Tetrahedron 74 (2018) 425–432

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

# High-efficiency blue OLEDs based on dendritic dinuclear iridium (III) complexes grafted with fluorene core and blue fluorescence chromospheres

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ARTICLE INFO

*Article history:*
Received 19 October 2017
Received in revised form
5 December 2017
Accepted 8 December 2017
Available online 9 December 2017

*Keywords:*
Electrophosphorescence
Dinuclear iridium (III) complexes
Blue-emitting fluorescent chromophore
Sky blue-emitting phosphorescent chromophore
OLEDs

ABSTRACT

Two novel dendrimer-like blue-emitting dinuclear cyclometalated iridium (III) complexes, namely $(DNaTPA)_2DBF(FIrpic)_2$ and $(DPyTPA)_2DBF(FIrpic)_2$, have been successfully synthesized and characterized. In which FIrpic is an iridium (III) bis[(4,6-difluorophenyl)pyridinato-*N*,*C2′*]picolate blue-emitting phosphorescent chromophore core, DBF is a 2,7-diphenyl-9H-fluorene bridging core, DNaTPA and DPyTPA are deep blue-emitting fluorescent chromophores composed by rigid high-triplet-energy dendrons of triphenylamine-functionalized naphthalene or pyrene units, and the peripheral dendrons are connected with the ancillary ligand of the emitting core through nonconjugated ether linkage. Their photophysical, thermal, electrochemical, as well as electrophosphorescent properties were primarily studied. Both iridium (III) complexes exhibit high efficient blue emission in solution (38.5% and 19.2%) and a typical FIrpic emission in 1,3-bis(*N*-carbzolyl)benzene (mCP) matrix (27.0% and 24.1%). Simple bilayer phosphorescent organic light-emitting diodes (PHOLEDs) with a configuration of ITO/PEDOT:PSS/mCP:dopants/TmPyPB/Liq/Al achieved high efficiencies of 12.96 cd/A for current efficiency (CE), 6162 cd/$m^2$ for brightness, 6.22% for external quantum efficiency (EQE), and 3.13 lm/W for power efficiency (PE) with Commission International de L'Eclairage (CIE) coordinates of (0.19 ± 0.01, 0.35 ± 0.02) at only 2 wt% blend of $(DNaTPA)_2DBF(FIrpic)_2$. $(DPyTPA)_2DBF(FIrpic)_2$-doped devices also reach efficiencies of (9.14 cd/A, 7167 cd/$m^2$, 4.41%, 2.61 lm/W) at the same doping concentration. The results demonstrate that the introduction of dendritic blue-emitting fluorescent chromophore grafted into the blue phosphorescent chromosphere core through nonconjugated linkage is an efficient way to achieve high-efficiency sky-blue emission.

## 1. Introduction

High-efficiency blue organic light emitting diodes (OLEDs) act as a power consumption reducer have been desired to realize high performance OLEDs in both flat-panel displays and solid-state lightings. Over the past two decades, various methods have been tried to demonstrate efficient blue OLEDs with both high external quantum efficiency (EQE) and power efficiency (PE). For example, in a host/guest doping system, by modifying high triplet energy and narrow $\Delta E_{ST}$ (energy between singlet and triplet) host materials (especially some bipolar host,[1–10] exciplex co-host systems,[11–16] etc.), excitons could strictly confined in the emitting layer (EML), the electrical balance in the emitting layer can be well tuned, and the operating voltage of the devices will be also reduced, thus a series of theoretical limit- breaking blue phosphorescent OLEDs (PHOLEDs) with a maximum EQE over 30% have been reported.[4,16]

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https://doi.org/10.1016/j.tet.2017.12.018

