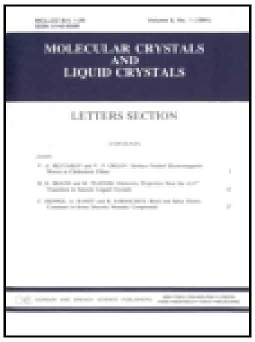
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Starburst-Type Carbazole Trimers as Host Materials for Solution-Processed Phosphorescent OLEDs

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Novel starburst-type carbazole trimers ***SB-1*** *and* ***SB-2*** *were developed as hole-transporting host materials for phosphorescent organic light-emitting diodes (PhOLEDs). The triplet levels (T_1s) of* ***SB-1*** *and* ***SB-2*** *were determined as at 2.81 and 2.73 eV, respectively. Also, these compounds afforded stable amorphous thin films upon spin-coating, and thus it was found that they are applicable to solution-processed devices. Indeed, blue PhOLEDs were fabricated by a solution method using* ***SB-1*** *and* ***SB-2*** *as host materials, where better device performance was obtained for the* ***SB-1****-based device due to its higher-lying T_1.*

Keywords Phosphorescent organic light-emitting diode; Hole-transporting material; Host material; Carbazole; Starburst oligomer; Solution-processing

Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have been receiving considerable attention because they utilize both singlet and triplet excitons to achieve as high as 100% of internal quantum efficiencies [1]. Blue PhOLEDs, however, still show relatively low quantum efficiencies and short device lifetimes in comparison with the green PhOLEDs, and thus the host materials optimized for blue phosphorescence emitters are eagerly required. Especially, those for solution-processed PhOLEDs have been receiving increasing attention from the viewpoint of low-cost device fabrication, and some polymers are often employed as represented by poly(9-vinylcarbazole) (PVCz) [2]. However, there are few examples of low-mass-type materials for this purpose [3]. We here report novel starburst-type carbazole trimers **SB-1** and **SB-2** (Scheme 1) as low-mass hole-transporting hosts, especially focusing on application to solution-processed blue PhOLEDs.

Results and Discussion

In **SB-1** and **SB-2**, the carbazole components are expected to promise high hole-transporting ability [4], and the peripheral tertiary butyl groups are introduced not only to get them

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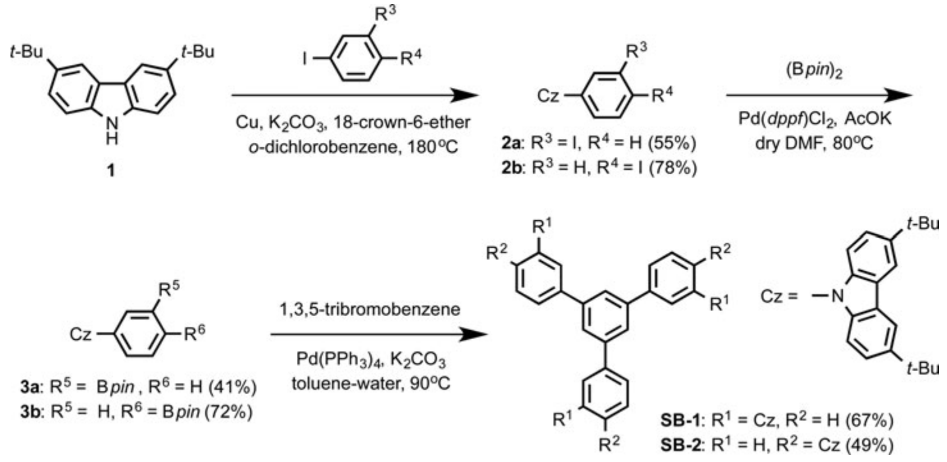

Scheme 1. Synthesis of **SB-1** and **SB-2**.

