

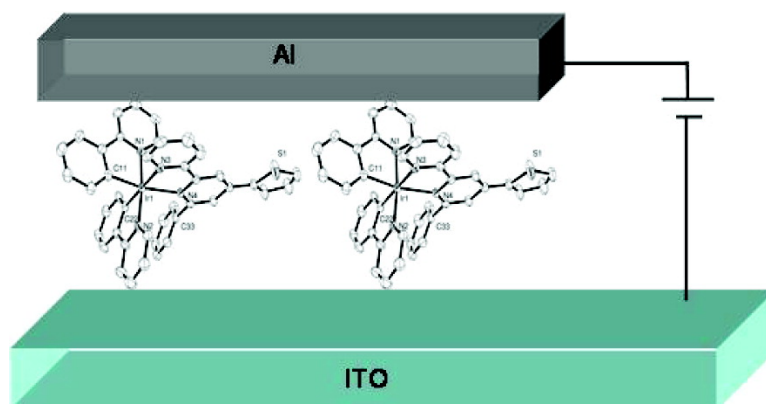
Communication

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## A Supramolecularly-Caged Ionic Iridium(III) Complex Yielding Bright and Very Stable Solid-State Light-Emitting Electrochemical Cells

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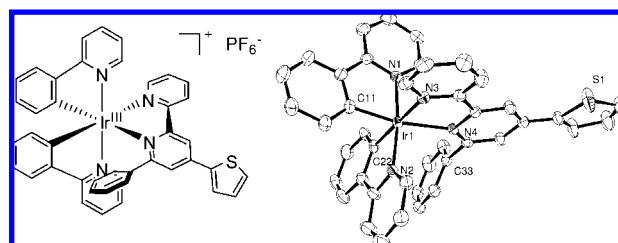
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Solid-state light-emitting electrochemical cells (LECs) have attracted considerable interest in the past years.<sup>1–3</sup> The main characteristic of these devices is the insensitivity to the workfunction of the electrodes employed. This is due to the generation of a strong interfacial electric field caused by the displacement of the mobile ionic species toward the charged electrodes when an external electric field is applied over the device. Therefore, in contrast to OLEDs, air-stable electrodes, such as gold, silver, or aluminum can be used, which is an initial requirement for obtaining unencapsulated devices. Recently, single-component, solid-state light-emitting devices based on ionic transition-metal complexes (iTMCs) have been reported.<sup>4,5</sup> In iTMC-based LECs, the complexes perform all the necessary roles to generate light: (a) the decrease of injection barriers via the displacement of the counterions, (b) the transport of electrons and holes via consecutive reduction and oxidation, respectively, of the iTMC, and (c) the generation of the photons. 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.<sup>6–9</sup>

iTMC-based LECs have limited stability, which was attributed (in the case of a [Ru(bpy)<sub>3</sub>]<sup>2+</sup>-based device) to a water-assisted ligand exchange reaction and the subsequent formation of a new complex that functions as an efficient luminance quencher.<sup>10,11</sup> Therefore, complexes that are less sensitive to these ligand-exchange reactions must be developed. In previous studies, we demonstrated that the lifetime can be significantly improved by increasing the hydrophobicity of the complex by introducing bulky aromatic groups on the periphery of the complex.<sup>12,13</sup> Recently, iridium-based iTMCs were reported in which the ligands were interacting with each other via  $\pi$ - $\pi$  stacking of the aromatic rings which can be viewed as a supramolecular cage formation.<sup>14,15</sup> Such an intramolecular interaction will increase the complex stability by decreasing the possibility of ligand-exchange reactions. We have adopted a similar approach and prepared a new supramolecularly caged iTMC, [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> (Hppy = 2-phenylpyridine, ptbpy = 6-phenyl-4-(2-thienyl)-2,2'-bipyridine), with the aim of improving the stability of LECs. This novel complex gave bright (2700 cd/m<sup>2</sup> at 5 V) and very stable (estimated *t*<sub>1/2</sub> of approximately 600 h at 3 V) LECs.

