Dipolar Dibenzothiophene *S,S*-Dioxide Derivatives Containing Diarylamine: Materials for Single-Layer Organic Light-Emitting Devices**

By Tai-Hsiang Huang, Jiann T. Lin,* Li-Yin Chen, Yu-Ting Lin, and Chung-Chih Wu*

Considerable progress has been made on organic light-emitting diodes (OLEDs) in the past decade since the seminal reports of the groups at Kodak^[1] and Cambridge^[2] on small-molecule- and polymer-based devices. In OLEDs, the balance of electron and hole mobility is extremely important in confining excitons at the desired region to assure color purity and good performance of the device. Towards this end, a common approach used for polymers is blending of different components. In contrast, small molecules of different functions are generally vacuum-deposited successively to form a multi-layered device. For instance, the three-layered structure typical for OLEDs consists of a hole-transporting layer (HTL), an emitting layer, and electron-transporting layers (ETLs). The device can be simplified to a two-layered structure if one of the carrier-transporting materials also possesses emission characteristics. Single-layered devices are also possible and desired if a balance of electron- and hole-transport inside the emitting materials can be achieved. It is conceivable that the overall cost will be reduced by a more simplified device fabrication.

So far, fabrication of single-layered small-molecule electroluminescent (EL) devices has not been actively pursued, and those reported in literature are far from satisfactory.^[3] Recently, we reported single-layered devices fabricated from benzo[1,2,5]thiadiazole-based compounds containing arylamines^[4] and 3-cyano-9-diarylmino carbazoles.^[5] In the latter case, we introduced a cyano substituent, the functional group used to enhance the electron mobility of poly(*p*-phenylenevinylene) (PPV) and its small-molecule homologues,^[6] at the hole-transporting carbazoyl amines. Current efficiency up to

~5.5 cd A⁻¹ at 100 mA cm⁻² current density can be achieved. In the former case, the electron-accepting benzo[1,2,5]thiadiazole^[7] was linked to the electron-donating arylamines.^[8] Despite the presence of the electron-transporting benzo[1,2,5]thiadiazole and hole-transporting arylamines, the current efficiency at 100 mA cm⁻² can only reach ~0.60 cd A⁻¹. In our continuing search for materials for single-layered devices, the thiophene-*S,S*-dioxide moiety attracted our attention. Both the thiophene-*S,S*-dioxide^[9] and benzothiophene-*S,S*-dioxide^[10] moieties were demonstrated to be beneficial for increasing electron affinity and solid-state photoluminescence efficiency. It is believed that the electron-deficient dibenzothiophene-*S,S*-dioxide moiety will behave similarly.^[11] We have successfully synthesized dibenzothiophene-*S,S*-dioxide-based dipolar compounds and fabricated single-layered devices from these materials.^[12]

Scheme 1 illustrates the synthesis of the new compounds **1–4** in this study. Compounds **1** and **4** were synthesized from 2,8-dibromo-dibenzothiophene-*S,S*-dioxide^[13] and diarylamines by the palladium-catalyzed C–N coupling strategy developed by Hartwig et al.^[14] Stille's cross-coupling reaction^[15] of triarylamino-stannyl reagents and 2,8-dibromo-dibenzothiophene-*S,S*-dioxide led to the compounds **2** and **3**. These compounds were isolated in moderate to good yields (**1**, 53 %; **2**, 32 %; **3**, 71 %; **4**, 60 %). The thermal properties of the compounds were determined by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) measurements (Table 1). Compound **3** exhibits sequential glass transition, crystallization, and melting behavior upon repetitive heating and cooling cycles according to DSC. Compounds **2** and **4** are amorphous once made. Upon fast cooling of the melt, **1** forms a stable glass which persists in the subsequent heating cycles. The thermal decomposition temperatures of all four materials range from 345 to 440 °C.

