**. However, the oxidative coupling of *N*-phenyl-1,2-phenylenediamine with 10-*n*-hexylphenothiazine-3-carbaldehyde and 10-*n*-hexylphenothiazine-3,7-dicarbaldehyde under the treatment of sodium metabisulfite readily produced **1d** and **2d**, respectively. Most of the molecules that we prepared are soluble in common organic solvents such as chloroform, dichloro-



Scheme 1. Reagents and conditions: (a) $Na_2S_2O_5$, DMF, 95 °C; (b) 1-bromopropane, NaH, DMF, r.t.; (c) 2-bromopyridine, CuI, 1,10-phenanthroline, Cs_2CO_3, DMF, 110 °C.



Scheme 2. The synthesis of **1d** and **2d**.

methane, 1,2-dichloroethane, THF and acetonitrile with the exception of **2a** which shows poor solubility in most of the solvents above-mentioned, and their structures were characterized by standard spectroscopic analyses. Especially, a crystal of **1d** was obtained from a hexane/ethyl acetate solution and its X-ray crystal structure was solved as illustrated in Figure 1.[17]

Structure Determination of 1d. Single crystals of **1d** were grown in a solution of hexane and ethyl acetate at room temperature. An X-ray structure determination confirmed the centrosymmetric nature (space group $P2_1/c$) of the crystal. As revealed by Figure 1, the dihedral angle between phenothiazine and benzimidazole rings was found to be 35.04 (9)°, indicating a slight distortion from the planar conformation that closely correlates the two ring. *N*-Substituted phenyl ring was largely twisted from the benzimidazole ring plane with a dihedral angle of 60.46 (10)°. Those conformations may affect the photophysical properties of the molecule.

Photophysical Properties. Figure 2 shows the absorption spectra of mono- and dibenzimidazole derivatives, **1** and **2** in CH_3CN (1.0×10^{-5} M). For monobenzimidazole derivatives **1**, the longest-wavelength absorption maxima (near 350 nm) were bathochromically shifted by about 40 nm in comparison with 10-hexylphenothiazine (311 nm),[11b] whereas those of dibenzimidazole derivatives **2** were red-shifted by about 60 nm. The attachment of the electron-donating alkyl group to the benzimidazole moieties such as **1b** and **2b** blue-

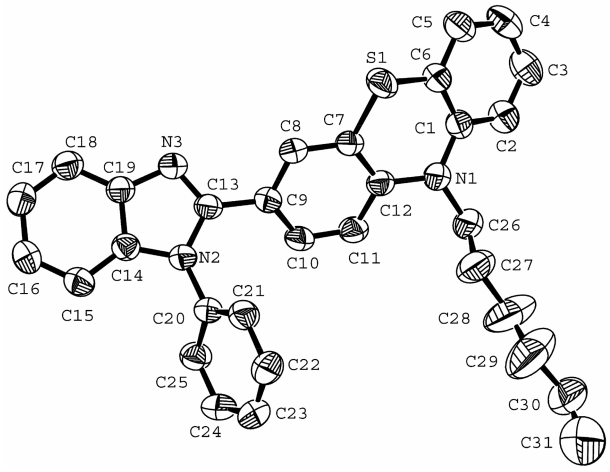


Figure 1. Crystallographic structure of **1d** (ORTEP drawing).

