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# Bipolar Heteroleptic Green Iridium Dendrimers Containing Oligocarbazole and Oxadiazole Dendrons for Bright and Efficient Nondoped Electrophosphorescent Devices

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Abstract: Bipolar heteroleptic green light-emitting iridium (Ir) dendrimers G(OXD) and G(DOXD) have been designed and synthesized under mild conditions in high yields, in which the first C^N and second O^O ligands are functionalized with oligocarbazole- and oxadiazole-based dendrons, respectively. To avoid affecting the optical properties of the emissive iridium core, all the functional moieties are attached to the ligands through a flexible spacer. Compared with the unipolar dendrimer G(acac), dendrimers G(OXD) and G-(DOXD) exhibit the close emission maxima of 511-512 nm and photoluminescence quantum yield of 0.39-0.40 in a solution of toluene. Moreover, on going from **G(acac)** to **G(OXD)** and **G(DOXD)**, we have found that the introduction of oxadiazole fragments decreases the lowest unoccupied molecular orbital (LUMO) energy levels to facilitate the electron injection and electron transporting, while their highest occupied molecular orbital (HOMO) energy levels remain unchanged. This means that, we can individually tune the HOMO and LUMO energy levels based on the heteroleptic structure to ensure the relative independence be-

**Keywords:** bipolar • dendrimers • iridium • nondoped devices • heter-oleptic ligands

## Introduction

Organic light-emitting diodes (OLEDs) based on phosphorescent dyes have entered the commercial stage owing to their prominent market share in large-area flat-panel-display technology,<sup>[1]</sup> as they can harvest both singlet and triplet excitons to realize a theoretical internal quantum efficiency of 100%.<sup>[2]</sup> Among these dyes, iridium (Ir) complexes are extensively studied because of their high photoluminescence quantum yields and appropriate exciton lifetimes.<sup>[3]</sup> To achieve high performance, doped electrophosphorescent devices are fabricated, in which the iridium complexes are dispersed into the host matrix.<sup>[4]</sup> Although this physical blending technique is usually effective, the inevitable phase segregation could deteriorate the device stability and lifetime.<sup>[5]</sup> To solve this problem, nondoped devices are employed, in which the host is no longer needed in the EML.

With this aim in mind, the iridium complexes are covalently attached to the polymeric host to form electrophosphorescent polymers.<sup>[6]</sup> Unfortunately, the device efficiency is still much lower than that of the corresponding physical blending counterparts. As an alternative, bifunctional phosphorescent iridium dendrimers with a "self-host" feature have been recently developed by our research group.<sup>[7–9]</sup> Here oligocarbazole is incorporated into the emissive iridi-

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Graduate School of Chinese Academy of Sciences Beijing 100039 (P. R. China) with **G(DOXD)** as the EML gives a maximum luminous efficiency of 25.5 cd A<sup>-1</sup> ( $\eta_{ext}$ : 7.4%) and a brightness of 33 880 cd m<sup>-2</sup>. In comparison to **G(acac)** (17.2 cd A<sup>-1</sup>, 17680 cd m<sup>-2</sup>), both the efficiency and brightness are improved by about 1.5 and 2 times, respectively. These state-of-the-art performances indicate the potential of these bipolar heteroleptic iridium dendrimers as solution-processible emitting materials for nondoped device applications.

um core as the dendron shell, and it plays the same role as the host. Through tuning the dendron generation, we obtained a maximum luminous efficiency of 34.7 cd  $A^{-1}$  for the second generation green dendrimer G2 based on nondoped device configuration.<sup>[7]</sup> Moreover, by increasing the number of dendrons, the efficiency was further improved to 45.7 cd  $A^{-1}$ , which is close to that of the doped devices.<sup>[9]</sup> However, the synthesis of all the above-mentioned homoleptic iridium dendrimers required high reaction temperatures and the yields were very low, especially for higher generation dendrimers, for example, G2 was obtained in only 8% yield.<sup>[7]</sup> In contrast, according to the literature,<sup>[10]</sup> the heteroleptic dendrimers were easily synthesized under mild conditions with high yields. By considering the large-scale preparation and the practical application, it is highly desirable to develop heteroleptic iridium dendrimers suitable for nondoped devices.

