# Efficient electroluminescence based on a novel binuclear rhenium complex 

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#### Abstract

A novel binuclear rhenium(I) ( $\left.\mathrm{Re}^{\mathrm{I}}\right)$ carbonyl complex with the formula $\left[\mathrm{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$, where DF represented 4,5-diazafluorene, was designed and synthesized for applications in organic light-emitting diodes (OLEDs). The OLEDs employing $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ as an emitter with the structure of ITO/m-MTDA$\mathrm{TA}(10 \mathrm{~nm}) / \mathrm{NPB}(20 \mathrm{~nm}) / \mathrm{CBP}:$ Re-complex $(\mathrm{x} \%, 30 \mathrm{~nm}) / \operatorname{Bphen}(10 \mathrm{~nm}) / \mathrm{Alq}_{3}(30 \mathrm{~nm}) / \mathrm{LiF}(1 \mathrm{~nm}) / \mathrm{Al}(100 \mathrm{~nm})$ were fabricated. The OLEDs based on $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ exhibited green-yellow emissions with a peak current efficiency of $8.2 \mathrm{~cd} / \mathrm{A}$ at $16 \mathrm{~cd} / \mathrm{m}^{2}$ and a maximum brightness of $2026 \mathrm{~cd} / \mathrm{m}^{2}$ at 17.5 V , respectively, which confirmed that the binuclear Re-complex could function as an efficient phosphor emitter. © 2009 Elsevier B.V. All rights reserved.


## 1. Introduction

Organic light-emitting diodes (OLEDs) remain a subject of intensive research due to their potential applications in full-color flat-panel displays and solid-state lighting [1-4]. Among these device applications, the use of phosphorescent ( Ph ) emitters may increase electroluminescence (EL) efficiency because they can harvest light from both singlet and triplet excitons and enable the internal quantum efficiency to theoretically approach $100 \%$ [5,6]. The transition-metal-based Ph complexes such as $\mathrm{Os}^{\mathrm{II}}[7,8]$, $\mathrm{Ir}^{\text {III }}$ [9-11] and $\mathrm{Pt}^{\mathrm{II}}[12,13$ ] have been extensively studied. Recent research results indicate that rhenium( I ) $\left(\mathrm{Re}^{\mathrm{I}}\right)$ complexes can also serve as a class of potential EL phosphor materials [14-17] because $\operatorname{Re}^{\mathrm{I}}$ phosphors present relatively short excited state lifetime ( $<1 \mu \mathrm{~s}$ ), excellent thermal and photochemical stability and so on. Up to now, most reported Ph materials used for OLEDs are mononuclear complexes because it seems challenging for the accepted view that binuclear or polynuclear metal complexes are unsuitable for OLEDs applications due to their low luminescence efficiencies. However, efficient EL of binuclear or polynuclear metal complexes such as Ir [18], Pt [19,20], Cu [21,22] and Eu [23,24] have been studied, but in this regard there has been few report for the binuclear $\mathrm{Re}^{\mathrm{I}}$ complexes [25].

In this paper, we designed and synthesized a binuclear $\mathrm{Re}^{\mathrm{I}}$ complex, $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$, where DF was 4,5 -diazafluorene, for appli-

[^0]cations in OLEDs. The fact that 9,9'-bis-(4,5-diazafluorene) (BDF) is selected as the ligand is due to facile reaction of 4,5-diazafluoren9 -one(DFO) with hydrazine hydrate and high electron affinity of DF [26]. Therefore, it is expected that the OLEDs based on [ $\operatorname{Re}(\mathrm{D}-$ $\left.\mathrm{F})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ can exhibit balanced carrier recombination, thus leading to highly efficient EL emission. As a result, the $7 \mathrm{wt} . \%$ $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped OLED exhibited a peak current efficiency of $8.2 \mathrm{~cd} / \mathrm{A}$ at $16 \mathrm{~cd} / \mathrm{m}^{2}$ and a maximum brightness of $2026 \mathrm{~cd} /$ $\mathrm{m}^{2}$ at 17.5 V .