The supramolecular complex was prepared using methods similar to those for other [Ir(ppy)<sub>2</sub>L]<sup>+</sup> species. In brief, 6-phenyl-4-(thiophen-2-yl)-2,2'-bipyridine was prepared from the reaction of 1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one with 1-(2-pyridinyl)pyridinium iodide and ammonium acetate. [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> was prepared in quantitative yield by the reaction of [(ppy)<sub>2</sub>Ir( $\mu$ -Cl)<sub>2</sub>Ir(ppy)<sub>2</sub>] with 2 equiv of ptbpy in refluxing CH<sub>2</sub>Cl<sub>2</sub>/MeOH (1:1 v/v) followed by precipitation of the hexafluorophosphate salt (Supporting Information, Scheme S1).<sup>16,17</sup>

Figure 1 depicts the crystal structure of the [Ir(ppy)<sub>2</sub>(ptbpy)]<sup>+</sup> cation showing the intracation face-to-face  $\pi$ -stacking. This interaction diminishes the possibility of water molecules to react with the



**Figure 1.** Chemical structure of [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> (left) and structure of the [Ir(ppy)<sub>2</sub>(ptbpy)]<sup>+</sup> cation present in [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> showing the intracation face-to-face  $\pi$ -stacking of the pendant phenyl ring containing C33 with the cyclometallated phenyl ring containing C22 of a ppy ligand. Hydrogen atoms have been omitted for clarity and thermal ellipsoids are represented at 50% probability (right).

metal complex and hence reduces the possibility of the formation of degradation products.

The [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> complex shows a strong emission at 608 nm in acetonitrile solution ( $\lambda_{\text{exc}} = 355$  nm) and presents a photoluminescence quantum efficiency (PLQE) of 0.06 and an excited-state lifetime of 1.5  $\mu$ s (see Figure S1 and Table S1 for photophysical characterization).

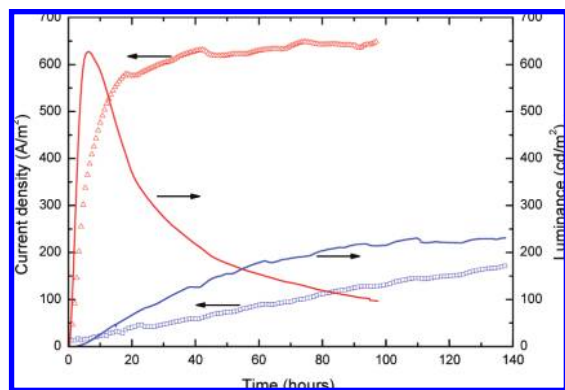
Electrochemical analysis using cyclic voltammetry (CV) of this complex revealed an irreversible oxidation peak that we attribute to adsorption processes at the electrode involving the thienyl substituent, as observed in similar complexes.<sup>18</sup> Multiple CV scans showed no significant changes in the oxidation wave indicating that the complex is electrochemically robust (see Figure S2a,b and Table S2).

A simple two-layer LEC was prepared to investigate the electroluminescent properties of the complex. Prior to the deposition of the photoactive 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 (90 nm) contained [Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub> and small amounts of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate to speed up the turn-on of the device.<sup>19</sup> Aluminum was used as the top electrode contact (see Supporting Information).

Upon applying a bias of 3 V to an ITO/PEDOT:PSS/[Ir(ppy)<sub>2</sub>(ptbpy)]PF<sub>6</sub>/Al device, no light emission was observed not even after applying this bias for as long as 24 h. To determine whether this device could emit light, a voltage sweep was applied and at 8 V weak electroluminescence was observed. Hence, a bias of 8 V was applied to the single-component LEC and the luminance was monitored versus time. This is a very high bias for such a thin film which should rapidly lead to degradation of the complex as has been observed for LECs using other iridium-based iTMCs.<sup>6,13,20</sup> However, surprisingly, the current density and the luminance increase slowly over a time frame of a couple of hours reaching luminance levels of 100 cd/m<sup>2</sup>. The luminance was uniform throughout the device and showed an emission spectrum with a maximum at 607 nm with CIE color points, *x* = 0.587

