Intramolecular π-Stacking in a Phenylpyrazole-Based Iridium Complex and Its Use in Light-Emitting Electrochemical Cells

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Solid-state light-emitting electrochemical cells (LECs) are a promising type of electroluminescent device.[1–4] LECs offer a number of advantages over traditional organic light-emitting diodes (OLEDs), in particular simpler architectures and production. LECs require only a single layer of a charged luminescent material, which can be processed directly from solution.[1] Furthermore, charge injection in LECs is insensitive to the work function of the cathode material, thus permitting the use of air-stable electrodes. Therefore, their encapsulation does not have to be as rigorous as that with OLEDs. These characteristics make LECs the simplest kind of electroluminescent devices.

The principal problem to date is the limited stability of LEC devices, which mainly originates from the degradation of the ionic transition-metal complexes (iTMCs) used as the active component in the emissive layer.[5–9] Recently, we reported on a breakthrough in the stability of iTMC-containing LECs reaching lifetimes of more than 1000 h (and with a prebiasing driving method more than 3000 h) using a supramolecularly caged ionic iridium complex as the single active component.[10–12] These complexes were obtained by the interaction of a 6-phenyl-2,2′-bipyridine (pbpy, N^N) with the precursor complex $[Ir(ppy)_2(\mu\text{-Cl})_2Ir(ppy)_2]$ containing cyclometalated *C,N*-donor ligands (Hppy = 2-phenylpyridine). The phenyl ring on the pbpy ligand π-stacks face-to-face with the phenyl ring of the ppy ligands, forming a supramolecular cage that closes the iTMCs in the ground state (S_0) and in the emitting (T_1) and metal-centered (^{3}MC) excited triplet states. This makes it more difficult for nucleophiles to attack the complex, which is believed to be the reason for the higher stability of the so-prepared LECs.

In this communication we extend the concept of supramolecular cage formation to an ionic iridium complex, $[Ir(dmppz)_2(pbpy)][PF_6]$ (**1**), incorporating 3,5-dimethyl-1-phenylpyrazole (Hdmppz) and pbpy as ligands. It was chosen as Ir-containing phenylpyrazole (ppz) complexes have slightly wider band gaps than those of their ppy-based equivalents.[13,14] To facilitate the evaluation of this new complex we compare it with the previously published complex, $[Ir(ppy)_2(pbpy)][PF_6]$ (**2**), described in the introduction. We show that the supramolecular cage formation can be extended to pyrazole-based iridium complexes and that LECs making use of them exhibit remarkably high stabilities.

The Hdmppz *C,N*-ligand was prepared in good yields by treating phenylhydrazinium chloride with pentane-2,4-dione in 1,2-dichloroethane at 70 °C for 24 h via a successive hydrazone formation, cyclization, and double bond isomerization sequence as described in the literature.[15] 6-Phenyl-2,2′-bipyridine was prepared using literature methods.[16] For $[Ir(dmppz)_2(\mu\text{-Cl})_2Ir(dmppz)_2]$, iridium(III) chloride hydrate and Hdmppz were refluxed in a mixture of
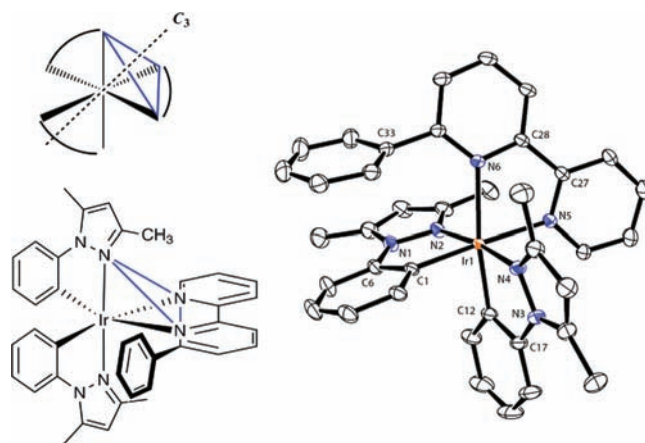

Figure 1. Left: chemical structure of complex **1** (bottom) where one octahedral face (blue) and the C_3 axis in an ideal octahedral coordination (top) are emphasized. Right: X-ray structure of the $[Ir(dmppz)_2(pbpy)]^+$ cation present in $[Ir(dmppz)_2(pbpy)][PF_6]$ (**1**) showing the intracation face-to-face π-stacking of the pendant phenyl ring containing C33 with the cyclometalated phenyl ring containing C1 of a dmppz ligand. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are represented at 50% probability.

