Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2011, 21, 9139

www.rsc.org/materials

Highly efficient deep-blue emitting organic light emitting diode based on the multifunctional fluorescent molecule comprising covalently bonded carbazole and anthracene moieties[†]

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Received 15th March 2011, Accepted 21st April 2011 DOI: 10.1039/c1jm11111f

High performance deep-blue organic light-emitting diodes (OLEDs) have been investigated using new multifunctional blue emitting materials 3-(anthracen-9-yl)-9-ethyl-9*H*-carbazole (AC), 3,6-di (anthracen-9-yl)-9-ethyl-9*H*-carbazole (DAC), 3-(anthracen-9-yl)-9-phenyl-9*H*-carbazole (P-AC), and 3,6-di(anthracen-9-yl)-9-phenyl-9*H*-carbazole (P-DAC) which comprise covalently bonded carbazole and anthracene moieties. We also have investigated the thermal, electrochemical, and morphological stability to find suitable molecular structure, consisting of carbazole and anthracene moieties. The non-doping deep-blue OLEDs using P-DAC, which showed the highest thermal, electrochemical, and morphological stability, proved the highest luminance efficiency and external quantum efficiency of 3.14 cd A⁻¹ and 2.75%, with the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (0.162, 0.136) at 100 mA cm⁻². Moreover, the doping devices using P-DAC as the host material showed blue emission, and the high luminance efficiencies and external quantum efficiencies of as high as 7.70 cd A⁻¹ and 4.86% with CIE chromaticity coordinates (0.156, 0.136) and (0.156, 0.217) at 100 mA cm⁻². Both the non-doping and doping devices using P-DAC uniquely exhibited high operational stability with virtually negligible efficiency roll-off over the broad current density range.

Introduction

Organic light-emitting diodes (OLEDs) have progressed into the most desirable next generation flat-panel display and solid state lighting devices over the past few decades after the pioneering work of Tang and Van Slyke in 1987.¹ Although OLEDs have achieved remarkable development to date, there remain several important problems to be solved currently. One of them is the inferior performance of blue OLEDs to those of green and red ones.^{2,3}

Blue emitting materials intrinsically possess high band gap energy, which results in the inferior OLED performance *via* limited carrier injection demanding higher driving voltage for appropriate operation.⁴ Due to the higher voltage applied for effective carrier injection, the more Joule heat is also generated during device operation. This Joule heat, in turn, brings about the degradation and recrystallization of the blue emitting materials. As a result, color purity and device life-time are seriously reduced. To address this problem, high thermal stability and amorphous film morphology are considered as important requirements in blue emitting materials.⁵ In addition, to obtain excellent color purity, blue emitting materials should have molecular structure not to form excimer which brings about broad and red-shifted electroluminescent (EL) emission.⁶

It is well-known that a host-dopant emitter system can significantly improve OLED performance in terms of the efficiency, color purity, and device life-time.⁷ Various host materials for blue emitting OLED have been reported to date, which include anthracene,^{4,8} strylarylene,⁹ fluorene,¹⁰ quinoline,¹¹ and pyrene¹² derivatives. In spite of their successful performance in a given aspect, satisfactory blue host materials are still rare which balance all the aspects of efficiency, color purity, and device life-time.

In this paper, we intended to report the multifunctional deepblue emitting host materials having carbazole and anthracene moieties to achieve high efficiency, color purity, and long device life-time all together in blue OLEDs. Carbazole-based compounds have been well known for their excellent hole transporting ability, luminescence efficiency, thermal stability, versatile structural derivatization, and unique ability to form amorphous film.¹³ Anthracene is more promising towards blueemitting OLED in terms of the excellent luminescence efficiency, thermal and electrochemical stability, and ease of structural modification.^{8a,8c,14} Unfortunately, however, it suffers from the unfavorable crystallization and excimer formation in the film

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[†] Electronic supplementary information (ESI) available: Synthesis and characteristics of deep-blue emitting molecules and charge carrier properties of P-DAC. See DOI: 10.1039/c1jm11111f

state.^{4,6a} It was rationally considered, therefore, that the covalent bonding of carbazole and anthracene may give a multifunctional molecule showing synergetic effect towards blue-emitting OLED application.

Herein, we report on the synthesis and OLED performances of a novel series of new deep-blue emitting materials consisting of covalently bonded carbazole and anthracene moieties; *i.e.* 3-(anthracen-9-yl)-9-ethyl-9*H*-carbazole) (AC), 3,6-di(anthracen-9-yl)-9-ethyl-9*H*-carbazole (DAC), 3-(anthracen-9-yl)-9-phenyl-9*H*-carbazole (P-AC), and 3,6-di(anthracen-9-yl)-9-phenyl-9*H*carbazole (P-DAC).

Results and discussion

Scheme 1 illustrates the synthetic routes to a series of deep-blue emitting materials AC, DAC, P-AC, and P-DAC. As shown in the scheme, these compounds were all synthesized through four step chemical reactions starting from carbazole. Carbazole was

N-alkylated or N-arylated to give 9-ethyl-9H-carbazole (1) and 9-phenyl-9H-carbazole (6), which were subsequently brominated with N-bromosuccinimide (NBS) to generate the compounds 3bromo-9-ethyl-9H-carbazole (2), 3,6-dibromo-9-ethyl-9Hcarbazole (4), 3-bromo-9-phenyl-9H-carbazole (7), and 3,6dibromo-9-phenyl-9H-carbazole (9). Then, these bromocompounds were transformed into boronic esters via lithiation with *n*-butyllithium followed by reaction with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Finally, AC, DAC, P-AC, and P-DAC were obtained by the Suzuki-Miyaura coupling reactions of boronic esters (3, 5, 8, 10) with 9-bromoanthracene. All the compounds were purified either by the silica column chromatography or recrystallization in solvent. The chemical structure and purity of the intermediates and final compounds were characterized by spectroscopic methods and elemental analysis (see Experimental section for details).

