Addition of a Phosphorescent Dopant in Electroluminescent Devices from Ionic Transition Metal Complexes

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Ionic transition metal complexes have emerged as promising candidates for applications in solid-state electroluminescent devices. This is due to the fact that a single, solution-processable layer sandwiched between two air-stable electrodes can yield high-efficiency devices. In this paper we demonstrate tuning of the emission of these devices in the red part of the spectrum by dispersing an ionic osmium complex into an ionic ruthenium complex matrix. This is shown to lead to devices that are more efficient than those from pristine films of the matrix or the dopant alone. These devices also show improved stability compared to devices based on the matrix and feature an emission spectrum that can be tuned by the concentration of the dopant.

Introduction

Ionic transition metal complexes (iTMCs), such as $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ (where bpy is 2,2′-bipyridine) and its derivatives are the focus of much research as materials for solid-state electroluminescent devices.[1−9] In such devices, electrons and holes, injected from two metal electrodes into a thin layer of the complex, recombine and give rise to light emission. A key feature of these multifunctional materials lies in the fact that the counterions (PF_6^-) redistribute under an applied bias so as to facilitate the injection of electrons and holes.[10] As a result, devices from iTMCs can operate efficiently, even with air-stable electrodes, and show low operating voltages.[7] External quantum efficiencies up to 5.5% have been reported in single-layer devices processed from solution.[3] As with any new class of electroluminescent materials, to be commercially viable iTMCs must show, among other things, emission that covers the visible spectrum. Devices based on ionic ruthenium complexes show electroluminescence in the orange-red part of the spectrum.[1−8] Color tuning can be achieved by changing the metal center or the ligand, a pathway that has been explored in neutral transition metal complexes.[11] By this approach, devices that emit in the yellow[9] and green part[12] of the spectrum were recently demonstrated for iridium iTMCs.

A different approach to tuning the emission from devices based on iTMCs is demonstrated here by means of doping with phosphorescent guests. Introduction of dopants in organic films is a common way to tune a number of device properties in organic light-emitting diodes (OLEDs) such as the color of emission and the device efficiency.[13−17] The use of phosphorescent dopants gave rise to a new era in OLEDs and led to large increases in device efficiency.[13] Color tuning by means of doping involves dispersing a highly fluorescent or phosphorescent molecule (dopant) in an organic semiconductor matrix. The matrix transports charge while the emission is delegated to the dopant, either via energy transfer (excitons are formed on the matrix) or by sequential electron and hole capture by the dopant (electrons and holes are transferred from the matrix to the dopant). Separating the processes of charge transport and emission allows their optimization and the avoidance of self-quenching that decreases the emission yield in organics. This approach has been demonstrated in small molecule[15,16] as well as polymeric[14,17] matrices.

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In this paper we explore the addition of a phosphorescent dopant, namely, the ionic osmium complex $[Os(phen)_3]^{2+}(PF_6^-)_2$ (where phen is 1,10-phenanthroline), into devices of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$. The choice of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ as a matrix is consistent with the fact that this complex, which shows bright emission in the orange region of the spectrum, is the most well-studied material in iTMC devices.[7] The osmium complex that was used as the dopant emits in the red part of the spectrum but with a rather low quantum yield.[18] A distinguishing feature of this dopant−matrix system is that since both materials are ionic, large amounts of $[Os(phen)_3]^{2+}(PF_6^-)_2$ can be dissolved in films of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ with no visible aggregation. In addition, since they both have the same counterion (PF_6^-), we expect no significant change in the ionic conductivity of the matrix upon the addition of small amounts of the dopant. Addition of the phosphorescent dopant in this system is shown to lead to devices that are more efficient than those from pristine films of the matrix or the dopant alone and feature an emission spectrum that can be tuned toward the red part of the spectrum. Preliminary studies also show improved stability of the doped devices compared to $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ devices.

