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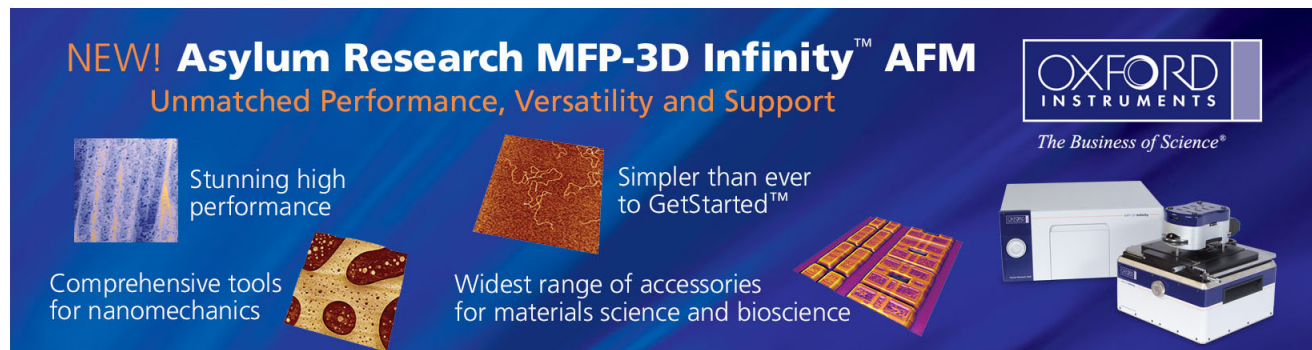J. Appl. Phys. **92**, 5971 (2002); 10.1063/1.1513886

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Bright red-emitting electrophosphorescent device using osmium complex as a triplet emitter

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A series of efficient and bright double-layer light-emitting devices have been fabricated using the osmium (Os) complex as the triplet emissive dopant in both a blue-emitting polyfluorene derivative (PF–TPA–OXD) containing hole-transporting triphenylamine (TPA) and electron-transporting oxadiazole (OXD) as side chains and a blend of 2-(4-*t*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD) in poly(*N*-vinylcarbazole) (PVK). Due to a balanced charge injection and transport in PF–TPA–OXD and very efficient energy transfer from this polymer to the Os complex, the resulting device (indium tin oxide/HTL/$OsCF_3$:PF–TPA–OXD/Ca/Ag) reaches a maximum external quantum efficiency of 2.1% with a peak brightness of 2920 cd/m^2. These results are significantly higher than those obtained from the commonly used host, PVK:PBD (0.49% and 1270 cd/m^2). © *2003 American Institute of Physics.* [DOI: 10.1063/1.1593230]

Recently, tremendous efforts have been focused on improving the efficiency of organic light-emitting diodes (OLEDs) through either the development of better materials or more efficient device structures. In an OLED, both the holes and electrons are injected form the opposite electrodes then combined together to form excitons. However, the radiative decay of the singlet excitons is very fast but that of the triplet excitons is usually inhibited by the rule of the spin conservation and is very inefficient. Therefore, the development of OLEDs has been mostly based on the fluorescent emissive materials. However, by employing triplet-based phosphorescent dye in small molecule- and polymer-based LEDs where both singlet and triplet excited states participate, the internal efficiency can reach as high as 100%.[1,2] Red-emitting LEDs based on the triplet emitters such as trivalent Ir complexes,[3,4] Pt phophyrine derivatives,[5,6] and tris(polypyridyl) Ru(II) complexes[7,8] have been demonstrated with very high efficiency. Compared to the analogues tris(polypyridyl) Ru(II) complexes, the Os(II)-based complexes have rarely been used in LED applications. This is because the tris(polypyridyl) Os(II) complexes usually possess relatively low quantum yields in the order of 0.1% and very short emission lifetimes in the order of 50 ns[9] when compared to those of the Ru complexes. In addition, the emission of the tris(polypyridyl) Os(II) complexes is significantly red-shifted compared to the tris(polypyridyl) Ru(II) complexes and is in the near-IR region. Nguyen *et al.*[10] showed that the use of strong π-acid ligands, such as phosphine and CH_3CN, combined with polypyridyl ligands will yield Os(II) complexes with triplet life time of up to 1.84 μs.