Fig. 1 shows three-dimensional optimized geometry, the calculated highest occupied molecular orbital (HOMO) and



Scheme 1 Synthetic routes to AC, DAC, P-AC, and P-DAC.

lowest unoccupied molecular orbital (LUMO) electron density maps, thermogravimetric analysis (TGA) trace, absorption and photoluminescent (PL) spectrum, repeated cyclic voltammograms, and scanning electron microscope (SEM) image of P-DAC (see the ESI† for those of AC, DAC, and P-AC).

Theoretical molecular orbital calculation was carried out using Gaussian03 at B3LYP/6-31g(dp)¹⁵ level, to characterize optimized geometries, orbital energy, and electron densities of the HOMO and LUMO states of each molecule. As shown in Fig. 1(a), all molecules, including P-DAC (see Fig. S1 in the ESI[†] for all molecules) have non-coplanar twisted conformation due to the large torsional angle between carbazole and anthracene moieties. Such a unique structural feature is beneficial in OLED application by preventing the excessive intermolecular interaction against fluorescence quenching and also by suppressing the crystallization problem to establish the uniform amorphous morphology in the film state of OLED device.



Fig. 1 (a) Three-dimensional optimized geometry of P-DAC. (b) The calculated HOMO and LUMO electron density maps of P-DAC. (c) TGA trace of P-DAC measured at a scan rate of 10 °C min⁻¹ under N₂. (d) Absorption and PL spectrum of P-DAC. (e) Repeated cyclic voltammograms of P-DAC. (f) SEM image of P-DAC in vacuum deposited film on Si wafer. The scale bar represents 10 μ m and image is magnified by a factor of 3000.

Table 1	Physical	properties of	AC,	DAC,	P-AC,	and P	-DAC	(ND: not	detected)
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Compound	$T_{\rm g}/T_{\rm m}/T_{\rm d}{}^a/^{\circ}{\rm C}$	λ_{abs}^{b}/nm	$\lambda_{\rm em}^{c}/{\rm nm}$	$\lambda_{\rm em}^{}^{d}/{\rm nm}$	AbPLQY ^e (%)	HOMO/LUMO ^f /eV
AC	ND/ND/300	351,368,387	443	456	45	-5.40/-2.36
DAC	ND/ND/395	351,368,388	441	464	44	-5.41/-2.37
P-AC	89/196/326	348,368,387	435	451	51	-5.47/-2.42
P-DAC	ND/ND/419	351,368,388	431	460	40	-5.50/-2.45

^{*a*} $T_{\rm g}$ determined by DSC with a heating rate of 10 °C min⁻¹ under N₂, $T_{\rm m}$ determined by DSC with a heating rate of 10 °C min⁻¹ under N₂, $T_{\rm d}$ obtained with 5% mass loss by TGA with a heating rate of 10 °C min⁻¹ under N₂. ^{*b*} Maximum absorption wavelength, measured in MC (10⁻⁵ M). ^{*c*} Maximum emission wavelength, measured in MC (10⁻⁵ M). ^{*d*} Maximum emission wavelength, measured in film state (films prepared on quartz plate by the thermal evaporation method). ^{*e*} AbPLQY values in film state were measured using the integrating sphere method. ^{*f*} HOMO energy level was measured by CV. LUMO energy level was determined from the HOMO level and the optical band gap.

Fig. 1(b) shows the calculated HOMO and LUMO electron density maps of P-DAC (see Fig. S2 in the ESI† for all the molecules). It was peculiarly noted that HOMO and LUMO electron densities of all the molecules are localized only at the anthracene moiety. Thus, it was expected that the absorption and emission properties of the multifunctional molecules are controlled mostly by π - π * transition of anthracene moiety, which means that the excellent luminescence efficiency of anthracene moiety is maintained, while the crystallization and aggregation problems are effectively suppressed.

The thermal properties of these multifunctional molecules were characterized by differential scanning calorimetry (DSC) and TGA in a N_2 atmosphere (Table 1, Fig. 1(c), and see Fig. S3 in the ESI†). All the molecules showed good thermal stability as

to have the onset decomposition temperatures (T_d) , defined for the 5% mass loss temperature by TGA, at 300, 395, 326, and 419 °C, respectively. DSC thermograms of these molecules barely showed glass transition temperatures (T_g) and melting temperatures (T_m) most likely due to their smaller heat capacity and crystallinity. However, P-AC exhibited a somewhat noticeable T_g at 89 °C and T_m at 196 °C.

Fig. 1(d) shows absorption and PL spectrum of P-DAC in CH_2Cl_2 (MC) solution and also the PL spectra of thermally evaporated film (see Fig. S4 in the ESI† for all other molecules). The precise photophysical data are summarized in Table 1. In MC solution state, all the multifunctional molecules showed the characteristic vibrational patterns of isolated anthracene moiety in the absorption spectra, while they were rather smooth and



Fig. 2 (a) Structures of non-doped devices and energy levels of materials. (b) Molecular structures of materials. (c) EL spectrum and emission photograph of non-doped devices at 10 mA cm⁻².