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and  $y = 0.411$ , representing an orange color. The remarkably slow turn-on time ( $t_{on}$ ) of several hours at an applied bias of 8 V combined with the fact that light is uniformly emitted implies that the ionic mobility in the solid film is very low and that the complex is electrochemically very stable. The low mobility of the counter-ions in solid films of  $[\text{Ir}(\text{ppy})_2(\text{tpbpy})]\text{PF}_6$  is indicative of a very densely packed morphology or even of the formation of nanoscale crystalline domains. AFM analysis of a pristine film of  $[\text{Ir}(\text{ppy})_2(\text{tpbpy})]\text{PF}_6$  and of one containing the IL only show very uniform and flat films (see Figure S5). The  $t_{on}$  can be decreased by using a smaller counterion,<sup>5</sup> by the addition of small amounts of IL,<sup>19</sup> and by the application of a short but intense voltage pulse.<sup>21</sup>



**Figure 2.** Current density (symbols) and luminance (line) versus time of an ITO/PEDOT:PSS/ $[\text{Ir}(\text{ppy})_2(\text{tpbpy})]\text{PF}_6/\text{Al}$  device containing 0.13 (blue squares) and 0.26 % (red triangles) of IL, at an applied bias of 3 V.

Figure 2 shows the current density and luminance evolution versus time at an applied bias of 3V of two  $[\text{Ir}(\text{ppy})_2(\text{tpbpy})]\text{PF}_6$  containing LECs to which small amounts of IL (0.13 and 0.26 % wt.) were added. The addition of the ionic liquid has a notable effect on the turn-on time of the device. The  $t_{on}$  of the LECs is reduced to 6 and 136 h for the high and low IL concentration, respectively. The device with 0.26% of IL reaches luminance levels significantly higher ( $626 \text{ cd/m}^2$ ) than the device with 0.13% of IL ( $230 \text{ cd/m}^2$ ) (Table 1).

**Table 1.** Device Data for the LEC Devices

IL (%)	$U$ (V)	$t_{on}$ (h)	$t_{1/2}$ (h)	luminance ( $\text{cd/m}^2$ )	eff. ( $\text{cd/A}$ )	EQE (%)
0	8	2.3		100	1.0	0.62
0.13	3	136	$\pm 600$	230	2.2	1.36
0.26	3	6	25	626	2.7	1.67
	5	1.5	2	2770	2.0	1.24

The  $t_{on}$  of 136 h for the device with 0.13% of IL is the longest value reported to date. Because of this slow turn-on, an accurate lifetime analysis was not performed. Such an analysis generally involves measuring the time to half the maximum brightness ( $t_{1/2}$ ). However, in all published lifetime data of LEC devices,  $t_{on}$  is less (generally at least 5 times) than  $t_{1/2}$ .<sup>10,12,20</sup> If this holds in our device, it implies that the  $t_{1/2}$  would be at least in the order of 680 h, which is a significant increase compared to the previous record. Unfortunately, we were not able to analyze the device during such a long time due to a limited number of testing positions available.

In LECs the luminance can not be easily increased by applying a higher bias voltage as the latter also causes a multitude of secondary effects in the device that enhance its decay. To amplify the possible uses of LECs, it is therefore important to establish if

higher brightness levels can be reached by using more stable complexes. Therefore, a bias of 5 V was applied to the ITO/ $[\text{Ir}(\text{ppy})_2(\text{tpbpy})]\text{PF}_6/\text{Al}$  device containing 0.26% of IL. This resulted in a maximum luminance value of  $2700 \text{ cd/m}^2$  which is by far the highest value reported for an iTMC device (see Figure S2). This value shows the potential of LECs for lighting and signage applications. It is remarkable that this maximum brightness is reached after applying the high bias for more than 1.5 h, confirming the extraordinary stability of the title complex.

In summary, the presence of interligand  $\pi-\pi$  stacking in a single ionic iridium complex greatly enhances its stability when used in a double-layer solid-state LEC. DFT calculations show that this stacking is maintained in the excited-state thus protecting the complex against ligand-exchange reactions. LECs using this complex show extraordinary stabilities and luminance values indicating the path toward stable iTMCs for use in LECs reaching stabilities required for practical applications.

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**Supporting Information Available:** Experimental details; supplemental figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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