In addition, bipolar hosts containing suitable electron-rich and electron-deficient moieties in one molecule have been intensively studied by several groups,<sup>[11]</sup> as they are believed to be beneficial to maintain the charge balance in the emissive layer so as to improve the device efficiency accompanied by a small roll-off. With the same concept, bipolar phosphorescent heavy-metal complexes, such as Pt<sup>II</sup>, Ru<sup>II</sup>, and Re<sup>I</sup> complexes,<sup>[12,13]</sup> are also explored. However, until now few endeavors have been paid to the development of bipolar iridium dendrimers. In this study, we report the effective synthesis of novel bipolar heteroleptic green iridium dendrimers and their application in nondoped electrophosphorescent devices. For the bipolar dendrimer G(DOXD), a promising efficiency as high as  $25.5 \text{ cd } \text{A}^{-1}$  together with a high brightness of 33880 cd m<sup>-2</sup> is realized. Compared to that of the corresponding unipolar dendrimer G(acac)  $(17.2 \text{ cd } \text{A}^{-1}, 17680 \text{ cd } \text{m}^{-2})$ , both the efficiency and the brightness are improved by about 1.5 and 2 times, respectively.

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tween the hole and electron in the

emitting layer (EML), which is a favor-

able feature for bipolar optoelectronic

materials. As a result, a bilayer non-

doped electrophosphorescent device

# **Results and Discussion**

# Synthesis

Scheme 1 depicts the functionalization procedure of the first C^N and second O^O ligands. As for the first C^N ligand, the second generation carbazole dendron 2 was linked to 2phenyl-1H-benzoimidazole (1) through a flexible spacer, which was prepared by condensation of ortho-phenylenediamine with benzoic acid.<sup>[14]</sup> As for the second O^O ligand, the oxadiazole moiety was introduced to one or both ends of acetylacetone through a reported modular synthetic methodology.<sup>[15]</sup> It is noteworthy that such functional entities and ligands are combined through a nonconjugated bond so as to weaken the electronic coupling between them, and thus retain the optical property of the iridium complex core. Furthermore, according to the literature,<sup>[16]</sup> the emission is mainly from the metal to the first C^N ligand transitions for the heteroleptic iridium complexes. This means that this heteroleptic dendritic skeleton, in which the hole- and electrontransporting units are individually incorporated into the different ligands, can ensure the relative independence between the hole and electron transporting in the emitting layer. This feature is very favorable, especially for the bipolar optoelectronic materials.

The synthesis of the bipolar heteroleptic dendrimers **G**-(**OXD**) and **G**(**DOXD**) was carried out in a modified twostep approach, as illustrated in Scheme 2.  $IrCl_3 \cdot nH_2O$  was first treated with an excess of the first ligand **LG** to form a chloride-bridged dimer in a solvent mixture of 2-ethoxyethanol, water (H<sub>2</sub>O), and tetrahydrofuran (THF). In the second step, we initially tried the typical reaction conditions by using Na<sub>2</sub>CO<sub>3</sub> as the base,<sup>[17]</sup> however, we could not obtain the desired product, as the nitrogen atom in the oxadiazole ring could affect this ligation reaction. Therefore, we modified the synthetic route, as illustrated in Scheme 2. After treatment of the second ligand with one equivalent of sodium *tert*-butoxide (*t*BuONa) in a mixed solvent of ethanol and dichloromethane (DCM), the monoanion was

# Abstract in Chinese:

基于咔唑功能化的第一 C<sup>^</sup>N 配体和噁二唑功能化的第二 0<sup>°</sup>0 配体,我们设计与合成了双极异配位绿光树枝状铱配 合物 G(OXD)和 G(DOXD)。它们的合成条件温和,反应产 率高。为了不改变中心发光核的发光性质,这些功能基 团通过柔性烷基链与中心发光核相连。与单极树枝状铱 配合物 G(acac)相比, G(OXD)和 G(DOXD)表现出相似的 光物理性质:甲苯溶液中的最大发射峰位于 511-512 nm,发光效率为 0.39-0.40。研究发现,随着噁二唑树枝 的增加,配合物的 HOMO 能级保持不变,而 LUMO 能级逐 渐降低。基于 G(DOXD)的双层非掺杂器件,最大电流效率 达到了 25.5 cd A<sup>-1</sup> (外量子效率为 7.4%),最大亮度达 到了 33,880 cd m<sup>-2</sup>,分别是 G(acac)</sup>(17.2 cd A<sup>-1</sup>, 17,680 cd m<sup>-2</sup>)的 1.5 倍和 2 倍。优良的器件性能表 明,这种双极异配位树枝状铱配合物在可溶液加工型的 非掺杂器件中有着广泛的应用前景。

