Improved Turn-on Times of Iridium Electroluminescent Devices by Use of Ionic Liquids

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We demonstrate an improvement in the turn-on time of electroluminescent devices based on the iridium complex $[Ir(ppy)_2(dtb-bpy)]^+(PF_6^-)$, where ppy is 2-phenylpyridine and dtb-bpy is 4,4′-di-*tert*-butyl-2,2′-dipyridine, by introduction of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate $BMIM^+(PF_6^-)$. Addition of 0.46 mol of the ionic liquid per mole of Ir complex reduces the turn-on time from 5 h to 40 min. However, the device lifetime is also reduced by a factor of 3 over this range, suggesting a tradeoff between device speed and stability. These results are discussed within the framework of the electrodynamic model of device operation and are found to be consistent with an increase in the ionic conductivity of the $[Ir(ppy)_2(dtb-bpy)]^+(PF_6^-)$ films upon the addition of ionic liquid.

Introduction

Electroluminescent devices based on ionic transition metal complexes (iTMCs) are being extensively studied as potential candidates for display and solid-state lighting applications.[1−8] These devices consist of a single solution-deposited layer of an iTMC sandwiched between two metal electrodes. Air-stable electrodes[1,9] that can be deposited by lamination[10] can be used, which allows the simple fabrication of large-area, fault-tolerant illumination panels.[11] These advantages stem from the high density of mobile ions in the iTMC film, which arises from the counterions associated with the complexes. Under an applied bias, these counterions drift and accumulate near one electrode, leaving uncompensated metal ions near the other electrode. The high electric fields caused by counterion accumulation and depletion enable the efficient injection of holes and electrons, leading to a high electroluminescence efficiency. As a result, after a few years of development, electroluminescent devices based on a single layer of an iTMC have reached external quantum efficiencies of 5%[2,3] and power efficiencies as high as 10 Lm/W.[2]

Although electroluminescent devices based on iTMCs offer several advantages, their turn-on time (time it takes to reach maximum emission upon the application of a dc bias) is dependent on the mobility of the counterions and can range from seconds to several hours.[1] In order for these materials to be considered in any practical applications, the turn-on time needs to be decreased substantially.[12] Reducing the thickness of the iTMC layer reduces the turn-on time, but leads to a decrease in the efficiency due to exciton quenching at the electrodes.[13] Increasing the applied bias makes the devices turn on faster, but iTMC-based devices show rapid degradation above their turn-on voltage.[4,5] Using pre-biasing schemes, where a high bias is applied only for a few seconds to switch the device on, can be used to circumvent this problem.[5] However, such schemes require complex driving electronics and are incompatible with some of the proposed device architectures.[11] Hence, iTMCs with a high intrinsic ionic conductivity represent the most preferable way to obtain devices with a fast turn-on time.

To this extent, several studies have focused on the relative abundance and mobility of the ions in the iTMC film. Addition of poly(ethylene oxide) (PEO) to films of a tris-(4,7-diphenyl-1,10-phenanthroline disulfonate)ruthenium(II) complex decreased the turn-on time from 2 min to 30 s.[14] Addition of $(LiCF_3^+)(SO_3^-)$ salt to these blends reduced the

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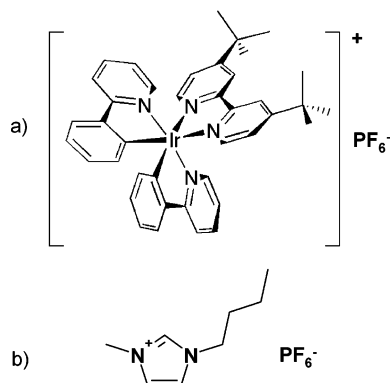
Figure 1. (a) Structure of $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$. (b) Structure of $BMIM(PF_6^-)$.

Figure 2. Radiant flux versus time of $ITO/[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$: $BMIM^+(PF_6^-)/Au$ devices with varying concentrations of ionic liquid under a -3 V bias.

turn-on time further to approximately 20 s. Similarly, a decrease in the turn-on time of devices from binuclear ruthenium complexes was demonstrated with the addition of lithium trifluoromethanesulfonate/crown ether complexes.[15] However, the external quantum efficiencies of all these devices were low—on the order of 0.02% or lower.[14,15] Finally, the nature of the counterions was found to have dramatic impact on the ionic conductivity. In devices based on ruthenium complexes, replacing the PF_6^- counterions with ClO_4^- or BF_4^- led to a reduction of the turn-on time from several minutes to a few seconds.[3,6,7] However, these experiments showed that a reduction of the turn-on time was also accompanied by an increase in the rate of degradation of the light output over time, suggesting a possible tradeoff between device speed and stability.

