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Green Light-Emitting Solid-State Electrochemical Cell Obtained from a Homoleptic Iridium(III) Complex Containing Ionically Charged Ligands

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Organic light-emitting diodes (OLEDs) are becoming increasingly successful as a new display technology.[1−3] Light-emitting electrochemical cells (LECs) are among the youngest generation of OLEDs and contain ionic charges as additional ingredients.[4] These ionic charges facilitate electronic charge injection into the light-emitting film independent of the metallic electrode employed. First examples of LECs were based on polymeric OLEDs, to which salts, such as $LiCF_3$, were added to facilitate the charge injection.[5] Later examples used a single molecule approach, in which a single molecule acts both as the charge transporting species and as the emitter. Most of these single molecule type LECs make use of the positively charged metal organic complex, tris-bipyridine ruthenium, balanced by a large negative counterion such as hexafluorophosphate.[6,7]

The possibility to use air stable electrodes combined with the architectural simplicity of the LEC devices is the main advantage over nonionic OLEDs. Additionally, large efficiencies can be obtained at low driving voltage which is needed for lighting applications.[8] As a result of the operation mechanism of LEC devices which involves displacement of ionic charges, the turn on time ranges from seconds to hours. Using high voltage pulses allows for a significant reduction in these turn on times, allowing the use of LEC for lighting and possibly display applications. With respect to nonionic OLEDs, LEC devices are limited by the reduced amount of emission colors available and their lifetimes. Because of their high quantum efficiencies iridium(III) based complexes are among the most appealing complexes for LEC devices. However, most of the reported high luminance efficiency Ir(III) complexes are neutral as they use cyclometalating ligands coordinated to Ir(III), such as phenylpyridine or acetyl acetate. To introduce a charge on this kind of complexes several approaches can be used. One possibility is that of designing heteroleptic complexes formed by a mixture of a neutral ligand as, for example, bipyridine derivatives, with cyclometalating ligands. Thus, a yellow and green LEC device has been obtained from a single molecular thin film of the complex cation Ir(III) bis(phenylpyridine)tertbutylbipyridine.[9,10] The drawback of using the bipyridine ligand is that it has a lower lying lowest unoccupied molecular orbital than the phenylpyridine leading to a red-shifted emission with respect to the neutral tris(phenylpyridine)iridium ($Ir(ppy)_3$) emitter. Wide band gap neutral ligands can also be used to prepare a variety of complexes with different emission wavelengths.[11] However, the necessity to use multiple ligands to obtain a charged Ir(III) complex does complicate the design. To overcome this problem a different approach to charged Ir(III) complexes is that of attaching a charged side group in the periphery of the cyclometaling ligands. This approach and the performance of the LEC using the resulting cationic Ir(III) complex are described in this communication. The complex, *fac*-tris[2-(2-pyridinyl-*k*-*N*)-5(tri-*n*-butylphosphonium)phenyl)-*k*-*C*]−iridium(III) formulated as $[Ir(ppy\text{-}Pbu_3)_3{:}(PF_6)_3]$, **1** (Figure 1), was prepared as the bromide salt using a slightly modified synthesis as described in the literature.[12,13] The raw product was repeatedly re-crystallized from ethyl acetate to yield 63.2% of the final product, with a purity of 99.5% by ^{1}H NMR.[19] The bromide anions were exchanged by hexafluorophosphonium anions using a metathesis reaction.

In **1** the three cyclometalating ligands are the same. As this ligand contains a net charged side group its net charge is +3. As the counterion we have chosen PF_6^- as this allows for an easier comparison with earlier LEC devices based on iridium compounds.

Thin films of **1** blended with 20% poly(methyl methacrylate) (PMMA) were prepared from acetonitrile solution via spin coating on patterned indium tin oxide (ITO) coated glass plates.[20] The absorption and emission spectra, from acetonitrile solution and the thin film, respectively, are depicted in Figure 2.

