# Improving the performance of phosphorescent polymer light-emitting diodes using morphology-stable carbazole-based iridium complexes<sup>†</sup>

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Received 10th April 2007, Accepted 6th June 2007 First published as an Advance Article on the web 21st June 2007 DOI: 10.1039/b705342h

A series of morphology-stable carbazole-based iridium(III) complexes with green to red emission have been prepared and characterized by elemental analysis, nuclear magnetic resonance, and mass spectroscopy. Their thermal, electrochemical, electronic absorption, and photoluminescent properties have been studied. Highly efficient polymer light-emitting devices by using these complexes as dopant emitters, both non-conjugated polymer (PVK) and conjugated polymer, polyhedral oligomeric silsesquioxane-terminated poly(9,9-dioctylfluorene) [PFO(poss)], as the host materials, have been achieved. With the device structure of ITO/PEDOT/(PFO(poss) + 30% PBD)–2 wt.% 1/Ba/Al, a maximum external quantum efficiency of 6.4% and a maximum luminous efficiency of 6.00 cd  $A^{-1}$  with red emission at 608 nm were obtained. With the device configuration of ITO/PEDOT/(PFO(poss) + 30% PBD)–4 wt.% 4/Ba/Al, a maximum external quantum efficiency of 22.4 cd  $A^{-1}$  with yellow–green emission at 544 nm were realized. The increased morphology stability of 1 and 2 imparted by the *N*-decyl long chains at the *N* atom of carbazole results in significantly better device performance than their short chain analogues 1a and 2a under identical device configurations.

#### Introduction

Phosphorescent heavy-metal complexes as emitters in organic light-emitting diodes (OLEDs) have attracted great attention because they can fully utilize both singlet and triplet excitons through the strong spin-orbital coupling of heavy-metal ions.<sup>1</sup> Phosphorescent OLEDs include vacuum-deposited smallmolecule-based devices and phosphorescent dye-doped polymer-based devices. The efficiencies of polymer light-emitting diodes (PLEDs) based on phosphorescent dyes are usually inferior to those of small-molecule-based devices. However, the advantage of ease of fabrication of PLEDs by processing the materials from solution, such as by spin coating or printing techniques, have made them attractive.<sup>2</sup> Most recently, considerable progress on PLEDs based on phosphorescent iridium complexes has been made.<sup>3</sup> For example, Gong et al.<sup>2b,c</sup> reported the high efficiency (external quantum efficiency ( $QE_{ext}$ ) = 10% ph el<sup>-1</sup>, luminous efficiency (LE) = 32 cd  $A^{-1}$ ) yellow-green phosphorescent PLED by doping tris[9,9-dihexyl-2-(pyridyl-2')fluorene] iridium(III) [Ir(DPF)<sub>3</sub>] into a blend of PVK and PBD. Jiang et al.<sup>3d</sup> reported the high efficiency (QE<sub>ext</sub> = 12% ph el<sup>-1</sup> and LE = 5.2 cd A<sup>-1</sup>) red phosphorescent PLED by incorporating iridium(III)

bis(2-phenyquinolyl- $N, C^{2'}$ ) acetylacetonate [PhqIr] into the blends of poly(9,9'-dioctylfluorene) (PFO) and PBD.

Several groups have studied the mechanism of the PLEDs based on phosphorescent complexes. They believe that the Förster energy transfer plays a minor role in achieving high device efficiency, instead that direct charge trapping plays the dominant role in electroluminescence.<sup>2b,4</sup> Moreover, a multi-layer architecture consisting of the hole-transporting (HT), the electron-transporting (ET) and the emissive layers is generally adopted to attain balanced injection and transport of holes and electrons, which are key points for a high efficiency OLED device.<sup>5</sup> Therefore, in order to fabricate high efficiency and/or simple configuration PLEDs, it would be reasonable to have the phosphorescent complexes contain structural features for optimizing charge injection and transport across the bulk.

Carbazole-based compounds have played very important roles in organic/polymeric optoelectronic materials. In organic light-emitting diodes (OLEDs), carbazole derivatives can usually be used as host materials for both small-molecule OLEDs (such as 4,4'-N,N'-dicarbazolebiphenyl, CBP) and polymer OLEDs (such as poly(vinylcarbazole), PVK) because of their high triplet energy and good hole-transporting ability.<sup>1d,6</sup> In addition, the energy levels of carbazole-based compounds can be tuned by substitution at the 3/6 or 2/7 positions due to their different electronic density.<sup>7</sup> We previously reported four novel carbazole-based Ir(III) and Pt(II) complexes, which exhibit emission from blue-green to red by altering the ligation of metal with carbon atom at the 2 or 3 position of the carbazole unit. Vacuum-deposited small-molecule-based electroluminescent devices with a configuration of ITO/NPB/CBP-dopant/BCP/AlQ3/LiF/Al (NPB = 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl;

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: TGA curves of **1–4**, PL and EL spectra of **1a** and **2a**, CIE coordinate plot for PLEDs. See DOI: 10.1039/b705342h

BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; AlQ<sub>3</sub> = tris(8-hydroxyquinoline)aluminium) perform with very high efficiencies by using these complexes as dopants.<sup>8</sup> However, the easy crystallization of these complexes due to the short alkyl chain at the *N* atom of carbazole is unfavorable for the fabrication of polymer-based devices because a crystalline dopant can not disperse well with an amorphous host polymer, which consequently gives rise to phase separation.<sup>9</sup>

Aiming to develop solution-processible phosphorescent PLEDs, we designed and synthesized four new carbazolebased iridium complexes, in which the long alkyl chain at the Natom of carbazole was introduced to prevent crystallization and improve the compatibility between the dopants and the host polymers, consequently to suppress the phase separation. In addition, the bulky ligand should also tend to diminish the aggregation of dopants. The four complexes can be divided into two types: one type is that the carbazole unit directly ligates with iridium by the C-2 or C-3 positions of carbazole, respectively; the other is that the carbazole unit does not directly bond to iridium. This provides us with access to evaluate the effect of coordinated or uncoordinated carbazole on the emission and the charge-transporting ability of these iridium complexes. By applying both non-conjugated polymer (PVK) and conjugated polymer (PFO) as host polymers for the four iridium-complex dopants, we have successfully fabricated high-performance PLEDs. The thermal, electrochemical and photophysical properties of these complexes will also be discussed.

#### **Results and discussion**

#### Synthesis and characterization

As shown in Scheme 1, two ligands, 2-pyridinyl-N-decylcarbazole (2-PyDeCz) and 3-pyridinyl-N-decylcarbazole (3-PyDeCz) were prepared from the corresponding bromosubstituted carbazole and 2-bromopyridine through the Negishi cross-coupling reaction. The other two ligands, 2-(4'-(2"-phenylpyridinyl))-*N*-(2-ethylhexyl)carbazole (2-PhPyCz) and 3-(4'-(2"-phenylpyridinyl))-N-(2-ethylhexyl)carbazole (3-PhPyCz) were prepared from the corresponding carbazole boronic acid and 2-(4-bromophenyl)pyridine via the Suzuki cross-coupling reaction. The cyclometalated iridium complexes were synthesized in two steps:<sup>10</sup> the ligands were first reacted with iridium trichloride hydrate to give the corresponding cyclometalated µ-chloro-bridged dimers, then subsequent treatment of the dimers with acetylacetone in the presence of  $Na_2CO_3$  afforded the desired complexes 1-4.

All the complexes were fully characterized by NMR, elemental analysis and mass spectroscopy. The <sup>1</sup>H NMR data of the iridium complexes reveal the symmetry in the complexes, with the iridium centers coordinated by the two cyclometalated ligands with *cis*-C,C and *trans*-N,N conformation.<sup>11</sup>

#### Thermal analysis

The thermal properties of these complexes were investigated by TGA (thermal gravimetric analysis) and DSC (differential scanning calorimetry) (Fig. 1 and Table 1). All complexes exhibit good thermal stability with 5% weight loss temperatures ranging from 328 °C to 388 °C. DSC analysis reveals the morphology of these complexes could be tuned by the ligand structures. Complex 2a with short alkyl chain at the N atom of carbazole is a crystalline solid, with no phasetransition signal from 30 to 300 °C. On the contrary, complexes 1-4 are amorphous solids, most likely due to the introduction of the long and flexible *n*-decyl or 2-ethylhexyl in the ligand frameworks.  $^{9a,12}$  1 and 2 undergo crystallization at 206 and 105 °C, followed by melting transitions at 257 and 244 °C, respectively, however, only 1 shows the glass transition at 110 °C. In contrast, both 3 and 4 with larger ligands all exhibit glass transition, with significantly higher  $T_{g}$  (140 °C for 3, and 170 °C for 4) than 1. Furthermore, no crystallization and melting transition are observed for 3 and 4 before decomposition. This suggests that 3 and 4, with long alkyl chain and bulky ligand structures, are more resistant to crystallization.

#### Electrochemistry

The electrochemical behavior of the complexes was examined using cyclic voltammetry, and the electrochemical data are given in Table 1. The four complexes all undergo a reversible one-electron oxidation wave ranging from 0.00 to 0.38 V during an anodic scan in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 2). These values fall within those of  $Ir(ppy)_2(acac)$  (ppy = 2-phenylpyridine) and other analogues.<sup>13</sup> The oxidations appearing at more positive positions may be assigned to the oxidation of ligand carbazole. A representative example for 3 is shown in Fig. 2. Cathodic sweeps in THF exhibit irreversible reduction processes. Based on the onset potentials of the oxidation and reduction, HOMO and LUMO energy levels of these complexes were estimated with regard to the energy level of ferrocene (4.8 eV below vacuum).<sup>14</sup> As shown in Table 1, the 3-position carbon of carbazole-ligated complex 1 reveals a higher HOMO and lower LUMO level than its isomeric 2-position-ligated complex 2. This electrochemical behavior is in agreement with the description of pyridine-localized LUMO and metal-involved HOMO.<sup>15</sup> The more electron-donating 3-position carbon of carbazole will destabilize the metal d-orbital when ligating to the iridium in 1, leading to a higher HOMO than 2 with the less electronic 2-position carbon bonding. Simultaneously, the connection of pyridine with carbon at the less electronic 2-position of the carbazole unit stabilizes the LUMO more than the connection at the 3-position. The two factors work together to narrow the energy gap of complex 1. Contrasting to the striking difference in energy levels between 1 and 2, the complexes 3 and 4 show almost the same HOMO and LUMO levels because their carbazole parts do not directly bond to iridium. The oxidation potentials of 3-4 raise significantly compared to 1-2, attributing to the increasing ligand size. The higher HOMO levels in 1 (-4.71 eV) and 2 (-4.86 eV) relative to 3(-5.03 eV) and 4(-5.02 eV) indicate that 1-2have lower ionization potentials than 3-4, thus have better hole-transporting abilities.<sup>5e</sup> The LUMO levels of 3-4 are similar to that of 1 and significantly lower than 2, attributing to the strong electron-donating properties of carbazole units connected at the phenyl ring of the phenylpyridine ligand.