formed and then was successfully treated with the dimer to afford the bipolar heteroleptic dendrimers. Notably, this reaction could be performed at room temperature with a yield over 90%, which is much higher than that of the homoleptic iridium dendrimers.<sup>[18]</sup> This made it possible to produce heteroleptic iridium dendrimers with higher yields on gram scale. For comparison, the model compound G(acac) was also synthesized. Additionally, the surface of all the dendrimers was decorated with tert-butyl groups to ensure their solubility. For instance, the dendrimers were highly soluble in common organic solvents, such as chloroform, chlorobenzene, toluene, and tetrahydrofuran at room temperature. From these solutions, high-quality films could be achieved by spin-coating. Furthermore, all dendrimers were thermally stable with the decomposition temperature  $(T_d)$  as high as 332-370 °C. The structures of the dendrimers were verified by using <sup>1</sup>H NMR spectroscopy, elemental analysis, and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry.

## **Photophysical and Electrochemical Properties**

Figure 1 shows the absorption spectra in dichloromethane and the photoluminescence (PL) spectra of the iridium dendrimers in toluene, and the related photophysical properties



Figure 1. The absorption spectra  $(10^{-5} \text{ M in CH}_2\text{Cl}_2 \text{ solution})$  and the PL spectra  $(10^{-5} \text{ M in toluene solution})$  of **G(acac)** (---), **G(OXD)** (---), and **G(DOXD)** (----).

are displayed in Table 1. All of the dendrimers show two major absorption bands. The absorption bands below 330 nm are attributed to the spin-allowed ligand-centered (LC) transitions and the weak absorption shoulders in the range of 330–500 nm are assigned to the metal-to-ligand charge-transfer (MLCT) transitions of the iridium complexes. Obviously, all the dendrimers display almost identical spectral features, except for the bands around 300 nm; these bands are ascribed to oxadiazole subchromophores, the intensity of which increases gradually in the order **G**-(acac) < **G**(**DXD**).

Simultaneously, their emission maxima in toluene as well as the triplet energy levels estimated from the phosphores-



Scheme 1. Synthesis of the dendritic ligands LG, OXDacac, and DOXDacac. PPA = polyphosphoric acid.

cence spectra measured at 77 K are close to the emissive iridium core. These results demonstrate that the introduction of oligocarbazole and oxadiazole dendrons through a flexible spacer does not alter the optical property of the emissive iridium core, as discussed before. In addition, the intensity of the shoulder around 540 nm for G(DOXD) is lower than that of G(acac), indicative of a reduced interaction between emissive iridium cores. However, there is still aggregation to some degree, because a red shift of 7–9 nm from solution to film for the emission peak is observed (Table 1). Moreover, the lifetimes increase gradually with the number of oxadiazole units; this indicates the effective tuning of intermolecular interactions.

Table 1. Photophysical and Electrochemical Properties of the Dendrimers.

	$\lambda_{\rm abs}  [{\rm nm}] \; (\log  \varepsilon)^{[{\rm a}]}$	$\lambda_{\mathrm{em}}  [\mathrm{nm}] / \boldsymbol{\Phi}_{\mathrm{p}}^{\mathrm{[b]}}$	$\lambda_{em} [nm]^{[c]}$	$ au_1  [\mu s]^{[d]}$	$ au_2  [\mu s]^{[d]}$	$T_1 [\mathrm{eV}]^{[\mathrm{e}]}$	$E_{\rm g}  [{\rm eV}]^{\rm [f]}$	HOMO [eV] <sup>[g]</sup>	LUMO [eV] <sup>[h]</sup>
G(acac)	239(5.4), 268(5.1), 297(5.0), 315(4.6), 347(4.5), 414(3.8), 499(3.3)	511/0.39	520	0.06	0.32	2.44	2.43	-5.1	-1.8
G(OXD)	239(5.4), 268(5.1), 297(5.1), 314(4.6), 248(4.4), 417(3.7), 407(3.2)	512/0. 39	520	0.08	0.51	2.44	2.43	-5.1	-1.9
G(DOXD)	348(4.4), 417(3.7), 497(3.2) 239(5.4), 270(5.1), 298(5.2), 315(4.7), 348(4.4), 417(3.7), 497(3.2)	512/0.40	519	0.13	0.58	2.44	2.43	-5.1	-2.1

