New deep-blue emitting materials based on fully substituted ethylene derivatives[†]

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New blue fluorescent compounds containing tetra-substituted ethylene moieties have been designed and synthesized. These materials, 1,2-di(4'-*tert*-butylphenyl)-1,2-bis(4'-(anthracene-9-yl)phenyl)ethene [BPBAPE, **1A**], 1,2-diphenyl-1,2-bis(4'-(anthracene-9-yl)phenyl)ethene [PBAPE, **1B**], 9,10-bis(4-(1,2,2-tris(4-*tert*-butylphenyl)vinyl)phenyl)anthracene [BTBPPA, **2A**], and 9,10-bis(4-(1,2,2-triphenylvinyl)phenyl)anthracene [BTPPA, **2B**], were synthesized through Suzuki and McMurry reactions. By fabricating multilayered non-doped OLED devices using these new blue materials, we achieved luminance efficiencies of 4.00 lm W⁻¹ (10.33 cd A⁻¹ at 8.1 V) for BPBAPE [**1A**] and 1.82 lm W⁻¹ (3.93 cd A⁻¹ at 6.8 V) for BTPPA [**2B**] at 10 mA cm⁻². The maxima in the electroluminescence spectra of ITO/2-TNATA (60 nm)/NPB (15 nm)/BPBAPE [**1A**] and BTPPA [**2B**] (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm) devices were found to be 475 and 452 nm respectively. The BPBAPE [**1A**] and BTPPA [**2B**] devices exhibited sky blue emission (0.195, 0.303) and deep blue emission (0.159, 0.135) at 10 mA cm⁻² respectively.

Introduction

Organic light-emitting diodes (OLEDs) based on organic molecules are currently the subject of intense research efforts due to their promise as devices for full-color large display applications.^{1–5} To date, numerous conjugated organic molecules have been synthesized and reported to exhibit electro-luminescence (EL) ranging from red to green and blue. In order to fabricate full-color OLED displays, we need high performance red,^{6–8} green,^{2,9} and blue^{10–13} materials with high EL efficiencies, good thermal properties and long lifetimes as well as pure color coordinates (Commission Internationale de l'Eclairage (CIE)). Both host and dopant methods have been used in fluorescence and phosphorescence systems to produce high efficiency OLEDs, and red and green emitters have been developed and improved to the standard required for commercializing full-color OLEDs.

In recent times, red materials with CIE coordinates (0.67, 0.23) and long lifetimes of more than 100 000 h at 11 cd A^{-1} have been produced. Green emitting materials with CIE coordinates (0.29, 0.64) and lifetimes of 100 000 h at 21 cd A^{-1} have also been developed. However, the best blue materials have lifetimes of only 12 000 h at 7 cd A^{-1} and CIE coordinates (0.14, 0.16).¹⁴

It is not easy to produce highly efficient blue materials with long device lifetimes. The electronic levels of blue materials with a wide band gap are generally mismatched with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the other OLED layers, such as the hole transporting layer (HTL) and the electron transporting layer (ETL). These differences between the electronic levels result in a mismatched carrier balance of electrons and holes and a low EL efficiency.

Many kinds of blue materials including diarylanthracene,¹⁵ di(styryl)arylene,¹⁶ fluorene,¹⁷ pyrene¹⁸ and fluoranthene¹⁹ have been intensively investigated and attempts made to improve their EL properties. 4,4'-Bis(2,2-diphenylvinyl)-1,1'-biphenyl (DPVBi)¹⁶ is a commercialized compound, but has a low glass transition temperature T_g of 64 °C,²⁰ undergoes recrystallization after long operation, and has a short device lifetime compared to those of green and red materials. In addition, some blue materials including DPVBi exhibit film roughening during EL operation or after storage. This is another issue that must be solved if longer lifetimes are to be achieved.

In a previous study, we have synthesized tetraphenylethylene derivatives, 1,1,2,2-tetrakis(4'-*tert*-butylphenyl)ethene [TBPE], 1,2-di(4'-*tert*-butylphenyl)-1,2-bis(4'-*tert*-butylbiphenyl)ethene [BPBBPE] and 1,1,2,2-tetrakis(4'-*tert*-butylbiphenyl)ethene [TBBPE], as new blue emitting materials.²¹ TBPE has the basic structure of these tetra-substituted ethylene derivatives, in which ethylene is connected to the tertiary butyl (*tert*-butyl) phenyl moiety. In this series of compounds, tetra-substituted ethylene is the core to which the chromophores are attached. TBBPE has a longer conjugation length than TBPE because of the biphenyl group. The biphenyl moiety has a higher fluorescence efficiency ($\Phi_{\rm f}$) (0.15²²) than the phenyl ring (0.04²³). BPBBPE combines the half segment chromophores of TBPE and TBBPE.