The σ^* or d orbitals of Os(II) are very high in energy compared to the π^* of the ligands. The metal-to-ligand-charge-transfer (MLCT) bands are dominantly from the t_{2g} of the Os metal to π^* of the ligands. When a polypyridyl ligand is replaced with a π-acid ligand (such as phosphine and arsine ligand), there is a shift to higher energy in the absorption and emission bands from the tris(polypyridyl) Os(II) complexes.[11–14] Therefore, these mixed-ligand systems are suitable for the triplet-based LED applications. It can blue-shift the emission colors from near-IR to orange-red and increase the emission quantum yields up to 45%.[11] Recently, a series of Os complexes have been developed and efficient red-emitting LEDs have been demonstrated using polymer blends as the host materials.[11,12]

In the dye doped systems for LEDs, two kinds of emission mechanisms are possible. One is based on the Föster or Dexter type energy transfer from the host to the dopant, the other is based on the direct recombination of the injected charges on the dopant site, i.e., charge trapping mechanism. In this letter, we demonstrate that by employing a host polymer with optimized charge injection and transport, we can take advantage of both mechanisms to improve device's efficiency and brightness. Figure 1 shows the chemical structures of the osmium complex ($OsCF_3$) and the *in situ* polymerizable hole-transporting material, bis - tetraphenylenebiphenyldiamine – perfluorocyclobutane (BTPD–PFCB), and the highly efficient blue-emitting poly-fluorene containing both hole- and electron-transporting moiety as side chains (PF–TPA–OXD)[15] used in this work. The electroluminescence (EL) devices were fabricated on indium tin oxide (ITO)-coated glass substrate that were cleaned and treated with oxygen plasma before use. A layer of 20-nm-thick BTPD–PFCB was first fabricated by spin coating the

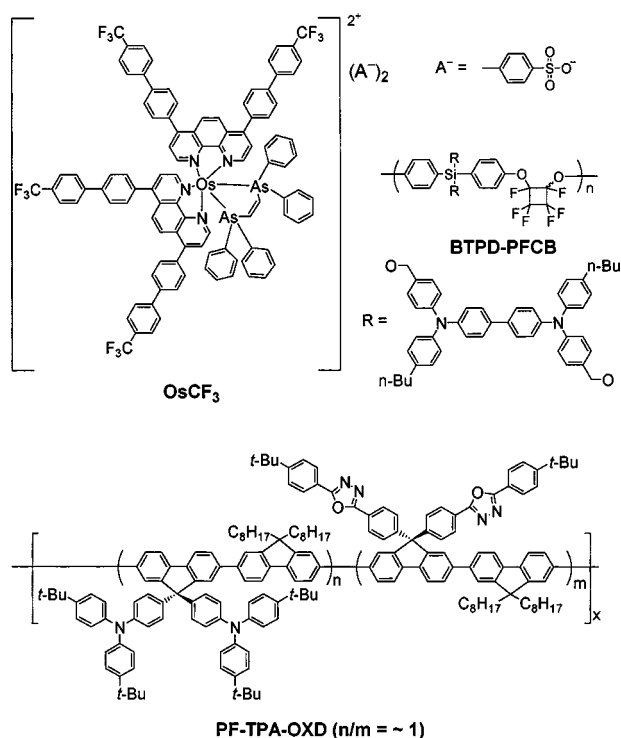[a)]Electronic mail: ajen@u.washington.edu

FIG. 3. EL spectra of (a) ITO/BTPD–PFCB/OsCF$_3$:PVK:PBD/Ca/Ag and (b) ITO/BTPD–PFCB/OsCF$_3$:PF–TPA–OXD/Ca/Ag (offset for clarity), (c) ITO/BTPD–PFCB/PF–TPA–OXD/Ca/Ag, and (d) ITO/BTPD–PFCB/PVK:PBD/Ca/Ag.

FIG. 1. Chemical structure of osmium complex (OsCF$_3$), hole transporting material (BTPD–PFCB), and polyfluorene derivative (PF–TPA–OXD).

monomer from its solution in 1,2-dichloroethane (DCE) and annealing at 225 °C for 1 h under nitrogen atmosphere.[16,17] Then, a layer of 3.0 wt % Os complex doped blend of poly(*N*-vinylcarbazole) (PVK)/2-(4-*t*-butylphenyl)-5-(4-biphenylyl)-1,3-4-oxadiazole (PBD) (PVK:PBD=7:3 by weight) or PF–TPA–OXD were spin coated, from their solution in DCE (~10 mg/mL), onto the top of the BTPD–PFCB layer. A cathode layer of 30-nm-thick Ca was vacuum deposited onto the top of the OsCF$_3$ doped polymer film at below 1×10^{-6} Torr, and then a layer of 120-nm-thick Ag was deposited as the protecting layer.

