Dendrimers

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Bifunctional Green Iridium Dendrimers with a “Self-Host” Feature for Highly Efficient Nondoped Electrophosphorescent Devices**

Junqiao Ding, Bin Wang, Zhengyu Yue, Bing Yao, Zhiyuan Xie, Yanxiang Cheng, Lixiang Wang, Xiabin Jing, and Fosong Wang*

Electrophosphorescent devices that contain transition-metal complexes have attracted much attention in recent years, as they can harvest both singlet and triplet excitons to realize a theoretical internal quantum efficiency of 100%.[1] Iridium complexes are of paramount importance in the field because of their high photoluminescence quantum yields and appropriate exciton lifetimes.[2–7] Unfortunately, either quenching of the luminescence caused by intermolecular interactions or poor carrier mobility has prevented them from being used in an undiluted form as the emissive layer (EML).[8] Therefore, in many cases, a doping technique must be employed in the fabrication of high-performance devices.[2–7] Dispersion of the Ir complex in a host matrix not only separates the phosphors and avoids self-quenching, but also contributes to charge transport. Although this technique is usually effective, phase segregation is often an inevitable problem. In addition, the doping concentration is usually lower than 10 wt% and cannot be controlled precisely, which could be a disadvantage for the preparation of reliable and reproducible commercial devices.

A nondoped electrophosphorescent device is a better alternative with which to overcome the aforementioned problems, because its EML is composed of a single Ir complex. However, few efforts have been made to design Ir phosphors suitable for nondoped devices. Wang et al.[8] have reported a fluorinated Ir complex [Ir-2h] (*fac*-tris[5-fluoro-2-(5-trifluoromethyl-2-pyridinyl)phenyl-C,N]iridium), which has a comparatively low efficiency of 20 cd A^{-1}. Interestingly, an even higher efficiency (47 cd A^{-1}) was recently obtained[9] in a device based on a dendritic framework,[10–11] in which an emissive Ir complex core was surrounded by the rigid phenylene-based dendrons to reduce the quenching of the luminescence in the solid state. However, the poor charge-transport capability of the phenylene dendrons significantly limited the performances of devices that contained these materials.

Recently, carbazole units have been introduced into transition-metal-based complexes to improve their charge-carrier injection and transport ability.[12] However, little attention has been paid to their host function.[13–14] In the development of nondoped phosphorescent materials, it is highly desirable to attach carbazole-based dendrons to the phosphorescent core to form bifunctional dendrimers, in which the core acts as the emissive dopant and the dendron plays the same role as the host. As shown in Figure 1, the main advantages of this design can be summarized in three points: 1) the high triplet energy (> 2.9 eV) of the dendrons can prevent the back energy transfer from the emissive Ir core to the peripheral dendrons; 2) the shielding effect of the dendrons can reduce or eliminate intermolecular interactions between emissive Ir cores; 3) the carbazole-based dendrons can render excellent charge-transport properties to the material. This “self-host” feature makes it possible to use these bifunctional dendrimers alone as EML for nondoped devices. We have previously shown that the efficiency of devices based on this scaffold has reached 34.7 cd A^{-1} by tuning the dendron generation.[15] However, this value is still much lower than that of the corresponding doped devices (50.4 cd A^{-1}), and great effort is required to further improve the performance of nondoped devices.

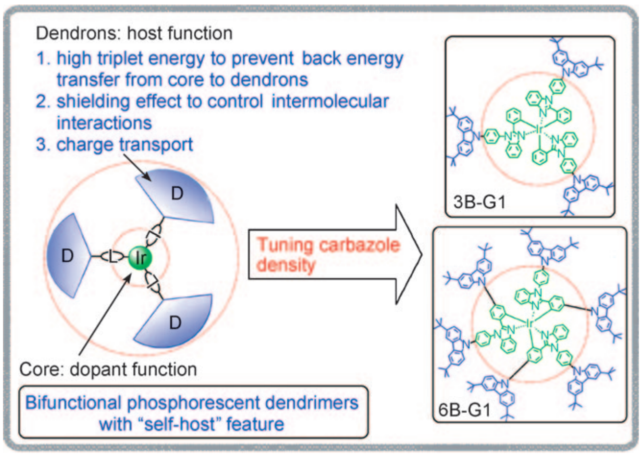

Figure 1. Features and structures of bifunctional phosphorescent iridium dendrimers.