soluble in organic solvents but also to add amorphous stability through thin film formation [5]. In PhOLEDs, host materials should keep their lowest-lying triplet levels (T_1s) so high as to suppress reverse triplet energy transfer from phosphorescent emitters [6]. In this term, **SB-1** and **SB-2** are expected to have high T_1s due to their distorted divergent oligo(phenylene)-based structures with their π-conjugation partially disconnected [7]. In Scheme 1 is shown the synthesis of **SB-1** and **SB-2**. 3,6-Di(*tert*-butyl)carbazole **1** was subjected to the Ullmann reaction with 1,3- and 1,4-diiodobenzene to give **2a** and **2b**, respectively, followed by conversion to the corresponding boronic acid pinacolate esters (**3a** and **3b**, respectively). Then, the Suzuki-Miyaura coupling reactions of these precursors with 1,3,5-tribromobenzene afforded **SB-1** and **SB-2**, the structures of which were characterized by ^{1}H and ^{13}C NMR and MALDI-TOF mass spectra as well as elemental analysis. From thermogravimetric analysis, the decomposition temperatures of 1 wt% loss were determined as 407 and 422°C, respectively, and thus **SB-1** and **SB-2** are thermally stable compounds.

Electronic absorption and phosphorescence spectra of **SB-1** and **SB-2** are shown in Figure 1, and the data are also summarized in Table 1. Optical band gaps (ΔE_{gap}s) were calculated from the spectral onsets of the electronic absorption spectra (λ_{onset}s), and the

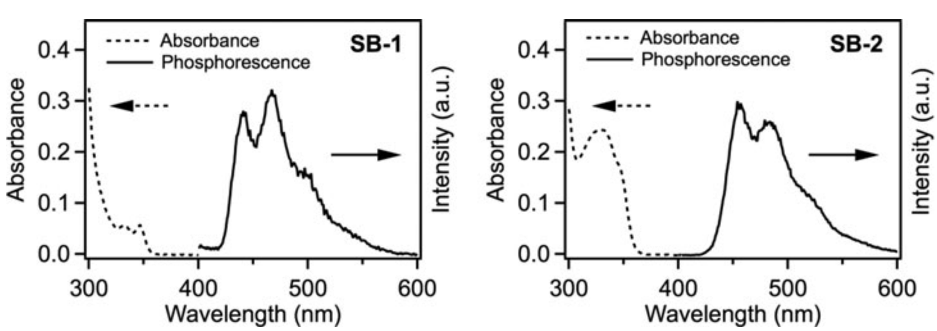

Figure 1. Electronic absorption and phosphorescence spectra of **SB-1** (left) and **SB-2** (right). The electronic absorption spectra were measured in toluene (10 μM) at rt, and the phosphorescence spectra were measured in deaerated 2-MeTHF glasses (10 μM) at 77 K.

Table 1. Optical, phosphorescent and electrochemical properties of **SB-1**, **SB-2** and FIrpic

Compd	λ_{onset} (nm)	λ_{phos} (nm)	T_1 (eV)	ΔE_{gap} (eV)	E_{HOMO} (eV)	E_{LUMO} (eV)
SB-1	356	441	2.81	3.48	–5.60	–2.12
SB-2	369	454	2.73	3.36	–5.56	–2.20
FIrpic	—	—	2.62[a]	2.90[a]	–5.90[a]	–3.00[a]

[a]Reported value in Ref. [8].

T_1s were determined from the emission maxima of the phosphorescence spectra (λ_{phos}s). As expected on the molecular design (*vide supra*), both of **SB-1** and **SB-2** have larger ΔE_{gap}s and higher T_1s in comparison with a representative blue phosphorescent emitter FIrpic [8], so they are potential host materials suitable to blue PhOLEDs. In comparison between the two starburst molecules, **SB-1** possesses a wider ΔE_{gap} and a higher T_1, and this is rationally explained by DFT calculations. The distributions of the HOMOs and LUMOs in **SB-1** and **SB-2** are shown in Figure 2. Each molecule has two degenerated HOMOs and LUMOs. The LUMOs are identical between these molecules, located at the triphenylbenzene components. On the other hand, the HOMOs of **SB-1** are localized at the carbazole moieties, whereas those of **SB-2** are delocalized from the carbazoles to the benzene core. This clearly indicates that the π-conjugation between the carbazole components and the benzene core is disrupted by *m*-phenylene linkage in **SB-1**, and thus the ΔE_{gap} gets more widened. Additionally, the small overlap between HOMO and LUMO in **SB-1** suppresses the decrease in the T_1 level, so it is indicated that **SB-1** shows the higher T_1 than **SB-2** [9].