In this paper, we describe a reduction in the turn-on time in devices based on $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$, where ppy is 2-phenylpyridine and dtb-bpy is 4,4′-di-*tert*-butyl-2,2′-di-pyridine, achieved by the use of the ionic liquid 1-butyl-3-methyl imidazolium hexafluorophosphate, $BMIM^+(PF_6^-)$, with chemical structures shown in Figure 1. We have chosen this particular iTMC because it yields devices with a high external quantum efficiency (5%), but with a remarkably long turn-on time of several hours.[2] We investigate the effects of $BMIM^+(PF_6^-)$ concentration on the device speed and stability.

Experimental Section

Details on the synthesis of $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$ are reported elsewhere.[2] The ionic liquid $BMIM^+(PF_6^-)$ was purchased from Sigma Aldrich, stored in a nitrogen glovebox, and used as received. All solutions were prepared and spin-cast in a nitrogen glovebox. The $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$ and $BMIM^+(PF_6^-)$ were initially dissolved separately in acetonitrile and then combined to form solutions of 24 mg of the Ir complex/mL of solution and varying percentages of the ionic liquid. The concentration percentages reported are for volume percentages (v/v) of $BMIM^+(PF_6^-)$ in this solution. For $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$, 0.125% $BMIM^+(PF_6^-)$ correlates to 0.23 mol of $BMIM^+(PF_6^-)$/mol of $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$ in the film. Likewise, 0.188%, 0.25%, and 0.5% $BMIM^+(PF_6^-)$ correspond to 0.345, 0.46, and 0.96 mol of $BMIM^+(PF_6^-)$/mol of $[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)$, respectively.
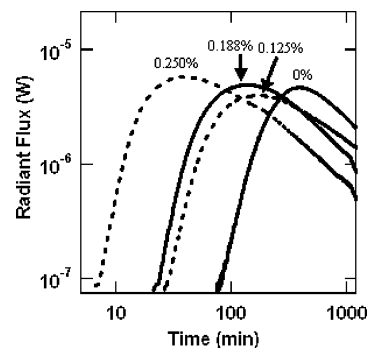
The films were spin-coated from solution onto glass substrates covered with prepatterned ITO electrodes (Thin Film Devices, Anaheim, CA). The thickness of the films was approximately 75 nm, as measured with profilometry. The ITO substrates were cleaned just before the deposition of the organic layer by a deionized water bath, followed by UV/ozone treatment. The films were dried for approximately 12 h at 80 °C under vacuum and were reintroduced in a dry nitrogen glovebox for further processing and characterization. A 200 Å thick Au top electrode was deposited through a shadow mask that defined six devices per substrate with a 3 mm² active area each. The deposition of Au was carried out intermittently to minimize heating of the organic film. The electrical characteristics of the devices were measured with a Keithley 236 source-measure unit, and the radiant flux measurements were collected with a calibrated UDT S370 optometer coupled to an integrating sphere. The electroluminescence spectra were measured with a calibrated S2000 Ocean Optics fiber spectrometer.

Results and Discussion

Ionic liquids, such as $BMIM^+(PF_6^-)$, have found use in a variety of electrochemical devices, including displays, actuators, and electrochromic windows.[16,17] Also called room-temperature molten salts, they often consist of an organic cation (e.g., $BMIM^+$) and an inorganic anion (e.g., PF_6^-). They are frequently used as electrolytes since they show reasonable ionic conductivity and are fluid at room temperature. Furthermore, the chemical structure of these materials can be manipulated to address polarity and solubility. Recently, ionic liquids have been introduced in films of the conjugated polymers poly(2-methoxy-5-(2′-ethylhexoxy)-1,4-phenylenevinylene) (MEH−PPV) and poly(9,9-dihexyl-fluorene-2,7-diyl) (PDHF) to endow them with ionic conductivity.[18−20] Since it is the ionic conductivity that determines the turn-on time of iTMC devices, the addition of ionic liquids to these films might prove to be a viable pathway for reducing turn-on time.

This is shown in Figure 2, where the temporal behavior of the radiant flux of $ITO/[Ir(ppy)_2(dtb\text{-}bpy)]^+(PF_6^-)/Au$

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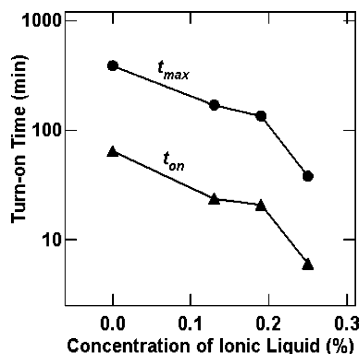(20) Ouisse, T.; Stéphan, O.; Armand, M.; Leprêtre, J. C. *J. Appl. Phys.* **2002**, *92*, 2795.