The absorption spectrum shows an intense maximum around 272 nm ($\epsilon = 10.4 \times 10^4$ $M^{-1}\cdot cm^{-1}$) and a broad absorption band centered around 360 nm ($\epsilon = 18.9 \times 10^3$ $M^{-1}\cdot cm^{-1}$) with an additional feature at 392 nm ($\epsilon = 10.5 \times 10^3$ $M^{-1}\cdot cm^{-1}$). It is shifted with respect to its parent complex $Ir(ppy)_3$ which has a maximum at 280 nm and a broader band around 375 nm which were assigned to a ligand

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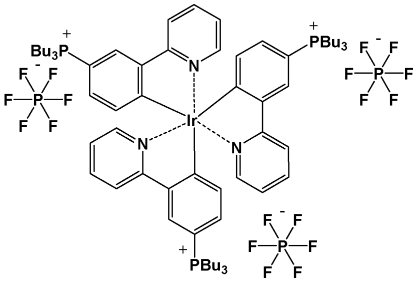

Figure 1. Chemical structure of the charged tris-phenylpyridine iridium compound, Ir(ppy-Pbu$_3$)$_3$:(PF$_6$)$_3$.

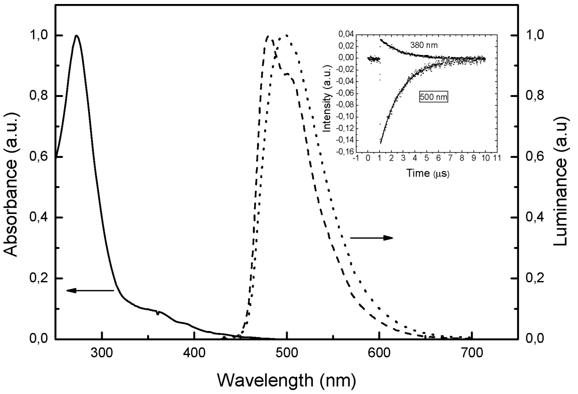

Figure 2. Absorption and emission spectrum of **1** in acetonitrile solution (solid and dashed lines, respectively) and the emission spectrum of a thin film of **1**/PMMA (80:20; dotted line). Inset shows the transient absorption of the excitated state at 380 and at 500 nm of compound **1** in degassed acetonitrile solution.

centered ($\pi-\pi^*$) transition and a metal-to-ligand charge-transfer (MLCT) transition, respectively.[14] Accordingly, in the absorption spectrum of **1** the first transition at 272 nm can be attributed to an allowed ligand centered ($\pi-\pi^*$) transition, while the broad absorption can be assigned to spin-allowed Ir to ligand charge-transfer (MLCT) transitions.

The emission spectrum was taken at room temperature using an excitation wavelength of 360 nm. A strong photoemission is observed with a maximum at 480 nm. This is blue-shifted with 35 nm compared to the emission spectrum of Ir(ppy)$_3$. A similar effect was observed when phenyl hydrogen atoms of the phenylpyridine ligands in Ir(ppy)$_3$ were substituted with inductive electron withdrawing fluorine atoms. This was attributed to an increase in the stabilization of the highest occupied molecular orbital (HOMO) which causes an increase of the optical gap.[15,16] In analogy, in our complex, due to the electron withdrawing nature of the tri-butyl phosphor group on the phenylpyridine ligand, the blue shift is attributed to a more stabilized HOMO level, corroborated by an increase in the oxidation potential. Additionally, the emission peak of compound **1** is more structured than that of Ir(ppy)$_3$, indicative of a more ligand centered transistion ($\pi-\pi^*$) with less MLCT character. This is corroborated by the decrease in MLCT/($\pi-\pi^*$) extension coefficients ratio with respect to Ir(ppy)$_3$.[15] Such a decreased MLCT behavior can result, according to Li et al., in a decrease in luminance quantum yield, which is indeed observed (Table 1).[17] The emission color of compound **1** in solution is a bluish-green with Commission Internationale de l'Eclairage (CIE)[18] coordinates $x = 0.171$ and $y = 0.439$; the photoemission from the solid film has shifted slightly toward the green, resulting in the CIE coordinates $x = 0.206$ and $y = 0.518$.

