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# Stable Single-Layer Light-Emitting Electrochemical Cell Using 4,7-Diphenyl-1,10-phenanthroline-bis(2-phenylpyridine)iridium(III) Hexafluorophosphate

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Light-emitting electrochemical cells (LEECs) are single-layer electroluminescent devices consisting of a luminescent material in combination with ionic charges.[1,2] The main characteristic of these devices is the insensitivity to the workfunction of the electrodes employed. This is due to the generation of a strong interfacial electric field caused by the displacement of the mobile ionic species toward the charged electrodes when applying an external electric field over the device. Additionally, these devices have a large tolerance to the thickness of the emitting layer, which simplifies the production process. First examples of these devices were based on conjugated polymers to which inorganic salts were added.[1] More recently, the focus has shifted to organometallic compounds that yield single-component solid-state light-emitting devices. The majority of the devices is based on charged organometallic complexes using iridium(III) and ruthenium(II) as the metal core.[3−7] The compound most widely used in these single-component devices is tris(bipyridine)ruthenium(II), $Ru(bpy)_3^{2+}$, balanced by a large negative counterion such as hexafluorophosphate.[2,8,9] The devices are interesting candidates for use in thin-film lighting applications as they operate at very low voltages, yielding high power efficient devices, and are easy to produce. There remain, however, a number of bottlenecks that impede their integration in products. These include a limited temporal stability and the lack of deep-blue light-emitting complexes. Using various chemical approaches, the range of available colors has increased recently up to a blueish-green device.[4] A more serious obstacle for implementation of the devices is their limited lifetimes. Detailed studies performed on $Ru(bpy)_3^{2+}$-based devices revealed that the device stability can be related to the formation of small amounts of quenching molecules during device operation.[10,11] In a recent paper, we showed that by using more bulky ligands the lifetime of a ruthenium(II)-complex-based device can be greatly enhanced.[12] One explanation for this increase in lifetime is the protection of the metal-ligand bond from chemical reactions that may lead to possible quenching molecules as unwanted products. Thus we showed that it is possible to significantly increase the lifetime of devices based on charged ruthenium organometallic complexes. However, to obtain devices emitting yellow, green, and blue light, other metals such as iridium have to be used as the core of the light emitting complexes. The lifetime of the devices using these complexes is generally low, ranging from minutes to a few hours. It is therefore of great interest to verify if the approach of introducing bulky shielding ligands in iridium complexes can also increase the device lifetime. In this Communication, a device is described based on the heteroleptic iridium(III) complex: 4,7-diphenyl-1,10-phenanthroline-bis(2-phenylpyridine)iridium(III) hexafluorophosphate (abbreviated as $[Ir(ppy)_2dpp]PF_6$), which shows a significant increase in lifetime compared to previous charged iridium-based electroluminescent devices.

The title complex was chosen as it resembles most of the other iridium complexes used in LEEC devices, namely, a complex based on two cyclometalating C^N ligands and one neutral diimine N^N ligand resulting in a 1+ overall charge, which is countered by one negative ion, hexafluorophosphate. The complex was synthesized by reacting 1 equiv of the dimeric iridium(III) complex $[Ir(ppy)_2(Cl)]_2$ with 2.5 equiv of 4.7-diphenyl-1,10-phenanthroline in dichloromethane under nitrogen. The photoluminescent quantum yield was determined to be 53% using $[Ru(dpp)_3]Cl_2$ as the standard (see Supporting Information).[13]

Solid films of $[Ir(ppy)_2dpp]PF_6$ were prepared by spin coating from acetonitrile solutions. Neat films were obtained without adding inactive polymers such as polymethylmethacrylate (PMMA). The thickness of the films ranged between 100 and 200 nm as determined using a profilometer. Devices were prepared by depositing gold, silver, or aluminum electrodes on top of the spin-coated films, which were thermally evaporated under vacuum ($<2 \times 10^{-6}$ mbar) to a thickness of 100 nm. Structured ITO-containing glass plates were used as the substrates. Device preparation and characterization were performed in inert atmosphere (<0.1 ppm $H_2O$ and <0.1 ppm $O_2$).

Upon applying a bias of 3 V to an ITO/$[Ir(ppy)_2dpp]PF_6$/Au device, light emission, slowly increasing in intensity with time, is observed (Figure 1). The electroluminescence spectrum of the $[Ir(ppy)_2dpp]PF_6$ device is broad with a maximum at 600 nm, very similar to the photoluminescence spectra obtained in solution (see Supporting Information for PL spectra).

The time-delayed response of the current density and the luminance is one of the striking features of the operation of an electrochemical cell and reflects the mechanism of device operation. The slow response is due to the low migration rate of the $PF_6^-$ ions through the solid film and can be enhanced by changing this counterion with smaller ones such as $BF_4^-$.[14]

For comparison, the current density and the luminance versus time are shown in Figure 1 for a similar device under the same external electric field but making use of the complex 3,4,7,8-tetramethyl-1,10-phenanthroline-bis(2-phenylpyridine)-iridium(III) hexafluorophosphate (abbreviated as $[Ir(ppy)_2phen]PF_6$). From this comparison it is obvious that the lifetime of the ITO/$[Ir(ppy)_2dpp]PF_6$/Au device is drastically improved with respect to the ITO/$[Ir(ppy)_2phen]PF_6$/Au device. The time to half of the maximum light intensity is approximately 65 h, in the same range as the previously reported 115 h for a ruthenium-based device.[12] It is, to our knowledge, the longest stability observed up to now for solid-state LEEC devices using charged iridium organometallic complexes under dc driving.