[a] Measured in CH<sub>2</sub>Cl<sub>2</sub> at 298 K at a concentration of  $10^{-5}$  M.  $\varepsilon$  is the absorption coefficient in the Beer–Lambert equation. [b] Measured in toluene at 298 K at a concentration of  $10^{-5}$  M and an excitation wavelength of 410 nm. [c] Neat-film data measured at 298 K. PL spectra were measured with an excitation wavelength of 409 nm. [d] Measured in solid films at 298 K in the air and the lifetimes are obtained by biexponential fit of emission decay curves. [e] Estimated from the highest energy peak of the phosphorescence spectra at 77 K. [f]  $E_g$ =The optical band gap estimated from the onset of the absorption edge. [g] HOMO = -e (4.8 V+ $E^{\text{red}}$ ), where  $E^{\text{red}}$  was taken from the onset of the oxidation potential. [h] LUMO = -e (4.8 V+ $E^{\text{red}}$ ), where  $E^{\text{red}}$  was taken from the onset of the reduction potential.

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Scheme 2. a) Synthesis of the bipolar heteroleptic dendrimers with G(DOXD) as an example; b) molecular structures of the bipolar heteroleptic dendrimers G(OXD) and G(DOXD) together with the model compound G(acac).

The electrochemical behaviors of dendrimers G(acac), G-(OXD), and G(DOXD) were examined by cyclic voltammetry (CV), and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels (Table 1) were calculated from the onset of the oxidation and reduction potential, respectively. Upon anodic sweeping in dichloromethane, as shown in Figure 2, all dendrimers showed multiple oxidation waves. The first oxidation wave located at the lowest potential was reversible, and could be assigned to the oxidation of the iridium-phenyl center. The other oxidation waves were irreversible, and were related to the peripheral carbazole-based dendrons. During the cathodic scan in acetonitrile, only irreversible reduction waves were found. In comparison to G-(acac), a new reduction wave corresponding to the oxadiazole fragment appeared toward the positive potential for G-(DOXD). As a result, on going from  $G(acac) \rightarrow G(OXD) \rightarrow$ G(DOXD), the LUMO energy level gradually decreased from -1.8 eV to -1.9 and -2.1 eV, respectively, while their HOMO energy level remained to be -5.1 eV. This observation suggests that the incorporation of an oxadiazole into

the second O^O ligand can facilitate efficient electron injection. Most importantly, it does not affect the hole injection and transporting at the same time.



Figure 2. The electrochemical spectra of **G(acac)** —, **G(OXD)** (---), and **G(DOXD)** (----), a) Measured in CH<sub>2</sub>Cl<sub>2</sub>, and b) in acetonitrile (scan rate =  $100 \text{ mV s}^{-1}$ ).

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#### **Electroluminescent Properties**

The solution-processibility and bipolar nature of the dendrimers render them suitable candidates for nondoped electrophosphorescent devices. Therefore, the single layer devices with the configuration of indium tin oxide (ITO)/ Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) (50 nm)/EML (100 nm)/Ca (10 nm)/Al (100 nm) (Structure A, Figure 3) were firstly fabricated, and



Figure 3. Schematic diagram of EL device configurations and the molecular structures of the relevant compounds used in these devices.

the device performances are listed in Table 2. Figure 4a and 4b show the current density-voltage-luminescence characteristics, and the current density dependence of the luminous efficiency together with the external quantum efficiency ( $\eta_{ext}$ ). Owing to the improved electron injection and transporting, the luminous efficiency gradually increases when **G**-(acac) is replaced with **G**(DOXD). Consequently, **G**-(DOXD) gives the best device performance among these dendrimers. A maximum luminous efficiency of 5.5 cd A<sup>-1</sup>

Table 2. Performance of the devices using the dendrimers.



Figure 4. a) The current density-voltage-luminescence characteristics and b) current density dependence of luminous efficiency as well as external quantum efficiency for devices with structure A.

and a maximum brightness of 12,730 cdm<sup>-2</sup> for **G(DOXD)** are obtained. Compared with **G(acac)** (2.8 cd A<sup>-1</sup>, 4810 cdm<sup>-2</sup>), both the efficiency and brightness are greatly enhanced due to the bipolar transporting nature. Nonetheless, we have noted that the performance is still very poor relative to the multilayer device, which may result from the large electron injection barrier (0.8 eV) between the EML and the calcium cathode (2.9 eV).<sup>[19]</sup> Therefore, studies on how to further lower the LUMO energy level of these bipolar dendrimers are under investigation, and it is beyond the focus of this article.