Scheme 1 Synthesis of the complexes.

#### **Photophysical properties**

The absorption spectra of **1–4** in dichloromethane solution are shown in Fig. 3. The intense absorptions in the ultraviolet region are assigned to transitions of ligand-centered states with mostly spin-allowed  ${}^{1}\pi$ - $\pi^{*}$  characters because their energies and extinction coefficients are comparable to those of the corresponding free ligands. The absorption bands of low energy that extend to the visible region are conventionally assigned to metal-to-ligand charge-transfer bands (including  ${}^{1}MLCT$ and  ${}^{3}MLCT$ ) and  ${}^{3}\pi$ - $\pi^{*}$  transitions.  ${}^{1g,13b}$  It is noteworthy that **1** exhibits significantly lower energy absorptions (extended to *ca.* 550 nm) than the other three complexes (extended to *ca.* 500 nm).

The photoluminescence (PL) spectra of 1-4 in CH<sub>2</sub>Cl<sub>2</sub> are shown in Fig. 4. Complex 1 emits orange–red light with emission peak at 594 nm, while 2-4 emits green or yellow– green light with an emission maximum ranging from 511 to 548 nm. The notable difference of emission wavelengths between 1 and 2-4 is consistent with the discrepancy of their low energy absorptions, implying the emissions come from the triplet excited state phosphorescence. In addition, the long luminescence decay lifetimes of these complexes dispersed in PVK film that fall between 1.57 to 3.22 µs (Table 2) indicate



Fig. 1 DSC scans of 1–4.  $T_g$  = glass-transition temperature,  $T_c$  = crystallization temperature,  $T_m$  = melting temperature.



**Fig. 2** Cyclic voltammogram of **1–4** in dichloromethane solution at 298 K. As an example, the ligand-centered oxidations for **3** are shown.

that their emitting states have triplet characters. The remarkable tuning (83 nm) is observed between the linkage isomers 1 and 2 where the carbazole unit directly ligates to the iridium. Contrasting to this, the offset of emission maxima is only 8 nm between the linkage isomers 3 and 4 where the carbazole unit does not directly bond to iridium. The above alteration of emission wavelength is in good correlation with the variation of energy gap evaluated from the results of cyclic voltammetry (*vide supra*). The emission spectra of 1-2 exhibit broad and featureless characters, suggesting that the lowest excited triplet states of these complexes are likely to be dominated by the



Fig. 3 Normalized absorption spectra of 1-4 in dichloromethane solution.



Fig. 4 Normalized PL spectra of 1-4 in dichloromethane solution.

<sup>3</sup>MLCT excited state. Differently, the emission spectra of **3–4** show vibrational fine structures, indicating that these complexes emit from a mixed <sup>3</sup>MLCT $^{-3}\pi$ - $\pi$ \* state with more  $^{3}\pi$ - $\pi$ \* character than those in **1–2**, owing to the increasing ligand size. <sup>1g,16</sup>

#### Polymer light-emitting devices

To evaluate the electroluminescent performance of these iridium complexes in PLEDs, the single-active-layer devices using them as dopant emitters were fabricated with both non-conjugated polymer (PVK) and conjugated polymer,

Table 1 Thermal and electrochemical data for the complexes

| Complex | $T_{\rm d}{}^a/{}^{\circ}{\rm C}$ | Phase-transition temperature/°C $(T_g/T_c/T_m)^b$ | $E_{1/2}^{\text{ox}}/\text{V}^c$ | HOMO/eV <sup>d</sup> | LUMO/eV <sup>e</sup> | Eg/eV <sup>f</sup> |
|---------|-----------------------------------|---|----------------------------------|----------------------|----------------------|--------------------|
| 1       | 351                               | 110/206/257                                       | 0.00                             | -4.71                | -2.31                | 2.40               |
| 3       | 328<br>375                        | /105/244<br>140//                                 | 0.15<br>0.34                     | -4.86<br>-5.03       | -2.04<br>-2.35       | 2.82<br>2.68       |
| 4       | 388                               | 167//   | 0.38                             | -5.02                | -2.38                | 2.54               |