Figure 3. Turn-on times t_{max} (circles) and t_{on} (triangles) versus concentration of ionic liquid for ITO/[Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$): BMIM$^+$(PF$_6^-$)/Au devices under a -3 V bias.

devices with various amounts of ionic liquid is compared. The data show that as the concentration of the ionic liquid is increased from 0% to 0.25%, the time for the onset of light emission t_{on} is reduced from 1 h to 6 min. Similarly, the time to achieve maximum emission t_{max} decreases significantly, from approximately 5 h to 40 min. The data shown were obtained for a reverse bias of -3 V (ITO biased positive), and a similar trend was observed under forward bias. The shape of these curves is consistent with previous observations. Initially, the radiant flux follows the device current (not shown here) and increases because as the counterions redistribute, electron and hole injection are enhanced. The radiant flux reaches a maximum at a time t_{max}, when steady state is achieved (the current also reaches its steady state at this point). The decrease in the radiant flux at later times corresponds to degradation seen in several iTMC devices, for reasons that are not entirely clear.[1,21]

According to the electrodynamic model,[22,23] the turn-on time of these devices is determined by the speed at which counterion redistribution near the electrodes takes place. If the concentration and/or the mobility of counterions is increased, it takes a shorter amount of time for these ions to redistribute near the electrodes, and the devices turn on faster. Hence, the results of Figure 2 can be understood by an increase in the ionic conductivity upon the addition of ionic liquid. The influence of ionic liquid on the turn-on time is quite dramatic. As shown in Figure 3, t_{on} and t_{max} decrease in an exponential fashion with ionic liquid concentration.

Devices with ionic liquid concentrations of 0.5% and above were unstable—that is, they turned on almost instantly after a voltage was applied but lasted only a few seconds. The poor characteristics of these devices were likely due to electrochemical degradation from extremely high ion accumulation (see below) rather than to poor morphology of the films. Optical microscopy revealed no phase separation between [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) and the ionic liquid for all concentrations investigated, including 0.5%, for which the molar ratio of ionic liquid to the Ir complex is nearly one-to-one. Previous work found that high-temperature processing often augments phase separation between an ionic

liquid and nonpolar polymers such as MEH−PPV and PDHF.[20] However, a high compatibility was found between the Ir complex and the ionic liquid, even when baked at 80 °C, presumably due to the intrinsically ionic nature of the former.

Ionic liquids have been used in light emitting diodes made from conjugated polymers to enhance charge injection.[18−20] The mechanism behind this enhancement involves accumulation of ions near the electrodes, which leads to high interfacial fields that decrease the barrier for tunneling of electronic carriers.[22,23] As a result, if the device performance (in terms of emission intensity and efficiency) is limited by injection, an enhancement is expected upon addition of ionic liquids. This has been observed in recent experiments. Panozzo et al. investigated the addition of the ionic liquid tetrahexyl-ammonium-bis-trifluoro-methyl-sulfonylimide (THA-TFSI) to PDHF and MEH−PPV.[18] They reported an improvement of the power efficiencies by over 1 and 2 orders of magnitude for the PDHF and MEH−PPV, respectively. Yang et al. investigated the influence of a series of 1-methyl-3-alkyl-imidazolium salts to MEH−PPV devices.[19] Changing the butyl substituent of BMIM$^+$ to a longer alkyl chain promoted phase compatibility with MEH−PPV and led to higher external quantum efficiencies (as high as 1.4% for a hexadecyl substituent). In a detailed investigation of the current behavior of such devices, Ouisse et al. examined the addition of molten TFSI salts to PDHF and related polymers.[20] Increased salt concentration led to higher emission intensity.

The addition of ionic liquid in [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) has, however, little effect on the emission intensity. The maximum radiant flux R_{max} of these devices increases only slightly with ionic liquid concentration (see Figure 2). Furthermore, we did not observe any systematic change in the maximum external quantum efficiency with ionic liquid content (data not shown). These results are consistent with previous data for iTMC devices incorporating modest levels of additional ions[14,15] and indicate that the increase in the ionic conductivity does not change appreciably the steady-state injection rates for electrons (from ITO) and holes (from Au). This is consistent with earlier work,[2] which established that ITO and Au are already very efficient injectors of electrons and holes, respectively, into [Ir(ppy)$_2$(dtb-bpy)]$^+$-(PF$_6^-$).