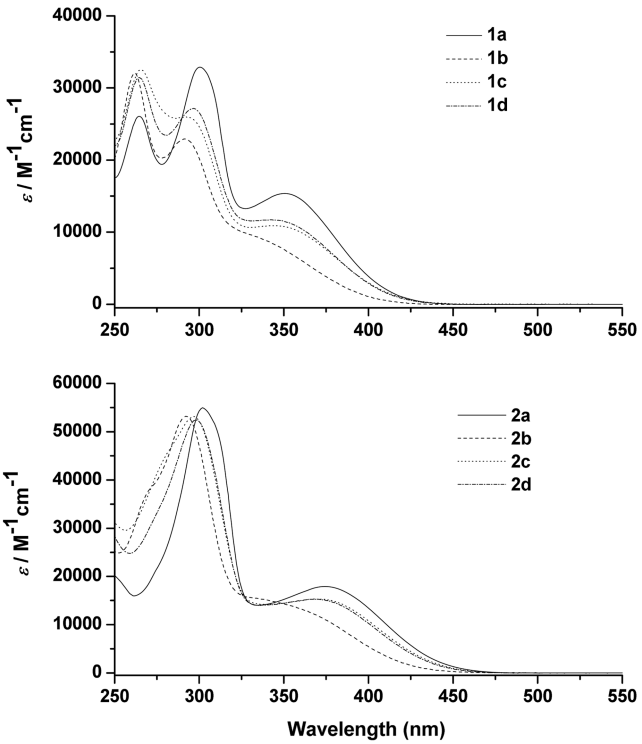


Figure 2. Absorption spectra of BP series (**1a**-**1d**, up) and DBP series (**2a**-**2d**, down) in acetonitrile (1.0×10^{-5} M).

shifted the absorption onset by about 9 and 17 nm relative to the parent molecules, **1a** and **2a**, respectively, whereas the shifts were not significant for **1c**-**d** and **2c**-**d**.

In contrast to the absorption spectra, the fluorescence spectra of asymmetric monobenzimidazole derivatives **1** showed a large positive solvatochromism compared with symmetric dibenzimidazole derivatives **2**. For example, the emission maximum of **1d** was red-shifted from the structured band at 455 nm in hexane to the structureless band at 492 nm in polar acetonitrile (Figure 3). Interestingly, the bathochromic shift was accompanied by broadening of the emission band, which is the characteristic of charge transfer (CT) emission band. We attribute this large solvatochromic

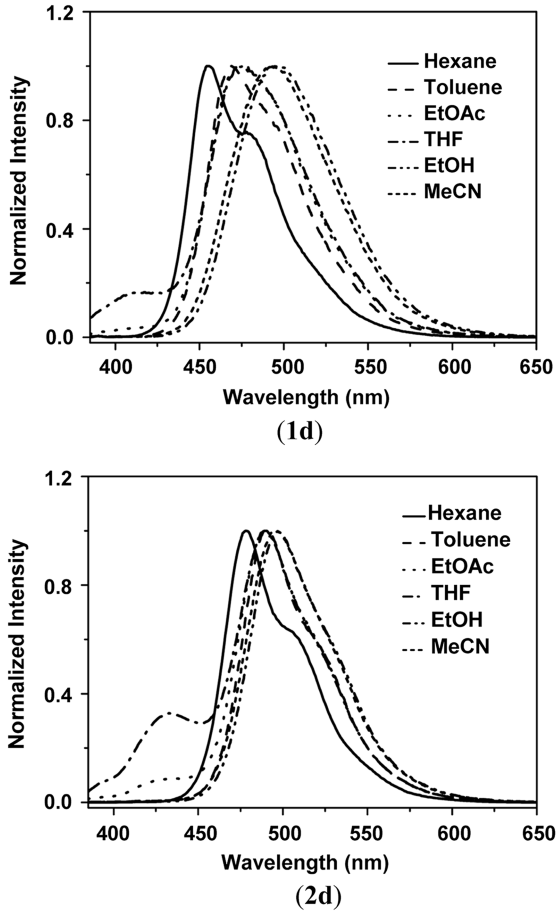


Figure 3. Normalized photoluminescence spectra of **1d** and **2d** in various solvents.

effect to the large induced dipole moment at the excited state generated by the charge transfer from the electron donating phenothiazine core to the electron withdrawing benzimidazole subunit in **1d**.[9a] The polar excited state of asymmetric **1d** may be efficiently stabilized by the polar solvent such as acetonitrile compared with symmetric **2d**. Therefore, the emission maxima of **1d** are similar to **2d** in polar solvents even though the latter have a longer π-conjugation length (Figure 3). It is interesting that the replacement of the hydrogen atom at 1 position of benzimidazole subunit by phenyl or pyridyl group gave rise to a red-shift in the emission by about 10-20 nm regardless of **1** or **2**, whereas the shifts in the alkyl substituted **1b** and **2b** were found to be negligible (Table 1).