UV-visible (UV–VIS) and photoluminescence (PL) spectrum of OsCF$_3$ in ethanol solution are shown in Fig. 2. The absorption spectrum of OsCF$_3$ in ethanol solution [Fig. 2(a)] shows a strong absorption at 280–330 nm, which corresponds to the $\pi-\pi^*$ transition of the ligands. The moderate absorption band in the region of 350–460 nm corresponds to
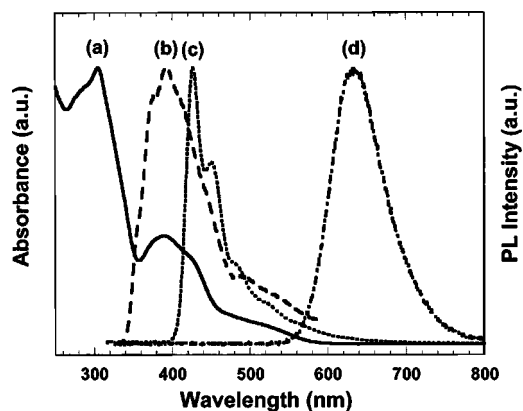

FIG. 2. (a) UV–VI spectrum of OsCF$_3$ solution in ethanol, (b) PL spectrum of PVK:PBD blend film, (c) PL spectrum of PF–TPA–OXD film, (d) PL spectrum of OsCF$_3$ solution in ethanol.
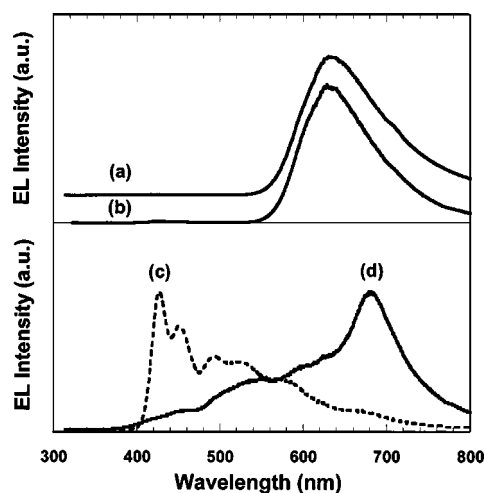
the singlet MLCT absorption. In addition, a weak absorption band between 460 and 560 nm corresponds to the triplet MLCT absorption. The extinction coefficients (ϵ) at 280 and 375 nm are 125 000 and 40 000 L^{-1} cm^{-1} mol^{-1}, respectively. The PL of the solution of OsCF$_3$ [Fig. 2(d)] emits red light with a maximum at 632 nm. As can be seen in both Figs. 2(b) and 2(c), the films of PVK:PBD blend and PF–TPA–OXD emit violet and blue light, respectively. Since the MLCT states of the OsCF$_3$ complex absorb light in the region of 350–580 nm, therefore, both the polymer and the blend can be used as host materials for efficient energy transfer.

In the EL devices based on the OsCF$_3$ complex doped in the blend of PVK:PBD, a doping ration of 3.0 wt % was employed and it is sufficient to quench the emission of the host. This matches well with our previous results that a doping level between 2.5 and 5.0 wt % gives the best device performance.[12] Although the energy transfer could be improved by increasing the concentration of the dopant, this will also increase the non-radiative decay due to self-quenching. As can be seen in Fig. 3(a), the EL spectrum of device 1 (ITO/HTL/OsCF$_3$:PVK:PBD/Ca/Ag) emits strong red light with a λ_{max} at 630 nm under the forward bias. The maximum external quantum efficiency (η_{max}) of device 1 was calculated to be 0.49% at a current density of 0.025 A/cm^2 (at a brightness of 109 cd/m^2 with a driving voltage of 13.0 V). The maximum brightness (B_{max}) of device 1 reaches 1270 cd/m^2 at a voltage of 19.0 V and a current density of 0.44 A/cm^2. In the EL device based on the PF–TPA–OXD host [ITO/HTL/OsCF$_3$:PF–TPA–OXD/Ca/Ag, device 2 in Fig. 3(b)], the peak wavelength (628 nm) and the shape of the spectrum is similar to that of the device 1. This indicates that the host materials do not affect the emission properties. However, device 2 shows a very weak emission which originates from the emission of polyfluorene backbone (in the region of 400–500 nm). The η_{max} of the device 2 was calculated to be 2.1% at a current density of 0.0085 A/cm^2 (at a brightness of 166 cd/m^2 with a driving voltage of 12.0 V), which is four times higher than the value obtained with host material of PVK:PBD (device 1). The B_{max} of device 2
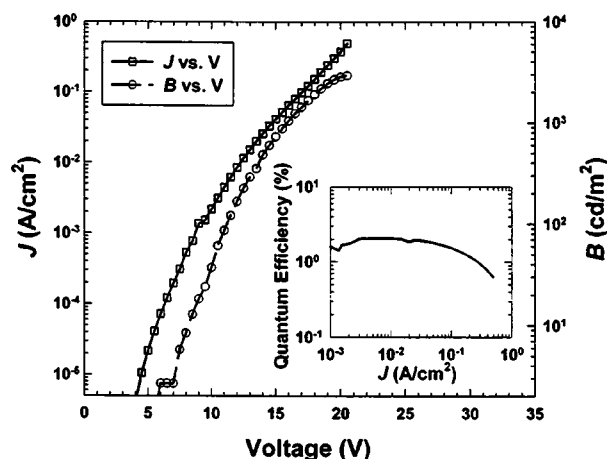
FIG. 4. Current density–bias voltage–brightness relationship of ITO/BTPD–PFCB/OsCF$_3$:PF–TPA–OXD/Ca/Ag. Inset is external quantum efficiency vs current density relationship.

