Molecular Modification of 2,7-Diphenyl[1]benzothieno[3,2-*b*]benzothiophene (DPh-BTBT) with Diarylamino Substituents: From Crystalline Order to Amorphous State in Evaporated Thin Films

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Introduction of diarylamino substituents on 2,7-diphenyl[1]benzothieno[3,2-*b*]benzothiophene (DPh-BTBT) caused morphological change in the evaporated thin-film state: from highly crystalline films with edge-on molecular orientation for DPh-BTBT to amorphous films for the diarylamino derivatives. The former was unsuitable as a hole-transporting layer in organic light-emitting diodes (OLEDs), whereas the latter acted as a superior hole-transporting layer in multilayered OLEDs.

Recent prevailing interest in organic electronics has encouraged synthetic chemists to develop new organic semiconductors as an active material for various electronic device applications such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells.[1] One of such organic semiconductors recently developed is 2,7-diphenyl[1]benzothieno[3,2-*b*]benzothiophene (DPh-BTBT, Figure 1) that gives high-performance OFETs with field-effect mobility (μ_{FET}) higher than 1.0 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$.[2] Not only the high mobility, but also its improved air-stability and ready availability[3] make DPh-BTBT an attractive material for other organic electronic devices, e.g. OLEDs or photovoltaic cells.

Preliminary experiments using DPh-BTBT as the hole-transporting material (HTM) in multi-layered OLED devices (ITO/DPh-BTBT/$\mathrm{Alq_3}$/LiF/Al) (Figure S1) however, gave discouraging results: most of the fabricated devices showed negligible emission. The reason for the poor results seemed to be two fold: one is energetic mismatching of the highest occupied molecular orbital (HOMO) of DPh-BTBT (≈5.6 eV below the vacuum level) with the work function of ITO electrode (≈5.0 eV). The other, presumably the major one, is unfavorable molecular orientation of DPh-BTBT in the thin film state as evidenced by an X-ray diffraction measurement (XRD) of the evaporated thin film on the ITO substrate (Figure S2). The film has a crystalline phase with edge-on molecular orientation similar to DPh-BTBT thin film on $\mathrm{Si/SiO_2}$ substrates. Such molecular orientation in the crystalline film is unsuitable in OLED devices, although it is optimal for high-performance OFET devices.

With these preliminary results, we planned to chemically modify DPh-BTBT with diarylamino substituents that are often employed in the development of HTMs, because the groups can raise the HOMO energy level and promote the formation of an amorphous phase in the thin film state.[4] In this communication, we report the synthesis of diarylamino derivatives of DPh-BTBT **2**–**4** (Scheme 1) and their characterization as an active electronic material in OFET and OLED devices.

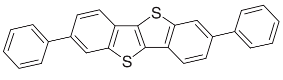
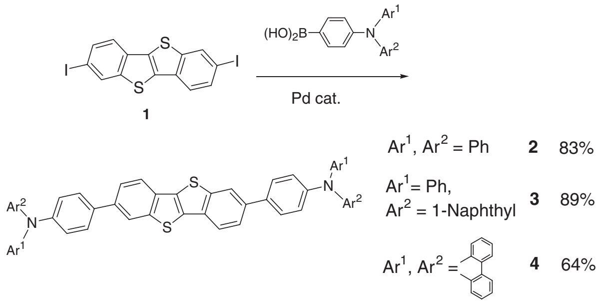


Figure 1. Molecular structure of DPh-BTBT.



Scheme 1. Synthesis of DPh-BTBT derivatives.

Synthesis of new DPh-BTBT derivatives **2**–**4** was easily achieved by the palladium-catalyzed Suzuki–Miyaura coupling between 2,7-diiodo[1]benzothieno[3,2-*b*]benzothiophene (**1**)[2] and the corresponding boronic acids, 4-(*N*,*N*-diphenylamino)phenyl boronic acid for **2**,[5] 4-[*N*-(1-naphthyl)-*N*-phenylamino]phenyl boronic acid for **3**,[6] and 4-(9-carbazolyl)phenyl boronic acid for **4**,[7] respectively (Scheme 1).[8,9]

Table 1 lists their oxidation potentials (E_{ox}), estimated HOMO energy levels,[10,11] energy gaps estimated from the absorption edge in dichloromethane solution, and glass-transition temperatures (T_{g}) together with those of a representative HTM, *N*,*N*′-diphenyl-*N*,*N*′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD) for comparison.[12]

Physical vapor deposition of **2**–**4** gave homogenous thin films on $\mathrm{Si/SiO_2}$ or ITO substrates. XRDs of evaporated thin films of **2**–**4** on both substrates showed no peak, indicating that

Table 1. Some molecular properties of **2**–**4**

	E_{ox}[a]/V	HOMO[b]/eV	E_{g}[c]/eV	T_{g}[d]/°C
2	+0.39	5.2	2.88	123
3	+0.41	5.2	2.88	140
4	+0.73	5.5	3.10	—[e]
α-NPD	+0.26	5.1		95

[a]Oxidation onset vs. $\mathrm{Fc/Fc^+}$. [b]Estimated from the oxidation onsets. [c]Estimated from absorption edges in solution UV–vis spectra. [d]Determined with DSC traces. [e]T_{g} was not confirmed on the DSC trace.