In this study, we sought to synthesize new blue-emitting chemical structures by making use of tetra-substituted ethylene and anthracene moieties. The chemical structure characteristics of tetra-substituted ethylene mean that it has more chromophores per molecule, and greater thermal stability due

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Scheme 1 Chemical structures of the synthesized materials and DPVBi.

to its higher molecular weight, than the conventional stilbene moiety. Anthracene is a very stable and highly efficient chromophore ($\Phi_{\rm f} = 0.27$) and several studies in this area have focused on it and related chemical structures.^{24–28}

Therefore, we synthesized new tetra-substituted ethylene derivatives containing anthracene moieties and characterized

their electrical and optical properties (Scheme 1). The materials 1,2-di(4'-*tert*-butylphenyl)-1,2-bis(4'-(anthracene-9-yl)phenyl) ethene [BPBAPE, **1A**], 1,2-diphenyl-1,2-bis(4'-(anthracene-9-yl) phenyl)ethene [PBAPE, **1B**], 9,10-bis(4-(1,2,2-tris(4-*tert*-butylphenyl)vinyl)phenyl) anthracene [BTBPPA, **2A**], and 9,10-bis(4-(1,2,2-triphenylvinyl)phenyl)anthracene [BTPPA, **2B**] were synthesized by using the Suzuki and McMurry reactions.

In the B series of synthesized molecules, we removed the *tert*-butyl group from compounds BPBAPE [1A] and BTBPPA [2A] to tune the maximum emitting wavelength.

The thermal and electro-optical properties of these materials were characterized with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), atomic force microscopy (AFM), cyclic voltammetry (CV), and UV-visible and photoluminescence (PL) spectroscopy. Multilayered EL devices were fabricated using these materials as non-doped emitting layers.

Results and discussion

Synthesis and characterization

The synthetic routes for the four compounds are shown in Scheme 2. We used titanium chloride and zinc catalyst mixed with THF solvent in the McMurry reaction for synthesizing ethylene moieties, and used boration and the Suzuki reaction to carry out the carbon–carbon coupling reactions. In the McMurry reaction, coupling results in two different coordinations, and there are also two competing factors, the steric hindrance of the phenyl ring derivatives and the electronic



Scheme 2 Synthetic routes of BPBAPE [1A], PBAPE [1B], BTBPPA [2A] and BTPPA [2B].



Fig. 1 ¹H NMR spectra of (*E*)- and (*Z*)-BPBAPE [**1A**] (a) and (*E*)-BPBAPE [**1A**] (b) in the range of 7.0 to 8.6 ppm; 600 MHz, d_8 -THF.

repulsion of the two anions. As a result, the asymmetric carbonyl compounds consist of equal proportions of the (E)-form and (Z)-form isomers. The mixed isomers of BPBAPE [1A] and PBAPE [1B] were separated by using recrystallization. We used (E)-form compounds in the EL experiments for BPBAPE [1A] and PBAPE [1B].

All compounds were purified with the silica column method and recrystallization, producing very pure powders that we characterized with NMR, FT-IR, and FAB-MS analysis. As the McMurry reactions proceeded, the FT-IR carbonyl stretching peak at 1650 cm⁻¹ completely disappeared, and overall the NMR proton peaks became more shielded with the loss of carbonyl groups from the compounds.

Fig. 1 shows the ¹H NMR (600 MHz, d_8 -THF) spectra of (*E*)- and (*Z*)-BPBAPE [**1A**] (a) and (*E*)-BPBAPE [**1A**] (b). As can be seen in Fig. 1(a), the mixed isomers result in mixed proton peaks, whereas after recrystallization the (*E*)-form compound exhibits clear spin splitting in Fig. 1(b). The protons that give rise to the peaks marked c, *i.e.*, c protons, are more shielded than d protons because c protons are closer to tertiary butyl groups and further from ethylene moieties than the d protons. In order to verify the chemical structure, we recrystallized BPBAPE [**1A**] and then obtained its XRD pattern, which confirms that only the (*E*)-form is present (Fig. 2). It was also confirmed that PBAPE [**1B**] contains only the (*E*)-form by comparing the NMR peak patterns.