Table 1. Photophysical Properties

	abs^a 298 K	emission 298^a K		
	λ (nm)	λ (nm)	τ^b (μs)	$\varphi_{em}{}^c$
1	300, 360	480	1.70	0.34
Ir(ppy)$_3$[15]	280, 375	515	1.9	0.40

^{a} Acetonitrile. ^{b} Luminescence emission lifetime (±10%). ^{c} Luminescence quantum yield (±10%), using Ru(bpy)$_3$:(PF$_6$)$_2$ as the reference.

The transient absorption spectra of a diluted, degassed solution of **1** in acetonitrile at two different wavelengths are depicted in the inset of Figure 2. Using an excitation wavelength of 355 nm, the absorption decay is probed at 380 and at 500 nm. At 380 nm, the positive signal represents the absorption decay of the excited state, while at 500 nm, the negative absorption represents the decay in emission from the excited state. Both decays result in an excited-state lifetime of 1.7 μs.

The introduction of charged groups onto the phenyl rings of the phenylpyridine ligands results in a considerable shift in the emission spectrum while maintaining a high quantum efficiency. The resulting blueish-green emission color is interesting for applications in light-emitting devices.

We have used compound **1** to prepare solid-state single layer light-emitting devices. A sandwiched device structure was prepared by spin-coating a thin layer of **1** intermixed with 20% PMMA on ITO coated glass plates followed by a thermally evaporated gold layer. To generate electroluminescence a bias was applied to this ITO/**1**:PMMA/Au device in an inert atmosphere. A green luminescence was observed, slowly increasing in intensity with time (Figure 3). The slow turn on times are typical for LECs and can be increased by applying voltage pulses prior to the direct current bias or by adding of more mobile ionic charge carriers.

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(19) Synthetic procedure: *fac*-tris[2-(2-pyridinyl-*k*-*N*)-5(tri-*n*-butylphosphonium)phenyl)-*k*-*C*]−iridium(III) initially prepared as the bromide salt was synthesized from *fac*-tris[2-(2-pyridinyl-*k*-*N*)(5-bromphenyl)-*kC*]−iridium(III), using the method as described in WO 2002/068435, by a modified procedure reported by Allen et al.[13] *N*,*N*-Dimethylformamide was used as the solvent instead of ethanol. The raw product was repeatedly re-crystallized from ethyl acetate to yield 63.2% of the final product, with a purity of 99.5% by ^{1}H NMR. The bromide anions were exchanged by hexafluorophosphonium anions using a metathesis reaction.

(20) Device preparation: **1** was blended with 20% PMMA to enhance the film forming properties. Thin films were prepared from acetonitrile solution via spin coating on patterned ITO coated glass plates. The ITO glass plates were extensively cleaned just before the deposition of the organic film. The thickness of these films ranged between 100 and 200 nm measured using a profilometer. Au was used as the cathode for these devices, which were evaporated under vacuum ($<2 \times 10^{-6}$ mbarr) to a thickness of 100 nm. Unless mentioned otherwise the device structure used is ITO/**1**:PMMA/Au. Devices were characterized in an inert atmosphere.