Electrochemical Properties. The electrochemical behaviors of **1** and **2** were investigated by cyclic voltammetry (CV). Typical CV curves for **1d** and **2d** are shown in Figure 4, which can be taken as the examples for a closer inspection of electrochemical properties of the 3-substituted (**1**) and 3,7-disubstitued (**2**) phenothiazins. The compound **1d** showed a reversible one-electron oxidative wave with a half-wave potential of + 0.78 V (i_{pa1} = 5.4 μA) *vs* Ag/AgCl, which is + 0.08 V higher than that of 10-*n*-hexylphenothiazine (**10-HP**, E^1_{ox} = + 0.70 V), whereas the half-wave potential of the first reversible one-electron oxidative wave of **2d** was

Table 1. Photophysical Data of **1a-2d**

	λ_{max}^{abs}/nm (ε^a)	λ_{max}^{em}/nm [b]	Φ_f [c]
1a	303(2.82), 353(1.49)	462	0.35
1b	295(2.25)	463	0.39
1c	266(3.03), 339(1.27)	479	0.38
1d	301(2.68), 348(1.18)	469	0.43
2a	304(4.88), 376(1.73)	485	0.46
2b	296(5.08)	483	0.50
2c	298(5.15), 362(1.69)	494	0.46
2d	303(5.24), 375(1.54)	491	0.47

[a] 10^4 $M^{-1}cm^{-1}$ in toluene; [b] for **1a-1d**, λ_{ex} = 350 nm, **2a-2d**, λ_{ex} = 370 nm; [c] Φ_f calculated with **DPA** (9, 10-diphenylanthracene) as standard(Φ_f = 0.91 in benzene).

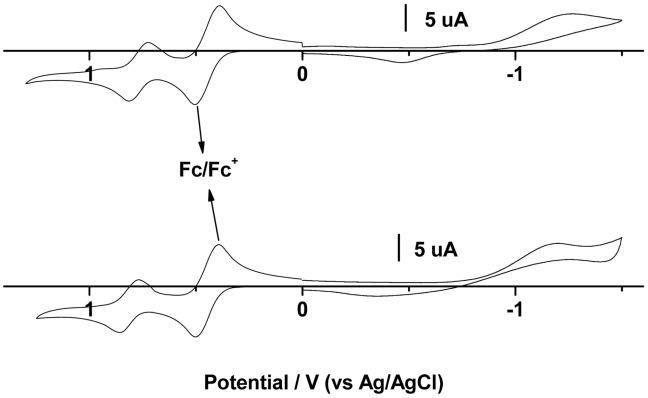


Figure 4. Cyclic voltammograms of 1 mM solutions of **1d** (top) and **2d** (down) in CH_2Cl_2 (oxidation process) and THF (reduction process) at a platinum electrode (0.1 M $TBAPF_6$; scan rate 100 mV/s).

appeared at + 0.80 V (i_{pa1} = 4.6 μA). The HOMO and LUMO energy levels of both **1** and **2** were deduced from the oxidative potentials and absorption onset (Table 2). The HOMO energy levels of those phenothiazine-based compounds were similar each other whereas LUMO energy levels varied dependent upon the substitutent. For example, **1b** with a propyl group at 1' position of the benzimidazole subunit had the same HOMO energy as the pyridyl-substituted **1c**, whereas the LUMO energy of the former was 0.12 eV higher than that of the latter. It is also interesting to notice that the LUMO energy levels of **2** were substantially lower than those of **1** which might be due to the delocalization of LUMO in **2**.