<sup>*a*</sup>  $T_d$  = Temperature at which 5% weight of sample is lost. <sup>*b*</sup>  $T_g$  = glass-transition temperature;  $T_c$  = crystallization temperature;  $T_m$  = melting temperature. <sup>*c*</sup> Oxidation potential *versus* Fc/Fc<sup>+</sup>. <sup>*d*</sup> Determined from the onset of oxidation potentials. <sup>*e*</sup> Determined from the onset of reduction potential. <sup>*f*</sup> Determined from the difference between HOMO and LUMO levels.

| Complex                  | $\lambda_{\rm abs}/{\rm nm} \ (\log \varepsilon)^a$      | $\lambda_{\rm em}/{\rm nm}^a$ | $arPsi^b$     | $\tau/\mu s^c$ | $\lambda_{\rm EL}/{\rm nm}^d$ | CIE $(x, y)^d$    |
|--------------------------|--|-------------------------------|---------------|----------------|-------------------------------|-------------------|
| 1                        | 289 (5.0), 344 (5.0), 478 (3.8), 518 (3.9)               | 594                           | 0.24          | 3.22           | 608                           | 0.62, 0.38        |
| 2                        | 323 (5.2), 420 (4.0), 453 (3.9)                          | 511                           | 0.31          | 1.57           | 524                           | 0.35, 0.62        |
| 3                        | 300 (1.9), 341 (1.9), 450 (1.0)                          | 548                           | 0.26          | 3.04           | 554 (592)                     | 0.41, 0.57        |
| 4                        | 269 (3.4), 332 (2.7), 454 (0.9)                          | 540                           | 0.32          | 2.87           | 544 (582)                     | 0.38, 0.60        |
| <sup>a</sup> Measured in | n dichloromethane at 298 K. <sup>b</sup> Measured in deg | assed dichloromet             | hane solution | by integrating | sphere. <sup>c</sup> Phospho  | rescence lifetime |
| of <b>1–4</b> disper     | sed in PVK film <sup>d</sup> Measured from PLEDs         |                               |               | , , ,          |                               |                   |

 Table 2
 Photophysical data for complexes

polyhedral oligomeric silsesquioxane-terminated poly(9,9'-dioctylfluorene) [PFO(poss)], as the host materials.

Fig. 5a shows the device configurations in which PVK acted as a host material for the complexes. When PFO acted as host material, an additional layer of PVK was used on the top of PEDOT–PSS as a hole-injection layer because PFO(poss) has a HOMO level at -5.77 eV (Fig. 5b). In all the devices, PBD was blended into the host material to increase the electrontransporting ability with concentration of 40 wt.% and 30 wt.% in PVK and PFO(poss), respectively. The doping concentration of iridium complexes varied from 2–4 wt.% in each type of devices.

The devices based on 1 exhibit red emissions at 608 nm with CIE (Commission Internationale de l'Eclairage ) coordinates of (0.62, 0.38), and those based on 2 show green emission at



Fig. 5 The configuration of devices (a) and (b), as well as the molecular structures of the host.

524 nm with CIE coordinates of (0.35, 0.62). The two emission peaks display bathochromic shifts of 13 and 14 nm, respectively, relative to their PL emissions in dichloromethane solution (Table 2). The emission maxima of EL devices based on **3** and **4** show a little red-shifts compared to their PL, however, the intensities of the lower energy shoulders observed in the solution PL spectra significantly increased in the EL devices (Fig. 6).

Fig. 7 shows the external quantum efficiency ( $QE_{ext}$ ) and luminance as a function of current density (J) for all the devices. Table 3 summarizes the operating conditions and the characteristics of these devices. For red-emitting complex 1, the devices with 2 wt.% doping concentration display better performances than those with 4 wt.% doping level where the PVK or PFO(poss) is applied as the host polymer. The best performance was achieved in the device based on 2 wt.% iridium complex doping into PFO-PBD(30 wt.%), in which a maximum brightness of 6402 cd m<sup>-2</sup> at J = 224 mA cm<sup>-2</sup>, a maximum external quantum efficiency of 6.4% and a luminance efficiency (LE) of 6.00 cd  $A^{-1}$  at  $J = 14 \text{ mA cm}^{-2}$ were obtained. For green- or yellow-green-emitting complexes 2-4, the devices with 4 wt.% doping concentration exhibit significantly better performances than those with 2 wt.% doping ratio where the PVK or PFO(poss) hosts the phosphorescent complexes. This phenomenon suggests that the devices with red-emitting complex as phosphorescent dyes are easier to get concentration saturation than those with green- or yellow-green-emitting complexes. The devices with 4 wt.% iridium complexes 2-4 doping exhibited maximum QEext in the range of 9.4 to 9.9%, maximum LE ranging from 21.2 to 22.4 cd  $A^{-1}$ , and maximum brightness between 11 845



Fig. 6 EL spectra of PLEDs using the iridium complexes as dopants.