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[*] Dr. J. Ding, B. Yao, Prof. Z. Xie, Prof. Y. Cheng, Prof. L. Wang, Prof. X. Jing, Prof. F. Wang
State Key Laboratory of Polymer Physics and Chemistry
Changchun Institute of Applied Chemistry
Chinese Academy of Sciences, Changchun 130022 (China)
Fax: (+86) 431-8568-5653
E-mail: lixiang@ciac.jl.cn

B. Wang, Prof. Z. Yue
School of Chemistry & Materials Science and Key Laboratory of Fundamental Inorganic Material Chemistry, Ministry of Education
Heilongjiang University, Harbin 150080 (China)

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Herein, we report a more effective strategy for performance improvement, which involves simply increasing the density of carbazole dendrons around the emissive Ir core. All of the first-generation carbazole branches in the target molecule 6B-G1 were directly attached to the core through their N positions to ensure the relative independence of the core's optical properties (Figure 1). With six carbazole branches located at the periphery, the core is expected to be encapsulated more efficiently in 6B-G1 than in 3B-G1, thus allowing a noticeable reduction of the intermolecular interactions in films. As a result, a promising peak efficiency of 45.7 cd A^{-1} (13.4%, 37.8 lm W^{-1}) for 6B-G1, which is about double that of 3B-G1, has been realized for a nondoped device. Furthermore, owing to the excellent charge-transport properties of carbazole dendrons, high luminance and high current density (18000 cd m^{-2}, 360 mA cm^{-2} at 12 V) are simultaneously achieved, and result in a low power consumption. To the best of our knowledge, this is the first report of the nondoped Ir phosphors with an overall performance that is very close to that of doped devices.

The photophysical and electrochemical properties of 6B-G1 and 3B-G1 were investigated. The UV/Vis spectra of 3B-G1 and 6B-G1 exhibit two major absorption bands (see Figure S1 in the Supporting Information). The absorption band below 380 nm is attributed to a spin-allowed ligand-centered (LC) transition and the weak absorption shoulder in the range 380–500 nm is assigned to the metal-to-ligand charge-transfer (MLCT) transition of the Ir complex. Additionally, the band around 239 nm, which is characteristic of carbazole units,[16] increases from 3B-G1 to 6B-G1 because of the increased density of carbazole branches.

Figure 2 shows the photoluminescence (PL) spectra of 6B-G1 and 3B-G1 both in toluene solution and in films. The PL spectrum of 6B-G1 in solution displays discernable vibronic progressions that are not observed in the spectrum of 3B-G1; this feature suggests increased molecular rigidity. It is noteworthy that on going from 3B-G1 to 6B-G1, only a small blue-shift of 3 nm is observed. The optical band gap (E_g) of 6B-G1 (2.43 eV) estimated from the onset of the absorption spectrum is the same as that of 3B-G1 (see Table S1 in the Supporting Information). These results indicate that an increase of the density of carbazole dendrons at the periphery of the dendrimer does not obviously change its emission properties, although its electrochemical properties are slightly affected. The highest occupied molecular orbital (HOMO) energy level of 6B-G1 decreases by about 0.1 eV compared to that of 3B-G1 (see Table S1 in the Supporting Information). This decrease indicates that the inner Ir complex core becomes somewhat less able to capture the charge when the carbazole density is enhanced, and is consistent with results obtained for red Ir dendrimers.[17]

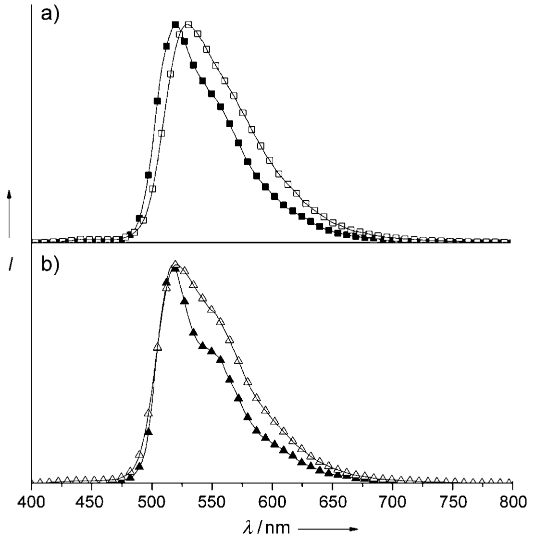

Figure 2. Solution (filled symbols) and film (empty symbols) PL spectra of a) 3B-G1 and b) 6B-G1.

The emission intensity of 6B-G1 at 555 nm is stronger in films than in solution, which indicates that aggregation occurs (Figure 2). However, the emission maximum of 6B-G1 shows a reduced bathochromic shift of 4 nm compared to 9 nm of 3B-G1; this shift suggests that the interactions between the emissive Ir complex cores in the solid state have been reduced because of the effective encapsulation by carbazole dendrons. This effect has been further confirmed by the decay lifetimes of the film PL, which increase with increasing dendron density and indicates the effective reduction of intermolecular interactions (see Table S1 in the Supporting Information).