Theoretical Calculations. To understand the influence of substituents on the electronic properties of **1** and **2**, theoretical calculations were performed using Gaussian 03 program. All the geometries were optimized at the B3LYP/6-31G(d) level.[18] The dihedral angles around the single bond connecting the phenothiazine and benzimidazole of **1d** and **2d** were found to be 30.08 and 30.29°, respectively, whereas that of *N*-substituted phenyl ring and benzimidazole ring were 55.51 and 55.29°, respectively, which are slightly smaller than the X-ray data. Table 2 lists the calculated HOMO/LUMO energy levels along with experimental HOMO/LUMO energy of **1** and **2** systems. Again, the calculated HOMO energy levels of **1** and **2** systems were similar each other whereas the calculated LUMO energy levels were strongly dependent upon the substituents at 1' position of benzimidazole subunit. Figure 5 illustrates the molecular

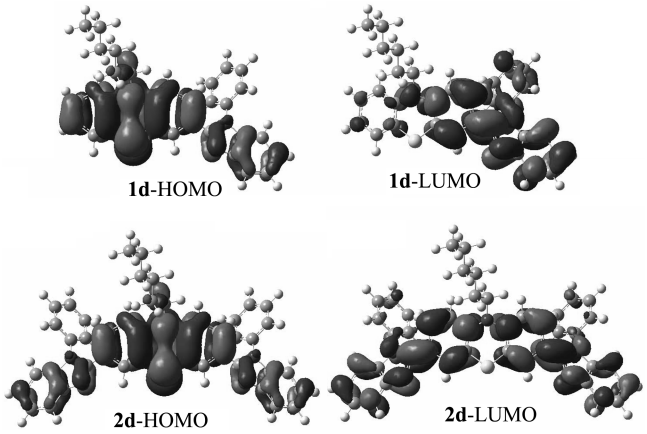


Figure 5. Pictorial presentation of HOMO (left) and LUMO (right) of **1d** and **2d**.

Table 2. Electrochemical Data and HOMO/LUMO energy levels of **1a-2d**

	E_{ox} (ΔEp)/(mV)[a]	E_{red}	E_g^{opt} (eV)[b]	HOMO[c] (Calc.)[d]	LUMO[c] (Calc.)[d]
1a	760(68), 1365(i)	–	3.02	5.14(5.05)	2.12(1.09)
1b	777(68), 1383(i)	−1211(i)	3.09	5.16(5.08)	2.07(0.84)
1c	779(64), 1311(i)	−1266(i)	2.97	5.16(5.08)	2.19(1.17)
1d	775(69), 1316(i)	−1276(i)	2.95	5.15(4.99)	2.20(0.98)
2a	771(65), 1336(i)	−1250(i)	2.81	5.15(5.08)	2.34(1.30)
2b	804(68), 1367(i)	−1130(i)	2.92	5.18(5.13)	2.26(1.03)
2c	804(68), 1248(i)	−1179(i)	2.81	5.18(5.08)	2.37(1.28)
2d	803(71), 1277(i)	−1199(i)	2.78	5.18(4.99)	2.39(1.14)
10-HP	702(72)	–	3.51	5.08	1.57

[a] Electrochemical measurement were recorded on a Bioanalytical System Bas 100B. Cyclic voltammograms were obtained in deoxygenated CH_2Cl_2 (oxidation process) and THF (reduction process) with a platinum working electrode, a platinum auxiliary electrode and a saturated Ag/AgCl reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. E_{ox}, E_{red} and ΔEp data are in mV units with reference to Ag/AgCl; i: irreversible peak potentials. [b] The E_g^{opt} optical band gap was derived from the onset of absorption spectra.(E_g = 1240/λ_{onset}). [c] The energy (eV) of the HOMO was calculated with reference to ferrocene (4.8 eV vs vacuum, $E_{HOMO} = E_{ox} + 4.8$) and the energy (eV) of the LUMO was obtained by equation: $E_{LUMO} = E_{HOMO} - E_g^{opt}$. The potential of *Fc/Fc*$^+$ in CH_2Cl_2 is 0.420 V. [d] Calculated energy using Gaussian 03 program.

orbitals of **1d** and **2d**. As shown in the figure, the HOMOs are more localized on the core of phenothiazine whereas the LUMOs are more localized on the benzimidazole explaining the large electronic effect of the substituents to the LUMO energy level of **1** and **2**. The localization of the LUMO of **1d** is more pronounced than that of **2d**, which may result in more CT emission character in compounds **1** compared with **2** as evidenced by the notable solvatochromism observed with **1d** (Figure 3).