## 2. Experimental

### 2.1. Sample

Scheme 1 outlines the synthetic pathways of the binuclear $\mathrm{Re}^{1}$ complex. First, 4,5-diazafluoren-9-one(DFO) was synthesized according to literature procedures [27]. And then, DFO was deoxidized to afford BDF in the presence of hydrazine hydrate [28]. Finally, $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ was obtained by direct complexation of BDF with $\operatorname{Re}(\mathrm{CO})_{5} \mathrm{Br}$ according to the conventional method [15]. The purity and structure of those compounds were confirmed by ${ }^{1}$ H NMR, Mass Spectroscopy and elemental analysis.

### 2.2. Optical measurements

UV-Vis absorption spectra and PL spectra were measured with a Perkin-Elmer Lambda-900 spectrophotometer and LS-55 luminescence spectrophotometer, respectively. UV-Vis and PL spectra


Scheme 1. Synthetic pathways of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$.
of the $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ complex were recorded in dichloromethane solution with the concentration of $10^{-5} \mathrm{M}$. The excited state lifetime of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ in deaerated dichloromethane solution was detected by a system equipped with a TDS 3052 digital phosphor oscilloscope pulsed Nd:YAG laser with a THG 355 nm output. The data were well fitted by single-order exponential decay. All measurements were carried out at room temperature under ambient conditions.

### 2.3. EL measurements

To examine the EL properties of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$, the devices with various doping concentrations were prepared employing $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ as a dopant and $4,4^{\prime}-\mathrm{N}, \mathrm{N}^{\prime}$-dicarbazole-biphenyl (CBP) as the host. The device configuration and molecular struc-



NPB


BPhen

m-MTDATA


CBP

$\mathrm{Alq}_{3}$

Fig. 1. The device configuration and molecular structures of the compounds used in the devices.
tures of the compounds used in these devices were depicted in Fig. 1. Here $4,4^{\prime}, 4^{\prime \prime}$-tris[3-methylphenyl(phenyl)amino]triphenylamine ( $m$-MTDATA), 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB), 4,7-diphenyl-1,10- phenanthroline (Bphen) and tris(8-hydroxyquinoline) aluminum ( $\mathrm{Alq}_{3}$ ) function as hole injection layer, hole transporting layer, exciton blocking layer and electron transporting layer, respectively. The organic layers were sequentially deposited onto the precleaned indium tin oxide (ITO) glass substrates with a resistance of $20 \Omega$ / sq. The pressure in the chamber was below $2 \times 10^{-4} \mathrm{~Pa}$. Deposition rates and thicknesses of the layers were monitored in situ using an oscillating quartz monitor. The evaporating rates were kept at $2-3 \AA / \mathrm{s}$ for organic layers and LiF layer, and $10 \AA$ /s for Al cathode, respectively. EL spectra were recorded with a Hitachi MPF-4 fluorescence spectrophotometer. The luminance-current-voltage ( $L-I-V$ ) characteristics of the OLEDs were measured with a 3645 dc power supply combined with a 1980a spot photometer and recorded simultaneously with measurements.

## 3. Results and discussion

Fig. 2 shows the PL and UV-Vis absorption spectra of [Re(D$\left.\mathrm{F})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ complex in dichloromethane solution. The strong


Fig. 2. Absorption spectrum (a) and PL spectrum (b) of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ in dichloromethane solutions $\left(10^{-5} \mathrm{M}\right)$, PL spectrum and (c) of CBP in neat film.

Table 1
EL performances of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped devices with different concentrations.

| Concentration (wt.\%) | $\eta_{\max }{ }^{\mathrm{a}}$ | $\eta^{\mathrm{b}}$ | $\eta^{\mathrm{c}}$ | $\eta^{\mathrm{d}}$ | $L_{\max }{ }^{\mathrm{e}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| 5 | 7.5 | 1.6 | 5.2 | 1.8 | 1225 |
| 7 | 8.2 | 2.4 | 7.2 | 3.5 | 2026 |
| 10 | 7.3 | 1.9 | 6.3 | 2.4 | 1334 |