Fig. 3 (a) *J–V–L* characteristics, (b) Luminance efficiency and power efficiency of non-doped devices with AC, DAC, P-AC, and P-DAC.

featureless in the emission spectra. The PL spectrum in film state was similarly shaped to that in solution but a little red-shifted probably due to the rather trivial solid-state effect (see Fig. 1(d) for the case of P-DAC).¹⁶ The absence of characteristic anthracene excimer peaks in these PL spectrum evidences the successful molecular design of our multifunctional blue emitting molecules. Attributed to the suppressed intermolecular interaction, absolute PL quantum yields (AbPLQY) of multifunctional molecules measured by an integrating sphere method in film state,¹⁷ were very high (>40%) as shown in Table 1. It should be noted that the maximum emission wavelength of ethyl carbazole derivatives is relatively larger than that of phenyl carbazole derivatives (AC *vs.* P-AC, and DAC *vs.* P-DAC) in the PL spectra due to the stronger electron donating properties of aliphatic group.

Table 1 also shows HOMO and LUMO energy levels of each molecule. HOMO energy levels of AC, DAC, P-AC, and P-DAC measured by cyclic voltammetry (CV) are -5.40, -5.41, -5.47, and -5.50 eV, respectively. The optical band gap energies (E_g) calculated from the threshold of the optical absorption are 3.04, 3.04, 3.05, and 3.05 eV, respectively, which are all appropriate for blue emission. LUMO energy levels were calculated to be -2.36, -2.37, -2.42, and -2.45 eV, respectively, from their HOMO energy levels and E_g . It is to be noted that the HOMO energy levels of ethyl carbazole derivatives (AC and DAC) are slightly higher than those of phenyl carbazole derivatives (P-AC and P-DAC). It is speculated that ethyl group at N9 position of

carbazole activates the carbazole ring system by increasing the electron density and makes the compound easier to oxidize than corresponding phenyl-substituted compounds.¹⁸

Fig. 1(e) shows repeated scans of cyclic voltammograms which were carried out to check the electrochemical stability of P-DAC (see Fig. S5 in the ESI† for all the multifunctional molecules). The oxidation process of AC and P-AC (compounds chemically substituted at C3 and N9 positions, but with open C6 position of carbazole moiety) was not reversible as to have the oxidation potential gradually shifted to the lower value with concomitant current increase in the repeated CV cycles (see Fig. S5(a) and (c) in the ESI†). Such characteristics are attributed to the electrochemical dimerization of carbazoles through the active C6 position.¹⁹⁻²² In contrast, DAC and P-DAC with substituents at all the C3, C6, and N9 positions, showed reversible oxidation process as shown in Fig. S5(b) and (d)†.

SEM images were obtained to check morphological characteristics of thermal evaporated films. Fig. 1(f) shows SEM image of P-DAC (see Fig. S6 in the ESI† for all the molecules). Except for AC, all molecules can form morphologically stable and uniform amorphous films. For carbazole-based compound to obtain sufficient morphological stability in thermally evaporated film, it has been proposed that the molecule size should be extended beyond the length of one carbazole molecule to obtain bulky and sterically hindered molecular configuration.²¹⁻²³ It is considered that AC, with only C3 positioned anthracene and N9 positioned ethyl group, is rather small in its molecular size to satisfy this condition.

In order to explore OLEDs characteristics of AC, DAC, P-AC, and P-DAC, we have fabricated non-doping (ND) blue devices, consisting of indium tin oxide (ITO) (150 nm)/4,4',4"-tris (N-(2-naphthyl)-N-phenyl-amino)triphenylamine (2-TNATA) (60 nm)/N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) (20 nm)/blue emitting layer (EML) (30 nm)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (10 nm)/tris(8-hydroxy-quinolinato) aluminium (Alq₃) (20 nm)/LiF (1 nm)/Al (100 nm). 2-TNATA was used as hole injection layer (HIL), NPB was used as hole transporting layer (HTL), AC, DAC, P-AC, and P-DAC were used as emitting layer (EML), BCP was used as hole blocking layer (HBL), and Alq₃ was used as electron transporting layer (ETL), respectively.

Fig. 2(a) shows the ND device structure and energy levels of materials, (b) the molecular structures of each material used in the device fabrication, and (c) the EL spectrum and emission photograph at 10 mA cm⁻². Fig. 3 shows current densityvoltage-luminance (J-V-L) characteristics, and luminance efficiency and power efficiency as a function of current density for each blue OLED. The important EL properties were analyzed from these graphs and summarized in Table 2. As shown in Fig. 2(c), all the blue OLED devices showed deepblue emission, although we find a rather small exciplex emission at around 580 nm range included in the EL spectra of DAC. The Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of purely blue emitting AC, P-AC, and P-DAC devices are (0.165, 0.151), (0.166, 0.152), and (0.167, 0.149) at 10 mA cm⁻² and (0.162, 0.134), (0.163, 0.132), and (0.162, 0.136) at 100 mA cm⁻², which show the deep-blue emission characteristics and very small change in the coordinate values as a function of current density. All the AC, P-AC,

Table 2 Electroluminescent characteristics of blue non-doped OLEDs (*V*: driving voltage, η_L : luminance efficiency, η_P : power efficiency, η_{ex} : external quantum efficiency)

EML	V^a/V	V^{b}/V	$\eta_L^{b}/cd A^{-1}$)	$\eta_{\mathrm{P}}{}^{b}/\mathrm{lm}~\mathrm{W}^{-1}$	$\eta_{\mathrm{ex}}{}^{b}$ (%)	CIE^b	V^c/V	$\eta_{\rm L}{}^c/{\rm cd}~{\rm A}{}^{-1}$)	$\eta_{\rm P}{}^c/{ m lm}~{ m W}^{-1}$	$\eta_{\mathrm{ex}}{}^{c}$ (%)	CIE^{c}
AC	4.40	7.91	3.45	1.39	2.84	0.165, 0.151	10.62	2.32	0.69	2.07	0.162, 0.134
DAC	4.60	7.54	2.09	0.87	1.38	0.193, 0.196	11.08	1.82	0.52	1.33	0.179, 0.171
P-AC	4.40	8.17	3.11	1.19	2.53	0.166, 0.152	11.18	2.56	0.72	2.35	0.163, 0.132
P-DAC	3.80	7.57	3.09	1.28	2.50	0.167, 0.149	10.66	3.14	0.92	2.75	0.162, 0.136

^a Turn-on voltage at 1 cd m⁻². ^b At 10 mA cm⁻². ^c At 100 mA cm⁻².