Accordingly, we demonstrated a material system whose LUMO energy levels can be fine-tuned without influencing HOMO energy levels by changing subtle substitution patterns. We are currently investigating EL properties of these molecules.

Conclusion

Two series of new organic fluorophores, asymmetrical (**1**) and symmetrical (**2**) donor-acceptor molecules based on phenothiazine and benzimidazole moieties have been synthesized. Study on electronic absorption, fluorescence emission and electrochemical behavior of those molecules indicated that the five-membered benzimidazole rings directly bonded to the phenothiazine donor facilitate effective charge transfer. The different molecular patterns such as a symmetrical bis-acceptor and an asymmetrical mono-acceptor skeletons, and the subtly different remote substituents at 1' position of benzimidazole subunit were found to influence the optical properties and electrochemical properties of **1** and **2**. Those approaches can lead to a fine-tuning of the LUMO levels without significantly affecting the energy levels of HOMO, and provide a new route for designing ambipolar molecules with energy levels matched with the Fermi levels of the electrodes to balance the electron or hole injection/transfer in OLEDS.

Experimental Section

General. Phenothiazine, *o*-phenylenediamine, 1-bromopropane, 2-bromopyridine, 1,10-phenanthroline, sodium hydride, sodium metabisulfite ($Na_2S_2O_5$), copper iodide, cesium carbonate, *n*-hexane, toluene, THF, ethyl acetate, ethanol, acetonitrile, deuterated dimethyl sulfoxide (DMSO-d_6) and deuterated chloroform were obtained from Aldrich and used as received. Phenothiazine-3-carbaldehyde and phenothiazine-3,7-dicarbaldehyde were synthesized using Vilsmeier-Haak reaction.[19] The ^{1}H and ^{13}C NMR spectra were collected on Jeol JNM-AL300 spectrometer at 300 MHz and 75 MHz, respectively. HRMS spectra were recorded on Jeol JMS-700 spectrometer. UV-vis absorption spectra were obtained on a Shimadzu UV-3100 spectrophotometer. Steady-state photoluminescence (PL) spectra were recorded on a Hitachi F-4500 spectrophotometer. The PL quantum yields of the compounds mentioned were determined relative to 9,10-diphenylanthracene (DPA) as a standard in benzene (λ_{exc} = 380 nm, Φ_f = 0.91). Cyclic voltammetry (CV) experiments were performed on a BASi C3 Cell Stand under nitrogen in dry and degassed CH_3CN at room temperature and at a scan rate of 100 mV/s. The working electrode was 1.6 mm platinum disk, the counter electrode was platinum wire and an Ag/AgCl electrode was used as the reference electrode. The potential values obtained in reference to Ag/Ag^+ were corrected to the internal standard of Fc/Fc^+ in CH_2Cl_2 ($E_{ox}^{1/2}$ = 0.420 V).

3-(Benzimidazol-2'-yl)-10-hexylphenothiazine (1a). To the solution of phenothiazine-3-carbaldehyde (1.0 g, 3.2 mmmol) and *o*-phenylenediamine (347 mg, 3.2 mmol) in 5 ml of DMF was added sodium metabisulfite (730 mg, 3.8 mmol), then the mixture was heated to 95 °C for 20 hours. After cooled to room temperature, 100 mL of ethyl acetate was added and washed with saturated aqueous NaCl and water. The organic phase was dried ($MgSO_4$) and concentrated at reduced pressure. Purification by chromatography (silica gel, hexane/acetone = 2:1) gave **1a** (1.18 g, 92%) as pale yellow glassy solid. Mp. 99-101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.81 (t, J = 6.6 Hz, 3H), 1.21-1.32 (m, 6 H), 1.67 (m, 2H), 3.67 (t, J = 6.9 Hz, 2H), 6.63 (d, J = 8.7 Hz, 1 H), 6.75(d, J = 8.1 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 6.09 (t, J = 8.1 Hz, 1H), 7.21-7.25 (m, 2H), 7.61-7.64 (m, 2H), 7.76 (s, 1H), 7.88 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.5, 26.5, 26.6, 31.3, 47.4, 115.2, 115.4, 122.6, 123.7, 124.1, 125.0, 125.6, 126.3, 127.1, 127.4, 144.1, 146.6, 152.1; IR (KBr, cm^{-1}): 1625; EI-HRMS cacld. for $C_{25}H_{25}N_3S$ 399.1769, found 399.1743.