To optimize the nondoped device performance, bilayer devices with the configuration of ITO/PEDOT:PSS (50 nm)/

Table 2. Terrormance of the devices using the deformations.									
EML	$V_{ m turn-on} \left[ { m V}  ight]$	$B_{\rm max}  [{\rm cd}/{\rm m}^2]^{[{\rm c}]}$	$\eta_{\mathrm{l}}  [\mathrm{cd}  \mathrm{A}^{-1}]^{[\mathrm{c}]}$	$\eta_{\mathrm{ext}}  [\%]^{[\mathrm{c}]}$	$\eta_l  [\operatorname{cd} \operatorname{A}^{-1}]^{[\operatorname{d}]}$	$\eta_{\mathrm{ext}}  [\%]^{\mathrm{[d]}}$	$\lambda_{em} [nm]$	CIE [x, y]	
G(acac) <sup>[a]</sup>	5.1	4810	2.8	0.8	_	_	520	(0.38, 0.58)	
$G(OXD)^{[a]}$	5.8	8740	3.7	1.1	3.7	1.1	520	(0.37, 0.59)	
G(DOXD) <sup>[a]</sup>	5.7	12730	5.5	1.6	5.5	1.6	520	(0.35, 0.60)	
G(acac)[b]	3.5	17680	17.2	5.0	13.3	4.0	520	(0.36,0.60)	
G(OXD) <sup>[b]</sup>	4.0	26140	19.6	5.7	16.4	4.6	520	(0.34, 0.60)	
G(DOXD) <sup>[b]</sup>	4.1	33880	25.5	7.4	19.8	5.7	520	(0.34,0.60)	

[a] Device data with structure A. [b] Device data with structure B. [c] The maximum values for brightness ( $B_{max}$ ), luminous efficiency ( $\eta_i$ ), and external quantum efficiency ( $\eta_{ext}$ ). [d] Data collected at a brightness of 5000 cd m<sup>-2</sup>.

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EML (45 nm)/TPBI (60 nm)/LiF (1 nm)/Al (100 nm) (Structure B, Figure 2) were prepared, in which 1,3,5-tris(2-*N*-phenylbenzimidazolyl)-benzene (TBPI) acted as the electrontransporting and hole-blocking material. As shown in Figure 5, all these dendrimers exhibit strong green electrolu-



Figure 5. The EL spectra at a driving voltage of 9 V for devices with structure B.

minescence (EL) at about 520 nm with similar Commission Internationale de L'Eclairage (CIE) coordinates of (0.36, 0.59), (0.34, 0.60), and (0.34, 0.60) for **G(acac)**, **G(OXD)**, and **G(DOXD)**, respectively. The EL spectra are identical to their PL counterparts, thus indicating that the emission occurs from the iridium core. Furthermore, their EL spectra are independent of the applied voltages from 5 V to 14 V, and no additional emission signals from aggregates or excimers have been observed. This further proves that the "selfhost" feature makes it possible to use these multifunctional light-emitting dendrimers alone as the EML for nondoped devices.

As illustrated in Figure 6a, the turn-on voltage (at a brightness of 1 cdm<sup>-2</sup>) reduces from 5.1-5.8 V of the singlelayer devices to 3.5-4.1 V of the bilayer ones, and a decrease of approximately 1.6-1.8 V is achieved because of the insertion of an additional electron-transporting and hole-blocking layer. Similar to the single-layer devices, both the luminous efficiency and brightness of the bilayer devices are improved when G(acac) is replaced with G(DOXD). For example, the luminous efficiency and brightness of G(DOXD) are nearly 1.5 and 2 times that of G(acac), respectively. As a consequence, a maximum luminous efficiency of  $25.5 \text{ cd } \text{A}^{-1}$ , and a maximum brightness of  $33\,880$  cd m<sup>-2</sup> for G(DOXD) have been realized. Considering the mild synthetic conditions as well as the high yields, the performance of the bipolar dendrimer G(DOXD) is very promising. In particular, the efficiency still remains as high as  $19.8 \text{ cd } A^{-1}$  when the brightness increases to 5000 cdm<sup>-2</sup>, indicative of a gentle roll-off at high current density. To the best of our knowledge, this is the first report of heteroleptic bipolar iridium dendrimers being used for bright and efficient nondoped electrophosphorescent devices.



