

A High T_g Carbazole-Based Hole-Transporting Material for Organic Light-Emitting Devices

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A new branched carbazole derivative, 1,3,5-tris(2-(9-ethylcarbazyl-3)ethylene)benzene (TECEB), was prepared as a hole-transporting material for organic light-emitting devices (OLEDs). TECEB is comparable to 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) in terms of highest-occupied molecular orbital/lowest-unoccupied molecular orbital energy levels, hole-drift mobility, as well as device performance (maximum luminance of about 10 000 cd m⁻² and current efficiency of 3.27 cd A⁻¹) in a standard hole-transporting layer/tris-(8-hydroxyquinoline)aluminum double-layer device, but is superior to NPB in terms of its higher glass-transition temperature (*T_g*, 130 °C) and ease of synthesis. The latter features suggest that TECEB can be a potential alternative material to NPB especially for high-temperature applications in OLEDs and other organic electronic devices.

Introduction

In recent years, organic light-emitting devices (OLEDs) have attracted much attention because of their applications in full-color flat-panel displays.^{1–3} Since the initial work on molecular and polymeric OLEDs, respectively, by Tang et al.⁴ and Burroughes et al.,⁵ there have been extensive studies on layered organic electroluminescent (EL) devices to improve device performance. High efficiency and good durability are particularly important for practical applications. The degradation mechanisms in the organic EL devices are not yet fully understood, but several studies indicate that one cause of the degradation is the morphological changes of amorphous organic layers, especially the hole-transporting layer (HTL).^{6,7} Such morphological changes seem to be caused by Joule heating during device operation.^{8,9} Therefore, thermally and morphologically stable thin films of organic materials having a high glass-transition temperature (*T_g*) are required to realize high-stability OLEDs. Shirota and co-workers^{10–13} have demonstrated several families of starburst aromatic amines that are useful HTMs for OLEDs with *T_g*

values as high as 165 °C. Of course, a useful HTM is not only characterized by a high *T_g* but should also have a low energy barrier for hole injection from the anode and then into the electron-transporting layer (ETL), an ability to block electron injection from the ETL to the HTL, and a high hole mobility. It is essential, therefore, to increase the *T_g* without compromising the other important properties.¹⁴

In this paper, we describe a facile synthesis of a new carbazole derivative, 1,3,5-tris(2-(9-ethylcarbazyl-3)-ethylene)benzene (TECEB), whose structure is shown in Scheme 1, for use as a HTM in OLEDs. Carbazole was introduced as an important moiety into the core molecule of TECEB for the following reasons: (1) The thermal stability or glassy-state durability of organic compounds can be greatly improved upon incorporation of the carbazole moiety due to its rigidity.^{8,14–15} (2) Carbazole is chemically stable itself and can be easily modified at the 3, 6, or 9 position.¹⁶ (3) The moderately high oxidative potential of carbazole-containing compounds make them promising as HTMs. The chemical structure of TECEB was designed in such a way that the carbazole moiety was introduced by C–C double-bond connection at its 3 position through a Wittig reaction. This is in contrast to the N–C single-bond connection as in other typical triaryl amines and carbazole-containing HTMs obtained either through palladium-catalyzed cross-coupling reactions requiring expensive and extremely air-sensitive palladium catalysts or through copper-catalyzed Ullmann

