

Stable and Efficient Light-Emitting Electrochemical Cells

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ABSTRACT

Three new heteroleptic iridium complexes that combine two approaches, one leading to a high stability and the other yielding a high luminescence efficiency, are presented. All complexes contain a phenyl group at the 6-position of the neutral bpy ligand, which holds an additional, increasingly bulky substituent on the 4-position. The phenyl group allows for intramolecular π - π stacking, which renders the complex more stable and yields long-living light-emitting electrochemical cells (LECs). The additional substituent increases the intersite distance between the cations in the film, reducing the quenching of the excitons, and should improve the efficiency of the LECs. Indeed, LEC devices employing these complexes as the primary active component show shorter turn-on times, higher efficiencies and luminances, and, surprisingly, also demonstrate longer device stabilities.

Keywords light-emitting electrochemical cells, iridium complexes, ionic transition-metal complexes, high efficiency, bulky substituents.

1 INTRODUCTION

Solid-state light-emitting electrochemical cells (LECs) have attracted considerable interest in the past few years.[1] LECs are single-component electroluminescent devices consisting of a charged luminescent material.[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 towards the charged electrodes when an external electric field is applied over the device. Therefore, in contrast to organic light-emitting diodes (OLEDs), air-stable electrodes, such as gold, silver, or aluminium, can be used, which is an initial requirement for obtaining unencapsulated devices.

In its simplest form, a LEC consists of a single active layer composed entirely of an ionic transition-metal complex (iTMC). iTMCs are triplet emitters similar to those used in OLEDs. iTMC-based LECs exhibiting low turn-on times and emitting blue, green, orange, red, and even white light have been reported.[1] Recently, we reported on a new approach to iTMCs that led to a significant increase in the lifetime of LECs that employed

them as the main component.[3, 4] This was achieved with an iridium complex exhibiting intramolecular π - π stacking of two of its phenyl rings, resulting in a supramolecular cage formation. The simplest example is mentioned in this work for comparison and is referred to as complex **1** (see Fig. 1). This demonstrated that LECs can reach lifetimes suitable for first applications. Hence, all requirements seem to have been met to allow LECs to be applied in first products.

However, the aforementioned achievements were obtained separately and never jointly in one device with a single complex. It is the object of this work to combine in one single complex two approaches, one leading to a high stability and the other yielding a high luminescence efficiency. High efficiencies can be reached by decreasing the quenching of the excitons by shielding the individual iTMCs from each other. This can be achieved by the introduction of bulky side groups to the periphery of the complex.[5] Bulky groups in the iTMC can also increase the stability of the LECs as they render the complex less susceptible for interaction with water.[6, 7] That interaction was identified as the primary reason for the short lifetimes of ruthenium based LECs.[8, 9] Three heteroleptic iridium complexes combining the above-mentioned features with cyclometallated 2-phenylpyridine ligands (Hppy = 2-phenylpyridine) were prepared, [Ir(ppy)₂(Meppbpy)]PF₆ (**2**, Meppbpy = 4-(3,5-dimethoxyphenyl)-6-phenyl-2,2'-bipyridine), [Ir(ppy)₂(C₁₀ppbpy)]PF₆ (**3**, C₁₀ppbpy = 4-(3,5-bis(decyloxy)phenyl)-6-phenyl-2,2'-bipyridine), and [Ir(ppy)₂(G1ppbpy)]PF₆ (**4**, G1ppbpy = 4-(3,5-bis(dodecyloxy)benzyloxyphenyl)-6-phenyl-2,2'-bipyridine), and are presented in Figure 1.