In addition to design host materials, blue-emitting materials act as the core components in OLEDs which determine device's efficiency and color purity are crucial important. To fully utilize both singlet and triplet excitons, and break the 25% internal quantum efficiency (IQE) limitation in fluorescent OLEDs, some newly-emerging up-conversion materials with kinds of triplet harvesting processes such as triplet-triplet annihilation (TTA),[17–22] thermally active delayed fluorescence (TADF),[15,23–27] hybrid local and charge transfer (HLCT),[28–31] and triplet-polaron interaction (TPI)[32,33] have also been used in high-efficiency blue OLEDs. And very recently, a spiroacridine-triazine hybrid sky-blue TADF emitter achieved a recorded EQE of nearly 37% in conventional planar OLED structures.[23]

By now, the most widely used and efficiently blue OLEDs are always phosphorescent OLEDs. A typical used phosphorescent iridium (III) bis(4,6- (difluorophenyl)-pyridinato-*N*,C2′)picolinate (FIrPic) has been widely applied as the dopant in blue PHOLEDs, by using various host and exciton blocking materials, quite high *EQE* of around 20–30% have already reported in sky blue PHOLEDs,[3–12] and even at 1000 cd/m$^2$, some excellent performances still remain *EQE* beyond 23.0%.[4,6,11,12] However, the optimum doping concentration of FIrPic-doped blue PHOLEDs was generally 10%–20%, which means a costly device manufacturing, and the quantum efficiency of such materials always dropped sharply at high luminance, except for some well-designed complicated device structures. So, it is urgently required to develop some other high efficient blue PHOLEDs. One successful approach to control efficiency roll-off is to develop phosphorescent dendrimer materials, for the purpose of preventing self-aggregation or providing charge transporting properties through peripheral moieties.[34–39] Wang et al. reported an efficient self-host blue-emitting iridium (III) dendrimer, which have the second-generation oligocarbazole as the dendrons and through a non-conjugated chain bridged with Ir(dfppy)$_3$ core, the non-doped device based on this iridium (III) complex exhibited a EQE of 15.3% along with CIE coordinates of (0.16, 0.29), which is even superior to the corresponding doped devices.[34] Samuel et al. obtained a kinds of blue phosphorescent dendrimer where twisted biphenyl-based dendrons are attached to the saturated blue emissive phenyl triazole-based iridium (III) core, quite high solution photoluminescence (PL) quantum yield of 94% was achieved. Unfortunately, for the relative lower triplet energies for ETL materials, excitons will be formed near the EML/ETL interface and easily quenched, hence the maximum EQE was only reached to 3.9% in bilayer devices.[35] Samuel et al. reported a dendrimer contains ethylhexyloxy surface group, biphenyl-based dendrimers with a FIrpic core, the bilayer devices have maximum *EQE* of 10.4% and maximum power efficiencies (*PE*) of 11.0 lm/W, the efficiencies are even higher than those more complicated evaporated device structures that contain FIrpic blended with mCP.[36] Huang et al. reported a series of nonconjugated dendritic iridium (III) complex based on tunable pyridine based ligands, interestingly, the introduction of the nonconjugated dendrons improved the solid-state luminescence quantum efficiencies of the iridium complexes in the case of no significantly alter the emissive wavelengths of the iridium core, and a highest *EQE* of 12.8% was achieved in its doped green PLEDs.[38] Although such materials provided an efficient way to overcome device' efficiency roll-off at high currents, however, most of the phosphorescent dendrimer are also performed at high doping concentration or even non-doped devices, there is still much room to improve device's properties to achieve a much simpler, high efficiency, and low optimum doping concentration blue PHOLEDs.