Fig. 7 The luminance and external quantum efficiency versus current density of PLED devices using complex 1 (a), 2 (b), 3 (c), and 4 (d) as phosphorescent dopant.

and 18 730 cd  $m^{-2}$ . These performance data are amongst the best green- and yellow-green-emitting PLEDs based on phosphorescent dyes under similar device configurations.<sup>2b,3f,17</sup> When evaluating the device with different host polymers, the devices with PFO(poss) as host material reveal comparable or even better performance than those with PVK as host at the same doping concentration. In most work, the conjugated polymer-hosted phosphorescent PLEDs generally have lower quantum efficiencies than non-conjugated polymer, PVK,<sup>2</sup> because of phosphorescence quenching by conjugated polymers with a low-energy triplet state.<sup>18</sup> We previously reported that high-efficiency red-phosphorescent PLEDs can be achieved with both non-conjugated polymers and conjugated polymers as the host materials doped with iridium(III) bis(2-phenylquinolyl- $N, C^{2'}$ ) acetylactonate.<sup>3d</sup> Here we demonstrated that green-, and yellow-green-emitting iridium complexes could also be compatible with both non-conjugated and conjugated host polymers for highly efficient PLEDs. This implies that host quenching is only one of the important factors limiting emission efficiency if the triplet energy level of PFO(poss) is not significantly different from that of PFO homopolymer ( $\sim 2.1 \text{ eV}$ ).<sup>18</sup> In addition, as proposed by Sudhakar *et al.*,<sup>18</sup> the phosphorescent quenching rate might be reduced in the solid state due to reduced intermolecular interactions between host and guest molecules in the solid film.

For comparison, the devices based on complexes 1a and 2a with short alkyl chains at the N atom of carbazole were also fabricated. The PL and EL spectra of 1a and 2a are almost the same with their analogues 1 and 2 (see ESI,† Fig. S2 and S3), respectively, indicating that the lengths of the alkyl chains have no effect on the emission energy. The external quantum efficiency and luminance versus current density for the comparative devices are shown in Fig. 8. It is obvious that the device performance based on 1 and 2 are significantly better than their short chain analogues 1a and 2a under the increased solubility and morphology stability of 1 and 2 imparted by long chains favor the formation of homogeneous film, and improve the compatibility between the dopants and the host polymer PVK, resulting in high device performance.

|                                       | 1a<br>2 wt.%<br>PVK | 1              |               |               | 2a            | 2             |               |               |               |               |
|---------------------------------------|---------------------|----------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
|                                       |                     | 2 wt.%<br>PFO  | 4 wt.%<br>PFO | 2 wt.%<br>PVK | 4 wt.%<br>PVK | 4 wt.%<br>PVK | 2 wt.%<br>PFO | 4 wt.%<br>PFO | 2 wt.%<br>PVK | 4 wt.%<br>PVK |
| $J/\mathrm{mA~cm}^{-2a}$              | 15.2                | 14.3           | 2.10          | 3.20          | 40.0          | 3.90          | 0.28          | 2.70          | 5.55          | 2.50          |
| $L/cd m^{-2a}$                        | 373                 | 863            | 100           | 202           | 1451          | 563           | 31.2          | 578           | 473           | 534           |
| LE <sub>max</sub> /cd A <sup>-1</sup> | 2.40                | 6.00           | 4.76          | 6.31          | 3.63          | 14.3          | 11.1          | 21.4          | 8.52          | 21.4          |
| QE <sub>ext.max</sub> (%)             | 3.60                | 6.42           | 4.99          | 6.59          | 3.75          | 7.40          | 6.43          | 9.56          | 4.83          | 9.60          |
| $J/mA \text{ cm}^{-2b}$               | 149                 | 224.3          | 74.5          | 76.9          | 45.1          | 134           | 169.9         | 71.7          | 88.4          | 72.2          |
| $L_{\rm max}/{\rm cd}~{\rm m}^{-2}$   | 2088                | 6402           | 2090          | 3409          | 1633          | 9899          | 9077          | 9367          | 5717          | 11845         |
| $LE/cd A^{-1b}$                       | 1.40                | 2.85           | 2.80          | 4.43          | 3.62          | 7.40          | 5.34          | 13.1          | 6.47          | 16.4          |
| $QE_{ext}$ (%) <sup>b</sup>           | 2.10                | 3.06           | 2.91          | 4.59          | 3.75          | 3.80          | 3.03          | 5.93          | 3.66          | 7.44          |
|                                       |                     | 3              |               |               |               |               | 4             |               |               |               |
|                                       |                     | 2 wt.%<br>PFO  | 4 wt.%<br>PFO | 2 wt.%<br>PVK | 4 wt.%<br>PVK |               | 2 wt.%<br>PFO | 4 wt.%<br>PFO | 2 wt.%<br>PVK | 4 wt.%<br>PVK |
| $J/mA \text{ cm}^{-2a}$               |                     | 5.30           | 10.5          | 18.5          | 23.0          |               | 9.30          | 8.10          | 13.3          | 25.0          |
| L/cd m - 2a                           |                     | 958            | 2115          | 2503          | 4884          |               | 1949          | 1812          | 2053          | 4666          |
| LE <sub>max</sub> /cd A <sup>-1</sup> |                     | 18.1           | 20.1          | 13.5          | 21.2          |               | 21.0          | 22.4          | 15.4          | 18.6          |
| OE <sub>ext max</sub> (%)             |                     | 8.00           | 8.94          | 5.99          | 9.41          |               | 9.30          | 9.90          | 6.80          | 8.30          |
| $J/mA \text{ cm}^{-2b}$               |                     | 197            | 178           | 187           | 202           |               | 196           | 191           | 142           | 198           |
| $L_{\rm max}/{\rm cd}~{\rm m}^{-2}$   |                     | 13644          | 16539         | 11816         | 18680         |               | 19692         | 18730         | 10673         | 16734         |
| $LE/cd A^{-1b}$                       |                     | 6.90           | 9.30          | 6.30          | 9.20          |               | 10.0          | 9.80          | 7.50          | 8.50          |
| $QE_{ext}$ (%) <sup>b</sup>           |                     | 3.06           | 4.12          | 2.78          | 4.07          |               | 4.50          | 4.30          | 3.30          | 3.70          |
| <sup><i>a</i></sup> The data at ma    | aximum QE           | ext. b The dat | a at maximun  | n brightness. |               |               |               |               |               |               |