From the data in Fig. 2, we determined the following structural characteristics of BPBAPE [1A]: bond distances, planarity, and bond angles. According to the dihedral and bond angles, [C(27)-C(22)-C(21)-C(21)#1] (112.4(8)°), [C(5)-C(6)-C(15)-C(16)] (98.6(7)°), [C(23)-C(22)-C(21)-C(18)] (109.4(6)°), [C(21)#1-C(21)-C(18)-C(19)] (-98.8(8)°), and [C(22)-C(21)-C(18)] (116.5(4)°), BPBAPE [1A] has a



Fig. 2 ORTEP drawing of BPBAPE [1A], along with selected dihedral and bond angles, and bond lengths. The ellipsoid probability is 35%. The #1 symbol in atom labels indicates that these atoms are at equivalent position (-x, -y + 2, -z + 1).

propeller-like structure. Also, it was confirmed that the angle between molecules is 30.3° . In particular, the phenyl and anthracene groups are perpendicularly oriented with an angle between them of $98.6(7)^{\circ}$. It is possible that this orientation prevents chromophore stacking between molecules because of cross dipole stacking, and that it maintains a high performance emission band and limits excimer formation.²⁹ However, since the film is generally created in an amorphous state after vacuum deposition, this explanation might have some limitations.

Optical and electrochemical properties

After vacuum deposition of the synthesized compounds onto glass, we determined their UV-visible and PL spectra. The data are summarized in Table 1.

The UV maximum values of BPBAPE [1A], PBAPE [1B], BTBPPA [2A], and BTPPA [2B] are 392, 394, 400, and 402 nm respectively, and their PL maximum values are 489, 486, 463, and 455 nm respectively. All four compounds contain anthracene moieties, so exhibit UV-visible absorption near 400 nm.

The spectrum of PBAPE [1B] is blue-shifted by 3 nm with respect to that of BPBAPE [1A], and the spectrum of BTPPA [2B] is blue-shifted by 8 nm with respect to that of BTBPPA

	Solution (toluene)		Film on glass									
Compound	UV _{max} /nm	PL _{max} /nm	UV _{onset} /nm	UV _{max} /nm	PL _{max} /nm	HOMO/eV	LUMO/eV	$E_{\rm g}/{\rm eV}$	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm c}/^{\circ}{\rm C}$	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$
BPBAPE [1A] PBAPE [1 B] BTBPPA [2 A] BTPPA [2B]	388 388 398 398	495 482 462 451	409 410 420 420	392 394 400 402	489 486 463 455	5.65 5.63 5.59 5.62	2.62 2.61 2.64 2.67	3.03 3.02 2.95 2.95	155.3 135.6 	232.0 211.3 —	345.0 290.0 398.0 337.0	356.3 381.5 408.4 401.7

 Table 1
 Optical, electrical and thermal properties of synthesized compounds

[2A]. This result can be explained in terms of the donating effect of the *tert*-butyl group, as is evident in the similar results of Chen *et al.*²⁸

In order to measure the HOMO values of the synthesized compounds, CV analyses were carried out. According to the CV data, all the compounds have an electrochemical stability of greater than 50 cycles.

The band gaps of BPBAPE [1A] and PBAPE [1B] were found to be 3.03 and 3.02 eV respectively, and the band gaps of BTBPPA [2A] and BTPPA [2B] are the same, 2.95 eV.

The band gaps and the HOMO and LUMO levels are summarized in Table 1. The HOMO levels of BPBAPE [1A], PBAPE [1B], BTBPPA [2A], and BTPPA [2B], which all contain anthracene groups, are all near 5.6 eV, which is about 0.4 V lower than those of TBPE, BPBBPE, and TBBPE.²¹ The presence of anthracene moieties is thought to be the principal factor determining the HOMO levels of these materials. It has been reported that the HOMO levels of 9,10-di(2-napthyl) anthracene (MADN) as well as of many other compounds that have an anthracene group are also near 5.5–5.6 eV.^{25–28} Our result is thus in agreement with the results of previous studies.

Thermal properties

We carried out TGA and DSC to examine the thermal properties of the synthesized molecules (Table 1).

Fig. 3 shows the DSC data for PBAPE [**1B**], which of the four compounds containing anthracene has the lowest molecular weight. $T_{\rm g}$, $T_{\rm c}$, and $T_{\rm m}$ of PBAPE [**1B**] are 135.6 °C, 211.3 °C, and 290.0 °C respectively. $T_{\rm g}$, $T_{\rm c}$, and $T_{\rm m}$ for BPBAPE [**1A**] are 155.3 °C, 232.0 °C, and 345.0 °C



Fig. 3 DSC (solid line) and TGA (dashed line) data of PBAPE[1B]; 10 $^{\circ}$ C min⁻¹, N₂ conditions.

respectively. These results can be explained in terms of the higher molecular weight of BPBAPE [1A] due to the presence in it of the *tert*-butyl group. The T_g and T_c of BTBPPA [2A] and BTPPA [2B] were not measured, but the T_m were found to be 398.0 °C and 337.0 °C respectively. Thus T_m also increases as the molecular weight increases, because of the addition of the *tert*-butyl group.

