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Communication

Near-Quantitative Internal Quantum Efficiency in a Light-Emitting Electrochemical Cell

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A green-light-emitting iridium(III) complex was prepared that has a photoluminescence quantum yield in a thin-film configuration of almost unity. When used in a simple solid-state single-layer light-emitting electrochemical cell, it yielded an external quantum efficiency of nearly 15% and a power efficiency of 38 Lm/W. We argue that these high external efficiencies are only possible if near-quantitative internal electron-to-photon conversion occurs. This shows that the limiting factor for the efficiency of these devices is the photoluminescence quantum yield in a solid film configuration. The observed efficiencies show the prospect of these simple electroluminescent devices for lighting and signage applications.

Ionic transition-metal complexes (iTMCs) based on organometallic ruthenium and iridium complexes are widely used in technological applications such as molecular-sensing photovoltaics and electroluminescence devices.[1,2] One of the latest successful applications of these complexes is in light-emitting electrochemical cells (LECs).[3,4] The main advantage of LECs over other electroluminescent devices is the insensitivity of the electrodes used as the anode and cathode. This insensitivity originates from the presence of ionic charges that migrate toward the electrode interfaces when an external electric field is applied, thus generating a strong interfacial field that facilitates the injection of electrons and holes.[5] In LECs, the iTMC acts both as the charge transporting species and as the emitter, and therefore, it should be ambipolar in transport and should have high photoluminescence quantum efficiencies (PLQE).[6] Various colors have been obtained ranging from blue-ish to red.[7−9] Recently, even a white-light-emitting LEC was reported by using two complementary emitters.[10] By doping a wide-bandgap iTMC with a low-bandgap iTMC, orange-light-emitting LECs with external quantum and power efficiencies as high as 16% and 44 Lm/W, respectively, have been obtained.[11] However, blue- and green-light-emitting LECs remain scarce, especially with high external quantum efficiencies (EQEs).[12] The EQE is defined as

$$\mathrm{EQE} = b\varphi/2n^2 \tag{1}$$

where b is the recombination efficiency (equal to 1 for two ohmic contacts[13]), φ is the fraction of excitons that decay radiatively, and n is the refractive index of the glass substrate and is equal to 1.5 (the factor $1/2n^2$ accounts for the coupling of light out of the device). As the Ir(III)-based complexes can efficiently harvest both singlet and triplet excitons, φ should resemble the PL efficiency. Hence, the efficiency of the device is mainly determined by the PLQE of the iTMC emitter.

In this communication, we report on a very efficient green-light-emitting complex that yields very high EQE values when processed into a double-layer LEC. The complex, 4,4′-di-*tert*-butyl-2,2′-dipyridyl-bis[2-(2′,4′-difluorophenyl)pyridine]iridium(III) hexafluorophosphate, abbreviated as $[\mathrm{Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)}]^+(\mathrm{PF_6}^-)$ (inset Figure 2), can be considered an

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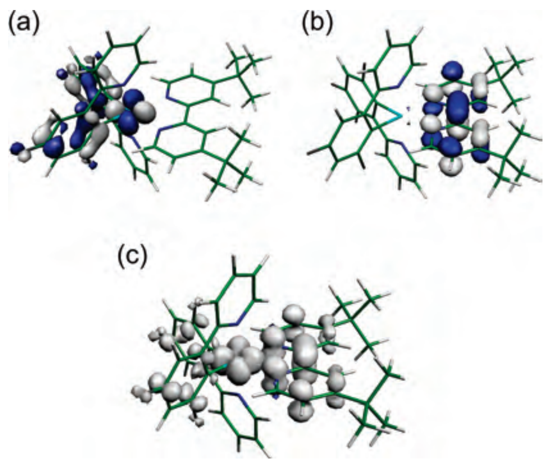

Figure 1. Electronic density contours (0.03 *e* bohr^{-3}) calculated for the HOMO (a) and LUMO (b) of the [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ complex in its S$_0$ ground state. (c) Spin-density distribution calculated for [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ in the T$_1$ excited state.

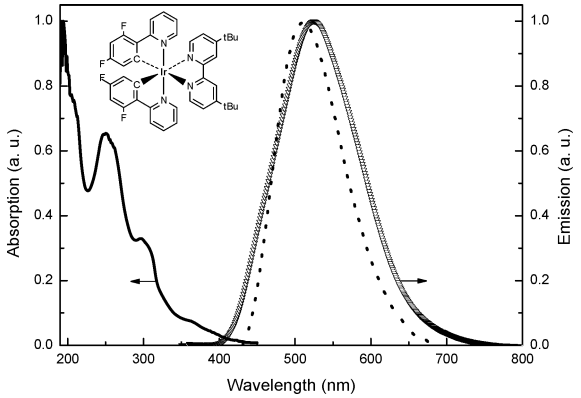

Figure 2. Absorption (solid line) and photoluminescence spectra (dotted line) of the [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ complex in acetonitrile solution. Electroemission spectra (open triangles) of an ITO/PEDOT:PSS/[Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$(PF$_6^-$):IL/Al device at an applied bias of 3 V. Inset shows the chemical structure of the [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ complex.