Table 3 Summary of the fabrication conditions and the characteristics of the PLEDs



Fig. 8 Comparison of the luminance and external quantum efficiency *versus* current density of devices using 1a, 1, 2a, and 2 as dopant.

#### Conclusion

In conclusion, we have developed a series of morphologystable carbazole-based iridium complexes for solution-processible phosphorescent PLEDs. For the linkage isomeric complexes with the carbazole carbon directly ligated with iridium, their energy levels and emissions can be significantly tuned, whereas these values show only a little difference between the linkage isomeric complexes with the carbazole carbon not bonded to iridium. Further more, the former shows better hole-transporting ability than the latter. By introducing the long and bulky alkyl chain in the ligand frame, the morphology stability of the complexes and the compatibility between the complexes and polymer host can be improved; as a consequence, the PLEDs using these complexes as emitters display better device performance than those based on their short chain analogues. We also note that the highly efficient PLEDs with green to red emission can be achieved where the non-conjugated PVK or conjugated PFO(poss) was applied as the host matrixes.

#### Experimental

#### General information

2-Bromo-N-decyl-carbazole and 3-bromo-N-decyl-carbazole were synthesized according to the literature procedures.<sup>19</sup> The preparation of the complexes 1a and 2a was reported in our previous paper.<sup>8</sup> PFO(poss) was kindly supplied by American Dye Sources Inc. PBD was purchased from Aldrich. 2-Bromopyridine, n-butyllithium, anhydrous zinc chloride and tetrakis(triphenylphosphine)palladium were purchased from Acros. Solvents were dried using standard procedures. <sup>1</sup>H NMR spectra were measured on a MECUYR-VX300 spectrometer in CDCl<sub>3</sub> using tetramethylsilane as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. Mass spectra were measured on a ZAB 3F-HF mass spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu 160A recording spectrophotometer. PL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields were measured from dilute dichloromethane solutions of complexes 1–4 (ca.  $10^{-6}$  mol L<sup>-1</sup>) by an absoluted method using the Edinburgh Instruments integrating sphere excitated with a Xe lamp. The photoluminescence lifetimes was recorded on a single-photon-counting spectrometer from Edinburgh Instruments (FLS920) with a hydrogen-filled pulse lamp as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrumentresponse function using the software package provided by

Edinburgh Instruments. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10 °C min<sup>-1</sup> from 30 to 300 °C under argon. Thermogravimetric analysis (TGA) was undertaken with a NETZSCH STA 449C instrument. The thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 20 °C min<sup>-1</sup> from 25 to 600 °C.

#### Electrochemistry

Cyclic voltammetry (CV) was carried out in nitrogen-purged anhydrous THF or dichloromethane at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudo-reference electrode with ferrocenium–ferrocene (Fc<sup>+</sup>/Fc) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s<sup>-1</sup>. Formal potentials are calculated as the average of cyclic voltammetric anodic and cathodic peaks.

#### Compounds

Synthesis of 2-pyridinyl-N-decylcarbazole (2-PyDeCz). 2-Bromopyridine (0.47 ml, 4.7 mmol) was added to 7.5 ml of anhydrous THF in a Schlenk tube filled with argon at -78 °C. n-BuLi (2.5 M in hexane, 4.0 ml, 9.4 mmol) was added dropwise. After this mixture had been stirred at -78 °C for 45 min, a solution of anhydrous ZnCl<sub>2</sub> (1.28 g, 9.4 mmol) in 15 ml of THF was added slowly and stirred for 1.5 h at room temperature. Then a solution of 2-bromo-N-decyl-carbazole (1.79 g, 4.6 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (55.3 mg, 0.05 mmol) in 15 ml of THF was added, and the reaction mixture was refluxed under an argon atmosphere for 16 h. After the mixture had cooled to room temperature, a solution of NH<sub>4</sub>Cl (2.2 g, 41 mmol) in water (10 ml) was added. Then the mixture was stirred for 15 min and extracted several times with CH<sub>2</sub>Cl<sub>2</sub>, and dried over anhydrous Na2SO4. The pure product was obtained after column chromatography on silica gel using chloroform-petroleum ether (1 : 10) as eluent. Yield: 65%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.74 (d, J = 4.5 Hz, 1H), 8.18-8.11 (m, 2H), 7.88-7.78 (m, 4H), 7.48-7.25 (m, 2H), 7.25 (t, J = 7.5 Hz, 2H), 4.32 (t, J = 7.5 Hz, 2H), 1.93 (m, 2H), 1.46-1.25 (m, 14H), 0.89 (t, J = 6.3 Hz, 3H).

