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Long-Living Light-Emitting Electrochemical Cells – Control through Supramolecular Interactions**

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Electroluminescent devices using organic semiconductors offer advantages over their inorganic counterparts such as processability, transparency, and the potential of lower-cost, large-area devices. They are becoming a serious alternative to conventional inorganic technology as their efficiencies and stabilities have improved dramatically over the last years.[1,2] The most efficient and stable organic light-emitting devices (OLEDs) are based on a multi-stack of small molecular-weight components that use air-sensitive injection layers or metals for efficient electron injection.[2] The multi-layer architecture is obtained by sequentially evaporating the active species under high-vacuum conditions. These devices require rigorous encapsulation to prevent degradation of the electron-injecting layers. Another type of electroluminescent device, referred to as a light-emitting electrochemical cell (LEC), has a much simpler architecture and does not rely on air-sensitive charge-injection layers or metals for electron injection.[3] This greatly simplifies their preparation and makes them more cost efficient. In its simplest form, it consists of a single active layer composed of an ionic transition-metal complex (iTMC).[4–6] The presence of mobile ions facilitates the formation of ionic junctions that lower the barrier for electron and hole injection and makes these devices independent of the work function of the electrode material.[7,8] Thus, electroluminescent devices based on iTMCs are simple devices, easy to prepare, and do not require rigorous encapsulation. These characteristics make them suitable for low-cost lighting and signing applications.[9]

A wide range of emission colors, including white,[10] and efficiencies as high as 36 lm W^{-1} have been reached with iridium(III) iTMCs.[11,12] Additionally, LECs using more abundantly available metals such as copper were also reported.[13] There remains, however, one important barrier to their practical application, which is their very low lifetimes ranging from several minutes to a few days.[14] The origin of the low lifetimes of iTMC-based electroluminescent devices has been studied in detail only for devices using $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) as the active component.[15,16] The intrinsic instability of the iTMC under working conditions was identified as the primary and predominant reason for device degradation. Moreover, these studies revealed that the instability of the iTMC complex leads with participation of water molecules to the generation of degradation products that act as efficient luminescence quenchers. Although no detailed study exists for iridium(III)-based iTMC devices, the use of more hydrophobic complexes significantly increased the device lifetime, indicating that the intrinsic stability of the complex is also in this case the limiting factor.[17]

Supramolecular interactions, such as π-stacking, between coordinated ligands of a single complex can potentially enhance its stability. For example they are known to influence the photophysical properties of copper-based iTMCs incorporating 2-aryl- or 2,9-diaryl-1,10-phenanthroline ligands.[18,19]

In this work, we describe the preparation and characteristics of a supramolecularly caged ionic iridium(III) complex $[Ir(ppy)_2(Hpbpy)][PF_6]$ where ppy is 2-phenylpyridine and Hpbpy is 6-phenyl-2,2′-bipyridine. It was compared with the parent complex $[Ir(ppy)_2(bpy)][PF_6]$, that does not have a phenyl group on the bipyridine (bpy) ligand. The lifetime of a simple electroluminescent device employing air-stable electrodes and using the supramolecularly-caged complex as the only active component is more than 3000 hours at an average luminance of 200 cd m^{-2} while operating at a driving voltage of 3 volts. This large increase in lifetime was obtained without sacrificing the device turn-on time of a few seconds. Compared with the record lifetime reported for an iridium based LEC (60 hours),[17] this lifetime is an enormous improvement and sufficient for first applications.

The prototype supramolecular complex was prepared using methods similar to those for other $[Ir(ppy)_2L]^+$ species. In brief, 6-phenyl-2,2′-bipyridine was prepared directly from 2,2′-bipyridine by reaction with PhLi at 0 °C and subsequent oxidation of the dihydro-intermediate with $KMnO_4$.[20]

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Table 1. Photophysical and electrochemical properties.