Figure 6. a) The current density-voltage-luminescence characteristics and b) current density dependence of luminous efficiency as well as external quantum efficiency for devices with structure B.

# Conclusions

In summary, we have demonstrated a novel approach, which is the integration of hole-transporting carbazole-based dendrons, electron-transporting oxadiazole-based dendrons, and an iridium complex core to form heteroleptic bipolar green dendrimers for nondoped electrophosphorescent device applications. Compared with the unipolar dendrimer **G(acac)**, both the luminous efficiency and brightness of the bipolar dendrimer **G(DOXD)** have been significantly improved. In terms of the mild synthetic conditions, high yields, the stateof-the-art luminous efficiency together with brightness, we believe that this strategy would be suitable for the design and synthesis of novel multifunctional heteroleptic bipolar iridium dendrimers for bright and efficient nondoped electrophosphorescent devices, which have an emission color other than green for use in full-color OLED displays.

# **Experimental Section**

#### Synthesis

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. All chemical reactions were carried out under an inert atmosphere. The intermediates 3,6,3",6"-tetra-kis-*tert*-butyl-9'*H*-[9,3';6',9"]tercarbazole,<sup>[20]</sup> 2-phenyl-1H-benzoimida-zole,<sup>[14]</sup> **H-OXD**, **OXDacac**, and **DOXDacac**<sup>[15]</sup> were prepared according

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to the literature procedures. TBPI was synthesized in our laboratory following a literature method.  $^{\left[ 21\right] }$ 

#### 2-phenyl-1H-benzoimidazole

A mixture of benzoic acid (12.2 g, 0.1 mol), *ortho*-phenylenediamine (10.8 g, 0.1 mol), and polyphosphoric acid (PPA, 65 mL) was heated at 210 °C for 6 h under argon, then permitted to cool to about 100 °C, and poured into rapidly stirred water (500 mL). The insoluble residue was collected by filtration, washed with water (3 × 20 mL), and reslurried in an excess of 10% sodium carbonate solution. The alkaline slurry was filtered, and the product was washed thoroughly with water and dried at 60 °C. The crude product was recrystallized from ethanol and water to obtain the pure product (14.9 g, 77%). <sup>1</sup>H NMR (300 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =12.94 (s, 11H), 8.23–8.15 (m, 2H), 7.76–7.44 (m, 5H), 7.26–7.16 ppm (m, 2H).

#### Intermediate 3

A mixture of 3,6,3",6"-tetrakis-*tert*-butyl-9'*H*-[9,3';6',9"] tercarbazole (2) (3.6 g, 5 mmol), 1,4-dibromobutane (10.8 g, 50 mmol), potassium hydroxide (2.8 g, 50 mmol), tetrabutyl ammonium bromide (0.2 g, 0.5 mmol), toluene (40 mL), and water (6 mL) was refluxed for 24 h under argon. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been completely removed, the excess 1,4-dibromobutane was distilled, then the residue was purified by column chromatography on silica gel with petroleum/ethyl acetate (12:1) as the eluent to give the product (2.5 g, 58%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.16 (s, 6H), 7.64 (s, 4H), 7.46–7.43 (m, 4H), 7.31 (d, *J*=8.7, 4H), 1.46 ppm (s, 36H).

## Ligand LG

A solution of *N*,*N*-dimethylformamide (DMF; 40 mL) and tetrahydrofuran (THF; 80 mL) was added dropwise over 20 min to a stirred mixture of 2-phenyl-1H-benzoimidazole (1.4 g, 7 mmol) and sodium hydride (1.3 g, 56 mmol). After that, the solution of intermediate **3** (6.0 g, 7 mmol) dissolved in DMF (10 mL) and THF (20 mL) was slowly added dropwise. When the addition was completed, the resulting solution was refluxed for 24 h under argon. After cooling to room temperature, the mixture was poured into water (125 mL) and extracted with DCM ( $3 \times 30$  mL). The organic extracts were washed with water and dried over anhydrous sodium sulfate. After the solvent had been completely removed, the residue was purified by column chromatography on silica gel with DCM/ ethyl acetate (30:1) as the eluent to give the product (5.2 g, 77%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  =8.17 (s, 6H), 7.89–7.86 (m, 1H), 7.69– 7.66 (m, 2H), 7.61–7.58 (m, 2H), 7.51–7.40 (m, 10H), 7.38–7.25 (m, 6H), 4.35 (s, 4H), 1.94 (s, 4H), 1.46 ppm (s, 36H).