Since BTBPPA [2A] and BTPPA [2B] have higher molecular weights than BPBAPE [1A] and PBAPE [1B], they have higher glass transition temperatures than of BPBAPE [1A] and PBAPE [1B], 135.6 °C and 155.3 °C respectively. These values are more than twice that of DPVBi, 64 °C.²⁰ Thus increased thermal stability has been achieved, which affects the lifetime of OLED devices. We also measured the degradation temperatures (T_d) of BPBAPE [1A], PBAPE [1B], BTBPPA [2A], and BTPPA [2B], which were determined from the onset points of weight loss, and found to be 356.3 °C, 381.5 °C, 408.4 °C, and 401.7 °C respectively. For BPBAPE [1A] and BTBPPA [2A], which have *tert*-butyl groups, the difference between T_m and T_d for PBAPE [1B] and BTPPA [2B], which do not contain *tert*-butyl groups, is 60–90 °C.

To investigate the morphological stabilities of BTBPPA [2A], BTPPA [2B] and DPVBi, we prepared thin films of these materials on indium tin oxide (ITO) substrates by vapor deposition and determined their surface morphologies with atomic force microscopy (AFM) before and after annealing at 65 °C for 3 days under a nitrogen atmosphere (see Fig. 4, 5, and 6). Fig. 4(a), 5(a), and 6(a) were obtained immediately after vacuum deposition, and Fig. 4(b), 5(b), and 6(b) were obtained after 3 days storage at room temperature under a nitrogen atmosphere. Fig. 4(c), 5(c), and 6(c) were obtained after 3 days at 65 °C under a nitrogen atmosphere. The root mean square (RMS) roughness of BTBPPA [2A] was found to be 3.407 nm (immediately after deposition), 3.430 nm (3 days), and 3.718 nm (3 days, 65 °C). Thus this material forms films that are stable for long periods of heat exposure and storage. In contrast, BTPPA [2B] undergoes re-crystallization at 65 °C under a nitrogen atmosphere (RMS = 38.72 nm), but maintains its film surface morphology in the absence of heating (immediately after deposition, 2.844 nm; 3 days, 3.062 nm). Thus when there is no *tert*-butyl group in the synthesized compounds, the packing between molecules is closer, which results in recrystallization during high temperature storage. This result agrees with the AFM results for ADN, 2-(tert-butyl)-9,10-di(2-naphthyl)anthracene (TBADN), and MADN.²⁸

As shown in Fig. 6, the appearance of DPVBi in the AFM images is better than those of BTBPPA [2A] and BTPPA [2B] right after deposition, but surface changes occur during storage, and the surface is also affected by heating (RMS



Fig. 4 AFM images of BTBPPA [2A]: (a) no treatment, (b) 3 days under nitrogen atmosphere, (c) heat treatment (65 $^{\circ}$ C for 3 days under nitrogen atmosphere).



Fig. 5 AFM images of BTPPA [2B]: (a) no treatment, (b) 3 days under nitrogen atmosphere, (c) heat treatment (65 $^{\circ}$ C for 3 days under nitrogen atmosphere).

Fig. 6 AFM images of DPVBi: (a) no treatment, (b) 3 days under nitrogen atmosphere, (c) heat treatment (65 $^{\circ}$ C for 3 days under nitrogen atmosphere).

roughness immediately after deposition, 2.050 nm; 3 days, 51.75 nm; 3 days with heating, 58.63 nm). Thus the synthesized compounds BTBPPA [2A] and BTPPA [2B] have better film morphologies than DPVBi. The results for BPBAPE [1A] and PBAPE [1B] are similar to those for BTBPPA [2A] and BTPPA [2B].

Electroluminescence properties

We fabricated EL devices with the synthesized compounds in the following configuration: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm). We compared the EL properties of these devices with those of a standard device: ITO/2-TNATA (60 nm)/NPB (15 nm)/DPVBi (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm).

The EL maximum values of the BPBAPE [1A] and PBAPE [1B] devices are 475 and 466 nm respectively, *i.e.*, in the sky blue range, and those for BTBPPA [2A] and BTPPA [2B] are 463 and 452 nm respectively, *i.e.*, in the deep blue range.