Complex	Emission (298 K)[a]				V_{ox} [V][e]	V_{red} [V]
	λ [nm]	$\varphi_{sol.}$[b]	φ_{film}[c]	τ [μs][d]		
$[Ir(ppy)_2(Hpbpy)][PF_6]$	595	0.03	0.37	0.5	1.19	1.41 2.04 2.23
$[Ir(ppy)_2(bpy)][PF_6]$	590	0.14	0.66	0.43	1.28	1.37 2.01 2.17

[a]λ_{exc} = 350 nm. [b]De-aerated CH_3CN solution (10^{-4} M). [c]5 wt % in PMMA. [d]Emission lifetime in CH_3CN solution ± 10%. [e]In CH_3CN solution versus Fc^+/Fc.

$[Ir(ppy)_2(bpy)][PF_6]$ and $[Ir(ppy)_2(Hpbpy)][PF_6]$ were prepared in quantitative yields by the reaction of $[(ppy)_2Ir(\mu\text{-}Cl)_2Ir(ppy)_2]$ with two equivalents of the corresponding ligand in refluxing CH_2Cl_2/MeOH (1:1 v/v) followed by precipitation of the hexafluorophosphate salts.[21,22] Details concerning the synthesis and the characterization of these complexes can be found in the Supporting Information.

The electrochemical and photophysical properties of $[Ir(ppy)_2(Hpbpy)][PF_6]$ and $[Ir(ppy)_2(bpy)][PF_6]$ (see Table 1) are similar, with the main difference being the lower photoluminescence quantum efficiency in a polymethylmethacrylate thin film, 37% versus 66%, respectively.

Figure 1a depicts the crystal structure of one of the two independent cations in the lattice of $[Ir(ppy)_2(Hpbpy)][PF_6]$. All metrical parameters within the cation are within the typical limits. The pendant phenyl ring exhibits an intracation face-to-face π-stacking interaction between the rings containing C61 and C77 (angle between least squares planes, 7.5°, centroid-centroid distance, 3.48 Å). This interaction diminishes the possibility of water molecules to react with the metal complex and hence reduces the possibility of the formation of degradation products capable of quenching the luminescence as was determined to occur in $[Ru(bpy)_3]^{2+}$-based devices.[15,16]

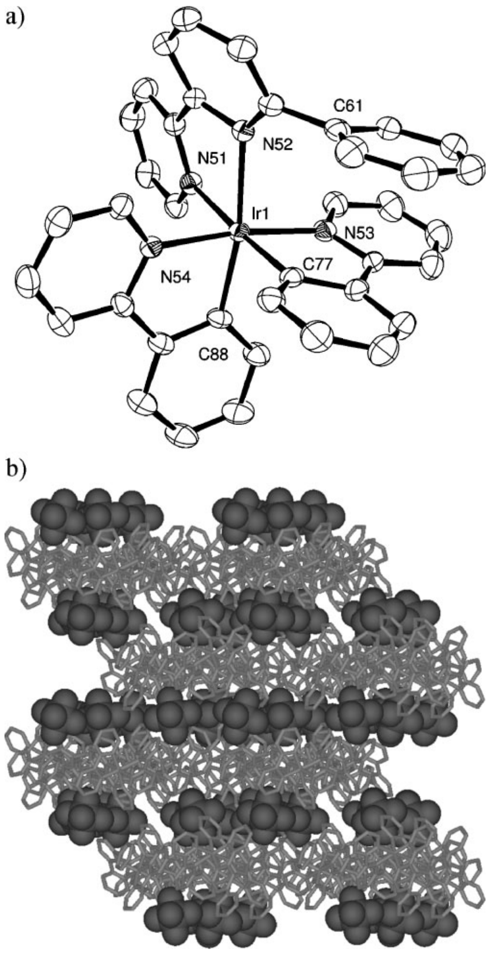

Figure 1. a) Structure of the $[Ir(ppy)_2(Hpbpy)]^+$ cation present in $[Ir(ppy)_2(Hpbpy)][PF_6]$ showing the intracation face-to-face π-stacking of the pendant phenyl ring containing C61 with the cylometallated phenyl ring containing C77 of a ppy ligand. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are represented at 50% probability. b) The lamellar structure with sheets of cations (light gray) and anions (dark gray).