However, the same result was found to be true at a forward bias of 3 V, namely, the maximum radiant flux and efficiency were not altered significantly by the addition of ionic liquid. This is surprising since earlier studies established that Au is a poor injector of electrons into [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$), confirmed by the fact that the radiant flux and efficiency are considerably lower at 3 V compared to -3 V.[2] Therefore, the data show that the Au/[Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) contact remains a poor electron injector even after the addition of ionic liquid. This means that the ion density near this contact does not change appreciably upon addition of the ionic liquid. This implies that the BMIM$^+$ ions, which are attracted toward the Au/[Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) contact at forward bias, cannot accumulate at high enough densities, probably due

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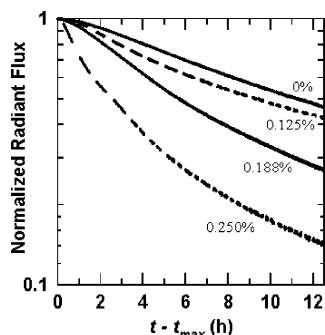(23) deMello, J. C. *Phys. Rev. B* **2002**, *66*, 235210.

Figure 4. Normalized radiant flux versus time from radiant flux maximum for ITO/[Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$): BMIM$^+$(PF$_6^-$)/Au devices with varying concentrations of ionic liquid under a -3 V bias.
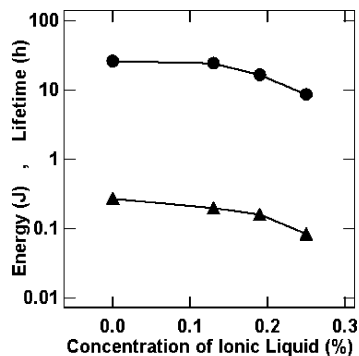

Figure 5. Lifetime (t_L, circles) and total emitted energy (E_{tot}, triangles) versus concentration of ionic liquid for ITO/[Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$): BMIM$^+$(PF$_6^-$)/Au devices under a -3 V applied bias.

to their relatively large size and/or low mobility in the [Ir-(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) matrix.

Unfortunately, addition of ionic liquids into [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) leads to a degradation of the device stability. Figure 4 shows the normalized radiant flux for each of these devices versus time from t_{max} at a bias of -3 V. Similar results were obtained at forward bias. Clearly, the rate of decay is enhanced by ionic liquid concentration. To quantitatively assess the stability of these devices, the lifetime t_L of each device was defined to be the time at which the radiant flux decayed to one-fifth of R_{max}. Furthermore, the total emitted energy E_{tot} over the lifetime of the device was calculated by integrating the radiant flux over time from the onset of emission up to t_L.[21] In Figure 5 t_L and E_{tot} are plotted against ionic liquid concentration. Both t_L and E_{tot} decrease with increasing ionic liquid concentration, and each are reduced by a factor of 3 in going from 0% to 0.25% ionic liquid.

A similar decrease in the lifetime upon the addition of mobile ions was observed in other iTMC devices.[15] One possible explanation is readily suggested by the electrodynamic model, which predicts that the field at the interface

increases dramatically with mobile ion density.[22,23] The increase in the density of PF$_6^-$ counterions that occurs upon the addition of ionic liquid can lead to very high fields near the positively charged electrode, possibly leading to multiple oxidation and subsequent decomposition of the [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) complex. This is in agreement with studies of Ohsawa et al.,[24] who found that although Ir complexes can be reversibly reduced with up to 4 electrons, reversible multiple oxidation is not possible. The only reversible oxidation is Ir(III) to Ir(IV), which corresponds to injection of one hole into the complex. Additional electron removal will lead to decomposition. Such a mechanism would be consistent with enhanced degradation observed not only upon the addition of mobile ions but also at a high applied bias, where high interfacial fields are expected.

Conclusions

We have demonstrated improved turn-on times of devices based on the iridium complex [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) by introduction of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate BMIM$^+$(PF$_6^-$). The ionic liquid showed excellent compatibility with the intrinsically ionic Ir complex. For a blend with 0.46 mol of the ionic liquid/mol of Ir complex, the time for onset of emission was reduced from 1 h to 6 min, and the time to achieve maximum emission was reduced from approximately 5 h to 40 min. Although the ultimate turn-on time in these devices is still too slow for any practical application, the magnitude of the decrease is substantial. An improvement of similar magnitude would be enough to bring the response of devices made from other iTMCs into practical time scales. The lifetime and total emitted energy were each reduced by a factor of 3 over this range of ionic liquid concentration. The results were consistent with the electrodynamic model of device operation and indicated an increase in the ionic conductivity of the [Ir(ppy)$_2$(dtb-bpy)]$^+$(PF$_6^-$) films upon addition of the ionic liquid.

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