It was identified that EL_{max} values of BPBAPE [1A] and PBAPE [1B] devices has been blue shifted compared to the PL_{max} values. We could not clearly understand the reasons for this blue shift in the EL spectra. Nonetheless, we assume that HIL (hole injection layer) and HTL are related to the blue shift in the EL spectra, and an additional experiment is being conducted separately.

Fig. 7 shows the EL spectra of BPBAPE [1A], PBAPE [1B], BTBPPA [2A], BTPPA [2B], and DPVBi. The spectrum of PBAPE [1B] is about 9 nm blue-shifted with respect to that of



Fig. 7 EL spectra of ITO/2-TNATA/NPB/BPBAPE [1A] (\blacksquare), PBAPE [1B] (\Box), BTBPPA [2A] (\bullet), BTPPA [2B] (\bigcirc) and DPVBi (\Rightarrow)/Alq₃/LiF/Al devices at 10 mA cm⁻².



Fig. 8 Current density-voltage characteristics of ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized material or DPVBi (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al devices.

BPBPAE [1A], and the spectrum of BTPPA [2B] is about 11 nm blue-shifted with respect to that of BTBPPA [2A]. Thus there is the same blue-shift effect in the EL spectra as found in the PL spectra.

Fig. 8 shows the I-V curves of the devices. When we compare the I-V curves for the BPBAPE [1A], PBAPE [1B], BTBPPA [2A], and BTPPA [2B] devices, which have similar HOMO and LUMO levels, we find that these compounds with

the exception of BTBPPA [2A] exhibit the same I-V characteristics as DPVBi or better.

We suggest that because BTBPPA [2A] has a high number of *tert*-butyl groups, *i.e.*, 6 *tert*-butyl moieties per molecule, its conductivity is lower, which results in a high turn-on voltage. PBAPE [1B] and BTPPA [2B] have no *tert*-butyl groups, so their devices exhibit the best I-V curves of the synthesized materials.

The device efficiency data of the compounds are shown in Table 2. In an earlier study, BPBBPE exhibited a greenish blue color, *i.e.* (0.218, 0.335) and an EL luminance efficiency of 2.31 cd $A^{-1.21c}$ The EL color of BPBAPE [1A], to which anthracene was added in order to increase its luminescence efficiency and to twist the molecular structure, is blue-shifted with sky-blue CIE coordinates (0.195, 0.303) compared to BPBBPE. In addition, the efficiency of the BPBAPE [1A] device is 10.33 cd A^{-1} , which is very high for an OLED device structure without doping, and it has the strongest brightness of the synthesized compounds. Most importantly, its efficiency is at least twice that of the conventional DPVBi device.

We conclude that the devices containing PBAPE [1B] and BTPPA [2B], which do not contain tert-butyl groups, have better I-V characteristics than the devices with BPBAPE [1A] and BTBPPA [2A]. However, the comparison of their luminance efficiencies produces a different result. The luminance efficiency of PBAPE [1B] is 40% lower than that of BPBAPE [1A], and that of BTPPA [2B] is 20% lower than that of BTBPPA [2A]. However, since BTBPPA [2A] has a high turn-on voltage, 9.5 V, BTPPA [2B] has a power efficiency that is about 10% higher. Further, in the absence of the electrondonating effects of tert-butyl groups, PBAPE [1B] and BTPPA [2B] exhibit CIE values that closely approach the blue color with respect to BPBAPE [1A] and BTBPPA [2A]. As a result, we conclude that the EL efficiencies and CIE values of these synthesized compounds are affected by the presence of tertbutyl groups and their inductive effect, as was also concluded in a previous study of ADN and TBADN.²⁸

The materials that combine anthracene and tetraphenylethylene moieties produce devices with better luminance efficiencies than DPVBi. In particular, the BPBAPE [1A] device exhibits a luminance efficiency of above 10 cd A⁻¹ even without using doping. This high luminance efficiency might be due to the propeller-like chemical structure of the molecule and its cross dipole stacking.²⁹ The PBAPE [1B] and BTBPPA [2A] devices also exhibit a high luminance efficiency, 5 cd A⁻¹, and so can also be used as blue emitting layers. Further, BTPPA [2B] has better thermal properties and a better luminance efficiency, a lower operating voltage, and a higher power efficiency than DPVBi. The deep blue CIE coordinates

Table 2 EL performance of multi-layered devices with the structure ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized material or DPVBi (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm) at 10 mA cm⁻²

Compound	EL _{max} /nm	Voltage/V	Luminance efficiency/cd A ⁻¹	Power efficiency/lm W ⁻¹	CIE (x, y)	
BPBAPE [1A]	475	8.1	10.33	4.00	(0.195, 0.303)	
PBAPE [1B]	466	6.3	6.09	3.05	(0.194, 0.268)	
BTBPPA [2A]	463	9.5	5.03	1.67	(0.165, 0.195)	
BTPPA [2B]	452	6.8	3.93	1.82	(0.159, 0.135)	
DPVBi	465	7.65	3.92	1.61	(0.150, 0.160)	

(0.159, 0.135) of the BTPPA [2B] device are further evidence of its superior properties.

