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Communication

Improving the Turn-On Time of Light-Emitting Electrochemical Cells without Sacrificing their Stability

Rubén D. Costa,[†] Antonio Pertegás,[†] Enrique Ortí,[†] and Henk J. Bolink*[,†,‡]

[†]*Instituto de Ciencia Molecular, Universidad de Valencia and* [‡]*Fundació General de la Universitat de València (FGUV), PO Box 22085, E-46071 Valencia, Spain*

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Light-emitting electrochemical cells (LECs) provide an attractive alternative to organic light-emitting diodes (OLEDs) due to their simple architecture and the use of air-stable electrodes. The concept of a polymer LEC, where the device consists of a single layer of a mixture of a conjugated polymer, an ion conducting polymer, and a salt, was introduced by Pei et al.[1,2] However, the simplest LECs are based on ionic transition-metal complexes (iTMCs) with Ru(II) and Ir(III) as the metal core.[3,4] The charge of the iTMCs is compensated with mobile counteranions such as PF_6^- or BF_4^- that make the addition of extra salts unnecessary. Furthermore, iTMCs present stable oxidized and reduced species and exhibit high emission quantum yields via phosphorescent processes.[5−8] Recently, it was reported that LECs using supramolecularly caged iridium complexes exhibited lifetimes as high as 3000 h at an average luminance of 200 cd/m^2, showing the potential of these devices for low-cost lighting and signage applications.[9−11]

The difference in the operation mechanism between LECs and OLEDs results from the mobile ions present in LECs and their redistribution during the device operation. As a consequence of the low ionic conductivity in the solid state, LECs show long turn-on times (t_{on}), defined as the time required to reach a luminance of 100 cd/m^2.[3,4] For practical applications, the turn-on time must be close to a few seconds, which is generally not observed. Unfortunately, all the strategies to improve the turn-on time come at a cost of the device stability.[12−21] The most promising strategy to decrease the turn-on time is by means of the addition of an ionic liquid (IL).[13,14] ILs have a high intrinsic ionic conductivity and when added to the iTMC layer they increase the density of the mobile ions. Despite their high potential for improving the turn-on time, only one IL, 1-butyl-3-methylimidazolium hexafluorophosphate [$BMIM^+$][PF_6^-] (Figure 1, right), has been used in LECs.[13,14]

In this communication, we evaluate the effect of ILs with different intrinsic ionic conductivities on the performance of LECs consisting of the archetype Ir-iTMC bis(2-phenylpyridine)-2,2′-bipyridine-iridium(III) hexafluorophosphate, [Ir(ppy)$_2$bpy]PF$_6$ (Figure 1, left), as the active electroluminescent component.[7] Three ILs were evaluated: [$BMIM^+$][PF_6^-] as the reference, and 1-ethyl-3-methylimidazolium hexafluorophosphate [$EMIM^+$][PF_6^-] and 1-hexyl-3-methylimidazolium hexafluorophosphate [$HMIM^+$][PF_6^-] as ILs with higher and lower ionic conductivities, respectively (Figure 1, right). They were chosen because they are similar in chemical structure and show significantly different ionic conductivities.[22−25] It was found that it is possible to decrease the turn-on time without sacrificing the stability of the iTMC-based LECs when the IL with a high intrinsic ionic conductivity was used.

Simple two-layer LECs were prepared for this study. Prior to the deposition of the active layer, a thin layer (100 nm) of poly(3,4-ethylenedioxythiophene)−poly(styrenesulfonate)

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*Corresponding author.

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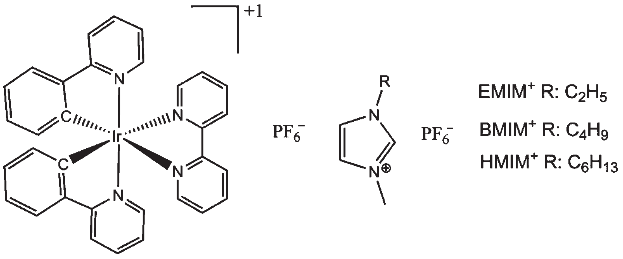

Figure 1. Chemical structure of the archetype [Ir(ppy)$_2$(bpy)]PF$_6$ complex (left) and the three ionic liquids with different alkyl substituents R (right).