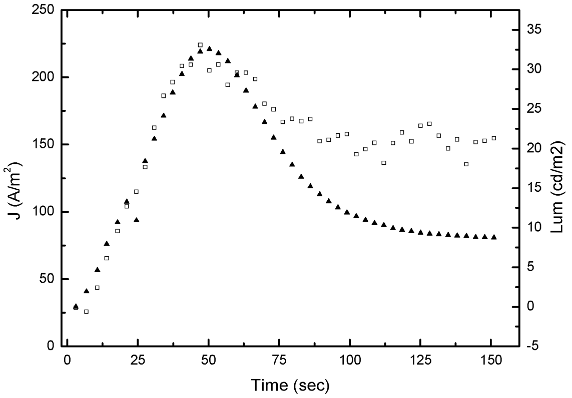

Figure 3. Current density (open squares) and luminance (closed up triangles) vs time at an applied bias of 4 V of a single layer ITO/Ir(ppy-Pbu$_3$)$_3$:(PF$_6$)$_3$/Au device.

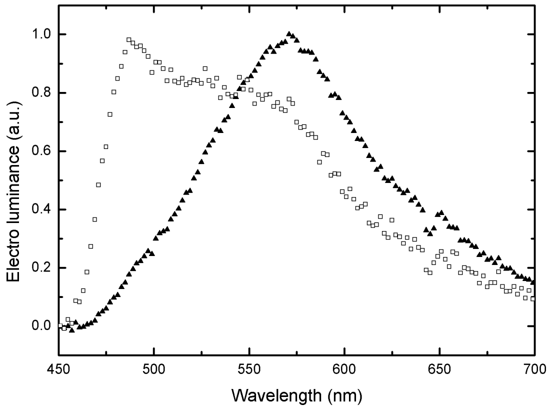

Figure 4. Electr-emission spectra of an ITO/**1**:PMMA/Au device, open squares taken after 10 s and closed triangles after 100 s with respect to turn on of electrical bias.

It takes around 50 s before the maximum light output is obtained (Figure 3). The build up of light output is synchronous with that of the current density. This time delayed response is one of the striking features of the operation of an electrochemical cell and reflects the mechanism of device operation.

Although the obtained efficiency is not very high, these results clearly show that the new approach to charged iridium-emitting complexes can be used to prepare solid-state LECs. After the maximum current density and light emission have been reached, the current density and the luminescence start to decline. Initially both current density and light emission decrease simultaneously indicating that there is a loss of charge transport or injection.

In Figure 4 two electroluminescence spectra are depicted taken at different times after turn on. The initial emission spectra show a resemblance to the photoluminescence spectra obtained from a thin film and has a first emission maximum at 487 nm. This is the lowest wavelength reported to date for devices based on ionic transition metal complexes. However, its stability is low, as can be seen from the shift in emission spectra with time.

During the build up of the emission intensity, the emission wavelength shifts toward a more yellowish green. Correspondingly the CIE values shift from $x = 0.337$ and $y = 0.501$ for the initial emission to $x = 0.429$ and $y = 0.515$ for the emission after 100 s. This shift in emission is only observed in electroluminescence. Photoluminescence measurements, using illumination of the electronically driven cell area that was used to record the electroluminescence spectra, revealed a photoluminescent spectrum identical to that of a pristine cell.

Although at this time we do not know the origin of the shift in emission, it appears to be associated with a chemical change of the emitting complex in the thin layer responsible for light generation. As the photoluminescence spectrum is unaffected, it appears that only a small number of emission centers are involved in the electroluminescent generation. This may be the reason for the low efficacy (0.25 cd/A) obtained at 4 V. When decreasing the driving voltage to 3 V a significant increase of efficacy (1.4 cd/A) was obtained. In a future study we will attempt to unravel this interesting phenomenon.

In conclusion, we have prepared a novel cationic iridium(III) complex by introducing positively charged side groups in the periphery of the phenylpyridine ligands. As a result of the electron withdrawing nature of the charged side groups the emission spectrum is blue-shifted with respect to its parent complex, resulting in an efficient bluish-green light-emitting complex. The up to now lowest wavelength LEC was obtained using a single layer of the novel complex. Although the stability of the device is limited it shows the potential of this approach toward ionically charged luminescent wide band gap emitters for electroluminescent devices.

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