Table 3 Electroluminescence data for the blue OLEDs (na: not available)

Materials code	Moiety	V/V	$\eta_{\rm L}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm P}/{ m lm}~{ m W}^{-1}$	η_{ex} (%)	CIE	Efficiency roll-off ^e (%)	Reference
P-DAC	Carbazole and anthracene	7 57 ^a	3.09^{a}	1.28^{a}	2.50 ^{<i>a</i>}	0 167 0 149 a	+2	This paper
TPVAn	Anthracene and strylarylene	6.7^{b}	$5.0^{\hat{b}}$	na	5.0^{b}	$0.14, 0.12^c$	-16	8d
MAM	Anthracene	7.99 ^a	2.94^{a}	1.28^{a}	3.90 ^a	$0.163, 0.124^a$	na	8 <i>e</i>
POAn	Anthracene	na	2.7^{a}	na	4.0^{a}	$0.15, 0.07^c$	-33	8 <i>f</i>
BFAn	Anthracene and fluorene	na	5.4 ^{<i>a</i>}	4.2^{a}	4.8^{a}	$0.15, 0.12^c$	-22	8g
DMIP-2-NA	Anthracene and indene	5.77^{b}	1.17^{b}	0.64^{b}	1.4^{b}	$0.151, 0.097^b$	na	8 <i>i</i>
9	Carbazole and arylamine	6.0^{d}	1.26^{d}	0.65^{d}	1.05^{d}	$0.15, 0.14^d$	na	13 <i>c</i>
MADN	Anthracene	6.2	1.4	0.4	na	0.15, 0.10	na	24
DPVPA	Anthracene and strylarylene	7.3	4.0	1.7	na	0.14, 0.17	na	24
^a At 10 mA cm ⁻	² . ^{<i>b</i>} At 20 mA cm ⁻² . ^{<i>c</i>} At 7 V. ^{<i>d</i>}	At 100 r	mA cm ^{-2} . ^{<i>e</i>} F	rom 10 mA cr	n^{-2} to 100	$mA cm^{-2}$.		

and P-DAC have shown high luminance efficiency larger than 3.0 cd A⁻¹ at the current density level of 10 mA cm⁻². In the case of AC and P-AC, however, the efficiencies were decreased at the higher current density level of 100 mA cm⁻². The luminance efficiency was reduced by 33% (3.45 cd A⁻¹ at 10 mA cm⁻² and 2.32 cd A⁻¹ at 100 mA cm⁻²) in AC ND device, and it was reduced by 18% (3.11 cd A^{-1} at 10 mA cm⁻² and 2.56 cd A⁻¹ at 100 mA cm⁻²) in P-AC device. In P-DAC device, on the contrary, the luminance efficiency was increased by 2% (3.09 cd A^{-1} at 10 mA cm⁻² and 3.14 cd A^{-1} at 100 mA cm⁻²). In fact, in the P-DAC deep-blue ND device, showed virtually invariant luminance efficiency as a function of current density. As shown in Fig. 3(b), such an excellent OLED performance of P-DAC consistent with its thermal, electrochemical, and morphological stability. The efficiency, color purity, and device stability of P-DAC non-doping device are the very good results, comparing with blue OLED devices reported in the literature (Table 3).8d-g,8i,13c,24 Especially, device operational stability in terms of efficiency roll-off tells that P-DAC is unique and excellent deep-blue emission material, which suggests further potential for the host material of deep-blue OLEDs. Fig. 4 shows the device life-time of each non-doping device at the initial luminance of 400 cd m^{-2} under constant current condition. Although the overall device life-time is relatively short by using BCP, which is lack of thermal and morphological stability,²⁵ luminance half life-time of the P-DAC non-doping device is largely superior to AC, DAC, and P-AC.

To further improve the device performance, doping devices have been fabricated and evaluated by using P-DAC as the host material which has shown the best performance among non-doping device. In P-DAC doping devices, BCzVBi and BDAVBi were investigated as blue-emitting dopants. The device structures were the same as that of non-doping device, when the each dopant was co-evaporated with P-DAC to give 3 wt% dopant content. Fig. 5(a) shows the device structures of P-DAC doping devices and energy levels of each material, (b) the molecular structures of dopants, (c) absorption spectrum of BCzVBi together with BDAVBi and PL spectra of P-DAC, and (d) the EL spectrum of doping devices and emission photographs at 10 mA cm⁻². P-DAC doping devices showed the deep blue emission whose shape is slightly different from that of P-DAC ND device (Fig. 2(c)) and included the intrinsic vibronic peak characteristics of dopants. Since the deep-blue host material, P-DAC has the larger band gap energy than dopants, and the spectral overlap efficiency between PL spectra of P-DAC and absorption spectrum of dopants is very high, Förster energy transfer was efficient from P-DAC to the dopants. Fig. 6 shows J-V-L characteristics, and luminance efficiency and power efficiency as a function of current density for different doping devices. The important EL properties were



Fig. 4 Device life-time of deep-blue non-doped OLEDs (initial luminance is 400 cd m^{-2} and device is operated with constant current).