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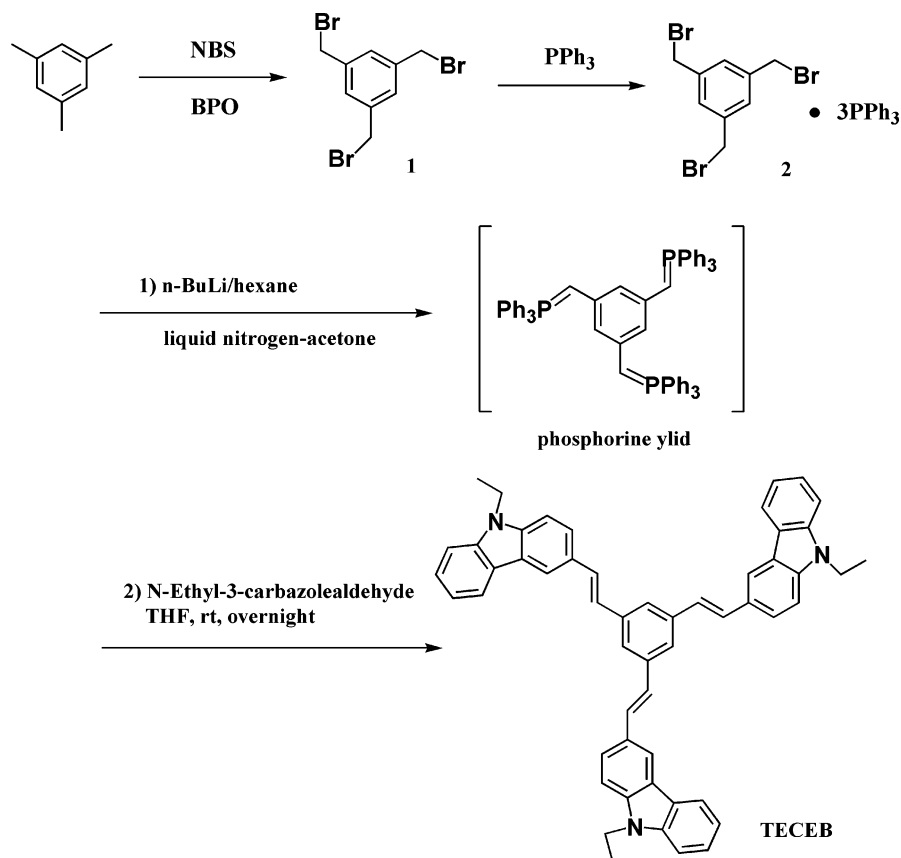
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Scheme 1. Molecular Structure and Synthetic Procedure of TECEB



condensations usually involving high temperatures and prolong reaction times.^{15–18} In the present work, the T_g and energy levels of TECEB were investigated, and its use as a HTM in OLEDs was also studied.

Experimental Section

Materials and Instruments. All the reagents and solvents used for the synthesis of TECEB were purchased from Aldrich and Acros companies and used without further purification. Tris-(8-hydroxyquinoline)aluminum (Alq_3) and 1,4-bis(1-naphthylphenylamino)-biphenyl (NPB) for EL device fabrication were synthesized in our laboratory and purified by train sublimation.

^1H NMR spectra were recorded on a Bruker DPX-400 spectrometer (300 MHz). The IR spectra were measured as KBr pellets on a BIO-RAD FTS-165 FT-IR spectrometer. Elemental analyses (EA) were performed by the Flash EA 1112 method. The photoluminescence (PL) and absorption spectra of red emitters in solution and in films were recorded with a Perkin-Elmer LS50 fluorescence spectrometer and a Perkin-Elmer Lambda 2S UV–visible spectrophotometer, respectively. Differential scanning calorimetry (DSC) measurement and thermogravimetric analysis (TGA) were performed on a Perkin-Elmer DSC 7 and a Dupont Instruments, 983 Dynamic Mechanical Analyzer, respectively.

Preparation of TECEB. The molecular structure of TECEB and its synthetic procedures¹⁹ are shown in Scheme 1. It can be prepared by traditional Wittig reactions along with the following procedures.

1. Mesitylene was brominated by a modified method different from the photochemical bromination previously reported.²⁰ A solution containing 12 g (0.1 mol) of mesitylene, 55 g (0.309 mol) of N-bromosuccinimide (NBS), 0.55 g of benzoyl peroxide (BPO), and 300 mL of benzene was heated to reflux to initiate the reaction. The reaction was strongly exothermic to keep the solution boiling even without further heating. The solution was reheated under reflux for another 1 h to ensure the complete bromination when it stopped to boil spontaneously. After filtering, the filtrate was washed with water and dried with anhydrous sodium sulfate. Upon concentration of the benzene solution, a colorless needle crystal was precipitated. Crystallization of the crude product in a 1:1 mixture of ethanol and hexane yielded 32.5 g (92%) of pure 1,3,5-tribromomethylbenzene (1). The chemical structure of 1 was confirmed by spectral data identical with those in the literature.²⁰

2. A solution including 7.2 g (20 mmol) of 1, 17.7 g (67.4 mmol) of triphenylphosphine, and 300 mL of ethanol was refluxed under nitrogen for 24 h. THF (200 mL) was added into the solution after it was concentrated to 150 mL. The produced white precipitate was filtered and thoroughly dried under a vacuum. Yield: 95%. MS: m/z 1143 (M^+).