2-methoxyethanol and water (3:1 v/v) for 24 h similarly to previously reported procedures.[17,18] Complex **1** was prepared using methods similar to those for other $[Ir(ppy)_2L]^+$ species by the reaction of $[Ir(dmppz)_2(\mu\text{-Cl})_2Ir(dmppz)_2]$ with 2 equiv of pbpy in refluxing CH_2Cl_2/MeOH (1:1 v/v) followed by addition of an excess of ammonium hexafluorophosphate and purification by column chromatography.[17,18] Details concerning the synthesis and the characterization of this complex can be found in the Supporting Information (SI).

Figure 1 depicts the crystal structure of the cation in the lattice of $[Ir(dmppz)_2(pbpy)][PF_6]$. It shows the same intracation face-to-face π-stacking of the pendant phenyl ring of the pbpy ligand as observed in $[Ir(ppy)_2(pbpy)][PF_6]$ (complex **2**).[10] The π-stacking interaction is observed between the rings containing C1 and C33 (centroid−centroid distance, 3.51 Å). Density functional theory (DFT) calculations show that the π-stacking interaction is preserved in the T_1 and ^{3}MC excited triplet states with centroid−centroid distances of 3.58 and 3.78 Å, respectively (see SI). This demonstrates that the concept of supramolecular cage formation can be extended to pyrazole-based ligands.

The photophysical and electrochemical properties of **1** are similar to those of complex **2**. The emission of **1** in acetonitrile solution (λ_{exc} = 355 nm) is blue-shifted (574 nm) with respect to complex **2** (595 nm). In addition, the photoluminescence quantum efficiency and the excited-state lifetimes are similar for both complexes (see

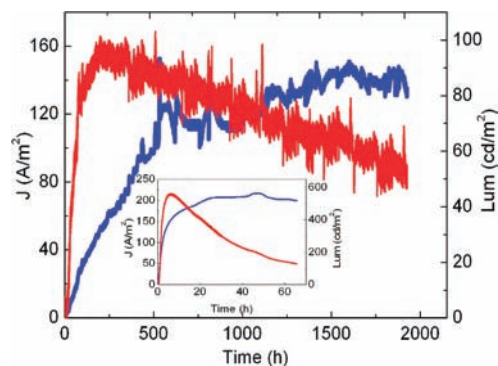[†] Universidad de Valencia.
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Figure 2. Current density (blue) and luminance (red) for ITO/PEDOT: PSS/**1**:IL/Al LEC devices at constant 3 V with 1:1 (inset) and 4:1**1**:IL molar ratios in the active layer.

Table 1. Performance of ITO/PEDOT:PSS/Ir-iTMC:IL/Al LEC Devices

(Ir-iTMC:IL)	U (V)	$t_{on}{}^a$ (h)	$t_{1/2}{}^b$ (h)	Luminance (cd/m²)	Efficiency (cd/A)	$E_{tot}{}^c$ (J)
1 (1:1)	3	0.94	33	563	4.2	6.6
1 (1:1)	4	0.08	3.1	1570	4.0	4.4
2 (1:1)	3	1.87	27	245	4.5	2.2
1 (4:1)	3	180	2000	105	4.0	18.7
1 (4:1)	4	52	550	191	5.0	12.6
2 (4:1)	3	204	1288	109	3.1	13.6

^{a} Time to reach 100 cd/m². ^{b} Time to reach half of the maximum luminance. ^{c} Total emitted energy up to the time the luminance reaches 1/5 of the maximum value for a cell area of 3 mm².