Fig. 5 (a) Structures of P-DAC doping devices and energy levels of materials. (b) Molecular structures of blue dopants. (c) UV-visible absorption spectrum of the BCzVBi, BDAVBi and PL spectra of the P-DAC. (d) EL spectrum and emission photographs of doping devices at 10 mA cm⁻².

analyzed from these graphs and are summarized in Table 4. The CIE chromaticity coordinates of BCzVBi and BDAVBi devices are (0.158, 0.142), (0.158, 0.219) at 10 mA cm⁻² and (0.156, 0.136), (0.156, 0.217) at 100 mA cm⁻², which show the blue emission characteristics and very small change in the coordinate values as a function of current density. Especially, BCzVBi doping device shows the deep-blue OLED characteristic. Luminance efficiency of BCzVBi doping device was 4.32 cd A^{-1} (E.Q.E: 3.65%) and that of BDAVBi was 7.36 cd A^{-1} (E.Q.E: 4.62%) at 10 mA cm⁻². The efficiency of BDAVBi doping device was superior to that of BCzVBi, it is because of the more spectral overlap between P-DAC and BDAVBi than that between P-DAC and BCzVBi, resulting in the more effective Förster energy transfer. Investigating the change in luminance efficiency in doping devices from 10 mA cm⁻² to 100 mA cm⁻², the efficiency of BCzVBi doping device was increased by 1% (4.32 cd A^{-1} at 10 mA cm⁻² and 4.37 cd A^{-1} at 100 mA cm⁻²) and the efficiency of BDAVBi doping device was also increased by 5% (7.36 cd A^{-1} at 10 mA cm⁻² and 7.70 cd A^{-1} at 100 mA cm⁻²). As shown in Fig. 6(b), it is noteworthy that there is little roll-off of luminance efficiency as a function of current density much like that of P-DAC non-doping device.

Conclusions

High efficiency deep-blue OLEDs have been investigated using new blue emitting materials AC, DAC, P-AC, and P-DAC which comprise covalently bonded carbazole and anthracene moieties. Theoretical molecular orbital calculations have shown that AC, DAC, P-AC, and P-DAC have non-coplanar structures. We also have investigated the thermal, electrochemical, and morphological stability to find suitable molecular structure, consisting of carbazole and anthracene moieties. The nondoping deep-blue EL device using P-DAC, which showed the highest thermal, electrochemical, and morphological stability, showed the highest luminance efficiency of 3.14 cd A^{-1} and 2.75%, with CIE chromaticity coordinates (0.162, 0.136) at 100 mA cm⁻². Moreover, the doping devices using P-DAC as the host material showed blue emission, and the high luminance efficiencies and external quantum efficiencies of as high as 7.70 cd A⁻¹ and 4.86%, with CIE chromaticity coordinates (0.156, 0.136) and (0.156, 0.217). Both the non-doping and doping devices using P-DAC uniquely exhibited high operational stability with virtually negligible efficiency roll-off over the broad current density range.



Fig. 6 (a) *J*–*V*–*L* characteristics, (b) Luminance efficiency and power efficiency of doping devices.

Experimental

Characterization

Chemical structures were fully identified by ¹H NMR (JEOL JNM-LA300, 300 MHz), ¹³C NMR (Bruker, Avance DPX-300), gas chromatography-mass spectrometry (GC-MS) (JEOL, JMS-AX505WA), and elemental analysis (EA1110, CE Instrument). The T_{g} and T_{m} of molecules were determined by DSC under N2 atmosphere using a TA instruments Q1000 model. The $T_{\rm d}$ of molecules were obtained by TGA under N₂ atmosphere using a TA instruments Q50 model. UV-visible spectra were recorded on a Varian Cary 100 Conc model, while PL spectra were taken using a Varian Cary Eclipse fluorescence spectrophotometer. AbPLQY was measured by the integrating method with IESP-150B (Optel) quantum efficiency measurement equipment. HOMO levels of molecules were obtained from the CV measurement. CV measurement was performed using a 273A (Princeton Applied Research) with a one-compartment electrolysis cell consisting of a platinum working electrode,

a platinum wire counter-electrode, and a quasi Ag⁺/Ag electrode as reference. Measurement was performed in 0.5 mM MC solution, with tetrabutylammonium tetrafluoroborate as supporting electrolyte, at a scan rate of 100 mV s⁻¹. Each oxidation potential was calibrated using ferrocene as a reference. LUMO levels were calculated from HOMO level and energy band gap which was obtained from the edge of the absorption spectra. SEM images were obtained from HITACHI S-4300.

Device fabrication and evaluation

The blue OLEDs were fabricated by thermal evaporation onto a cleaned glass substrate precoated with ITO without breaking the vacuum. Prior to organic layer deposition, the ITO substrates were exposed to UV-ozone flux for 20 min following degreasing in isopropyl alcohol. All layers were grown by thermal evaporation at the base pressure of $< 5 \times 10^{-7}$ Torr. Layers were deposited in following order: HIL/HTL/blue EML/HBL/ETL/ cathode. 60 nm-thick 2-TNATA (LT-E203 purchased from Lumtec) was used as the HIL, 20 nm-thick NPB (LT-E101 purchased from Lumtec) was used as the HTL, 30 nm-thick AC, DAC, P-AC, and P-DAC were used as the blue EML, 10 nmthick BCP (LT-E304 purchased from Lumtec) was used as the HBL, 20 nm-thick Alq₃ (LT-E401 purchased from Lumtec) was used as the ETL, respectively. Finally, the cathode consisting of a 1 nm-thick LiF and a 100 nm-thick layer of Al were deposited onto the sample surface. In P-DAC doping devices, BCzVBi (LT-E601 purchased from Lumtec) and BDAVBi (LT-E608 purchased from Lumtec) were investigated as blue-emitting dopants. The doping device structures were the same as that of non-doping device, when the each dopant was co-evaporated with P-DAC to give 3 wt% dopant content. All the materials were purified using train sublimation before use.