To identify the influence of the intramolecular π-stacking on the excited state properties, density functional theory (DFT) calculations were performed at the B3LYP/(6-311G** + LANL2DZ) level on $[Ir(ppy)_2(bpy)]^+$ and $[Ir(ppy)_2(Hpbpy)]^+$ cations. The geometries of the singlet ground state (S_0), the lowest triplet state (T_1), and the metal-centered triplet state (^{3}MC) were fully optimized for both complexes. The $[Ir(ppy)_2(Hpbpy)]^+$ cation exhibits the intramolecular π-π interaction both in the S_0 and in the triplet states.

Metal-centered states result from the excitation of one electron from the occupied t_{2g} (dπ) HOMO to the unoccupied e_g (dσ*) orbitals of the metal[23] and are assumed to be the origin of complex instability in $[Ru(bpy)_3]^{2+}$ devices.[24] These ^{3}MC states are calculated after geometry relaxation to lie at approximately 0.6 eV above the lowest energy T_1 state for both complexes. Although these states are somewhat higher in energy than those on $[Ru(bpy)_3]^{2+}$, they are still accessible.[23] As shown in Figure 2a the relevant dσ* orbital in $[Ir(ppy)_2(bpy)]^+$ is σ-antibonding between the metal and the nitrogen of the ppy ligands. Electron promotion thus leads to the elongation of the Ir–N_{ppy} bonds, from 2.08 Å in S_0 to 2.50 Å in the resulting ^{3}MC state, and to the virtual decoordination of the two N_{ppy} atoms (Fig. 2b). The rupture of the metal-ligand bonds and consequently the opening of the complex enhances the reactivity of the complex in the excited ^{3}MC state and facilitates its degradation. For the $[Ir(ppy)_2(Hpbpy)]^+$ complex (Fig. 2c), the intramolecular π-stacking prevents the weakening of the Ir–N_{ppy} bond of the ppy ligand involved in that interaction and this bond only lengthens from 2.08 Å in S_0 to 2.24 Å in the ^{3}MC state. The pendant phenyl ring thus exerts a cage effect that restricts the opening of the structure of the complex in the excited ^{3}MC state. This makes the complex more robust reducing the possibility of degradation reactions.

Using the $[Ir(ppy)_2(Hpbpy)]$ $[PF_6]$ salt as the single active component we have prepared a LEC device that consists of a double layer of poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS) (100 nm) and $[Ir(ppy)_2$