Conclusions

We have successfully designed and synthesized four useful blue emitting materials, BPBAPE [1A], PBAPE [1B], BTBPPA [2A] and BTPPA [2B], which are composed of tetra-substituted ethylene as a new core site and anthracene chromophore.

We fabricated EL devices with the synthesized compounds in the following configuration: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (30 nm)/Alq₃ (30 nm)/LiF (1 nm)/Al (200 nm). The EL maximum values of BPBAPE [1A], PBAPE [1B], BTBPPA [2A], and BTPPA [2B] were found to be 475, 466, 463, and 452 nm, respectively. All the materials that combine anthracene and tetraphenylethylene moieties exhibit better luminance efficiencies than DPVBi. BPBAPE [1A] exhibits a luminance efficiency above 10 cd A^{-1} without doping. It might be due to the propeller-like chemical structure of the molecule and its cross dipole stacking. PBAPE [1B] and BTBPPA [2A] also exhibit a high luminance efficiency, 5 cd A^{-1} , which means they too can be used as blue emitting layers. In particular, the BTPPA [2B] device has better thermal properties, a better luminance efficiency, a lower operating voltage, and a higher power efficiency than the conventional DPVBi device. Its deep blue CIE coordinates (0.159, 0.135) are further evidence of its superior properties.

Experimental

General information

¹H NMR spectra were recorded on Bruker Avance 500 and Avance 600 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL, JMS-AX505WA, HP5890 series II. Atomic force microscopy (AFM) imaging was performed in air using a PicoScan system (Molecular Imaging) equipped with a 5 \times 5 µm scanner. Magnetic-ac (Mac) mode (a non-contact mode) was used for all the AFM images. The optical absorption spectra were obtained with a HP 8453 UV-VIS-NIR spectrometer. The melting temperatures (T_m) , glass-transition temperatures (T_g) , crystallization temperatures (T_c) , and degradation temperatures (T_d) of the compounds were measured by carrying out differential scanning calorimetry (DSC) under a nitrogen atmosphere using a DSC2910 (TA Instruments) and thermogravimetric analysis (TGA) using a SDP-TGA2960 (TA Instruments). A Perkin Elmer luminescence spectrometer LS50 (xenon flash tube) was used for photo- and electro-luminescence spectroscopy. The redox potentials of the compounds were determined with cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 50–200 mV s⁻¹. The synthesized materials were dissolved in N,N-dimethylformamide (DMF) with 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte. We used a platinum working electrode and a saturated Ag/AgNO₃ reference electrode. Ferrocene was used for potential calibration and for reversibility criteria.

Crystals of BPBAPE [1A] were obtained from CHCl₃/ isopropyl alcohol at room temperature, sealed in glass capillaries under nitrogen, and mounted on the diffractometer. The structures were characterized by the application of direct methods using the SHELXS-96 program and least-squares refinement using SHELXL-97.

For the EL devices, all organic layers were deposited under 10^{-6} Torr, with a rate of deposition of 1 Å s⁻¹ to give an emitting area of 4 mm². The LiF and aluminium layers were continuously deposited under the same vacuum conditions.

The current–voltage (I-V) characteristics of the fabricated EL devices were obtained with a Keithley 2400 electrometer. Light intensity was obtained with a Minolta CS-100A.

Selected crystal data for BPBAPE [1A]

C₆₂H₅₂, M_r = 797.04, a = 20.268(3) Å, b = 10.0519(13) Å, c = 22.389(3) Å, α = 90°, β = 90°, γ = 90°, V = 4561.5(10) Å³, Z = 4, ρ_{calc} = 1.161 mg m⁻², F(000) = 1696, crystal size 0.16 mm × 0.08 mm × 0.07 mm, λ = 0.71073 A, T = 293(2) K, μ = 0.065 mm⁻¹, final R indices $[I > 2\sigma(I)] R_1$ = 0.1204, ωR_2 = 0.2709.†