J-V-L characteristics, EL spectra, and CIE chromaticity coordinates of the blue OLEDs were measured simultaneously using a Keithley 237 programmable source meter and a SpectraScan PR650 (Photo Research). Assuming Lambertian emission, the external quantum efficiency (EQE) was calculated from the luminance, current density, and electroluminescence spectrum.

Synthesis

P-DAC was synthesized according to the procedure in Scheme 1. Unless stated otherwise, all reagents were purchased from Sigma Aldrich, TCI, and Alfa Aesar (see Scheme S1 in the ESI[†] for all molecules).

9-Phenyl-9*H***-carbazole (6).** Carbazole (10 g, 59.8 mmol), iodobenzene (12.445 g, 61 mmol), copper powder (11.628 g, 183 mmol), and potassium carbonate (25.293 g, 193 mmol) were

Table 4 Electroluminescent characteristics of blue doping OLEDs

Dopant V	V^a/V	V^{b}/V	$\eta_{\rm L}{}^{b}$ /cd ${\rm A}^{-1}$	$\eta_{\mathrm{P}}{}^{b}/\mathrm{lm}~\mathrm{W}^{-1}$	$\eta_{\mathrm{ex}}{}^{b}$ (%)	CIE^b	V^c/V	$\eta_{\rm L}{}^c$ /cd A ⁻¹	$\eta_{\mathrm{P}}{}^{c}/\mathrm{lm}~\mathrm{W}^{-1}$	$\eta_{\mathrm{ex}}{}^{c}$ (%)	CIE ^c
BCzVBi 4	4.00	7.94	4.32	1.71	3.65	0.158, 0.142	10.77	4.37	1.27	3.83	0.156, 0.136
BDAVBi 3	3.80	7.42	7.36	3.12	4.62	0.158, 0.219	10.15	7.70	2.39	4.86	0.156, 0.217

dissolved in dimethylformamide (DMF) (120 mL) and stirred overnight at 140 °C under nitrogen atmosphere. After the reaction was finished, the reaction mixture was poured into the brine, washed, and the mixture was extracted by MC. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. Purification of solid residue by column chromatography (ethyl acetate (EA) : *n*-hexane = 1 : 10) gave product (8.1 g, 33 mmol, 56%). ¹H NMR (300 MHz, CDCl₃, δ): 8.12 (d, J = 7.8 Hz, 2H), 7.54–7.64 (m, 4H), 7.37–7.50 (m, 5H), 7.26–7.32 (m, 2H).

3,6-Dibromo-9-phenyl-9H-carbazole (9). To a solution of 9phenyl-9*H*-carbazole (3.44 g, 14.13 mmol) in DMF (150 mL), NBS (5.15 g, 28.97 mmol) was added slowly. The mixture was stirred overnight at room temperature. After pouring into brine, and washing, the mixture was extracted with MC. The organic extracts were dried over MgSO₄ and concentrated by rotary evaporation. Purification of solid residue by reprecipitation with methanol and tetrahydrofuran (THF) gave white powder (5.36 g, 13.36 mmol, 95%). ¹H NMR (300 MHz, CDCl₃, δ): 8.2 (s, 2H), 7.58–7.64 (d, J = 7.5 Hz, 2H), 7.48–7.53 (m, 5H), 7.23–7.26 (d, J = 7.5 Hz, 2H).

9-Phenyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (10). To a solution of 3,6-dibromo-9-phenyl-9*H*carbazole (5 g, 12.5 mmol) in anhydrous THF (100 mL) at -78 °C, 22 mL (3.17 mmol) of *n*-butyllithium (1.6 M in hexane) was added. The mixture was stirred at -78 °C for 2 h. 7.63 mL (37.4 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred overnight. The mixture was poured into water and extracted with MC. The organic extracts were washed with brine and dried over MgSO₄. The solvent was removed by rotary evaporation, and reprecipitation with methanol and THF gave product (5.15 g, 10.4 mmol, 83%). ¹H NMR (300 MHz, CDCl₃, δ): 8.7 (s, 2H), 7.82–7.86 (d, J = 8.1 Hz, 2H), 7.45–7.62 (m, 5H), 7.34–7.38 (d, J = 8.1 Hz, 2H), 1.40 (s, 24H).

3,6-di(anthracen-9-yl)-9-phenyl-9H-carbazole. P-DAC, 9-Phenyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9Hcarbazole (5.15 g, 10.4 mmol), 9-bromoanthracene (5.62 g, 21.84 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.216 g, 0.188 mmol) were added to a round-bottomed flask equipped with a reflux condenser and dissolved in 80 mL of THF. After adding 40 mL of aqueous 2 N sodium carbonate solution, the reaction mixture was heated at 85 °C for 24 h. The cooled crude mixture was poured into water and extracted with MC and dried over MgSO₄, filtered, and evaporated to yield a crude product. Flash column chromatography using CHCl₃ followed by reprecipitation with methanol and THF gave a product (3.7 g, 6.21 mmol, 60%). ¹H NMR (300 MHz, CDCl₃, δ): 8.48 (s, 2H), 8.17 (s, 2H), 8.02-8.06 (d, J = 8.4 Hz, 4H), 7.83-7.87 (d, J = 8.1 Hz, 2H), 7.76–7.80 (d, J = 8.4 Hz, 4H), 7.69–7.76 (t, J = 8.1 Hz, 2H), 7.67–7.72 (d, J = 8.4 Hz, 2H), 7.55–7.62 (t, J = 7.5 Hz, 1H), 4.48– 4.53 (d, J = 8.4 Hz, 2H), 7.40–7.47 (t, J = 8.1 Hz, 4H), 7.29–7.36 $(t, J = 8.1 \text{ Hz}, 4\text{H}); {}^{13}\text{C} \text{ NMR} (500 \text{ MHz}, \text{CDCl}_3, \delta): 131.6, 131.0,$ 130.3, 129.8, 128.5, 127.9, 127.4, 127.3, 126.5, 125.4, 125.2, 123.3, 110.0; GC-MS (FAB+) (m/z): calcd for C₄₆H₂₉N, 595.23; found,

595.23. Anal. calcd for $C_{46}H_{29}N$: C 92.74, H 4.91, N 2.35; found: C 92.58, H 4.93, N 2.32%.

Acknowledgements

This work was supported in parts by the Basic Science Research Program (CRI; RIAMIAM0209 (0417-20090011)) and WCU (World Class University) Program (R31-2008-000-10075-0) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology.