Photophysical properties of the compounds are also presented in Table 1. The absorption bands in the region from ~250 to 300 nm are attributed to π – π^* and n – π^* transitions of the conjugated aromatic segments, and those at longer wavelengths are due to charge-transfer (CT) transitions from the peripheral amines to the dibenzothiophene-*S,S*-dioxide core. The large solvatochromism of the emission spectra indicates that these molecules permit strong intramolecular charge transfer from the donor (amine) to the acceptor (dibenzothiophene-*S,S*-dioxide). The emission maximum λ_{em} of the compound increases as the solvent polarity increases, and the

[*] Dr. J. T. Lin, T.-H. Huang
Institute of Chemistry, Academia Sinica
Taipei, Taiwan 115 (Republic of China)
E-mail: jtlin@chem.sinica.edu.tw

Dr. J. T. Lin
Department of Chemistry, National Central University
Chungli, Taiwan 320 (Republic of China)

Dr. C.-C. Wu, L.-Y. Chen, Y.-T. Lin
Department of Electrical Engineering,
Graduate Institute of Electro-optical Engineering, and
Graduate Institute of Electronics Engineering
National Taiwan University
Taipei, Taiwan 106 (Republic of China)
E-mail: chungwu@cc.ee.ntu.edu.tw

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Scheme 1. Synthesis of compounds **1–4**. Ac: acetyl; Bu: butyl; Ph: phenyl; DMF: dimethylformamide.

Table 1. Physical data for the compounds.

Compound	λ_{abs} [a] [nm]		λ_{em} [nm] (ϕ_f [%]) [b]			$T_m/T_c/T_g/T_d$ [c] [°C]	E (ΔE_p) [d] [mV]	HOMO/LUMO [e] [eV]
	CH ₂ Cl ₂	toluene	CH ₂ Cl ₂	CH ₃ CN	film			
1	290,357	450(7)	495(15)	520(14)	483	299/NA/102/345	670(322), –2034(117)	5.47/2.56
2	257,300,376	444(98)	524(55)	572(8)	505	NA/NA/123/362	553(123), –1935(82)	5.35/2.61
3	255,292,418	477(48)	543(19)	583(4)	554	231/170/112/440	406(98), –2065(116)	5.21/2.74
4	261,288,332,352	444(7)	493(11)	512(7)	476	NA/NA/138/395	711(230), –2124(102)	5.51/2.57

[a] λ_{abs} : absorption maximum. [b] Quantum yield (ϕ_f) was measured relative to coumarin 6 (63 % in CH₃CN). Corrections due to the change in solvent refractive indices were applied. λ_{em} : emission maximum. [c] T_m : melting point; T_c : crystallization temperature; T_g : glass-transition temperature; T_d : decomposition temperature. [d] $E = 1/2(E_{\text{pa}} + E_{\text{pc}})$, $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$, where E_{pa} and E_{pc} are anodic and cathodic potentials, respectively. Samples were measured in CH₂Cl₂ and dimethylformamide. All the potentials are reported relative to ferrocene, which was used as the internal standard in each experiment. The ferrocene oxidation potential was located at +332 mV relative to the Ag/AgNO₃ non-aqueous reference electrode. The concentration of the compound was 1×10^{-3} M. [e] Highest occupied molecular orbital (HOMO) energy was calculated with reference to ferrocene (4.8 eV). Solvent-to-vacuum correction was not applied. The bandgap was derived from the observed absorption onset, and the lowest unoccupied molecular orbital (LUMO) energy was derived from subtracting the bandgap from the HOMO.

emission color ranges from blue to orange. Compound **3** emits at the longest wavelength of all four compounds, indicating the most prominent charge-transfer character in **3**, which contains a thiophene unit between the donor and the acceptor. The quantum yields of **1** and **4** are much lower than those of **2** and **3**, possibly due to electron-transfer quenching from the peripheral diarylamines.

Each compound displays two quasi-reversible waves in the cyclic voltammetry measurements (Table 1). The one that appears at a positive potential relative to ferrocene/ferrocenium is a two-electron process attributed to the oxidation of the two peripheral amine units; the reduction of the dibenzothienophene-*S,S*-dioxide core occurs at a notably negative potential (–1.9 to –2.1 V) relative to ferrocene/ferrocenium. Compound

3 has the lowest oxidation potential due to the presence of an electron-rich thieryl ring next to the nitrogen atom.^[16] Nevertheless, it appears at significantly higher values than those of the diphenylthienylamine analogue we reported earlier.^[17] This, together with the higher oxidation potential of **1** (or **4**) relative to **2**, points out the influence of the electron-withdrawing dibenzothienophene-*S,S*-dioxide core. The phenyl ring between the dibenzothienophene-*S,S*-dioxide core and the peripheral diarylamine will decrease the mutual electronic coupling between the two. Accordingly, the reduction of dibenzothienophene-*S,S*-dioxide core in **2** is shifted anodically relative to that of **1**. The cathodic shift of the reduction potential of **3** compared to **1** and **2** stems from the more effective charge transfer in the former (vide supra).