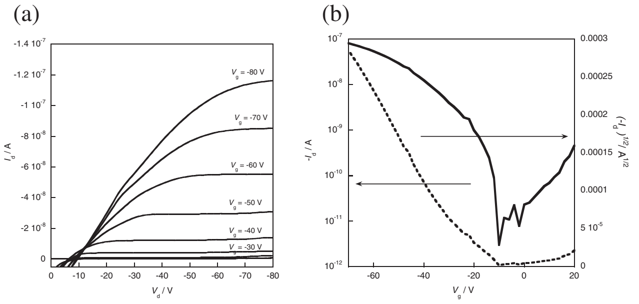


Figure 2. Output (a) and transfer (b) curves of **2**-based OFETs.

formation of amorphous thin film was highly likely (Figure S6). These results strongly implied that introduction of the diarylamino substituents deters the edge-on molecular orientation and is effective to change the thin-film morphology from crystalline order to an amorphous state.

In order to evaluate the hole-transporting properties of **2**–**4** in the thin-film phase, we fabricated their OFET devices with the top contact configuration ($L = 50\,\mu\mathrm{m}$, $W = 1.5\,\mathrm{mm}$). The output and transfer characteristics of **2**-based devices under negative gate bias are depicted in Figure 2 as a representative. In accordance with the amorphous nature of the thin film, its μ_{FET} ($2.0 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) was significantly reduced by four orders of magnitude compared with that of DPh-BTBT-based OFETs (Table 2). **3**-based devices showed μ_{FET} in the same order of magnitude as **2**-based ones, while **4**-based ones showed slightly lower μ_{FET}. These μ_{FET}s are on the other hand, in a similar range of reported values for OFETs with an amorphous thin film-based active channel:[13] actually, α-NPD-based OFETs[14] showed almost the same μ_{FET} ($1.4 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) when evaluated using the same device structure under identical conditions.[15] These results suggested that the present DPh-BTBT derivatives, in particular **2** and **3**, have a potential as HTM for OLEDs.

The standard device configuration of OLED (ITO (110 nm)/HTM (50 nm)/$\mathrm{Alq_3}$ (50 nm)/LiF (0.8 nm)/Al (100 nm)) was employed for evaluating **2**–**4** as HTM. For each HTM, more than ten devices were fabricated and evaluated to eliminate device-to-device deviation. All the devices except for the **4**-based devices showed an emission band centered at around 520 nm, typical emission from the $\mathrm{Alq_3}$ layer (Figure S7). The device characteristics, current efficiency ($LJ^{-1}{}_{1000}$) and driving voltage (V_{1000}) at the luminescence of $1000\,\mathrm{cd\,m^{-2}}$ extracted from typical devices are listed in Table 2 together with those of OLEDs with α-NPD.[12] As can be seen from Table 2, new HTMs **2** and **3** give comparable current efficiency and driving voltage with those of α-NPD, whereas **4** gives lower performances. The better performances of **2** and **3** as HTM can be partially attributed to their higher mobility and better energetic matching of their HOMOs with the work function of ITO electrode.[11]

Table 2. Some device characteristics extracted from OFETs and OLEDs based on **2**–**4**

	OFET		OLED	
	μ_{FET}[a] $/\mathrm{cm^2\,V^{-1}\,s^{-1}}$	$I_{\mathrm{on/off}}$	LJ^{-1}_{1000}[b] $/\mathrm{cd\,A^{-1}}$	V_{1000}[c] /V
2	2.0×10^{-4}	5×10^3	2.44	7.5
3	1.1×10^{-4}	10^3	1.92	8.4
4	2.8×10^{-5}	10^3	0.53	9.4
α-NPD	1.4×10^{-4}	5×10^3	2.38	8.5

[a] Extracted from the saturation regime. [b] Current efficiency at $1000\,\mathrm{cd\,m^{-2}}$. [c] Driving voltage at $1000\,\mathrm{cd\,m^{-2}}$.

Although the performances of the OLEDs using **2**–**4** as HTM are not necessarily far superior to standard OLED devices with α-NPD, the present results suggest that new DPh-BTBT derivatives, in particular **2** and **3**, showing comparable mobilities to α-NPD, have a potential as HTM for practical applications owing to their better thermal stability as expected from higher T_{g}s.[4] As a matter of fact, preliminary durability tests of **2**-based devices showed a longer lifetime than that of the standard OLEDs using α-NPD as HTM (Figure S9).

In summary we synthesized a series of diarylamino derivatives of DPh-BTBT **2**–**4** via the Suzuki–Miyaura coupling. Introduction of the diarylamino groups on DPh-BTBT induced morphological change in the vapor-deposited thin-films. In accordance with the amorphous nature of **2**–**4** thin films, μ_{FET}s evaluated using the OFET configuration were significantly lower than that of DPh-BTBT. In turn, the capability of **2**–**4** forming amorphous thin films makes them useful as HTM in multilayered OLEDs, and thus examined OLEDs showed comparable performances with a standard OLEDs using α-NPD as HTM.

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