SI, Table S1). The electrochemical data show that complexes **1** and **2** have very similar band gaps (2.58 versus 2.67 V).

Simple two-layer LECs were prepared to investigate the electroluminescent properties of complex **1**. Prior to the deposition of the active layer, a thin layer (100 nm) of poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) was spin-coated to increase the reproducibility of the devices. The active layer contains complex **1** and small amounts of the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate at different molar ratios (**1**:IL; 1:1 and 4:1). The IL is added to reduce the turn-on time (t_{on}) defined as the time to reach 100 cd/m².[19] Aluminum was used as the top electrode contact (see SI for details).

All LECs based on complex **1** show the same electroluminescence spectra (see Figure S2) with a maximum at 585 nm and CIE coordinates $x = 0.4883$, $y = 0.5035$.[20] The evolution of the current density and the luminance over time for LECs using complex **1** mixed with IL at different ratios are depicted in Figure 2. Independent of the **1**:IL ratio, the current density (J) and the luminance (Lum) profiles are similar, both increasing slowly with time. The luminance starts to decay slowly immediately after reaching its maximum value, whereas the current density levels off and appears to reach a plateau. This is indicative that the device stability is directly related to the emission process and not to the charge injection and charge transport processes; this was also observed for polymer-based LECs.[21] The devices were also evaluated at other driving constant voltages, and the results are summarized in Table 1 and shown in Figure S6.

The turn-on times for devices using complex **1** depend on the amount of IL present in the active layer and are comparable to those obtained for devices using complex **2**. The extraordinary long turn-on times are difficult to understand but may be related to the presence of nanoscale crystalline domains that hinder the movement of ions as was observed in spin-coated films of ruthenium iTMCs.[22] The figures of merit of the stability are the lifetime ($t_{1/2}$), time to

reach the half of the maximum luminance, and the total emitted energy (E_{tot})[7] up to the time the luminance reaches 1/5 of the maximum value for a cell area of 3 mm². Both $t_{1/2}$ and E_{tot} are significantly higher for LECs using complex **1** compared to those employing complex **2** independently of the IL concentration (see Table 1). For example, at a molar ratio of 4:1, LECs using complex **1** reach values of 2000 h and 18.7 J, respectively, at an applied bias of 3 V.

As mentioned above, the evolution of the luminance and current density curves with time hints toward a degradation mechanism that primarily affects the emitting properties of the complex. Only for $[Ru(bpy)_3]^{2+}$-based LECs has the degradation been studied in detail.[5–9] A water-assisted N^N ligand exchange reaction has been suggested to be at the origin of the degradation of the iTMC, generating products that are efficient quenchers of the excited state both in solution and in LEC devices. The water molecules make their closest approach to the central metal atom in $[Ru(bpy)_3]^{2+}$ along the C_3 axes of the coordination octahedron (see Figure 1).[8,9] For $[Ir(dmppz)_2(pbpy)]^+$, the pendant methyl groups of the dmppz ligands are located over the octahedral faces containing the N^N ligand (see Figure 1) and are a clear impediment to the entrance of water molecules, thus rendering the degradation more difficult. Therefore, the use of alkyl groups in these positions may shield the iTMC against the degradation, which can explain the observed enhancement of the LEC stability. This assumption is corroborated by the lowered stabilities ($t_{1/2}$ 142 h and E_{tot} 0.33 J) of LECs employing a similar complex without the methyl groups on the pyrazole ligands, $[Ir(ppz)_2(pbpy)][PF_6]$ (**3**). Device data can be found in the SI.

In summary, a supramolecular cage formation with a novel C^N ligand (dmppz) is reported. LECs based on this new cage-iTMC show an extraordinary stability of around 2000 h. We believe that the observed stability arises from the intramolecular π-stacking and from the position of the pendant methyl groups, both hindering the entrance of nucleophilic molecules.

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

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