3,7-Bis(benzimidazol-2'-yl)-10-hexylphenothiazine (2a). was prepared by a procedure similar to that of **1a** except that phenothiazine-3,7-dicarbaldehyde was used as the reactant and 2.4 equiv. of diamine and 3.0 equiv of $Na_2S_2O_5$ were reacted. After purification by chromatography, **2a** was obtained in 85% yield as yellow solid. Mp. 177-179 °C; ^{1}H NMR (300 MHz, DMSO): δ 0.82 (t, J = 6.6 Hz, 3H), 1.26-1.42 (m, 6H), 1.73 (m, 2H), 3.99 (t, 2H), 7.16-7.23 (m, 6H), 7.54-7.57 (m, 4H), 7.96 (d, J = 1.8 Hz, 2H), 8.01 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO) δ 13.9, 22.1, 25.8, 26.2, 30.8, 46.8, 111.2, 116.2, 118.6, 121.7, 122.3, 123.2, 124.8, 124.9, 126.2, 135.0, 143.9, 145.2, 150.5; Anal. Calcd. for $C_{23}H_{29}N_5S$: C, 74.53, H, 5.67, N, 13.58, S, 6.22 or for $C_{23}H_{29.5}N_5SO_{0.25}$ ($M \cdot 0.25H_2O$): C, 73.89, H, 5.72, N, 13.46, S, 6.16. Found: C, 73.92, H, 5.70, N, 13.54, S, 6.19.

3-(1'-Propylbenzimidazol-2'-yl)-10-hexylphenothiazine (1b). To the solution of **1a** (300 mg, 0.75 mmol) in 10 ml DMF was added 36 mg of NaH (60% dispersion in mineral oil, 0.9 mmol) at 0 °C. The mixture was stirred 30 minutes for 30 minutes and then warmed to room temperature. After another 30 minutes, 0.082 mL (0.9 mmol) of bromopropane was added and the solution was stirred for 16 hours. The reaction was quenched by water and extracted with ethyl acetate. The organic phase was washed by water and brine, then dried over $MgSO_4$ and concentrated at reduced pressure. Purification by chromatography on silica gel gave **1b** (320 mg, 97%) as pale yellow glassy solid. Mp. 107-109 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 6 H), 1.30-1.45 (m, 6H), 1.83 (m, 4H), 3.87 (t, J = 6.9 Hz, 2H), 4.17 (t, J =

7.8 Hz, 2H), 6.86-6.95 (m, 3H), 7.12-7.16 (m, 2H), 7.26-7.29 (m, 2H), 7.36 (m, 1H), 7.47-7.50 (m, 2H), 7.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.1, 13.8, 22.4, 23.0, 26.4, 26.5, 31.2, 46.1, 47.4, 109.9, 114.9, 115.4, 119.5, 122.0, 122.3, 122.6, 123.9, 124.3, 125.0, 127.2, 127.3, 127.7, 128.1, 135.5, 142.9, 144.3, 146.2, 152.8; EI-HRMS cacld. for $C_{28}H_{31}N_3S$; 441.2239, found 441.2271.