Notes and references

- 1 C. W. Tang and S. A. Van Slyke, Appl. Phys. Lett., 1987, 51, 913.
- 2 T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikeda, H. Yamaoto, F. Moriwaki and C. Hosokawa, *Dig. Tech. Pap. -Soc. Inf. Disp. Int. Symp.*, 2006, 37, 37.
- 3 S.-K. Kim, Y.-I. Park, I.-N. Kang and J.-W. Park, J. Mater. Chem., 2007, 17, 4670.
- 4 Y.-Y. Lyu, J. Kwak, O. Kwon, S.-H. Lee, D. Kim, C. Lee and K. Char, *Adv. Mater.*, 2008, **20**, 2720.
- 5 (a) D. F. O'Brien, P. E. Burrows, S. R. Forrest, B. E. Koene, D. E. Loy and M. E. Thompson, *Adv. Mater.*, 1998, **10**, 1108; (b) F. Steuber, J. Staudigel, M. Stössel, J. Simmerer, A. Winnacker, H. Spreitzer, F. Weissörtel and J. Salbeck, *Adv. Mater.*, 2000, **12**, 130.
- 6 (a) G. Klärner, M. H. Davey, W.-D. Chen, J. C. Scott and R. D. Miller, Adv. Mater., 1998, 10, 993; (b) T. Noda, H. Ogawa and Y. Shirota, Adv. Mater., 1999, 11, 283; (c) J. Thompson, R. I. R. Blyth, M. Mazzeo, M. Anni, G. Gigli and R. Cingolani, Appl. Phys. Lett., 2001, 79, 560.
- 7 C. W. Tang, S. A. Van Slyke and C. H. Chen, J. Appl. Phys., 1989, 65, 3610.
- 8 (a) J. Shi and C. W. Tang, Appl. Phys. Lett., 2002, 80, 3201; (b) Y. Kan, L. Wang, L. Duan, Y. Hu, G. Wu and Y. Qiu, Appl. Phys. Lett., 2004, 84, 1513; (c) Y.-H. Kim, H.-C. Jeong, S.-H. Kim, K. Yang and S.-K. Kwon, Adv. Funct. Mater., 2005, 15, 1799; (d) P. I. Shih, C. Y. Chuang, C. H. Chien, E. W.-G. Diau and C. F. Shu, Adv. Funct. Mater., 2007, 17, 3141; (e) S.-K. Kim, B. Yang, Y. Ma, J.-H. Lee and J.-W. Park, J. Mater. Chem., 2008, 18, 3376; (f) C.-H. Chien, C.-K. Chen, F.-M. Hsu, C.-F. Shu, P.-T. Chou and C.-H. Lai, Adv. Funct. Mater., 2009, 19, 560; (g) C.-H. Wu, C.-H. Chien, F.-M. Hsu, P.-I. Shih and C.-F. Shu, J. Mater. Chem., 2009, 19, 1464; (h) C.-J. Zheng, W.-M. Zhao, Z.-Q. Wang, D. Huang, J. Ye, X.-M. Ou, X.-H. Zhang, C.-S. Lee and S.-T. Lee, J. Mater. Chem., 2010, 20, 1560; (i) Z.-Y. Xia, Z.-Y. Zhang, J.-H. Su, Q. Zhang, K.-M. Fung, M.-K. Lam, K.-F. Li, W.-Y. Wong, K.-W. Cheah, H. Tian and C. H. Chen, J. Mater. Chem., 2010, 20, 3768.
- 9 (a) C. Hosokawa, H. Higashi, H. Nakamura and T. Kusumoto, *Appl. Phys. Lett.*, 1995, **67**, 3853; (b) J.-U. Kim, H.-B. Lee, J.-S. Shin, Y.-H. Kim, Y.-K. Joe, H.-Y. Oh, C.-G. Park and S.-K. Kwon, *Synth. Met.*, 2005, **150**, 27; (c) Y. Duan, Y. Zhao, P. Chen, J. Li, S. Liu, F. He and Y. Ma, *Appl. Phys. Lett.*, 2006, **88**, 263503.
- 10 (a) C.-C. Wu, Y.-T. Lin, K.-T. Wong, R.-T. Chen and Y.-Y. Chien, *Adv. Mater.*, 2004, 16, 61; (b) T.-C. Chao, Y.-T. Lin, C.-Y. Yang, T. S. Hung, H.-C. Chou, C.-C. Wu and K.-T. Wong, *Adv. Mater.*, 2005, 17, 992; (c) S. Tang, M. Liu, P. Lu, H. Xia, M. Li, Z. Xie, F. Shen, C. Gu, H. Wang, B. Yang and Y. Ma, *Adv. Funct. Mater.*, 2007, 17, 2869; (d) Z. Q. Gao, Z. H. Li, P. F. Xia, M. S. Wong, K. W. Cheah and C. H. Chen, *Adv. Funct. Mater.*, 2007, 17, 3194; (e) C.-C. Chi, C.-L. Chiang, S.-W. Liu, H. Yueh, C.-T. Chen and C.-T. Chen, *J. Mater. Chem.*, 2009, 19, 5561; (f) N. Cocherel, C. Poriel, L. Vignau, J.-F. Bergamini and J. R.-Berthelot, *Org. Lett.*, 2010, 12, 452; (g) S. Tao, Y. Zhou, C.-S. Lee, X. Zhang and S.-T. Lee, *Chem. Mater.*, 2010, 22, 2138; (h) A. L. Fisher, K. E. Linton, K. T. Kamtekar, C. Pearson, M. R. Bryce and M. C. Petty, *Chem. Mater.*, 2011, 23, 1640.
- (a) A. P. Kulkarni, A. P. Gifford, C. J. Tozola and S. A. Jenekhe, *Appl. Phys. Lett.*, 2005, **86**, 061106; (b) Y. Zhu, A. P. Kulkarni and S. A. Jenekhe, *Chem. Mater.*, 2005, **17**, 5225; (c) A. P. Kulkarni, X. Kong and S. A. Jenekhe, *Adv. Funct. Mater.*, 2006, **16**, 1057; (d) C. J. Tonzola, A. P. Kulkarni, A. P. Gifford, W. Kaminsky and