To evaluate 6B-G1 as a nondoped triplet emitter, electrophosphorescent devices with the configuration ITO/PEDOT:PSS (50 nm) /EML/TPBI (60 nm) /LiF (1 nm) /Al (100 nm) were fabricated (ITO = indium tin oxide, PEDOT:PSS = poly(ethylenedioxythiophene):poly(styrenesulfonic acid), TPBI = 1,3,5-tris(2-*N*-phenylbenzimidazolyl)-benzene). In this configuration, TPBI acts as an electron-transporting and hole-blocking material, while 6B-G1 alone is used as the EML. For comparison, the control device with 3B-G1 as the EML was also prepared under the same conditions. The electroluminescence (EL) spectrum of a 6B-G1 film is identical to its PL counterpart (see Figure S3 in the Supporting Information), with Commission Internationale de L'Eclairage (CIE) coordinates of (0.39, 0.58), which indicates that the emission occurs from the Ir core. Moreover, the EL spectra are independent of the applied voltages from 4 V to 14 V and no additional emission signals from aggregates or excimers have been observed.[18] These factors are the prerequisites for high efficiency as well as high color purity for nondoped devices.

Figure 3 shows the current density–voltage–brightness characteristics of the devices based on 6B-G1 and 3B-G1. Both the current density and the luminance at the same driving voltage decrease from 3B-G1 to 6B-G1. This effect can be ascribed to the larger hole-injection barrier between the anode and the EML for 6B-G1 because of its lower HOMO energy level (see above). However, the luminance and the current density of the nondoped device based on 6B-G1 are still much higher than those of the device based on the phenylene-based green dendrimer (about 3500 cd m^{-2}, 16 mA cm^{-2} at 12 V).[9] For 6B-G1, a brightness as high as 18000 cd m^{-2} and a current density as high as 360 mA cm^{-2} at 12 V have been realized, which are indicative of the superior charge-transport ability of carbazole-based dendrons com-

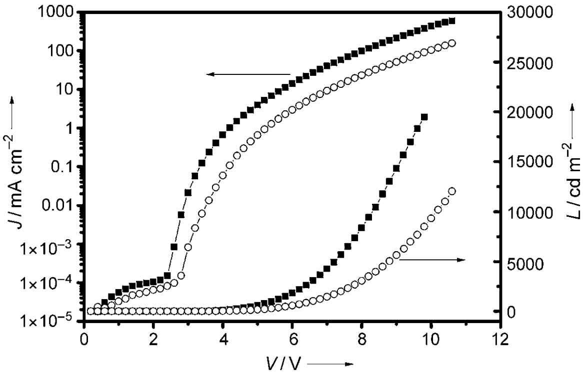

Figure 3. Current density–voltage–brightness (J–V–L) characteristics of 6B-G1 (○) and 3B-G1 (■).

pared to phenylene-based ones (see details in the Supporting Information).[19]

As shown in Figure 4, 6B-G1 gives a promising peak luminous efficiency of 45.7 cd A^{-1} (13.4%), which is about double that of 3B-G1 (23.6 cd A^{-1}, 7.0%) because of reduced PL quenching in the solid state. This efficiency is also much higher than that of the nondoped device fabricated from the second-generation green dendrimer with same Ir complex core (34.7 cd A^{-1}, 10.3%), and very close to that of the 3B-G1-based doped device (50.4 cd A^{-1}).[15] All these results indicate that increasing the density of the carbazole-based dendron is more efficient than employing a high-generation dendron for improving the nondoped device performance. The state-of-the-art efficiency combined with the high luminance and current density render this bifunctional Ir dendrimer a promising solution-processible emissive material for high performance nondoped organic light-emitting diodes (OLEDs).

In summary, a very effective strategy for the design of bifunctional phosphorescent dendrimers with a self-host feature has been demonstrated for improving the performance of non-doped electrophosphorescent devices. By increasing the density of carbazole dendrons at the edge of the emissive core, luminescence self-quenching caused by the intermolecular interactions in the solid state can be significantly reduced, while excellent charge-transport properties are still maintained. As a result, a peak luminous efficiency of 45.7 cd A^{-1} accompanied by high luminance has been realized for a nondoped device. This performance is very close to that of doped devices. We believed that this strategy would be suitable for the design and synthesis of novel solution-processible nondoped phosphorescent materials that have an emission color other than green for use in full-color OLED displays or white-emitting OLEDs.

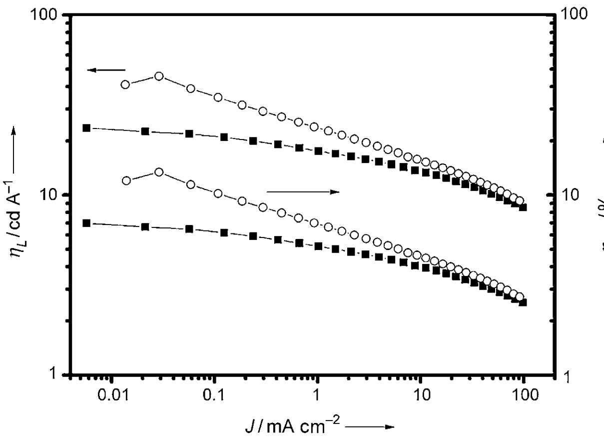

Figure 4. The current density dependence of luminous efficiency (η_L) and external quantum efficiency (η_{ext}) of 6B-G1 (○) and 3B-G1 (■).

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