Synthesis of 3-pyridinyl-*N*-decylcarbazole (3-PyDeCz). Ligand of 3-PyCz was synthesized according to the same method as 1a except using 3-bromo-*N*-decyl-carbazole to replace 2-bromo-*N*-decylcarbazole. Yield: 32%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.74 (d, *J* = 4.5 Hz, 1H), 8.19–8.11 (m, 1.5 Hz, 2H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.80 (t, *J* = 7.1 Hz, 1H), 7.51–7.40 (m, 4H), 7.23–7.18 (m, 2H), 4.35 (t, *J* = 3.9 Hz, 2H), 1.89 (m, 2H), 1.35–1.23 (m, 14H), 0.88 (t, *J* = 4.5 Hz, 3H).

Synthesis of 2-(4'-(2"-phenylpyridinyl))-*N*-(2-ethylhexyl)carbazole (2-PhPyCz). A mixture of 2-boronic-*N*-(2-ethylhexyl)carbazole (0.536 g, 1.67 mmol), 2-(4-bromophenyl)pyridine (0.356 g, 1.52 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (3% mmol, 10 mg) and Na<sub>2</sub>CO<sub>3</sub> (15 mmol, 1.59 g) in 15 ml of toluene and 5 ml of distilled water was stirred at 70 °C for 24 h. After reaction, the resulting mixture was poured into water and extracted with anhydrous ethyl ether. The crude product was purified by chromatography using dichloromethane–petroleum ether (1 : 1) as eluent. Yield: 46%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.73 (d, *J* = 4.8 Hz, 1H), 8.13 (t, *J* = 8.4 Hz, 4H), 7.85–7.75 (m, 4H), 7.63 (s, 1H), 7.55–7.39 (m, 3H), 7.21 (m, 2H), 4.23 (d, *J* = 6.0 Hz, 2H), 2.12 (m, 1H), 1.27–1.43 (m, 8H), 0.85–0.96 (m, 6H).

Synthesis of 3-(4'-(2"-phenylpyridinyl))-*N*-(2-ethylhexyl)carbazole (3-PhPyCz). Ligand of 3-PhPyCz was synthesized according to the same method as 2-PhPyC except using 3-boronic-*N*-(2-ethylhexyl)carbazole to replace 2-boronic-*N*-(2-ethylhexyl)carbazole. Yield: 73%. <sup>1</sup>H NMR(CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.73 (d, J = 4.2 Hz, 1H), 8.38 (s, 1H), 8.18 (d, J = 7.8 Hz, 1H), 8.13 (d, J = 8.4 Hz, 2H), 7.86–7.77 (m, 6H), 7.51–7.40 (m, 2H), 7.28–7.24 (m, 2H), 4.20 (d, J = 5.4 Hz, 2H), 2.10 (m, 1H), 1.30–1.40 (m, 8H), 0.86–0.96 (m, 6H).

Synthesis of complexes. A mixture of ligand (1.42 mmol),  $IrCl_3 \cdot 3H_2O$  (0.21 g, 0.59 mmol), 2-ethoxyethanol (12 ml) and distilled water (4 ml) was stirred under argon at 120 °C for 24 h. Cooled to room temperature, then the precipitate was collected by filtration and washed with water, ethanol and hexane successively, and then dried in vacuum to give  $\mu$ -chlorobridged cyclometallated Ir(III) dimer. Then the dimer complex (0.08 mmol), acetylacetone (0.24 mmol) and Na<sub>2</sub>CO<sub>3</sub> (86 mg, 0.8 mmol) were dissolved in 2-ethoxyethanol (8 ml), and the mixture was refluxed under argon at 100 °C for 16 h. After cooling to room temperature, the precipitate was filtered off and washed with water, ethanol and hexane. The crude product was flash chromatographed through a silica column using CH<sub>2</sub>Cl<sub>2</sub> as eluent to afford the desired iridium complex.

**Ir(2-PyDeCz)<sub>2</sub>(acac)** (1). Yield: 58%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.63 (d, J = 5.4 Hz, 2H), 8.03 (d, J = 8.1 Hz, 2H), 7.80 (t, J = 8.1 Hz, 2H), 7.60 (d, J = 7.2 Hz, 4H), 7.20–7.09 (m, 4H), 6.93–6.85 (m, 6H), 5.23 (s, 1H), 4.65 (t, J = 7.2 Hz, 4H), 1.79 (s, 6H), 1.31–1.22 (m, 32H), 0.85 (t, J = 6.3 Hz, 6H). Anal. Calcd for C<sub>59</sub>H<sub>69</sub>IrN<sub>4</sub>O<sub>2</sub> (%): C 66.95, H 6.57, N 5.29; Found: C 66.42, H 6.77, N 4.78. MS (FAB): *m/z* 1058 (M<sup>+</sup>).