In this article, two sky-blue phosphorescent dinuclear iridium (III) complexes grafted with naphthalene- or pyrene-functionalized triphenylamine blue-emitting fluorophore dendrimer through a nonconjugated ether link, namely (DNaTPA)$_2$DBF- (FIrpic)$_2$ and (DPyTPA)$_2$DBF(FIrpic)$_2$, were successfully synthesized and characterized (Scheme 1), in which DBF is 2,7-diphenyl-9H-fluorene blue fluorescent bridged core, FIrpic is blue phosphorescent core, and DNaTPA and DPyTPA are naphthalene- and pyrene-functionalized triphenylamine dendrimers, respectively. As expected, this kind of molecular structure not only enable complex retain most luminescence features of FIrpic, but also the bulky structure of fluorescent groups can suppress molecular aggregation at high currents in device. The influence of dendritic naphthalene and pyrene groups on the photophysical and electrochemical properties were systematically investigated, respectively. As results, a single-emissive-layered (SEL) device with a structure of ITO/PEDOT:PSSS/mCP:(DA)$_2$DNaTPBF(FIrpic)$_2$/TmPyPB/Liq/Al shows a maximum CE of 12.96 cd/A, a brightness of 7356 cd/m$^2$, a EQE of 6.22% and a PE of 3.13 lm W$^{-1}$ along with CIE coordinates of (0.19 ± 0.01, 0.35 ± 0.02) at the dopant concentration of 2 wt%. Meanwhile, at the same doping concentration, the pyrene-substituted analogues (DPyTPA)$_2$DBF(FIrpic)$_2$ exhibited device performances of 9.14 cd/A, 7167 cd/m$^2$, 4.41% and 2.61 lm/W with CIE coordinates of 0.19 ± 0.01, 0.33 ± 0.02. Besides, both devices show no obvious efficiencies roll-off at high currents. The results indicate that grafting dendrons blue-emitting fluorescent chromophore into the dinuclear iridium (III) complexes through nonconjugated ether link is an efficient way to achieve high-efficiency sky-blue emission in PHOLEDs.

## 2. Result and discussion

### 2.1. Thermal properties

The thermogravimetric analyses (TGA) curves of (DNaTPA)$_2$DBF(FIrpic)$_2$ and (DPyTPA)$_2$DBF(FIrpic)$_2$ under nitrogen atmosphere are depicted in Fig. 1, and the corresponding data are listed in Table 1. The decomposition temperature ($T_d$) of 341.0 °C for (DNaTPA)$_2$DBF(FIrpic)$_2$ and 322.0 °C for (DPyTPA)$_2$DBF(FIrpic)$_2$ are observed at 5% weight loss, respectively, which means such the non-conjugated configurations dendron iridium (III) complexes exhibit good thermal stability and can be applied for using in OLEDs.

### 2.2. Optical properties

The photophysical properties of (DNaTPA)$_2$DBF(FIrpic)$_2$ and (DPyTPA)$_2$DBF- (FIrpic)$_2$ were detected by using ultraviolet–visible (UV–vis) and photoluminescence (PL) spectrometers. Fig. 2 depicts the UV–vis absorption and PL spectra of the complexes in dilute DCM solution and in mCP matrix at RT, the corresponding values are summarized in Table 1. As shown in Fig. 2, (DNaTPA)$_2$DBF(FIrpic)$_2$ shows a wide absorption band peaks at 331 nm which could be ascribed to the π-π* electron transitions of molecular backbone, and some intramolecular charge transfer character to a certain extent. The weak absorption bands in the region of 380–450 nm is originated from the spin-allowed singlet as well as spin-forbidden triplet metal-to-ligand charge transfer ($^1$MLCT and $^3$MLCT) of the FIrpic portion.[43] Meanwhile, (DPyTPA)$_2$DBF(FIrpic)$_2$ exhibits a similar absorption profile peaks at 341 nm, and a higher-energy absorption band peaks at 278 nm could be ascribed to the spin-allowed π-π* electron transition of the pyrene unit,[40] an enhanced absorption band at lower-energy could be ascribed to the FIrpic emission as well as the charge transfer of the more delocalized DPyTPA chromophore.[42] The additional absorption band from the DPyTPA is available to improve energy-transfer from the host matrix to (DPyTPA)$_2$DBF(FIrpic)$_2$ in OLEDs.[44] Furthermore, the optical energy gap ($E_g^{opt}$) of (DNaTPA)$_2$DBF(FIrpic)$_2$ and