(PEDOT:PSS) was spin-coated to increase the reproducibility of the devices. The active layer consisted of [Ir(ppy)$_2$bpy]PF$_6$ mixed with one of the three different ILs at Ir-iTMC:IL molar ratios of 1:0, 1:1, and 4:1. The active layer had a thickness of approximately 100 nm for all devices. Aluminum was used as the top electrode contact. Details concerning the device preparation can be found in the Supporting Information.

All LECs containing the different ILs showed the same electroluminescence (EL) spectrum as the pristine device (Figure 2). The maximum of the EL spectrum lies at around 576 nm and is independent of the Ir-iTMC:IL molar ratio. The devices emit in the yellow region of the visible spectrum with CIE coordinates $x = 0.508$ and $y = 0.486$.[26] All of them showed a homogeneous emitting area, which together with the similar emission spectra is an indication of a high compatibility of the Ir-iTMC with the different ILs. This compatibility is due to the intrinsic ionic nature of both components.[13,27]

The luminance versus time curves of the LECs containing the different ILs are presented in Figure 3. Most notably, the luminance increases with increasing the intrinsic conductivity of the IL and, at the same time, the turn-on time decreases (see Table 1). Compared to the device without IL, which shows a t_{on} of 11.5 h, all the devices containing ILs are more than 1 order of magnitude faster. The t_{on} parameter also decreases with increasing the concentration of the ILs, in accord with what has been previously observed.[13,14]

One very important additional observation is that the luminance level of the device containing [EMIM$^+$][PF$_6^-$] remains above that of the device using [BMIM$^+$][PF$_6^-$] for as long as 350 h (Figure 2). This indicates that the stability of the device containing the IL with a higher intrinsic conductivity is superior. To be able to compare the device stability in a more systematic way, it is usually presented either as the time to reach half of the maximum luminance ($t_{1/2}$) or as the total emitted energy (E_{tot}). E_{tot} is estimated by integrating the radiant flux over time up to the time the luminance reaches 1/5th of the maximum value for a cell area of 3 mm^2.[28] The comparison of $t_{1/2}$ values is the simplest method but it is only valid when

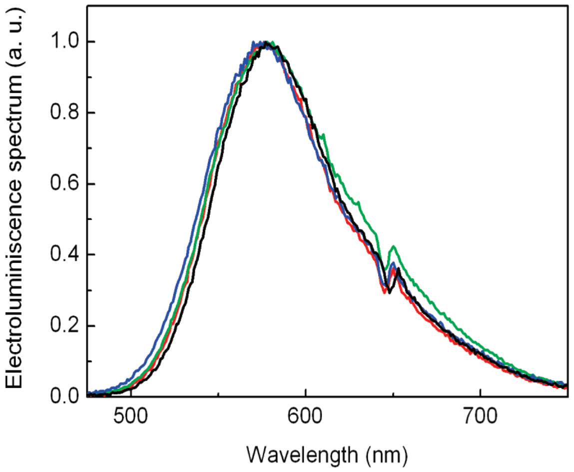

Figure 2. Electroluminiscence spectra of LECs containing different ionic liquids (iTMCs:IL molar ratio = 1:1): [EMIM$^+$][PF$_6^-$] (blue), [BMIM$^+$][PF$_6^-$] (red), and [HMIM$^+$][PF$_6^-$] (green) under an applied bias of 3 V. The electroluminescence spectrum of the LEC device without IL is also shown as a reference (black).

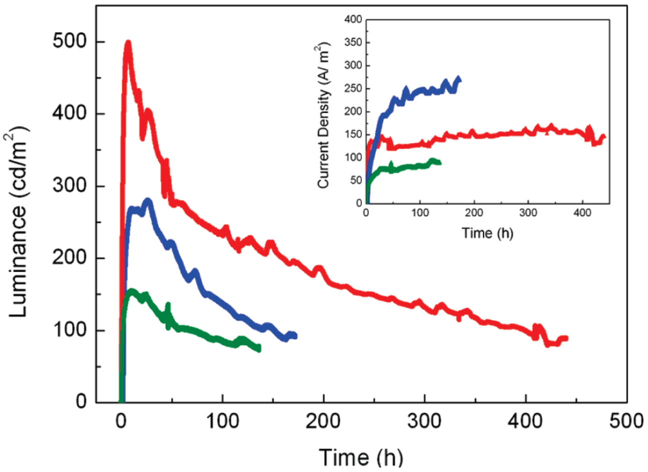

Figure 3. Luminance and current density (inset) versus time for ITO/PEDOT:PSS/Ir-iTMC:IL(4:1)/Al LEC devices under a constant voltage of 3 V. Devices incorporating [EMIM$^+$][PF$_6^-$], [BMIM$^+$][PF$_6^-$], and [HMIM$^+$][PF$_6^-$] ionic liquids are in red, blue, and green, respectively.