Experimental Section

The synthesis of $[Os(phen)_3]^{2+}(PF_6^-)_2$ and $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ and their device fabrication and characterization procedures have been reported earlier.[18,5] Doped films were prepared by mixing appropriate amounts of ruthenium and osmium complexes in solution to yield $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ films (matrix), doped with 0.5%, 1%, 5%, 10%, and 20% (w/w) $[Os(phen)_3]^{2+}(PF_6^-)_2$ (dopant). The films were clear, showing no evidence of dopant aggregation. For the fabrication of devices, films were cast from acetonitrile solutions (at 24 mg/mL) onto prepatterned ITO substrates (Thin Film Devices, Anaheim, CA), yielding films 90−100 nm thick, as measured by profilometry. Immediately before the film deposition, the ITO substrates were cleaned in a deionized water bath followed by UV/ozone treatment. The spun films were dried in a vacuum oven for 8 h at 80 °C, before a 20 nm thick Au layer was deposited through a shadow mask that defined six devices per substrate. All devices were prepared from the same stock of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ and $[Os(phen)_3]^{2+}(PF_6^-)_2$ and the same bottle of acetonitrile solvent, to achieve good device-to-device reproducibility. Devices based on the same material but fabricated on different substrates showed a variation in their efficiency that was on the order of 10%. A calibrated S2000 Ocean Optics fiber spectrometer was used to obtain electroluminescence spectra, and a UDT S370 optometer coupled to an integrating sphere was used to obtain the radiant flux. A Keithley source-measure unit was used to drive the devices, with the ITO electrode wired as the anode. The photoluminescence spectra were measured on reference films deposited on quartz substrates by use of a SPEX 1681 Minimate-2 spectrofluorometer. The excitation wavelength for all photoluminescence (PL) measurements was 470 nm. The preparation of the solutions, the deposition of the films, and the device characterization were conducted in a dry nitrogen glovebox, to minimize exposure to moisture and oxygen. The samples were briefly exposed to ambient conditions before and after the drying step and during the photoluminescence measurements.

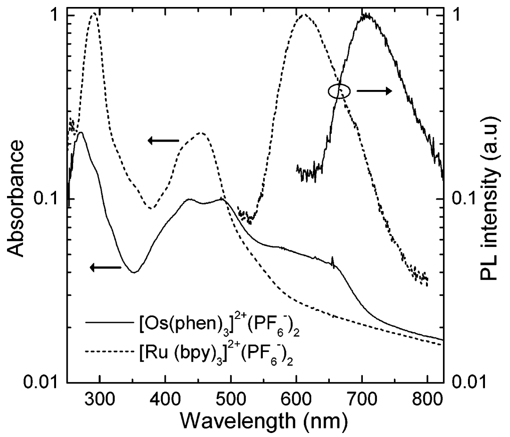

Figure 1. Absorption and (normalized) emission spectra of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ and $[Os(phen)_3]^{2+}(PF_6^-)_2$ films.

Results and Discussion

Figure 1 shows the absorption and emission spectra measured in pristine films of the two complexes. The ruthenium complex shows strong absorption with peaks around 290 and 450 nm, corresponding to ligand-to-ligand ($\pi-\pi^*$) and metal-to-ligand charge transfer (MLCT) transitions, respectively.[19] The emission, which arises from a ligand-to-metal charge-transfer transition,[19] shows a maximum at 610 nm. The absorption of the osmium complex shows similar peaks, with the $\pi-\pi^*$ transitions at 270 nm and the MLCT absorption band peaking around 500 nm but rather broad and with good overlap with the emission of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$. Such overlap between the matrix emission and dopant absorption is necessary for efficient energy transfer (one should keep in mind, though, that the absorption of the osmium complex in solid solution might be different). Finally, the emission of the osmium complex is shown to peak at 710 nm.

The normalized photoluminescence spectra from solid solutions of 1% and 5% (w/w) of the osmium complex into the ruthenium complex films are shown in Figure 2 (top panel). The spectra of pristine $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ and $[Os(phen)_3]^{2+}(PF_6^-)_2$ films are also shown for comparison. At 1% doping, we observe two peaks of nearly equal intensity at 610 and 675 nm. At 5%, most of the matrix emission is quenched as seen by the peak intensities at 610 and 695 nm. At such low dopant concentrations, most of the incident energy is absorbed by the matrix, and a fraction of it is subsequently transferred to the dopant. What is interesting and potentially useful is the shift seen in the emission of the $[Os(phen)_3]^{2+}$, which peaks at 675 nm in the 1% film, and at 695 nm in the 5% film, compared to 710 nm in the pristine $[Os(phen)_3]^{2+}(PF_6^-)_2$ film. Similar shifts have been observed in the emission of laser dyes doped in organic semiconductor films and have been attributed to solid-state solvation.[20,21] This is analogous to solvatochromism seen in liquid solutions,[22] leading to differential stabilization of the ground and excited states. Here the