#### Chloro-bridged iridium dimer

A mixture of LG (4.4 g, 4.4 mmol), iridium chloride trihydrate (0.7 g, 2.0 mmol), 2-ethoxyethanol (60 mL), THF (20 mL), and water (20 mL) was refluxed under argon for 48 h. After cooling to room temperature, the precipitate was collected by filtration and washed with water and ethanol. Then the crude product was purified by column chromatography on silica gel with DCM as an eluent to give the chloro-bridged iridium dimer.

## Dendrimer G(acac)

The chloro-bridged iridium dimer (480 mg, 0.11 mmol), pentane-2,4dione (**Hacac**; 45 mg, 0.44 mmol), and sodium carbonate (116 mg, 1.1 mmol) in 2-ethoxyethanol (15 mL), and CHCl<sub>3</sub> (5 mL) were refluxed under argon for 48 h. After cooling to room temperature, water was added. The mixture was extracted with DCM ( $3 \times 15$  mL), washed with water, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed, the residue was purified by column chromatography on alkaline alumina with DCM/petroleum (1:1) as an eluent to afford **G(acac)** (456 mg, 93%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.15 (s, 12 H), 7.72 (d, *J*=8.0 Hz, 2 H), 7.65 (d, *J*=8.2 Hz, 2 H), 7.57 (d, *J*= 8.3 Hz, 4H), 7.45–7.37 (m, 16 H), 7.32–7.29 (m, 10 H), 6.82 (t, *J*=6.9 Hz, 2 H), 6.57 (t, J=7.5 Hz, 2 H), 6.46 (d, J=7.5 Hz, 2 H), 5.11 (s, 1 H), 4.80 (s, 4 H), 4.44–4.29 (m, 4 H), 2.35–2.17 (m, 8 H), 1.65 (s, 6 H), 1.45 ppm (s, 72 H); Anal. Calc. for C<sub>143</sub>H<sub>147</sub>N<sub>10</sub>O<sub>2</sub>Ir: C 77.02, H 6.64, N 6.28; found: C 76.98, H 6.69, N 6.12; MALDI-TOF (*m*/*z*): 2229.1 [*M*<sup>+</sup>].

#### Dendrimer G(OXD)

A solution of sodium tert-butoxide (34 mg, 0.35 mmol) in ethanol (3 mL) was added dropwise to the stirred solution of ancillary ligand OXDacac (157 mg, 0.35 mmol) in DCM (15 mL) and ethanol (10 mL) at 0°C. After the reaction temperature returned to 25°C, the reaction was stirred for another 1 h. Then the chloro-bridged iridium dimer (0.60 g, 0.14 mmol) in DCM (8 mL) was added dropwise at room temperature. The reaction was stirred for another 2 h at room temperature before completion. The mixture was extracted with DCM (3×10 mL), washed with water, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed, the residue was purified by column chromatography on alkaline alumina with DCM/methanol (100: 1) as an eluent to afford G-(OXD) (686 mg, 95%) <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 8.15$  (s, 12H), 7.98 (t, J=8.4 Hz, 4H), 7.73-7.55 (m, 8H), 7.50-7.24 (m, 28H), 6.81 (d, J=8.7, 4H), 6.58-6.46 (m, 4H), 5.12 (s, 1H), 4.77 (s, 4H), 4.43-4.28 (m, 4H), 3.57-3.45 (m, 2H), 2.35-2.20 (m, 8H), 1.88 (s, 2H), 1.66 (s, 3H), 1.57 (s, 2H), 1.45 (s, 74H), 1.34 ppm (s, 11H); Anal. Calc. for C165H171N12O4Ir: C 76.86, H 6.68, N 6.52; found: C 76.56, H 6.71, N 6.12; MALDI-TOF (*m*/*z*): 2578.6 [*M*<sup>+</sup>+H]