Compounds **2** and **3**, having higher emission quantum yields, were subjected to EL studies using different device structures on an indium tin oxide (ITO) anode. Compounds NPB (1,4-bis[(1-naphthyl)phenyl]amino)biphenyl^[18] and TPBI (1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene)^[19] were used as hole- and electron-transporting materials, respectively, while LiF and Al were used as the electron-injection layer and the cathode. These device structures were: I) ITO/**2** (or **3**) (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (150 nm); II) ITO/NPB (40 nm)/**2** (or **3**) (40 nm)/LiF (1 nm)/Al (150 nm); III) ITO/**2** (or **3**) (80 nm)/LiF (1 nm)/Al (150 nm). The device performances are summarized in Table 2. Representative current–luminance (*I*–*L*) characteristics are shown in Figure 1. All devices exhibit low turn-on voltages (2.0–3.5 V) and emission (and thus, exciton confinement) in **2** (or **3**). It is worth noting

Table 2. Electroluminescent data of the devices. V_{on} : turn-on voltage; L_{max} : maximum luminance; CIE: Commission Internationale de l'Eclairage coordinates; FWHM: full width at half maximum; $\eta_{ext,max}$: maximum external quantum efficiency; $\eta_{p,max}$: maximum power efficiency; $\eta_{c,max}$: maximum current efficiency.

	2	3
V_{on} [V]	2.5; 2.3; 2.2	2.2; 2.5; 2.0
L_{max} [cd m ⁻²]	85475 (12.5); 9537 (15.0);	40140 (13.0); 10521 (11.5);
(V at L_{max} , [V])	37699 (12.5);	25159 (14.5)
λ_{em} [nm]	492; 492; 496	540; 536; 542
CIE [x,y]	0.16, 0.40; 0.16, 0.38;	0.37; 0.59; 0.36, 0.59;
	0.16, 0.44	0.37, 0.59
FWHM [nm]	68; 70; 68	82; 92; 82
$\eta_{ext,max}$ [%]	4.9; 1.3; 3.1	1.4; 0.87; 1.3
$\eta_{p,max}$ [lm W ⁻¹]	9.7; 3.3; 7.2	4.9; 3.3; 5.0
$\eta_{c,max}$ [cd A ⁻¹]	11; 3.1; 7.7	5.1; 3.1; 4.7
L [cd m ⁻²] [a]	10778; 2107; 7529	4904; 2272; 4245
η_{ext} [%] [a]	4.7; 0.94; 3.1	1.4; 0.65; 1.2
η_p [lm W ⁻¹] [a]	6.5; 1.3; 3.9	2.8; 1.7; 2.1
η_c [cd A ⁻¹] [a]	10.8; 2.1; 7.5	4.9; 2.3; 4.2

[a] Measured at a current density of 100 mA cm⁻². V_{on} was obtained from the x-intercept of a plot of log(luminance) versus applied voltage.

Figure 1. Luminance versus current density characteristics for the devices I, II, and III for compounds **2** and **3**.

that although the type I devices have the best device performances among the three types of devices, the unoptimized single-layered type III devices containing **2** and **3** show very promising performances comparable to those of the type I devices. In particular, the **2**-containing device III has the best performances (3.1 %; 3.9 lm W⁻¹; 7.5 cd A⁻¹ at 100 mA cm⁻²) among small-molecule single-layered devices reported in the literature.