TECEB. To a slurry containing 2.3 g (2 mmol) of dry 2 and 75 mL of dry THF under nitrogen atmosphere in a 500-mL three-necked round flask placed in liquid nitrogen–acetone bath, 5 mL (8 mmol) of 1.6 M n -butyllithium solution in hexane was added dropwise under stirring within a period of 1 h. Stirring was continued for another hour, and a red solution was formed. The red product is believed to be the phosphorine ylid of mesitylene, which is usually extremely sensitive to the air. Therefore, it was not isolated but converted directly into the final product. To the

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above solution maintained in liquid nitrogen–acetone bath, a solution of 1.5 g (8 mmol) of 9-ethylcarbazole-3-aldehyde in 25 mL of dry THF was added slowly. The system was stirred under nitrogen atmosphere at room temperature overnight. Followed by filtration and concentration, the residue was isolated by column chromatography on silica gel with mixed hexane and ethyl acetate (20:1 in volume) as eluent. A pale-yellow product was obtained. Recrystallization in ethanol and dichloromethane (1:1) yielded the pure product TECEB (1.25 g, yield 85%). ^1H NMR (300 MHz, CDCl_3) δ [ppm]: 1.38–1.5 (m, 9H), 4.32–4.50 (m, 6H), 6.66 (d, 3H, $J = 16.5$ Hz), 6.88 (d, 3H, $J = 16.5$ Hz), 7.06–8.32 (m, 24H). IR (KBr): 3047, 3011, 2970, 2930, 1626, 1598, 1578, 1486, 1466, 1329, 1233, 1153, 1125, 960, and 739 cm^{-1} . MS: m/z 736 (M^+). Anal. Calcd For $\text{C}_{54}\text{H}_{45}\text{N}_3$: C, 88.16; H, 6.12; N, 5.71%. Found: C, 87.96; H, 6.35; N, 5.59%.

Fabrication and Characterization of OLEDs. A double-layer OLED was fabricated by vacuum deposition with a configuration of indium tin oxide (ITO) (100 Ω/\square)/TECEB (70 nm)/Alq₃ (60 nm)/Mg:Ag, in which TECEB was used as HTL and Alq₃ was used as the ETL and emitting layer. Before being loaded into a deposition chamber, the ITO substrate was cleaned with detergent and deionized water, dried in an oven at 120 $^\circ\text{C}$ for about 2 h, and finally treated with UV ozone for 25 min. The device was fabricated by evaporating organic layers at a rate of 0.1–0.3 nm/s onto the ITO substrate sequentially at a pressure below 5×10^{-6} mbar. Onto the Alq₃ layer, a 200-nm-thick Mg:Ag (mass ratio of 9:1) alloy was deposited at a rate of 0.6 nm/s as the cathode. For comparison, a standard device with similar configuration but using NPB as HTL was also prepared under identical conditions. The EL spectra and current–voltage–luminescence characteristics were measured with a Spectrascan PR 650 photometer and a computer-controlled DC power supply under ambient conditions. The emission area of the devices was 0.1 cm^2 as determined by the overlap area of the anode and the cathode.

Results and Discussion

Design and Synthesis of TECEB. Most of the current HTMs used in OLEDs are triarylamine derivatives such as NPB, TPD, and *m*-MTDATA. In addition, carbazole-containing compounds such as CBP,¹⁷ TCTA,¹⁸ and PCA-TA²¹ are also of increasing interest for use as HTMs in OLEDs. Carbazole moieties are usually introduced into the core structure of the present carbazole-containing HTMs at their 9 position. In the present study, carbazole is chosen as an important substitute to compose the desired TECEB due to its merits of rigidity, high stability, strong electron-donating nature, and easy chemical modification. TECEB is designed in such a way that carbazole was introduced into the core structure at the 3 position through a C–C double-bond formed by the Wittig reaction so as to avoid the necessary usage of palladium or copper catalysts if introduced at the 9 position. TECEB is synthesized through a typical Wittig reaction between the phosphorine ylid of mesitylene and *N*-ethylcarbazole-3-aldehyde as illustrated in Scheme 1. The phosphorine ylid can be easily prepared from mesitylene through bromination by NBS, reaction with the triphenylphosphorine, and alkalization by *n*-butyllithium at high yields. The ylid intermediate is usually sensitive to oxygen and moisture and consequently converted into final product

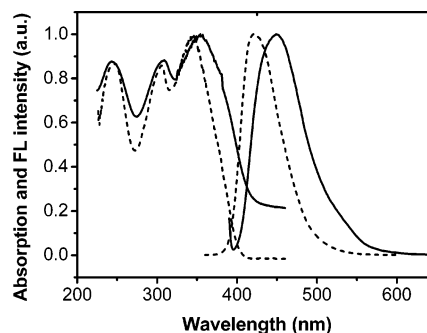


Figure 1. Normalized absorption and fluorescence spectra of TECEB in dilute dichloromethane solution (dashed line) and in pure films on quartz substrates (solid line).