archetype wide-bandgap charged Ir(III) complex. We choose this complex since it can be easily obtained using chemical procedures similar to those previously published.[14,15] The use of the difluorinated phenylpyridine cyclometalating ligands results, like in the case of neutral Ir-based complexes, in a significant stabilization of the HOMO, which is located partially on the iridium metal and on the phenyl groups of the phenylpyridines (see Figure 1). B3LYP/6-31G** calculations on the electronic ground state (see the Supporting Information for computational details) predict the HOMO of [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ (-8.06 eV) to be 0.24 eV lower in energy than the HOMO of the unsubstituted complex [Ir(ppy)$_2$bpy]$^+$ (-7.82 eV), where ppy stands for 2-phenylpyridine and bpy for 2,2′-bipyridine. The LUMO is fully located on the diimine ligand, and it is calculated at -4.86 eV, 0.19 eV above the LUMO of [Ir(ppy)$_2$bpy]$^+$ (-5.05 eV). This destabilization is due to the insertion of the *tert*-butyl groups on the bpy ligand. Thus, substitution on the ppy and bpy ligands effectively increases the energy gap between the HOMO and the LUMO in passing from [Ir(ppy)$_2$bpy]$^+$ (2.77 eV) to [Ir(ppy-F$_2$)$_2$(dtb-bpy)]$^+$ (3.20 eV). The introduction of the large *tert*-butyl groups in the bipyridine ligand furthermore increases the effective distance between the complexes and therefore decreases the self-quenching.[16]

The absorption and photoluminescence spectra of the complex in acetonitrile solution are shown in Figure 2. The absorption spectrum shows the typical intense bands observed for iridium complexes in the ultraviolet part of the spectrum between 200 and 300 nm. These bands are assigned to spin-allowed $^1\pi-\pi^*$ ligand-centered transitions in both the 2′,4′-difluorophenylpyridine (C∧N) and the 4,4′-di-*tert*-butyl-2,2′-dipyridyl (N∧N) ligands.

The less-intense, lower-energy absorption features from 300 to 450 nm are assigned to both spin-allowed and spin-forbidden charge transfer (CT) transitions. These bands are described as metal-to-ligand CTs (MLCT bands), in analogy to features seen at similar energies in related diimine Ir complexes.[12,17]

The emission spectrum was taken at room temperature using an excitation wavelength of 350 nm. A strong emission with a maximum at 512 nm is observed, which is considerably shifted compared to that of the parent complex [Ir(ppy)$_2$bpy]$^+$ (580 nm).[18] The hypsochromic shift is due to both the stabilization of the HOMO and the destabilization of the LUMO. The unstructured and broad emission band is typical of complexes containing a combination of orthometalating and neutral diimine ligands.[12,14,17] The lowest triplet state, T$_1$, originates from the HOMO → LUMO excitation and is calculated 2.66 eV above the S$_0$ state (adiabatic energy difference). The nature of T$_1$ should be therefore described as a mixture of metal-to-ligand and ligand-to-ligand charge transfer (^{3}MLCT and ^{3}LLCT, respectively) due to the participation of both the Ir atom and the phenyl rings of the ppys in the HOMO (see Figure 1). The spin densities calculated for the optimized geometry of T$_1$ (Ir, 0.48; ppy-F$_2$, 2×0.24; dtb-bpy, 1.04) confirm the mixed ^{3}MLCT$-^3$LLCT character of this state. To estimate the phosphorescence emission energy, the vertical energy difference between T$_1$ and S$_0$ was computed by performing a single-point calculation of S$_0$ at the optimized minimum-energy geometry of T$_1$. Calculations led to a vertical emission of 2.31 eV (532 nm), slightly underestimating the experimental emission observed at 2.42 eV (512 nm). The emission is thus attributed to a transition from a ^{3}MLCT triplet state showing some ^{3}LLCT character.

The photoluminescence quantum yield in a deaerated acetonitrile solution is approximately 70%, which is significantly higher than that measured for [Ir(ppy)$_2$(bpy)]$^+$ (14%).

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Table 1. Photophysical Properties of the $[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+$ Complex

complex	emission^a 298 K				
	λ (nm)	$\varphi_{sol}{}^b$	$\varphi_{film}{}^c$	$\varphi_{film}{}^d$	τ (μs)^e
$[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+$	512	70	≥96	72	1.4
$[Ir(ppy)_2(bpy)]^+$	580	14	66		0.43

^{a} $\lambda_{exc} = 350$ nm. ^{b} Deaerated CH_3CN solution (10^{-4} M). ^{c} 5% by wt. in PMMA. ^{d} Solid film of $[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+(PF_6^-)$ and 1-butyl-3-methylimidazolium hexafluorophosphate (molar ratio = 1:1.1). ^{e} Luminance emission lifetime ± 10%.