All complexes contain a phenyl group at the 6-position of the neutral 2,2'-bipyridine (bpy) ligand, which holds an additional, increasingly-bulky substituent on the 4-position. The phenyl group allows for the intramolecular π - π stacking, which renders the complex more stable and yields long-living LECs.[3, 4] The additional substituents increase the intersite distance between the cations in the film reducing the quenching of the excitons and should increase the efficiency of the LECs. Density functional theory (DFT) calculations indicate that all iTMCs have the desired π - π intramolecular interactions between the pendant phenyl ring of the bpy ligand and the phenyl ring of one of the ppy ligands. The photoluminescence quantum

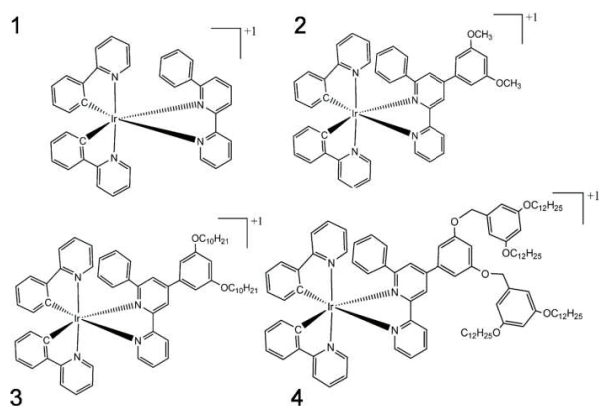


Figure 1: Chemical structures of the new complexes **2**, **3**, and **4**, and of the reference compound **1**

efficiency (PLQE) of films with the same composition than the active layer of the LEC device improves with the increasing size of the bulky groups indicating that the adopted strategy is successful. LEC devices employing these complexes as the primary active component show high efficiencies in the case of complexes **2** and **3**, however, no electroluminescence was obtained from the devices using complex **4**. When compared with devices employing the reference complex **1**, LECs using complexes **2** and **3** show shorter turn-on times, higher efficiencies and luminances, and, surprisingly, also demonstrate longer device lifetimes.

2 EXPERIMENTAL SECTION

Synthesis: The complexes were prepared using methods similar to those for other $[\text{Ir}(\text{ppy})_2\text{L}]^+$ species. However, the dendronised 6-phenyl-2,2'-bipyridine ligands were prepared using a "green" solvent-free method developed for aldol condensation and *Michael* addition to give ligand Meppbpy. After demethylation of Meppbpy by heating with molten pyridinium chloride, the free phenolic hydroxyl groups were reacted with an appropriate electrophile to give the desired ligands C₁₀ppbpy and G1ppbpy (bearing a 1st generation Fréchet-type Dendron), respectively.

Computational Details: Density functional calculations (DFT) were carried out with the C.02 revision of the Gaussian 03 program package, using Becke's three-parameter B3LYP exchange-correlation functional together with the 6-31G** basis set for C, H, and N atoms and the "double- ζ " quality LANL2DZ basis set for the Ir element. An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core $[(5s)^2(5p)^6]$ electrons and the $(5d)^6$ valence electrons of Ir(III). The geometries of the singlet ground state (S_0) and of the triplet excited states T_1 and ^3MC were fully optimized. Triplet states were calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. The expected values calculated for S^2 were always smaller than 2.05.

Device Preparation and Characterization: Poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS) was purchased from HC-Starck and solvents used were obtained from Aldrich. Indium tin oxide (ITO)-coated glass plates ($15 \Omega^{-1}$) were patterned using conventional photolithography (obtained from Naranjosubstrates, www.naranjosubstrates.com). The substrates were extensively cleaned using sonification in subsequently water-soap, water, and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 minutes.

The electroluminescent devices were prepared as follows. Transparent thin films of complexes **1–3** containing different amounts of the ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) were obtained by spinning from acetonitrile solutions using concentrations of 20 mg mL^{-1} at 2000 rpm for 40 seconds, resulting in a 80 nm thick films. Prior to the deposition of the emitting layer, a 100 nm layer of PEDOT:PSS was deposited to increase the device preparation yield. The thickness of the films was determined using an Ambios XP1 profilometer. After spinning the organic layers, the samples were transferred to an inert atmosphere glovebox ($< 0.1 \text{ ppm O}_2$ and H_2O , MBraun) and dried on a hot plate at 80°C for 1 hour. Aluminium metal electrodes (80 nm) were thermally evaporated using a shadow mask under a vacuum ($< 1 \times 10^{-6} \text{ mbar}$) using an Edwards Auto500 evaporator integrated into an inert atmosphere glovebox.