3,7-Bis(1'-propylbenzimidazol-2'-yl)-10-hexylphenothiazine (2b) was prepared by a procedure similar to that of **1b**. After purification by chromatography, **2b** was obtained in 85% yield as pale yellow glassy solid. Mp. 74-76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90-0.94 (m, 9H), 1.26-1.50 (m, 6H), 1.87-1.90 (m, 6H), 3.95 (t, J = 6.9 Hz, 2H), 4.21 (t, J = 7.8 Hz, 4H), 7.00 (d, J = 8.4 Hz, 2H), 7.28-7.31 (m, 4H), 7.39-7.42 (m, 2 H), 7.49 (d, J = 1.8 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.79-7.82 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.2, 13.9, 22.5, 23.1, 26.4, 26.5, 31.3, 46.3, 47.7, 110.0, 115.2, 119.6, 122.2, 122.4, 124.5, 124.9, 127.9, 128.4, 135.6, 142.9, 145.6, 152.6; EI-HRMS cacld. for $C_{38}H_{41}N_5S$ 599.3083, found 599.3102.

3-(1'-Pyrid-2''-ylbenzimidazol-2'-yl)-10-hexylphenothiazine (1c) An oven-dried two-necked flask was charged with 1a (200 mg, 0.5 mmol), CuI (142 mg, 0.75 mmol), 1,10-phenanthroline (270 mg, 1.5 mmol) and Cs_2CO_3 (326 mg, 1 mmol), then evacuated and backfilled with nitrogen. The flask was capped with a rubber septum and 2-bromopyridine (100 μL, 1 mmol) and 5 mL of DMF were added through the septum via syringe. The mixture was heated in an oil bath (110 °C) with stirring until the starting **1a** had been completely consumed as judged by TLC analysis. The mixture was cooled to room temperature, diluted with dichloromethane (50 mL), filtered through Celite, and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel (eluting with ethyl acetate/hexane mixtures). **1c** was obtained as a pale yellow solid (200 mg, 84%). Mp. 125-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, J = 6.6 Hz, 3H), 1.26-1.38 (m, 6 H), 1.74 (m, J = 6.6 Hz, 2H), 3.77 (t, J = 7.2 Hz, 2H), 6.70 (d, J = 8.7 Hz, 1H), 6.81 (d, J = 8.1 Hz, 1H), 6.88 (t, J = 7.2 Hz, 1 H), 7.05-7.11 (m, 3H), 7.16 (dt, J = 8.4 Hz, J = 2.1 Hz, 1H), 7.23-7.39 (m, 4H), 7.49 (d, J = 7.5 Hz, 1H), 7.33 (dt, J = 7.8 Hz, J = 1.8 Hz, 1H), 7.85 (d, J = 7.8 Hz, 1H), 8.67 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 22.4, 26.4, 26.5, 31.3, 47.4, 111.0, 114.6, 115.4, 119.5, 121.7, 122.6, 123.1, 123.2, 123.4, 123.7, 124.0, 124.8, 127.2, 127.3, 127.9, 128.4, 136.1, 138.5, 143.0, 144.2, 146.3, 149.7, 150.5, 151.4; EI-HRMS cacld. for $C_{30}H_{28}N_4S$ 476.2035, found 476.2006.

3,7-Bis(1'-pyrid-2''-ylbenzimidazol-2'-yl)-10-hexylphenothiazine (2c) was prepared by following the same procedure as that of **1c**. After purification by chromatography, **2c** was obtained in 41% yield as yellow solid. Mp. 153-155 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.86 (t, J = 6.6 Hz, 3H), 1.25 (m, 6H), 1.72 (m, 2H), 3.74 (t, J = 7.2 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.20-7.38 (m, 10H), 7.48 (d, J = 7.8 Hz, 2H), 7.76-7.86 (m, 4H), 8.68 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.4, 26.3, 26.4, 31.2, 47.6, 110.9, 114.8, 119.6, 121.7, 123.2, 123.5, 124.2, 124.3, 127.9, 128.5, 136.1, 138.6, 143.0, 145.4, 149.8, 150.4, 151.2; Anal. Calcd. for $C_{42}H_{35}N_7S$: C, 75.31, H, 5.27, N, 14.64, S, 4.79; Found: C, 75.48, H, 5.50, N, 14.61, S, 4.72.