This strong increase in PL efficiency is accompanied by an increase in the excited-state lifetime in a deaerated solution (see Table 1). In fact, thin films of the complex in polymethylmethacrylate (PMMA; 5% by weight) reach a PLQE value of almost 100%, making this one of the most efficient ionic iridium emitters. Thus, the use of the difluorophenylpyridine cyclometalating ligands together with the bulky di-*tert*-butylbipyridine neutral ligand shifts the emission toward the blue and additionally makes the complex one of the most efficient phosphorescent complexes reported. The high PLQE makes this complex an interesting candidate for high-efficiency LECs. The PLQE of the $[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+$ complex in deaerated solution is comparable to that of similar complexes that have a broad emission band, originating from a triplet excited-state with a predominant MLCT character.[8]

A simple two-layer LEC was prepared to investigate the electroluminescent properties of the complex. Prior to the deposition of the active layer, a thin layer (100 nm) of polyethylene dioxythiophene:polystyrene sulfonic acid (PEDOT:PSS) was spin-coated to increase the reproducibility of the devices. The active layer contained the $[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+(PF_6^-)$ complex and small amounts of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate to speed up the turn-on of the device.[19] Aluminum was used as the top electrode contact. Details concerning the device preparation can be found in the Supporting Information.

The electroluminescence spectrum is slightly broadened and shifted (13 nm) with respect to the photoluminescence spectrum (Figure 2), indicating that the same optical transition is responsible for the light emission. The CIE coordinates[20] of the emitted light are $x = 0.299$ and $y = 0.451$, corresponding to a green emission color. Figure 3 shows the typical evolution of the current density and light emission for a LEC device, namely, a slow turn-on followed by a gradual decay over time. The turn-on time and time to half of the maximum luminance depend on the driving voltage and are respectively 50 min and 9 h at 3 V and 4 and 17 min at 4 V. A remarkable feature of this device is its high current efficiency, which reaches 38 cd/A at 3 V. This value corresponds to a power efficiency of 39.8 Lm/W. At a driving voltage of 4 V, the luminance reaches 50 cd/m^2, and slightly lower current efficiencies (27 cd/A) and power efficiencies (21 Lm/W) are obtained. The corresponding EQE values at 3 and 4 V are 14.9% and 10.7%, respectively.

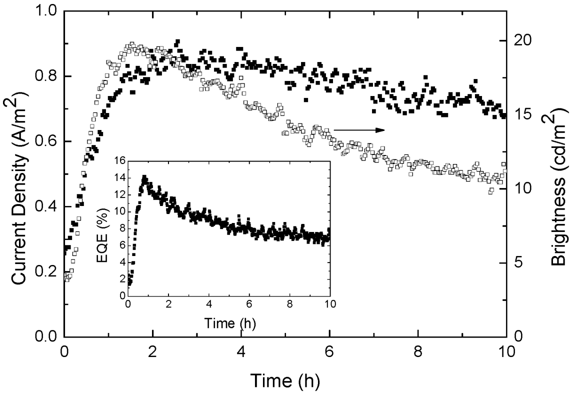

Figure 3. Current density (closed symbols) and brightness (open symbols) versus time at 3 V for an ITO/PEDOT:PSS/$[Ir(ppy\text{-}F_2)_2(dtb\text{-}bpy)]^+(PF_6^-)$:IL/Al device. Inset shows efficiency versus time at an applied voltage of 3 V.

According to eq 1, an EQE of 14.9% leads to a φ value of 67%. The PL efficiency of this complex in a thin film equal to that in the device configuration was determined to be 72%. Thus, for this device, φ = PLQE, which demonstrates that the recombination rate is close to unity. Additionally, this indicates that the complexes in the excited state are not experiencing an electric field, as this would decrease the PLQE. Such an observation is in line with the results described by Slinker et al., who report that the potential drop in LECs occurs predominantly at the electrode-emitting layer interfaces.[5]

In conclusion, we have shown that with small chemical modifications of the simplest ionic iridium(III) heteroleptic complex it is possible to achieve a green emission with a photoluminescence quantum yield in a solid film close to unity, and we demonstrate that this figure is the figure of merit for the design of complexes for use in LECs. The LEC based on this complex has unsurpassed external and power efficiencies of 15% and 40 Lm/W, respectively, with a green emission color. These high efficiencies demonstrate the promise these devices hold for high-efficiency lighting and signing applications.

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

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