Photophysical Characterization: The thin-film quantum yield measurements were performed in a nitrogen environment and determined on thin films (70 nm) with the same configuration than the LEC device with an ionic liquid at 4:1 molar ratio of Ir-iTMC/1-butyl-3-methylimidazolium hexafluorophosphate for the four complexes (**1**, **2**, **3**, and **4**) using the quantum yield measurement system from Hamamatsu, model C9920-01.

3 RESULTS AND DISCUSSION

The stability of iTMCs depends, at least partly, on their molecular structure and, in particular, on the ability to form π - π intramolecular interactions.[3, 4] Unfortunately, we were unable to obtain X-ray quality crystals of complexes **2–4**. Instead, DFT calculations were performed at the B3LYP/(6-31G** + LANL2DZ) level to fully optimize the structure of complexes **2** and **3** both in the ground and the excited states. In the ground state (S_0), the pendant phenyl ring of the bpy ligand stacks face-to-face with the phenyl ring of the adjacent ppy ligand. The average stacking distance between both phenyl rings calculated for complexes **2** and **3** ($\sim 3.5 \text{ \AA}$) is similar to the X-ray value reported for the reference compound **1** (3.48 \AA). [3] Similar results are to be expected for complex **4**, which was not calculated due to the larger size of the substituent in 4-position. Calculations therefore indicate that complexes **2–4** maintain the π - π intramolecular interaction observed for **1**. The optimized structures calculated for the lowest triplet

state (T_1) and the metal-centered triplet state (3MC) show that the π - π interaction is preserved in the excited state.

Metal-centered states result from the excitation of one electron from the occupied $d\pi$ HOMO to the unoccupied $d\sigma^*$ orbitals of the metal[10] and are assumed to be the origin of complex instability in $[Ru(bpy)_3]^{2+}$. [11, 12] In the iridium complex **1**, the 3MC states are calculated after geometry relaxation to lie approximately 0.6 eV above the lowest energy T_1 state. Although these states are somewhat higher in energy than those on $[Ru(bpy)_3]^{2+}$, they are still accessible. Hence, we assume that for iridium(III)-based iTMCs the relative position of the 3MC states is related to the complex stability. For complexes **2** and **3**, 3MC states are computed to lie 0.5 eV above the emitting triplet state (T_1) similarly to what is obtained for complex **1** (0.6 eV). Therefore, the probability of populating the 3MC states should be approximately the same for the three complexes.

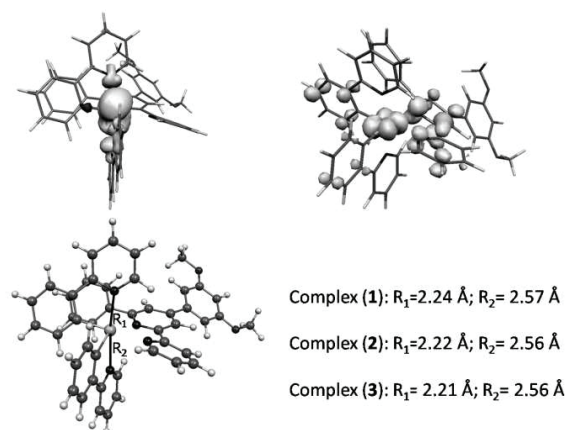


Figure 2: Top. Spin density distribution (0.005 e bohr⁻³) of the 3MC (left) and T_1 (right) excited states of complex **2**. Bottom. Minimum-energy structure calculated for the 3MC state of complex **2**, where R_1 and R_2 are the lengths of the Ir-N_{ppy} bonds.