Compared to other thiophene-*S,S*-dioxide and benzothio-phenene-*S,S*-dioxide derivatives, our compounds appear to have a better balance of electron- and hole-transport properties upon inspecting the EL performances of single-layered devices. Indeed, the amorphous compound **2** was found to have similar electron and hole mobilities of over 10⁻⁴ cm² V⁻¹ s⁻¹, as measured by the time-of-flight (TOF) transient photocurrent technique^[20] in vacuum at room temperature. These values are about one order-of-magnitude lower than the hole mobility (~10⁻³ cm² V⁻¹ s⁻¹) of the typical HTL material NPB^[21] and two orders-of-magnitude higher than the electron mobility (~10⁻⁶ cm² V⁻¹ s⁻¹) of the typical ETL material tris(8-hydroxy-quinoline) aluminum (Alq₃).^[22] Figure 2 shows representative TOF transients of holes for **2**. No clear plateaus are observed in the TOF transients, indicating dispersive transport behaviors (i.e., with carrier trapping) for both holes and electrons. Nevertheless, in the double logarithmic representations of the TOF transients (Fig. 2, inset), the carrier transit time t_T needed for determining carrier mobilities can still be clearly evaluated from the intersection point of two asymptotes. The field dependence of mobilities thus determined (Fig. 3) follows the nearly universal Poole–Frenkel relationship: $\mu \propto \exp(\beta E^{1/2})$, where β is the Poole–Frenkel factor and $E^{1/2}$ is the square root of the electric field.^[23] Knowledge of the bipolar transport properties of the present compounds provides a better understanding of the characteristics of single-layered devices. Although the EL performances of the current single-layered devices (type III) are still slightly lower than

Figure 2. TOF transients for **2** (1.43 μm thick) of holes at an electric field $E = 4.2 \times 10^5$ V cm⁻¹. The inset shows a double-logarithmic plot. t_T : transit time.

Figure 3. Electron and hole mobilities versus $E^{1/2}$ for **2**.

those of the best two-layered devices (type I), one should, however, note that the devices have not yet been subjected to thorough optimization, such as optimizing the electrodes (e.g., cathode), carrier injection, the layer thicknesses, etc. These factors could have subtle influences on the balance of carrier injection, the position of the carrier recombination zone, etc.

In summary, we have developed a convenient synthesis of dipolar compounds with a dibenzothiophene-*S,S*-dioxide core and two peripheral arylamines. These compounds exhibit intriguing ambipolar carrier transport properties and can be used to fabricate single-layered EL devices possessing excellent performances, comparable to those of multilayered devices. Future studies include modification of peripheral arylamines and spacers for emissive materials with non-dispersive ambipolar carrier-transport character.

Experimental

2,8-Di(diphenylamino)-5H-5λ⁶-dibenzo[*b,d*]thiophene-5,5-dione (1), and **2,8-di(1-naphthylamino)-5H-5λ⁶-dibenzo[*b,d*]thiophene-5,5-dione (4)** were synthesized by the same procedure: A mixture of diarylamine (2 equiv. per halogen atom), halides (5 mmol), *t*-BuONa (1.2 equiv. per halogen atom), Pd(OAc)₂ (1 mmol-% per halogen atom), tri-*tert*-butylphosphine (2 mmol-% per halogen), and toluene (40 mL) was heated at 80 °C for 16 h. After cooling, the mixture was treated with water and extracted with diethyl ether. The organic extract was dried over MgSO₄ with removal of the volatiles. The residue was purified by column chromatography on silica gel using ethyl acetate (EA)/*n*-hexane as an eluent.

Compound 1: White solids, yield = 470 mg (53 %). ¹H NMR (CDCl₃): δ 6.97 (dd, 2H, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz, C₆H₃), 7.06–7.12 (m, 14H, C₆H₃, *ortho*-, *para*-C₆H₅), 7.24–7.29 (m, 8H, *meta*-C₆H₅), 7.55 (d, 2H, *J* = 8.5 Hz, C₆H₃). Fast-ion bombardment mass spectroscopy (FAB MS) (*m/e*): 550 (*M*⁺). Elemental analysis calculated for C₃₆H₂₆N₂O₂S: C, 78.52; H, 4.76; N, 5.09. Found: C, 78.09; H, 4.42; N, 5.12.