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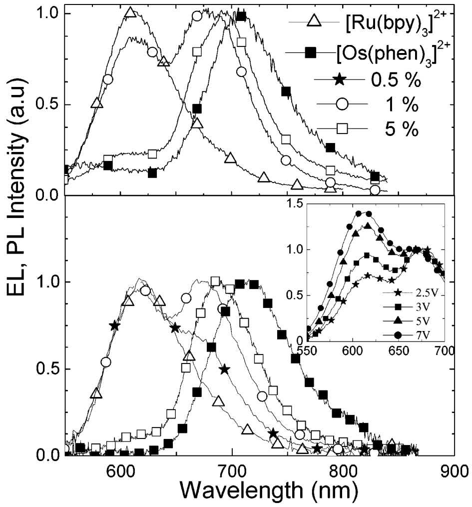

Figure 2. (Top panel) Normalized photoluminescence spectra of doped and pristine films under 470 nm excitation. (Bottom panel) Normalized electroluminescence spectra from devices made with doped and pristine films at 3 V. (Inset) Bias dependence of the emission spectrum for the 1% doped film.

metal−ligand excited states of $[Os(phen)_3]^{2+}$ undergo energy shifts due to increasing self-polarization (from other $[Os(phen)_3]^{2+}$) inside the $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ matrix, leading to a change in the energy gap and the observed behavior.

Normalized electroluminescence spectra of devices made from pristine and doped films and driven at 3 V are shown in Figure 2 (bottom panel). The spectra from these devices are identical to the film photoluminescence, indicating that the same optical transitions and energy exchange mechanisms are involved. The solid-state solvation shift of the $[Os(phen)_3]^{2+}$ emission seen in photoluminescence is also present in the electroluminescence. By 5% doping, nearly all of the emission is coming from $[Os(phen)_3]^{2+}$, with very little contribution from the matrix. The electroluminescence spectra were found to vary with bias, as shown in the inset of Figure 2 for the film with 1% doping. Increasing the bias from 2.5 to 7 V leads to an increase in the relative emission intensity of the matrix peak at 610 nm by a factor of 2. Such increases of the matrix emission with bias are attributed to saturation of the dopant excited states.[23] As expected, the effect was found to be much smaller for the 5% doped film (data not shown).

Figure 3 shows the external quantum efficiency (η) of electroluminescent devices made from pristine films of the ruthenium and the osmium complexes, as well as a film doped at 5%. The efficiency of the $[Os(phen)_3]^{2+}(PF_6^-)_2$ device is only a fraction of that of the $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ one, consistent with the lower emission quantum yield of the osmium complex.[18] However, the $[Os(phen)_3]^{2+}(PF_6^-)_2$ device shows better stability, consistent with the improved metal−ligand bond stability and ligand field splitting energy expected by a complex utilizing a third-row transition metal.[18,24−25] The device based on the doped film is shown to be the most efficient, showing an order of magnitude higher efficiency than the device made with the pristine osmium complex. This indicates that substantial self-quenching takes place in pristine $[Os(phen)_3]^{2+}(PF_6^-)_2$ films. The peak external quantum efficiency in this device reaches 0.75% (with a luminance of 220 cd/m^2 at 3 V applied bias and with 120 mA/cm^2 flowing through the device), which is high for a highly red EL device.[26−27] The dependence of the (peak) quantum efficiency on the degree of doping is shown in the inset of Figure 3. The dependence is the expected one for addition of phosphorescent dopants, with the decrease observed past 5% attributed to self-quenching.[14]

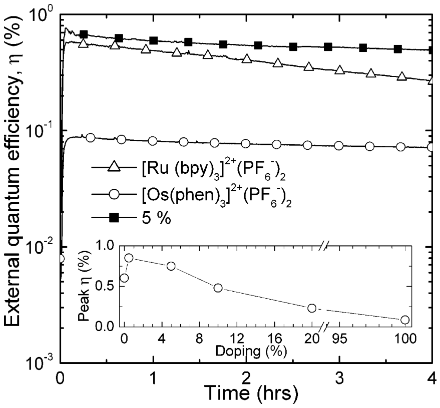

Figure 3. Temporal evolution of the external quantum efficiency devices made with the pristine and the 5% doped film under 3 V forward bias. (Inset) Dependence of peak efficiency on dopant concentration.

Conclusions

In conclusion, we explored the addition of phosphorescent dopants in electroluminescent devices based on an ionic transition metal complex. By use of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ as the matrix and $[Os(phen)_3]^{2+}$ $(PF_6^-)_2$ as the dopant, devices with emission that can be tuned by the dopant concentration were fabricated. Their efficiency was found to be higher than that from devices based on pristine films of the matrix or the dopant. Preliminary studies suggest that device stability was improved upon addition of the phosphorescent dopant.

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