reaches 2920 cd/m^2 at a voltage of 20.5 V and a current density of 0.49 A/cm^2.

The efficiency of the devices can be explained from the energy transfer point of view, which is most likely through the Föster mechanism in these devices, from the host to the Os complex dopant. In Föster energy transfer, the energy transfer efficiency is proportional to the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor. In order to investigate the overlap integral between the emission of the host and the absorption of OsCF$_3$, we also fabricated bilayer EL devices based on the host materials, which do not contain OsCF$_3$. The EL spectra of the devices show quite different features from their PL spectra [Figs. 2(b) and 2(c)]. As can be seen in Fig. 3(d), EL intensity of the bilayer device based on PVK:PBD (ITO/HTL/PVK:PBD/Ca/Ag) around 580–800 nm is much higher than that of 350–580 nm. The emission at 580–800 nm is due to the exciplex formation,[13] which arise from the interface between the HTL and the PVK:PBD layer. On the other hand, the EL spectrum of the bilayer device based on the PF–TPA–OXD (ITO/HTL/PF–TPA–OXD/Ca/Ag) showed quite different feature. The EL intensity in the region of 400–580 nm is higher than that in the region of 580–800 nm. As a result, the overlap integral between the absorption of OsCF$_3$ and the emission of PF–TPA–OXD is better than that of OsCF$_3$ and PVK:PBD. Therefore, the efficiency of the device based on PF–TPA–OXD is much higher compared to the device based on PVK:PBD host. The η_{max} and B_{max} of ITO/HTL/PF–TPA–OXD/Ca/Ag are 1.1% and 8900 cd/m^2, respectively, which are significantly higher than those derived from the ITO/HTL/PVK:PBD/Ca/Ag (0.11% and 82.4 cd/m^2). This imply that OsCF$_3$ dopant in device 2 can receive more emitted photons from the host than that from device 1 based on PVK:PBD. Figure 4 shows the current density and brightness as a function of the bias voltage respectively. The turn-on voltage (defined as the voltage required to give a luminance of 1 cd/m^2) of device 2 is 8.0 V, which is similar to that of device 1 (7.5 V). In addition, the current density of the OsCF$_3$ doped devices is smaller than that of the undoped devices. This is because OsCF$_3$ complex also acts as trap site for injected charges from the opposite electrodes (both holes and electrons). The p orbital of the

polypyridine ligands in the Os complex (correspond to the lowest unoccupied molecular orbital level of the complex, -3.33 eV) can be easily reduced and can act as the trapping sites for electrons injected from the cathode. The d orbital of the Os(II) ion (correspond to the highest occupied molecular orbital level, -5.47 eV) can also act as the trapping sites for holes injected from the ITO anode.[18] The external quantum efficiency of the device slightly decreases with the increasing of current density (inset of Fig. 4). This may be due to the EL originates from the recombination of long lifetime triplet excitons,[5] which causes saturation of emissive sites and triplet–triplet annihilation. This will result in significant decrease in efficiency.[2]

In summary, we have developed very bright red-emitting LEDs with high quantum efficiency by using Os complex as dopant in a conjugated polymer host. Due to a balanced charge injection and transport and very efficient energy transfer from this polymer to the Os complex, the resulting device (ITO/HTL/OsCF$_3$:PF–TPA–OXD/Ca/Ag) reaches a maximum external quantum efficiency of 2.1% with a peak brightness of 2920 cd/m^2. These results are significantly higher than those obtained from the commonly used host, PVK:PBD (0.49% and 1270 cd/m^2).

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