Compound 4: White solids, yield = 920 mg (60 %). ¹H NMR (CDCl₃): δ 6.75 (dd, 2H, *J*₁ = 8.6 Hz, *J*₂ = 2.1 Hz, C₆H₃), 6.89 (d, 2H, *J* = 2.1 Hz, C₆H₃), 7.06 (t, 2H, *J* = 7.3 Hz, *para*-C₆H₅), 7.09 (d, 4H, *J* = 7.5 Hz, *ortho*-C₆H₅), 7.21 (t, 4H, *J* = 7.3 Hz, *meta*-C₆H₅), 7.27 (d,

2H, *J* = 7.4 Hz, C₁₀H₇), 7.36 (t, 2H, *J* = 7.6 Hz, C₁₀H₇), 7.42–7.49 (m, 6H, C₁₀H₇), 7.78 (d, 2H, *J* = 8.6 Hz, C₆H₃), 7.79 (d, 2H, *J* = 8.2 Hz, C₁₀H₇), 7.88 (d, 2H, *J* = 8.4 Hz, C₁₀H₇). FAB MS (*m/e*): 702 (*M*⁺). Elemental analysis calculated for C₄₄H₃₀N₂O₂S: C, 81.20; H, 4.65; N, 4.30. Found: C, 81.22; H, 4.82; N, 4.43.

2,8-Di[4-(diphenylamino)phenyl]-5H-5λ⁶-dibenzo[*b,d*]thiophene-5,5-dione (2) and **2,8-di[5-(diphenylamino)-2-thienyl]-5H-5λ⁶-dibenzo[*b,d*]thiophene-5,5-dione (3)** were synthesized by the same procedure: A mixture of triarylaminostannyl reagents (2.3 equiv. per halogen atom), 2,8-dibromo-dibenzothiophene 5,5-dioxide (0.20 mmol), PdCl₂(PPh₃)₂ (2 mmol-% per halogen atom), and *N,N*-dimethylformamide (7 mL) was stirred at 90 °C for 24 h. After cooling, methanol (25 mL) was added to precipitate the product, and the precipitate was extracted with dichloromethane. The organic phase was washed with KF solution (10 %). The organic extract was dried over MgSO₄ with removal of the volatiles. The residue was purified by column chromatography on silica gel using EA/*n*-hexane.

Compound 2: Yellow solids, yield = 290 mg (32 %). ¹H NMR (CDCl₃): δ 7.06 (t, 4H, *J* = 7.5 Hz, *para*-C₆H₅), 7.12–7.16 (m, 12H, C₆H₄, *ortho*-C₆H₅), 7.26–7.31 (t, 8H, *J* = 7.8 Hz, *meta*-C₆H₅), 7.50 (d, 4H, *J* = 8.5 Hz, C₆H₄), 7.68 (d, 2H, *J* = 8.2 Hz, C₆H₃), 7.84 (d, 2H, *J* = 7.9 Hz, C₆H₃), 7.96 (s, 2H, C₆H₃). FAB MS (*m/e*): 651 (*M*⁺). Elemental analysis calculated for C₄₈H₃₄N₂O₂S: C, 82.02; H, 4.88; N, 3.99. Found: C, 82.07; H, 5.14; N, 3.89.

Compound 3: Yellow solids, yield = 906 mg (71 %). ¹H NMR (CDCl₃): δ 7.63 (d, 2H, *J* = 4.0 Hz, C₄H₂S), 7.09 (t, 4H, *J* = 7.3 Hz, *para*-C₆H₅), 7.19 (d, 8H, *J* = 7.5 Hz, *ortho*-C₆H₅), 7.27–7.32 (m, 10H, C₄H₂S, *meta*-C₆H₅), 7.59 (dd, 2H, *J*₁ = 7.9 Hz, *J*₂ = 1.3 Hz, C₆H₃), 7.72 (d, 2H, *J* = 7.9 Hz, C₆H₃), 7.79 (d, 2H, *J* = 1.3 Hz, C₆H₃). FAB MS (*m/e*): 714 (*M*⁺). Elemental analysis calculated for C₄₄H₃₀N₂O₂S₃: C, 73.92; H, 4.23; N, 3.92. Found: C, 73.62; H, 4.21; N, 4.03.

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