Synthesis

i) 1,2-Bis(4-bromophenyl)-1,2-bis(4-tert-butylphenyl)ethene (1) and 4,4',4"-(2-(4-bromophenyl)ethene-1,1,2-triyl)tris(tertbutylbenzene) (2). Bis(4-tert-butylphenyl)methanone (5 g, 17 mmol), (4-tert-butylphenyl)(4-bromophenyl)methanone (16 g, 51 mmol) and Zn powder (10.6 g, 170 mmol) were added to dried THF solvent (500 mL), then TiCl₄ (15 mL, 136 mmol) was added into the reaction mixture. The mixture was heated to 60 °C for 1 h under nitrogen. The reactant mixture was cooled after 1 h and then the product was extracted with diethyl ether. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered off and washed with methanol.

The mixture powder was separated by using column chromatography with $CHCl_3$ -n-hexane (1 : 10) eluent to afford a white solid 1,2-bis(4-bromophenyl)-1,2-bis(4-*tert*-butylphenyl)ethene (1) (5.2 g) and 4,4',4"-(2-(4-bromophenyl) ethene-1,1,2-triyl)tris(*tert*-butylbenzene) (2) (5.7 g).

ii) 1,2-Bis(4-tert-butylphenyl)-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (3). 1,2-Bis(4-bromophenyl)-1,2-bis(4-tert-butylphenyl)ethene (1) (5 g, 8.3 mmol) was dissolved in 200 mL of dry THF solution and stirred at -78 °C. then 1.6 M n-BuLi (20 mL) was added. Next, isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.5 mL, 34 mmol) was added to the reaction mixture after 30 min. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in acetone and added to methanol. The precipitate was filtered off and washed with methanol. The mixture powder was separated by using column chromatography with ethyl acetate-*n*-hexane (1:9) eluent to afford a white solid 1,2-bis(4-tert-butylphenyl)-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene (3) (3.2 g, 55%).

¹H NMR (CDCl₃, 500 MHz): δ 7.53 (m, 4H), 7.08 (m, 4H), 6.69 (m, 8H), 1.58 (d, 24H), 1.23 (d, 18H); FAB⁺-MS: 696.

iii) 1,2-Bis(4'-tert-butylphenyl)-1,2-bis(4'-(anthracene-9yl)phenyl)ethene [BPBAPE, 1A]. 1,2-Bis(4-tert-butylphenyl)-1,2-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) ethene (3) (3 g, 4.3 mmol), 9-bromoanthracene (2.5 g, 10 mmol) Pd(OAc), (0 29 g, 1 29 mmol) and (tris-a-tolyl).P

ethene (3) (3 g, 4.3 mmol), 9-bromoanthracene (2.5 g, 10 mmol), Pd(OAc)₂ (0.29 g, 1.29 mmol), and (tris-o-tolyl)₃P (0.39 g, 1.29 mmol) were added to DME (200 mL) solution, then a prepared K₂CO₃ solution, which was dissolved in a DME and H₂O (1 : 1, 100 mL) solvent, was added to the reaction mixture. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered off and washed with methanol. The yellowish powder was purified by using column chromatography with CHCl₃–n-hexane (1 : 2) eluent to afford a beige solid (BPBAPE, 1A) (3 g, 86%).

¹H NMR (THF, 600 MHz): δ 8.52 (s, 2H), 8.05 (d, 4H), 7.67 (d, 4H), 7.44 (t, 4H), 7.36 (t, 12H), 7.27 (d, 4H), 7.20 (d, 4H), 1.36 (s,18H); ¹³C NMR (CDCl₃, 500 MHz):149.9, 143.5, 141.4, 140.8, 137.4, 136.7, 131.61, 131.56, 131.48, 130.8, 130.4, 128.5, 127.1, 126.6, 125.4, 125.3, 124.7, 34.8, 31.7; FT-IR (KBr, cm⁻¹): 3049, 3026, 2960, 2901, 2865, 1510, 1441, 1409, 1360, 883, 843, 792, 736; FAB⁺-MS: 796.

iv) 1,2-Diphenyl-1,2-bis(4'-(anthracene-9-yl)phenyl)ethene [PBAPE, 1B]. PBAPE was synthesized as for the above series by using the McMurry and Suzuki coupling reactions.