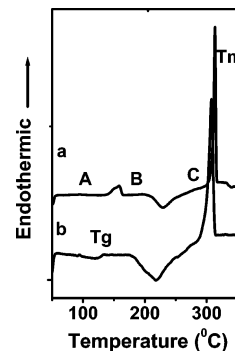


Figure 2. DSC curves for TECEB at the scan rate of 10 $^\circ\text{C min}^{-1}$. (a) The first run shows only crystalline behavior with two crystal transitions at 150 and 225 $^\circ\text{C}$, respectively, and a melting transition at 313 $^\circ\text{C}$ (T_m). (b) Upon rapid cooling and reheating, the second run displays a glass transition at 130 $^\circ\text{C}$ (T_g).

without isolation. It is notable that the synthesis of TECEB failed when Na_2CO_3 or *t*-BuOK was used as alkali to convert the phosphonium bromide 2 into the corresponding ylid, while it succeeded only when *n*-BuLi was used, implying that the phosphorine ylid of mesitylene can be formed and condensed with the *N*-ethylcarbazole-3-aldehyde only under strongly alkali conditions.

Photophysical and Thermal Properties of TECEB.

Figure 1 shows the absorption and the PL spectra of TECEB in dilute dichloromethane solution and in a vacuum-evaporated film on a quartz substrate. The absorption spectra both in the film and in the solution reveal the characteristic absorption peaks of carbazole between 250 and 350 nm. A redshift of 8 nm in the film relative to that in dichloromethane solution implies that interaction between TECEB molecules exists in the ground state. The PL spectra of TECEB in solution and in solid film are structureless and mirror the low-energy absorption band. The PL of TECEB in film shows a 30-nm redshift and is broader compared with that in dichloromethane solution. These features are usually observed for organic and polymer materials mainly due to the different polarity of the environments.

The morphological and thermal stabilities of TECEB were measured by DSC and TGA analysis. Figure 2 shows the DSC thermograms of TECEB measured at a scanning rate of 10 $^\circ\text{C/min}$. When a crystalline sample of TECEB obtained from crystallization from common organic solvents (crystal A) was heated from room temperature for the first run, an endothermic peak at 150 $^\circ\text{C}$ was observed, probably due to solid–solid-phase transition to form a different crystal form

(crystal B).²² With increasing temperature, an exothermic peak appeared at about 225 °C probably due to another solid–solid-phase transition, and the crystal B was consequently transformed into crystal C. Upon further heating, crystal C melted at 313 °C to give an isotropic liquid. Upon accelerated cooling by swirled water within the instrument, the melted sample changed into an amorphous glass. When the amorphous glass was reheated for the second run at the same scanning rate, an endothermic glass-transition phenomenon was detected at 130 °C, which corresponds to the transition of TECEB from amorphous glass to a rubbery state. On further heating above the T_g , an exothermic crystallization corresponding to the formation of crystal C again was detected at 225 °C, followed by the melting of crystal C at 313 °C. While further supporting experiments are still being carried out to confirm the above-mentioned polymorphism of TECEB, it is clear that the TECEB underwent a glass transition at 130 °C as shown by the DSC thermograms. The T_g of TECEB is higher by 34 °C than that of the widely used HTM NPB (96 °C), suggesting that better morphological stability of TECEB is expected. In addition, TECEB also shows excellent thermal stability as TGA measurement revealed no decomposition below 400 °C.

The highest-occupied molecular orbital (HOMO) energy level of TECEB was determined as 5.2 eV by ultraviolet photoelectron spectroscopy. The HOMO–LUMO (lowest-unoccupied molecular orbital) band gap of TECEB was determined from the absorption spectrum of TECEB film to be 2.8 eV. The LUMO energy level was calculated to be 2.4 eV by subtraction of the optical band gap from the HOMO energy level. The HOMO and LUMO energy levels of TECEB are comparable to those of NPB (HOMO, 5.2 eV; LUMO 2.2 eV).