${ }^{a}$ Maximum current efficiency (cd/A).
${ }^{\mathrm{b}}$ Current efficiency at $100 \mathrm{~mA} / \mathrm{cm}^{2}$.
${ }^{\text {c }}$ Current efficiency at $100 \mathrm{~cd} / \mathrm{m}^{2}$.
${ }^{\text {d }}$ Current efficiency at $1000 \mathrm{~cd} / \mathrm{m}^{2}$.
${ }^{\mathrm{e}}$ Maximum luminance ( $\mathrm{cd} / \mathrm{m}^{2}$ ).
absorption bands in the ultraviolet region at $260-305 \mathrm{~nm}$ with distinct vibronic features can be assigned to spin-allowed ${ }^{1} \pi-\pi^{*}$ transitions from the cyclometalated ligand. The relatively broad, weak absorption bands in the range ca. 400 nm are tentatively ascribed to the metal-to-ligand charge transfer $\mathrm{d} \pi(\mathrm{Re}) \rightarrow \pi^{*}$ (BDF) (MLCT) transitions. An intense PL spectrum of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ complex in dichloromethane solution at room temperature is observed centering at around 535 nm . It can be clearly seen that there is a sufficient overlap between PL spectrum of CBP film and MLCT absorption bands of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$, which indicates that CBP doped with $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ may meet the requirement for efficient Förster energy transfer from the singlet excited state of the host CBP to the ${ }^{1} \mathrm{MLCT}$ state of the guest $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$. The PL quantum yield of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ measured in deaerated dichloromethane is $5.2 \times 10^{-3}$ by using quinine sulfate as a reference which has a quantum yield of 0.546 [16].

To investigate the EL properties of the binuclear complexes, the devices using the complex as a dopant emitter were fabricated. It was found that the doping concentrations of Re-complex in the devices greatly affected EL performances. The EL performances of the devices based on different concentrations of Re-complex are summarized in Table 1. Obviously, the $7 \mathrm{wt} . \%$ Re-complex doped device shows a maximum efficiency.

The EL spectra based on $7 \mathrm{wt} . \%$ Re-complex doped device are displayed in Fig. 3. It can be found that the EL spectra consist of only a green-yellow emission peak without any residual emission such as from the host or adjacent organic layers even at high drive voltages, which means complete energy transfer from the host to the emitter upon electrical excitation. The EL spectra from the device exhibit no significant changes under the variation of the drive current and bias from 8 to 18 V . Furthermore, there is a close resemblance between the EL and PL spectra, indicating that the


Fig. 3. EL spectra of the $7 \mathrm{wt} . \%\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped device at different bias.


Fig. 4. $L-I-V$ characteristics of the device based on $7 \mathrm{wt} . \%\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$. Inset: current efficiency versus current density characteristics of $\mathrm{x} \%\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped devices.

EL emissions of the device originate from the triplet excited state of $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$.

Fig. 4 depicts $L-I-V$ characteristics of the device with $7 \mathrm{wt} . \%$ $\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ in CBP , and the relationships between current efficiency and current density of the $\mathrm{x} \%\left[\mathrm{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped devices are also given in inset of Fig. 4. The $7 \mathrm{wt} . \%\left[\operatorname{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$ doped device shows a turn-on voltage of 6.5 V , a maximum brightness of $2,026 \mathrm{~cd} / \mathrm{m}^{2}$ at a bias of 17.5 V and a peak current efficiency of $8.2 \mathrm{~cd} / \mathrm{A}$ at $16 \mathrm{~cd} / \mathrm{m}^{2}$, respectively. The current efficiency decreases slowly in low current density range, suggesting that the effect of triplet-triplet annihilation is neglectable probably due to the existence of steric hindrance of two diazafluorene rings and the short excited state lifetime of $0.1 \mu$ s of the binuclear $\operatorname{Re}^{1}$ complex. The abrupt decline of EL efficiencies under high current density should result from a coexistence of triplet-triplet annihilation [29] and field-induced exciton dissociation [30].

## 4. Conclusion

In summary, we reported a novel binuclear $\mathrm{Re}^{1}$ complex containing diazafluorene ligand, $\left[\mathrm{Re}(\mathrm{DF})(\mathrm{CO})_{3} \mathrm{Br}\right]_{2}$, for applications in OLEDs. The OLEDs based on the complex exhibited a maximum luminance of $2,026 \mathrm{~cd} / \mathrm{m}^{2}$ and a peak current efficiency of $8.2 \mathrm{~cd} /$ A, which confirmed that the binuclear $\mathrm{Re}^{1}$ complex could serve as an efficient emitter for electrophosphorescent devices. Our results indicate that it is practicable to acquire very efficient OLEDs by rational design of molecular structure in binuclear Re ${ }^{\mathrm{I}}$ complexes.

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