¹H NMR (THF, 500 MHz): δ 8.50 (s, 2H), 8.00 (d, 4H), 7.65 (d, 4H), 7.42 (t, 4H), 7.35–7.29 (m, 12H), 7.20 (t, 4H), 7.17 (t, 2H), 7.00 (t, 4H); ¹³C NMR (CDCl₃, 500 MHz):143.8, 143.4, 143.1, 137.2, 137.0, 131.8, 131.68, 131.49, 130.9, 130.3, 128.5, 128.1, 127.1, 126.9, 126.7, 125.7, 125.3; FT-IR (KBr, cm⁻¹): 3073, 3049, 3024, 1508, 1491, 1441, 1410, 1358, 943, 887, 753, 736, 699; FAB⁺-MS: 684.

v) 4,4,5,5-Tetramethyl-2-(4-(1,2,2-tris(4-tert-butylphenyl)vi-4,4',4"-(2-(4-Bromonyl)phenyl)-1,3,2-dioxaborolane (4). phenyl)ethene-1,1,2-triyl)tris(tert-butylbenzene) (2) (5 g, 8.6 mmol) was dissolved in 200 mL of dry THF solution and stirred at -78 °C, then 1.6 M n-BuLi (21 mL) was added. Next, isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.7 mL, 35 mmol) was added to the reaction mixture after 30 min. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in acetone and added to methanol. The precipitate was filtered off and washed with methanol. The mixture powder was separated by using column chromatography with ethyl alcohol-n-hexane (1:9)eluent to afford a white solid 4,4,5,5-tetramethyl-2-(4-(1,2,2tris(4-*tert*-butylphenyl)vinyl)phenyl)-1,3,2-dioxaborolane (4) (3.9 g, 72%).

¹H NMR (CDCl₃, 500 MHz): δ 7.54 (d, 2H), 7.24 (m, 6H), 6.99 (m, 8H), 1.48 (d, 12H), 1.23 (d, 27H); FAB⁺-MS: 626.

vi) 9,10-Bis(4-(1,2,2-tris(4-*tert*-butylphenyl)vinyl)phenyl)anthracene [BTBPPA, 2A]. 4,4',4"-(2-(4-Bromophenyl)ethene-1,1,2-triyl)tris(*tert*-butylbenzene) (2) (3.5 g, 5.6 mmol), 9,10-dibromoanthracene (0.84 g, 2.5 mmol), Pd(OAc)₂ (0.38 g, 1.68 mmol), and (tris-*o*-tolyl)₃P (0.51 g, 1.68 mmol) were added to DME (200 mL) solution, then a prepared K₂CO₃ solution, which was dissolved in a DME and H₂O (1 : 1, 100 mL) solvent, was added to the reaction mixture. After the reaction had finished, the reaction mixture was extracted with diethyl ether and water. The organic layer was dried with anhydrous MgSO₄ and filtered. The solution was evaporated. The residue was dissolved in CHCl₃ and added to methanol. The precipitate was filtered off and washed with methanol. The yellowish powder was purified by using column chromatography with CHCl₃–hexane (1 : 1) eluent to afford a beige solid (BTBPPA, **2A**) (1.3 g, 44%).

¹H NMR (CDCl₃, 500 MHz): δ 7.65 (q, 4H), 7.33 (q, 4H), 7.25 (d, 4H), 7.20 (d, 4H), 7.17 (m, 8H), 7.14–7.07 (m, 12H), 7.02 (d, 4H), 1.30 (d, 36H), 1.25 (s, 18H); ¹³C NMR (THF, 500 MHz):148.8, 148.6, 143.3, 140.8, 140.3, 136.5, 136.4, 130.9, 130.7, 130.5, 130.2, 129.9, 129.4, 128.2, 126.2, 124.3, 123.9, 123.7, 33.7, 33.2, 31.5, 30.4; FT-IR (KBr, cm⁻¹): 3061, 3024, 2962, 2902, 2865, 1508, 1460, 1439, 1390, 1361, 1109, 1020, 942, 836, 800, 771, 741, 693; FAB⁺-MS: 1175.

vii) 9,10-Bis(4-(1,2,2-triphenylvinyl)phenyl)anthracene [BTPPA, 2B]. BTPPA was synthesized as for the above series by using the McMurry and Suzuki coupling reactions.

¹H NMR (CDCl₃, 500 MHz): *δ* 7.63 (q, 4H), 7.34 (q, 4H), 7.25–7.12 (m, 38H); ¹³C NMR (CDCl₃, 500 MHz): 144.1, 143.7, 143.6, 143.3, 141.8, 141.2, 137.2, 137.1, 131.76, 131.6, 131.45, 130.9, 129.9, 128.03, 127.95, 127.95, 127.81, 127.18, 126.82, 126.78, 125.07; FT-IR (KBr, cm⁻¹): 3058, 3025, 1491, 1443, 1394, 1074, 1027, 942, 765, 755, 700; FAB⁺-MS: 838.

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