EL Performances of TECEB-Based Devices. On the basis of the merits of TECEB including good thermal and morphological stabilities, proper energy levels, and strong electron-donating and consequently hole-transporting nature of carbazole-containing compounds, TECEB is expected to serve as a good HTM in OLEDs. A double-layer OLED with a configuration of ITO/TECEB (70 nm)/Alq₃ (60 nm)/Mg:Ag, which utilizes TECEB as HTL and Alq₃ as emitting layer and ETL was fabricated. For comparison, a standard device with the similar structure but using NPB as the HTL was also prepared. Green emission from Alq₃ with a peak at 530 nm was obtained, suggesting that the charge recombination is localized in the Alq₃ layer and TECEB acts primarily as a hole transporter without causing exciplex formation at the interface with Alq₃. This should be attributed to the proper HOMO energy level of TECEB which is favorable for hole injection from ITO to TECEB layer and then to the Alq₃ layer. Similarly, the proper LUMO level of TECEB blocks electron injection from Alq₃ to itself. The current density–luminance–voltage (J – L – V) characteristics of the device are shown in Figure 3. The device turns on at a voltage of 3.5 V, and the luminance of the device can reach 9680 cd m⁻² at 20 V. In Figure 3, the J – L – V curves of the NPB standard device are shown as well. It is clear that both the

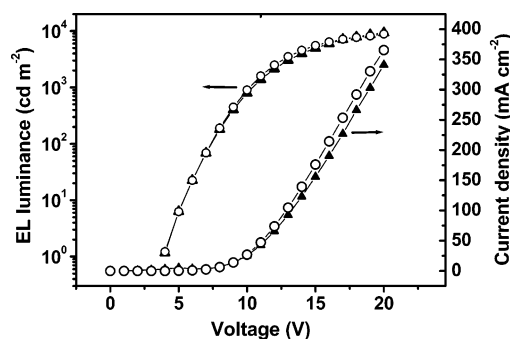


Figure 3. The current density–luminance–voltage curves of the ITO/TECEB (70 nm)/Alq₃ (60 nm)/Mg:Ag device (▲) and the ITO/NPB(70 nm)/Alq₃(60 nm)/ Mg:Ag standard device (○).

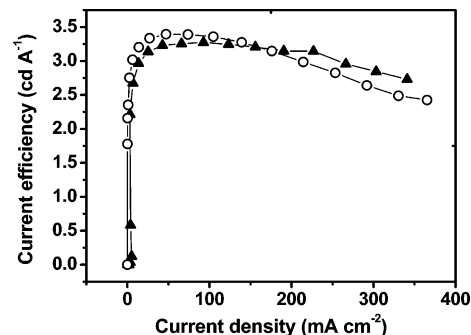


Figure 4. The current efficiency–current density characteristic of the ITO/TECEB (70 nm)/Alq₃ (60 nm)/Mg:Ag device (▲) and the ITO/NPB (70 nm)/Alq₃ (60 nm)/Mg:Ag standard device (○).

current density and the luminance of the TECEB device are comparable with the NPB standard device. Figure 4 illustrates the current efficiency–current density characteristics of the TECEB device and the NPB standard device. The TECEB device has a maximum current efficiency of 3.27 cd A⁻¹, which remains almost constant with current density up to 230 mA cm⁻² and shows only a small decline even when the current density increases to 350 mA cm⁻². While the current efficiency for the NPB standard device is slightly higher than that of the TECEB device in the low current density region, i.e., below 150 mA cm⁻², it decreases more rapidly with increasing current density. Significantly, even at the present stage when the device has yet to be optimized, the EL performances of the TECEB-based device are already comparable to those of the standard NPB/Alq₃ device. This suggests that TECEB is at least as good as NPB when used as a HTM in EL devices, but TECEB is expected to be more thermally stable based on its higher T_g value. The device stabilities of the TECEB-based and the NPB standard device are under investigation.

The hole-drifting mobility of TECEB was determined by transient electroluminescence measurements of the TECEB single-layer device by using the method described in the literature.^{23,24} The hole mobility of TECEB is about 10⁻⁴ cm² (V s)⁻¹, which is comparable with that of NPB.

To summarize, TECEB has similar hole mobility, energy levels, and performance in double-layer HTL/Alq₃ devices as NPB. Yet TECEB has a major advantage because its T_g

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is considerably higher than that of NPB, and thus better morphological stability and thermal durability are expected. In addition, the synthetic of TECEB avoids usage of palladium or copper catalysts, which are generally involved for the synthesis of triarylaminines or 9-position carbazole-containing hole-transporting materials. This merit is important for large-scale commercial applications where material cost is a major concern. Since neither the molecular structure of TECEB nor the device configuration has been optimized in the present work, further performance improvement may

be expected by fine tuning the molecular and/or device structure. The present results suggest that TECEB and possibly its analogues are potentially good candidates for large-scale applications as HTMs in OLEDs and related optoelectronic devices.

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