We next estimated the energy levels of HOMO (E_{HOMO}) and LUMO (E_{LUMO}) of **SB-1** and **SB-2**. The E_{HOMO}s were determined by cyclic voltammetry ([**SB-1** (or **SB-2**)] =

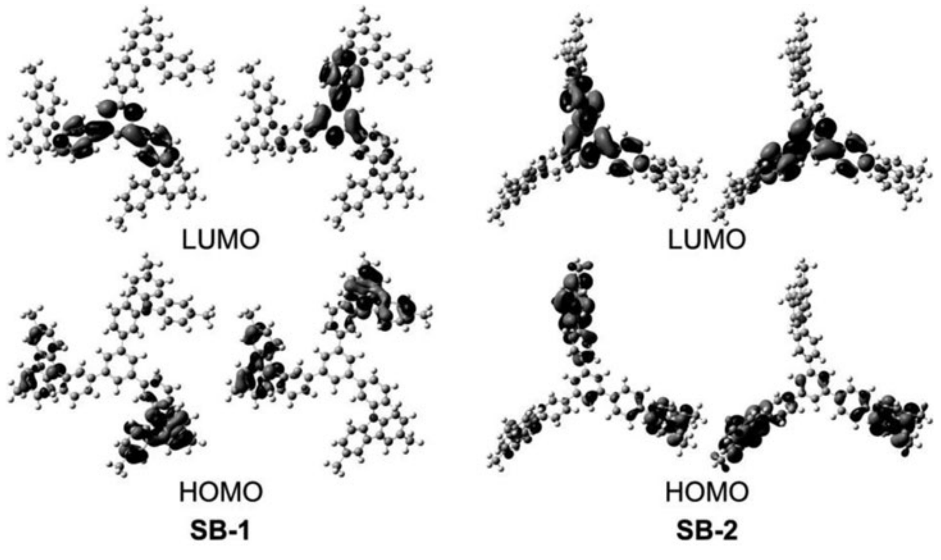

Figure 2. Calculated distributions of HOMOs and LUMOs of **SB-1** (left) and **SB-2** (right) (DFT, B3LYP/6-31G(d), Gaussian 09). The peripheral tertiary butyl groups are replaced by methyl ones.

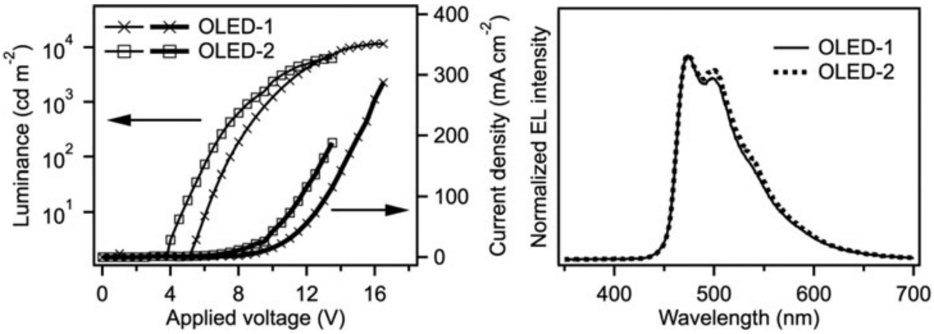

Figure 3. *J-V-L* curves (left) and EL spectra (right, @L_{max}) of OLED-1 and OLED-2.

1.0 mM in DMF with 0.1 M Bu_4NClO_4, *v.s.* Ag/AgCl, relative to ferrocenium/ferrocene redox couple (E_{HOMO} of ferrocene = –4.80 eV)), and the E_{LUMO}s were calculated from E_{HOMO}s and ΔE_{gap}s ($E_{LUMO} = E_{HOMO} + \Delta E_{gap}$). The obtained values of E_{HOMO} and E_{LUMO} are summarized in Table 1, along with those of FIrpic. Both of **SB-1** and **SB-2** possess almost comparable E_{HOMO}s and much higher E_{LUMO}s in comparison with FIrpic. Thus, providing that FIrpic is doped into **SB-1** and **SB-2** in OLEDs, smooth hole injection into FIrpic is possible [10] without trapping the electron injected into FIrpic.