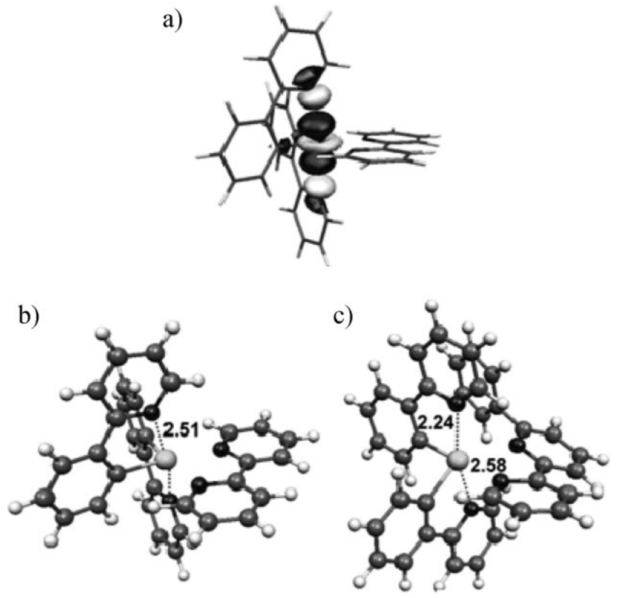

Figure 2. a) Electron density contours (0.03 e bohr^{-3}) calculated for the unoccupied e_g molecular orbital of $[Ir(ppy)_2(bpy)]^+$ showing σ-antibonding interactions along the vertical N_{ppy}–Ir–N_{ppy} axis. b) and c) Minimum-energy structures calculated for the ^{3}MC states of $[Ir(ppy)_2(bpy)]^+$ and $[Ir(ppy)_2(Hpbpy)]^+$, respectively. Ir–N_{ppy} distances are given in Å.

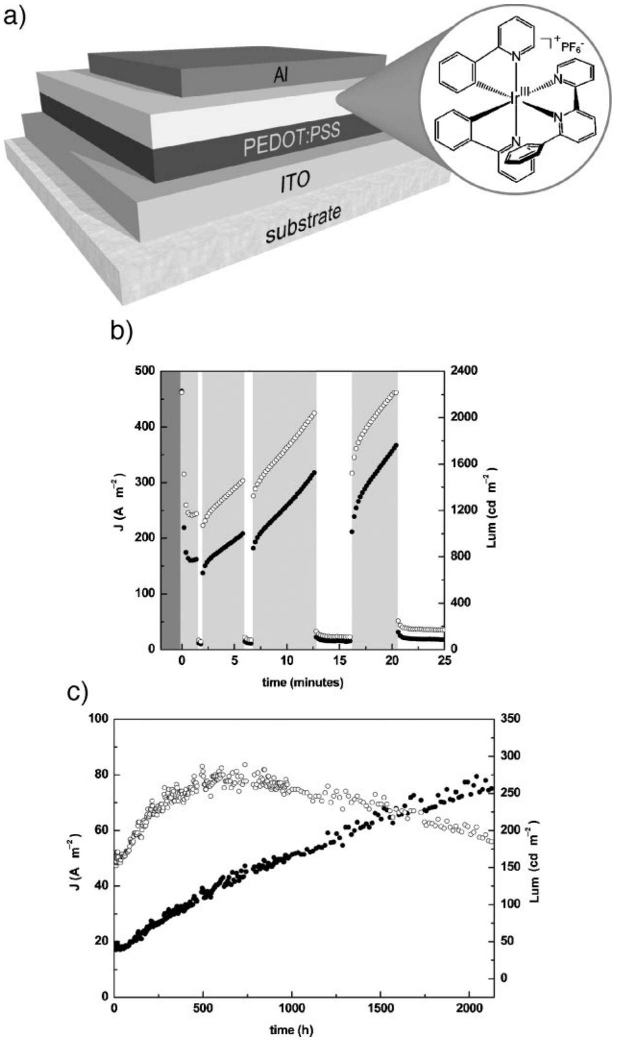

Figure 3. a) Schematic presentation of the simple electroluminescent device using the $[Ir(ppy)_2(Hpbpy)][PF_6]$ complex as the single active component. b) The device response to short pulses at higher biases (7 and 5 V, dark and light grey regions, respectively). c) Current density (closed squares) and luminance (open diamonds) versus time for an ITO/PEDOT:PSS/$[Ir(ppy)_2(Hpbpy)][PF_6]$:IL(4:1)/Al device under an applied bias of 3 V.

(Hpbpy)]$[PF_6]$ (80 nm) sequentially spin-coated from an aqueous and an acetonitrile solution, respectively, on top of a patterned ITO substrate (Fig. 3a). Subsequently, 80 nm of aluminium as the top electrode contact was thermally evaporated under high vacuum. Details concerning the device preparation can be found in the Supporting Information.