S. A. Jenekhe, *Adv. Funct. Mater.*, 2007, **17**, 863; (e) S. J. Lee, J. S. Park, K.-J. Yoon, Y.-I. Kim, S.-H. Jin, S. K. Kang, Y.-S. Gal, S. Kang, J. Y. Lee, J.-W. Kang, S.-H. Lee, H.-D. Park and J.-J. Kim, *Adv. Funct. Mater.*, 2008, **18**, 3922.

- 12 K.-C. Wu, P.-J. Ku, C.-S. Lin, H.-T. Shih, F.-I. Wu, M.-J. Huang, J.-J. Lin, I.-C. Chen and C.-H. Cheng, *Adv. Funct. Mater.*, 2008, 18, 67.
- 13 (a) Y. Kuwabara, H. Ogawa, H. Inada, N. Noma and Y. Shirota, Adv. Mater., 1994, 6, 677; (b) K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, Adv. Mater., 2000, 12, 1949; (c) K. R. J. Thomas, J. T. Lin, Y.-T. Tao and C.-W. Ko, J. Am. Chem. Soc., 2001, 123, 9404; (d) Y. Li, J. Ding, M. Day, Y. Tao, J. Lu and M. D'iorio, Chem. Mater., 2004, 16, 2165; (e) N. Blouin, A. Michaud and M. Leclerc, Adv. Mater., 2007, 19, 2295.
- 14 (a) Y.-H. Kim, D.-C. Shin, S.-H. Kim, C.-H. Ko, H.-S. Yu, Y.-S. Chae and S.-K. Kwon, *Adv. Mater.*, 2001, 13, 1690; (b) M.-T. Lee, H.-H. Chen, C.-H. Liao, C.-H. Tsai and C.-H. Chena, *Appl. Phys. Lett.*, 2004, 85, 3301.
- 15 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov,

- G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin,
- D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03*,
- Revision D.02, Gaussian, Inc., Wallingford, CT, 2004.
 16 J. Salbeck, N. Yu, J. Bauer, F. Weissörtel and H. Bestgen, Synth. Met., 1997, 91, 209.
- 17 J. C. de Mello, H. F. Winmann and R. H. Friend, Adv. Mater., 1997, 9, 230.
- 18 K. Brunner, A. van Dijken, H. Börner, J. J. A. M. Bastiaansen, N. M. M. Kiggen and B. M. W. Langeveld, *J. Am. Chem. Soc.*, 2004, **126**, 6035.
- 19 J. F. Ambrose and R. F. Nelson, J. Electrochem. Soc., 1968, 115, 1159.
- 20 J. F. Ambrose, L. L. Carpenter and R. F. Nelson, J. Electrochem. Soc., 1975, 122, 876.
- 21 M.-H. Tsai, H.-W. Lin, H.-C. Su, T.-H. Ke, C.-C. Wu, F.-C. Fang, Y.-L. Liao, K.-T. Wong and C.-I. Wu, Adv. Mater., 2006, 18, 1216.
- 22 M.-H. Tsai, T.-H. Ke, H.-W. Lin, C.-C. Wu, S.-F. Chiu, F.-C. Fang, Y.-L. Liao, K.-T. Wong, Y.-H. Chen and C.-I. Wu, ACS Appl. Mater. Interfaces, 2009, 1, 567.
- 23 M.-H. Tsai, Y.-H. Hong, C.-H. Chang, H.-C. Su, C.-C. Wu, A. Matoliukstyte, J. Simokaitiene, S. Grigalevicius, J. V. Grazulevicius and C.-P. Hsu, *Adv. Mater.*, 2007, **19**, 862.
- 24 S.-W. Wen, M.-T. Lee and C. H. Chen, J. Disp. Technol., 2005, 1, 90.
 25 (a) T. Watanabe, K. Nakamura, S. Kawami, Y. Fukuda, T. Tsuji, T. Wakimoto and S. Miyahuchi, Proc. SPIE-Int. Soc. Opt. Eng., 2000, 4105, 175; (b) R. C. Kwong, M. R. Nugent, L. Michalski, T. Ngo, K. Rajan, Y.-J. Tung, M. S. Weaver, T. X. Zhou, M. Hack, M. E. Thompson, S. R. Forrest and J. J. Brown, Appl. Phys. Lett., 2002, 81, 162; (c) N. Li, P. Wang, S.-L. Lai, W. Liu, C.-S. Lee, S.-T. Lee and Z. Liu, Adv. Mater., 2010, 22, 527.