The solution-processed blue PhOLEDs were fabricated using **SB-1** and **SB-2** (OLED-1 and OLED-2, respectively, device structure; ITO (anode, 150 nm)/PEDOT:PSS (40 nm)/**SB-1** (or **SB-2**):FIrpic:OXD-7 (8.5:1.2:3.0, wt/wt/wt, 85 nm)/CsF (1.0 nm)/aluminum (cathode, 250 nm)). The *J-V-L* curves as well as the electroluminescence (EL) spectra are shown in Figure 3. In Table 2 is summarized the device performance, along with the data for the device employing PVCz as a host material (OLED-3). The EL spectra of OLED-1 and OLED-2 were almost the same, identical to emission from FIrpic. Relatively high maximum luminance (L_{max}) of 12000 cd m^{-2} was obtained for OLED-1, more efficient than OLED-2. This should be because **SB-1** has wider ΔE_{gap} and higher T_1 than **SB-2**. Intriguingly, the device performance of OLED-1 is comparable to OLED-3. Therefore, **SB-1** is a good host material for solution-processed blue PhOLEDs.

Table 2. Device performance of solution-processed blue PhOLEDs employing **SB-1**, **SB-2** and PVCz as host materials

Device	Host	$V_{turn\text{-}on}$[a] (V)	L_{max} (cd m^{-2}) [@V]	η_j[b] (cd A^{-1})	η_p[b] (lm W^{-1})	η_{ext}[b] (%)	CIE (x, y)[c]
OLED-1	**SB-1**	5.0	12000 [@16.5]	7.99	2.51	3.45	(0.19, 0.39)
OLED-2	**SB-2**	4.0	6300 [@13.5]	5.60	1.95	2.36	(0.20, 0.40)
OLED-3	PVCz	4.0	11000 [@15.0]	11.0	3.64	4.47	(0.20, 0.42)

[a] Voltage at which the luminance of 1 cd m^{-2} is obtained. [b] Current efficiency, power efficiency, and external quantum efficiency at 1000 cd m^{-2}. [c] Commission Internationale de L'Eclairage chromaticity coordinate at 1000 cd m^{-2}.

Conclusions

Novel carbazole-based low-mass host materials **SB-1** and **SB-2** were developed. They showed good amorphous film formation and excellent thermal stability. The wider ΔE_{gap}s and higher T_1s made them applicable to blue PhOLEDs. Indeed, FIrpic-based PhOLEDs using **SB-1** and **SB-2** were successfully fabricated by solution processing. Especially, the **SB-1**-based device exhibited excellent performance comparative to the PVCz-based device.

Experimental

Synthesis of **SB-1**: general procedure for the starburst-type host materials.

A mixture of **3a** (750 mg, 1.56 mmol), 1,3,5-tribromobenzene (102 mg, 0.32 mmol), tetrakis(triphenylphosphine)palladium(0) (64.7 mg, 0.056 mmol) in toluene (19 ml) with 2 M K_2CO_3aq (9.7 ml) was heated at reflux for 12 h under N_2. After cooling, the mixture was evaporated to dryness, and the residue was extracted with dichloromethane. The obtained organic was washed with water and sat. brine, and then dried over anhydrous magnesium sulfate. The solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; dichloromethane:hexane = 1:5) to afford a white solid **SB-1** (245 mg, 0.22 mmol).

SB-1: yield, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.45$ (s, 54H), 7.38 (d, $J = 8.7$ Hz, 6H), 7.43 (dd, $J = 1.8$ and 8.7 Hz, 6H), 7.56 (d, $J = 7.8$ Hz, 3H), 7.66 (t, $J = 7.8$ Hz, 3H), 7.73 (d, $J = 7.8$ Hz, 3H), 7.85−7.87 (m, 6H), 8.12 (d, $J = 1.8$ Hz, 6H); MALDI-TOF MS $m/z = 1137$ (M^+); Anal. Calcd for $C_{84}H_{87}N_3$: C, 88.61; H, 7.70; N, 3.69. Found: C, 88.56; H, 7.69; N, 3.68.

SB-2: yield, 49%; ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 1.48$ (s, 54H), 7.45−7.52 (m, 12 H), 7.72 (d, $J = 8.2$ Hz, 6H), 7.99 (d, $J = 8.7$ Hz, 6H), 8.03 (s, 3H), 8.16 (d, $J = 1.8$ Hz, 6 H); MALDI-TOF MS $m/z = 1138$ ($[M + H]^+$); Anal. Calcd for $C_{84}H_{87}N_3$: C, 88.61; H, 7.70; N, 3.69. Found: C, 88.44; H, 7.89; N, 3.55.

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