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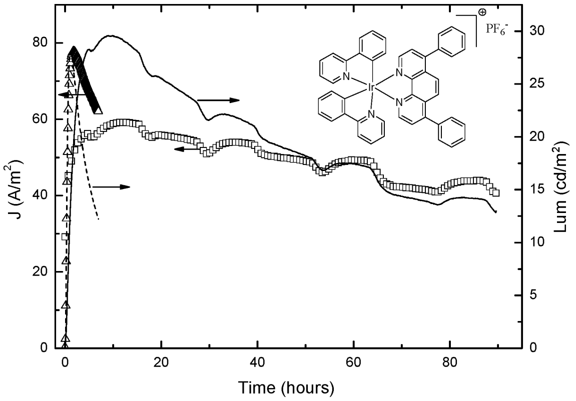

***Figure 1.*** Current density and luminance evolution as a function of time for an ITO/[Ir(ppy)$_2$dpp]PF$_6$/Au device (open squares and solid line, respectively) and for an ITO/[Ir(ppy)$_2$phen]PF$_6$/Au device (open triangles and dashed line, respectively) under an applied bias of 3 V. Inset shows the chemical structure of the [Ir(ppy)$_2$dpp]PF$_6$ complex.

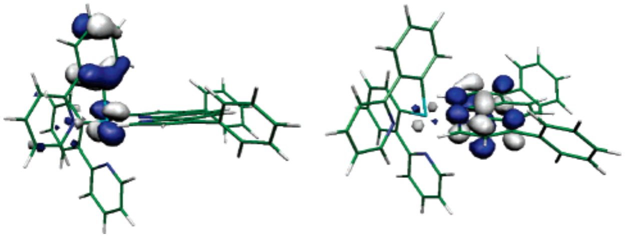

***Figure 2.*** Electron density contours (0.03 e bohr$^{-3}$) calculated for the HOMO (left) and the LUMO (right) of the Ir(ppy)$_2$dpp$^{+1}$ complex.

As the decay of the luminance coincides with the decay in current density for both devices studied, it is likely originating from a decrease in charge injection or transport capability rather than from a decay mechanism purely associated with a decrease in emission efficiency. Although it is difficult to relate device stabilities to physicochemical properties of the complexes used, we made an attempt by performing density-functional theory (DFT) calculations at the B3LYP/(6-31G**+LANL2DZ) level (see Supporting Information). The geometries of the singlet ground state (S$_0$) and the lowest triplet state (T$_1$) were fully optimized for both complexes without imposing any symmetry restriction.

Figure 2 sketches the atomic orbital composition calculated for the frontier molecular orbitals of Ir(ppy)$_2$dpp$^{1+}$. The HOMO and the LUMO are the levels in which holes and electrons are respectively injected at the electrodes, and they are involved in the charge transport processes. As sketched, the HOMO mostly resides on the Ir atom and on the phenyl ring of one ppy ligand, whereas the LUMO is mainly located on the phenanthroline core of the dpp ligand. Identical topologies are found for the HOMO and the LUMO of the Ir(ppy)$_2$phen$^{1+}$ complex. Actually, replacing phen by dpp has an almost negligible effect on the energies of the HOMO and the LUMO, which change from $-7.78$ to $-7.77$ eV and from $-4.58$ to $-4.68$ eV, respectively. In both complexes, the emitting exciton resulting from the recombination of the hole and the electron would be therefore equivalent to the triplet excited state T$_1$ resulting from the HOMO → LUMO excitation. This triplet shows a mixed metal-to-ligand and ligand-to-ligand charge transfer (MLCT/LLCT) character. The vertical energy difference between T$_1$ and S$_0$ at the optimized geometry of T$_1$ is calculated to be similar for both complexes [Ir(ppy)$_2$phen$^{1+}$, 2.04 eV (607 nm); Ir(ppy)$_2$dpp$^{1+}$, 1.93 (643 nm) eV].

The major difference between both complexes is, therefore, neither the energy nor the nature of the frontier orbitals but the presence of the phenyl rings on the dpp unit. These rings do not play any relevant role on the electronic properties of the complex but they act as physical barriers that protect the negative charge injected in the LUMO concentrated on the phenanthroline moiety (Figure 2). This shielding of the LUMO invokes two effects on the complex: (i) it renders the complex more hydrophobic and thereby less sensitive toward water-based chemical reactions,[7] and (ii) it sterically hinders a close overlapping of ppy ligands, on which holes partially reside, and dpp ligands on neighboring molecules, thus reducing the possibility for nonradiative intermolecular charge recombination. The long lifetime is mostly due to the suppression of chemical reactions, caused by the hydrophobocity and steric hindrance. This increase in lifetime is already obtained when substituting only one of the three ligands with bulky substituents. Therefore the research directed toward the synthesis of tailored molecules incorporating more hydrophobic and sterically bulky groups in the cyclometallating ligands is in progress.

In conclusion, we have shown that the introduction of bulky substituents in charged organometalic iridium complexes dramatically increases the lifetime of single layer devices consisting of such a complex when compared with similar complexes not having such bulky groups. From the analysis of the orbital energies and structural analysis it is deduced that the increase in device stability is originating from a steric rather than from an electronic effect, which is in analogy with what was suggested for the stability of LEEC devices based on organometallic complexes using ruthenium as the metal core.

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**Supporting Information Available:** Experimental and theoretical procedures and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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