## Dendrimer G(DOXD)

This compound was prepared according to the procedure for the synthesis of **G(OXD)** in a yield of 99%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =8.14 (s, 12 H), 8.00 (t, *J*=9.0 Hz, 8 H), 7.72–7.64 (m, 4 H), 7.57 (d, *J*=8.7 Hz, 4 H), 7.49–7.38 (m, 16 H), 7.35–7.20 (m, 14 H), 6.86–6.79 (m, 6 H), 6.61–6.51 (m, 4 H), 5.13 (s, 1 H), 4.79 (s, 4 H), 4.39–4.29 (m, 4 H), 3.55–3.44 (m, 4 H), 2.35 (s, 4 H), 2.22 (s, 4 H), 1.95–1.86 (m, 4 H), 1.58 (s, 4 H), 1.44 (s, 76 H), 1.34 ppm (s, 22 H); Anal. Calc. for C<sub>187</sub>H<sub>195</sub>N<sub>14</sub>O<sub>6</sub>Ir: C 76.74, H 6.72, N 6.70; found: C 76.66, H 6.78, N 6.40; MALDI-TOF (*m*/*z*): 2926.4 [*M*<sup>+</sup>].

## Measurement and Characterization

<sup>1</sup>H NMR spectra were recorded with a Bruker Avance 300 NMR spectrometer. The elemental analysis was performed by using a Bio-Rad elemental analysis system. MALDI/TOF (matrix assisted laser desorption ionization/time-of-flight) mass spectra were performed on AXIMA CFR MS apparatus (COMPACT). Cyclic voltammetry experiments were performed on an EG&G 283 (Princeton Applied Research) potentiostat/galvanostat system. All measurements were carried out with a conventional three-electrode system consisting of a platinum working electrode, a platinum counter electrode, and an Ag/AgCl reference electrode. The supporting electrolyte was tetrabutylammonium perchlorate (*n*Bu<sub>4</sub>NClO<sub>4</sub>; 0.1 M). Ferrocene was used as a standard to calibrate the system. With regard to the energy level of the ferrocene reference (4.8 eV relative to the vacuum level), the HOMO and LUMO energy levels were calculated according to the following two equations: HOMO = -e (4.8 V+ $E^{ox}$ ) and LUMO = -e (4.8 V+ $E^{red}$ ). Here,  $E^{ox}$  and  $E^{red}$  were taken from the onset of the oxidation and reduction potential, respectively.[22] The UV/Vis absorption and PL spectra were measured by using a Perkin-Elmer Lambda 35 UV/Vis spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. Solution spectra were recorded in DCM or toluene with a concentration of  $10^{-5}$  M. Thin films on quartz for spectroscopic measurements were prepared by spin-coating. All the above experiments and measurements were carried out at room temperature under ambient conditions. Solution PL quantum efficiency was measured in nitrogen-saturated toluene by a relative method using fac-[Ir(ppy)<sub>3</sub>] (factris(2-phenylpyridyl)iridium(III),  $\mathcal{O}_{p} = 0.40$  in toluene) as the standard.<sup>[23]</sup> Phosphorescence spectra at 77 K were measured in a mixed solvent of toluene/ethanol/methanol (5:4:1). The triplet energies were estimated as the maximum of the first vibronic mode  $(S_0^{v=0} \leftarrow T_1^{v=0})$  of the corresponding phosphorescence spectra at 77 K. The lifetimes of phosphorescence from the samples were measured in the air by exciting the samples with 355 nm light pulses with approximately a 3 ns pulse width from a Quanty-Ray DCR-2 pulsed Nd:YAG laser.

#### Device Fabrication and Testing

To fabricate the OLEDs, 50 nm thick PEDOT:PSS films were first deposited on precleaned ITO-coated glass substrates, and then cured at 120 °C in air for 1 h. The emissive layer was then prepared by spin-coating from a chlorobenzene solution of the dendrimer at a concentration of 10 mg mL<sup>-1</sup>. Successively, a 60 nm thick TPBI film was deposited, followed by deposition of the LiF/Al (1 nm/100 nm) cathode at a base pressure of less than  $10^{-6}$  torr through a shadow mask with an array of 14 mm<sup>2</sup> openings. The EL spectra and CIE coordinates were measured using a PR650 spectra colorimeter. The current density-voltage and brightness-voltage curves of the devices were measured using a Keithley 2400/2000 source meter and a calibrated silicon photodiode. All the experiments and measurements were carried out at room temperature under ambient conditions.

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