3-(1'-Phenylbenzimidazol-2'-yl)-10-hexylphenothiazine (1d) To the solution of phenothiazine-3-carbaldehyde (2.0 g, 6.4 mmol) and *N*-phenyl-1,2-phenylenediamine (1.31 g, 7.1 mmol) in 15 mL of DMF was added sodium metabisulfite (1.7 g, 9.0 mmol), then the mixture was heated to 95 °C for 12 hours. After cooled to room temperature, 100 mL of ethyl acetate was added and washed with saturated aqueous NaCl and water. The organic phase was dried ($MgSO_4$) and concentrated at reduced pressure. Purification by chromatography (silica gel, hexane/acetone = 2:1) gave **1d** (2.68 g, 88%) as pale yellow solid. Mp. 164-165 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85 (t, J = 6.6 Hz, 3H), 1.26-1.38 (m, 6H), 1.74 (m, 2H), 3.767 (t, J = 7.2 Hz, 2H), 6.66 (d, J = 8.7 Hz, 1H), 6.79 (d, J = 8.1 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 7.10 (m, 1H), 7.19-7.24 (m, 3H), 7.29-7.31 (m, 3H), 7.43 (s, 1H), 7.48-7.50 (m, 3H), 7.85 (d, J = 7.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.5, 26.4, 26.6, 31.3, 47.4, 110.2, 114.5, 115.4, 119.4, 122.6, 122.8, 123.0, 123.6, 124.1, 124.6, 127.2, 127.3, 128.0, 128.3, 128.6, 129.8, 136.9, 137.2, 142.8, 144.3, 146.2, 151.5; Anal. Calcd. for $C_{31}H_{29}N_3S$: Cald: C, 78.28; H, 6.15; N, 8.83; S, 6.74; Found: C, 78.51; H, 6.19; N, 8.75; S, 6.95.

3,7-Bis(1'-phenylbenzimidazol-2'-yl)-10-hexylphenothiazine (2d) was prepared by following the same procedure as that of **1d** except that phenothiazine-3,7-dicarbaldehyde was used as reactant and 2.4 equiv. of diamine and 3.0 equiv of $Na_2S_2O_5$ was consumed. After purification by chromatography, **2d** was obtained in 54% yield as yellow solid. Mp. 180-182 °C, ^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, J = 6.3 Hz, 3H), 1.28-1.33 (m, 6H), 1.72 (m, 2H), 3.71 (t, J = 6.6 Hz, 2H), 6.66 (t, J = 7.5 Hz, 2H), 7.21-7.26 (m, 6H), 7.32-7.35 (m, 6H), 7.41-7.44 (m, 2H), 7.52-7.54 (m, 6H), 7.90 (t, J = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.3, 22.4, 26.2, 31.2, 47.4, 110.2, 114.6, 119.4, 122.8, 123.0, 124.0, 124.1, 127.3, 127.9, 128.2, 128.6, 129.8, 136.8, 137.1, 142.8, 145.1, 151.2; Anal. Calcd. for $C_{44}H_{37}N_5S$: C, 79.13; H, 5.58; N, 10.49; S, 4.80; Found: C, 78.97; H, 5.92; N, 10.27; S, 5.02

Single crystal X-ray structure determination of 1d. Suitable crystals were obtained by recrystallization in hexane/ethyl acetate solution. Data were recorded using an Enraf-Nonius Kappa CCD diffractometer with graphite-monochromated Mo Kα-radiation (λ = 0.71073 Å). Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects using DENZO.[20] The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares with SHELXL-97.[21] A sulfur atom is disordered into two site and the structure was refined with 0.95 and 0.05 of occupation factors for each site. All non-hydrogen atoms were refined anisotropically. And all hydrogen atoms not involving the

hydrogen bonding were treated as idealized contributions.

Acknowledgement. This work was supported by the Korea Research Foundation (KRF-2005-005-J00801, K. H. A.) and the Korea Science and Engineering Foundation (KOSEF R01-2004-000-10610-0, S. I. Y.)

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