**Ir(3-PyDeCz)<sub>2</sub>(acac)** (2). Yield: 53%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.56 (d, *J* = 5.7 Hz, 2H), 8.22 (d, *J* = 6.3 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.24–7.20 (m, 4H), 7.11–6.99 (m, 6H), 5.25 (s, 1H), 3.83 (t, *J* = 7.2 Hz, 4H), 1.82 (s, 6H), 1.26–1.16 (m, 32H), 0.90 (t, *J* = 6.0 Hz, 6H). Anal. Calcd for C<sub>59</sub>H<sub>69</sub>IrN<sub>4</sub>O<sub>2</sub> (%): C 66.95, H 6.57, N 5.29; Found: C 66.38, H 6.51, N 4.77. MS (FAB): *m/z* 1058 (M<sup>+</sup>).

**Ir(2-PhPyCz)<sub>2</sub>(acac)** (3). Yield: 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.62 (d, J = 5.4 Hz, 2H), 7.97 ~ 8.05 (m, 4H), 7.9 (d, J = 5.1 Hz, 2H), 7.75 (t, J = 7.2 Hz, 2H), 7.65 (d,

 $J = 5.1 \text{ Hz}, 2\text{H}, 7.34-7.42 \text{ (m, 6H)}, 7.14-7.22 \text{ (m, 8H)}, 6.68 \text{ (s, 2H)}, 5.27 \text{ (s, 1H)}, 4.11 \text{ (d, } J = 3.9 \text{ Hz}, 4\text{H}), 2.03 \text{ (m, 2H)}, 1.85 \text{ (s, 6H)}, 1.26-1.37 \text{ (m, 16H)}, 0.86-0.92 \text{ (m, 12H)}. \text{ Anal. Calcd for } C_{67}\text{H}_{69}\text{IrN}_4\text{O}_2 \text{ (\%)}: \text{ C } 69.70, \text{ H } 6.02, \text{ N } 4.85; \text{ Found: C } 69.22, \text{ H } 6.35, \text{ N } 4.93. \text{ MS } \text{ (FAB): } m/z \text{ 1055 } \text{ (M}^+ - \text{acac)}.$ 

**Ir**(3-PhPyCz)<sub>2</sub>(acac) (4). Yield: 74%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ [ppm]: 8.55 (d, J = 5.4 Hz, 2H ), 8.05–7.99 (m, 4H), 7.83 (d, J = 5.4 Hz, 2H), 7.75 (t, J = 7.8 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.40–7.48 (m, 6H), 7.36 (d, J = 8.1 Hz, 2H), 7.15–7.20 (m, 6H), 6.57 (s, 2H ), 5.19 (s, 1H ), 4.04 (d, J = 3.6 Hz, 4H), 1.97 (m, 2H), 1.76 (s, 6H), 1.18–1.27 (m, 16H), 0.77–0.85 (m, 12H ). Anal. Calcd for C<sub>67</sub>H<sub>69</sub>IrN<sub>4</sub>O<sub>2</sub> (%): C 69.70, H 6.02, N 4.85; Found C 69.79, H 6.41, N 4.98. MS (FAB): m/z 1055 (M<sup>+</sup> – acac).

#### **PLED** Fabrication and measurements

The device configuration was ITO/PEDOT(40 nm)/(PVK + 40% PBD)-Ir-complex (80 nm)/Ba(4 nm)/Al(120 nm) and ITO/ PEDOT(40 nm)/PVK(40 nm)/(PFO(poss) + 30% PBD)-Ircomplex (80 nm)/Ba(4 nm)/Al(120 nm). The fabrication of electrophosphorescent devices followed our previous procedure.<sup>3d</sup> A 40 nm-thick layer of poly(ethylenedioxythiophene)poly(styrene sulfonic acid) (PEDOT-PSS) was spin-cast onto pre-cleaned ITO-glass substrates. A mixture of Ir-complex with host was spin-cast from a chlorobenzene solution (for PVK + PBD) and *p*-xylene-chlorobenzene = 7 : 3 (for PFO(poss) + PBD). The deposition speed and the thickness of the barium and aluminium layers were monitored with a thickness-rate meter model STM-100 (Sycon Instrument, Inc.). Device fabrication was carried out in a controlled atmosphere dry-box (Vacuum Atmosphere Co.) under N<sub>2</sub> circulation. Current density(I)-voltage(V)-luminance(L) data were collected using a Keithley 236 source measurement unit and a calibrated silicon photodiode. External EL quantum efficiencies (QEext) were obtained by measuring the total light output in all directions in an integrating sphere (IS-080, Labsphere). The luminance (cd m<sup>-2</sup>) and luminous efficiency  $(cd A^{-1})$  were measured by a silicon photodiode and calibrated using a PR-705 SpectraScan spectrophotometer (Photo Research). Electroluminescence spectra were recorded using a CCD spectrophotometer (Instaspec 4. Oriel).

#### Acknowledgements

We thank the National Natural Science Foundation of China (project no. 20474047 and 20371036) and the Program for New Century Excellent Talents in University, the Ministry of Education of China for financial support.

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