The rise-time of this electroluminescent device is of the order of several days at a driving voltage of 4 V. The slow rise of the current density and luminance is typical for these iTMC-based LECs and reflects their operational mechanism. The observed rise-time of several days, however, is extraordinary long and is indicative of a low ionic mobility in the $[Ir(ppy)_2(Hpbpy)][PF_6]$ thin film. In fact, from the crystal structure (Fig. 1b) it can be observed that $[PF_6]^-$-rich domains are separated in a laminar manner from the domains containing the cations, partly as a consequence of the extended π-stacking in the lattice. Such a laminar ordering of the cations and the $[PF_6]^-$ counter-ions, if also present, in the spin-coated films can explain the low mobility of the ions. It was reported that nanoscale crystalline domains are formed when spin-coating concentrated films of iTMCs.[25] To speed up the occurrence of the electroluminescence, small amounts of ionic liquid (IL) can be added to the active layer[26] or short high-voltage pulses can be applied.[27] A rapid turn-on of the luminescence is achieved when a combination of these techniques is used (Fig. 3b). At a bias of 7 V, the luminance reaches values as high as 2200 cd m^{-2}, associated with a current efficiency of 8 cd A^{-1}, within one minute. Such voltage levels, however, are detrimental for the device stability. That is why they are applied in a sequential way while stepwise lowering the applied bias. During these cycles the light is emitted continuously. After 5 short cycles, one at 7 V and the remaining four at 5 V, a luminance of 170 cd m^{-2} is obtained at a bias of 3 V after which the device is kept at 3 V and the evolution of the current density and the luminance is monitored over time (Fig. 3c). Surprisingly, even after the pre-stressing of the device, the luminance slowly increases and reaches a maximum of 290 cd m^{-2} after approximately 650 hours. The continuous rise of the luminance and current density observed after the pre-biasing indicates that there is a remaining fraction of ions in the film with a very low mobility that over longer timescales contribute to the ionic junction at the interfaces. The evolution of the current density is similar to that of the luminance up to the time the maximum is reached, indicative of the fact that the device is controlled by the injection limitation.

At a bias of 3 V, a maximum brightness of 290 cd m^{-2} is obtained with a current efficiency of 9.7 cd A^{-1}. The maximum power efficiency and external quantum efficiency for this electroluminescent device emitting orange light with a maximum wavelength of 594 nm are 10.1 lm W^{-1} and 4%, respectively. These efficiencies are among the best observed for iTMC-based LECs. The major improvement, however, concerns the device stability. This factor is reported in different ways, but normally either as the time taken to reach the half of the maximum luminance ($t_{1/2}$), or as the total photon flux emitted up to the time the luminance reaches 1/5th of the maximum value ($t_{1/5}$) for a cell area of 3 mm^2.[6,15] In this particular device, due to the continuous increase of the luminance after the rapid switch-on up to 650 hours the first figure is somewhat misleading. Therefore, a more correct way is to take the time starting just after the pre-biasing phase, thus from the point when the device is biased at 3 V, until it reaches $t_{1/2}$, which is extrapolated to be beyond 3000 hours. Compared to the device lifetime obtained when using the parent complex, $[Ir(ppy)_2(bpy)][PF_6]$, which is approximately 30 hours,[17] this value is an enormous improvement. The remarkable properties of our device are also demonstrated by the total photon flux emitted by the device. By extrapolating the lifetime curve up to $t_{1/5}$ this value is 73 Joule, which is two orders of magnitude larger that the best value reported before (0.27 J).[6] In comparison, the most-stable conjugated-polymer-based LECs showed lifetimes in the order of several days.[28]

In conclusion, the use of an ionic transition-metal complex containing weak intramolecular π-π interactions as the single active component in a light-emitting electrochemical cell results in an efficient and stable electroluminescent device. The observed lifetimes of more than 3000 hours and the short switch-on times are sufficient for low-cost lighting applications. The concept of using weak intramolecular interactions to form a cage-like structure can easily be extended to stabilize a wide range of charged and neutral transition metal complexes used in multi-layer OLEDs, molecular solar cells and sensing applications.

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