the luminance of the devices presents similar values. Hence, in this study, $t_{1/2}$ is not a meaningful parameter because the luminance values change drastically as a function of the IL used. For that reason, we estimated the total emitted energy E_{tot} for the different devices. The E_{tot} values and other data deduced from the luminance and current density versus time graphs are presented in Table 1.

Surprisingly, the total emitted energy obtained for the device using the IL with the highest intrinsic conductivity at a molar ratio of 4:1 is slightly above that of the reference device without IL (6.7 vs 6.6 J, respectively). This is the first time that a strategy to decrease the turn-on time of LECs does not result in a decrease of device stability. For higher IL concentrations (Ir-iTMC:IL, 1:1), the device using [EMIM$^+$][PF$_6^-$] again presents the fastest t_{on} and the highest stability of the series tested (see Table 1), albeit for this IL concentration the stability is not higher than that found for the pristine device.

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Table 1. Device Data for the LEC Devices Operating at 3 V

IL	intrinsic conductivity (mS/cm)	iTMC:IL	t_{on}[d] (min)	$t_{1/2}$[e] (h)	luminance (cd/m^2)	power efficiency lm/W	E_{tot} (J)
[EMIM$^+$][PF$_6^-$]	5.2[a]	4:1	24	81	497	4.6	6.7
		1:1	2.9	4.1	615	4.9	0.6
[BMIM$^+$][PF$_6^-$]	1.5[b]	4:1	82	103	269	8.6	2.3
		1:1	3.5	4.3	586	16.7	0.2
[HMIM$^+$][PF$_6^-$]	1.1[c]	4:1	132	134	153	5.6	1.1
		1:1	22	5.5	302	14.1	0.1
without		1:0	690	668	219	6.1	6.6

[a] Value at 298.15 K from ref 23. [b] Value at 298.15 K from ref 25. [c] Value at 295.1 K from ref 24. [d] Time to reach 100 cd/m^2. [e] Time to reach half of the maximum luminance.

Additionally, the devices employing the ILs at a molar ratio of 1:1 have lower t_{on} times, higher luminances, and lower stabilities than those with a molar ratio of 4:1. The lower turn-on times are in line with the current understanding of the operation mechanism of LECs, which depends strongly on the amount of free ions for the build-up of a thin interlayer close to the electrodes. With more IL there are more free ions and, hence, the build-up of the interlayer is faster.

The current densities of the devices do not show a clear trend with respect to the intrinsic conductivity of the ILs used. The devices with [EMIM$^+$][PF$_6^-$] have a lower current density than those using [BMIM$^+$][PF$_6^-$]. Hence, there is little influence of the IL on the magnitude of the electronic currents. This indicates that the observed increase in luminance is due to a higher emissivity of the emitter used. As the emitter used is the same for all the devices, apparently degradation reactions have evolved to a lesser extent for the devices incorporating [EMIM$^+$][PF$_6^-$] and, hence, the luminance is higher. The device efficacy is determined as the ratio between luminance and current density. In most cases, the maximum efficacy is reported. However, it usually drops rapidly with time effectively determining the useful lifetime of the device. For practical applications, a more constant device efficacy is desired. The devices employing the IL with the highest intrinsic conductivity show efficacy decay curves that are more similar to the luminance decay curves and hence maintain a rather constant efficacy over time.

In summary, the impact of different ILs on the performance of LECs based on the archetype Ir-iTMC [Ir(ppy)$_2$-(bpy)]PF$_6$ is reported. The ionic liquids were selected in view of their different intrinsic conductivity. In contrast to what is normally observed, it is possible to simultaneously optimize the turn-on time, the maximum luminance, and the stability of the device upon the addition of an ionic liquid with a high intrinsic ionic conductivity.

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Supporting Information Available: Experimental procedures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.