As indicated in Figure 2, the spin density of the 3MC state clearly indicates the σ -antibonding interaction between the metal and the nitrogen of the ppy ligands. Electron promotion to this orbital has various effects on the different Ir-N_{ppy} bonds. While the Ir-N_{ppy} bond of the ppy ligand not involved in the intramolecular π -stacking drastically lengthens from 2.08 Å in S_0 to ~2.55 Å, the π -stacking prevents the weakening of Ir-N_{ppy} bond involved in this interaction and this bond only lengthens to ~2.20 Å. The pendant phenyl ring thus exerts a cage effect that restricts the opening of the structure of the complex in the excited 3MC state for these complexes (see Fig. 2). This supramolecular cage effect makes complexes **1–4** more robust reducing the possibility of ligand-exchange reactions.

The photophysical properties of complexes **1–4** are summarized in Table 1 and are generally similar. This is an expected result since the modification of the complex is done at the periphery and does not affect the conjugation

pattern of the central core. The main difference between the complexes is the increase in the photoluminescent efficiency in going from **1** to **4**. In concentrated films prepared in the composition of the LEC devices the PLQE value is as large as 0.38 demonstrating that the presence of the bulky substituents results in a strong increase in the PLQE.

Table 1: Photoluminescence and electroluminescence properties of ITO/PEDOT:PSS/iTMC:IL(4:1)/Al LECs at 3 V.

iTMC	PLQE _{dev} [%]	t_{on} [h]	Lum _{max} [cd/m ²]	$t_{1/2}$ [h]	E_{tot} [J]	EQE [%]
1	21	237	109	1290	13.6	1.3
2	24	77	183	950	17.2	3.4
3	34	33	284	660	17.4	6.1
4	38	-	-	-	-	-

LECs were prepared from complexes **2**, **3**, and **4** using the methodology previously reported.[3] An ITO-covered substrate was coated with a 0.1 µm spin-coated layer of polyethylenedioxythiophene/polystyrene sulfonic acid (PEDOT:PSS) followed by a 90 nm spin-coated layer of a 4:1 molar mixture of the iTMC and the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate and finally an aluminium layer was evaporated as cathode. The ionic liquid is incorporated to improve the turn-on time of the device.[1] Details concerning the device preparation and characterization can be found in the experimental section.

The devices employing complex **4** showed neither an increase in current density nor luminance (Lum) at applied biases of 3 and 4 volts over a period of 48 hours. The reason for the inactivity of these devices is not clear, but might be due to the very large intercomplex distance resulting from the bulky dendritic substituent. As LECs are unstable when operated at higher biases, the devices using complex **4** were not further investigated. The devices using complexes **2** and **3** exhibited the typical responses for LECs, namely a slow rise of the current density and luminance upon applying a low bias to the device. The turn-on times (t_{on} , time to reach the maximum luminance value) are very long (77 and 33 hours, for devices using complex **2** and **3**, respectively) but considerably lower than that observed from the reference device employing complex **1** (237 hours). The extremely long t_{on} for the device using complex **1** was reported earlier but is not fully understood.[3].

The efficiencies found for the devices using complex **2** and **3** were significantly higher than those obtained from the devices using complex **1** (see Table 1). This is expected in view of the difference in PLQE for films of the complexes using the device composition (see Table 1). The external quantum efficiency (EQE) for LECs is defined as:

$$EQE = bq/2n^2 \quad (1)$$

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 PLQE. Hence, the efficiency of the device is mainly determined by the PLQE values of the iTMC emitter in the thin film configuration used in the devices. According to this simple relationship the EQE's for the device using complex **1**, **2**, and **3** should then be 4.6, 5.3, and 7.5 %, respectively. These predicted values are higher than those obtained experimentally for the different LECs, indicating that either the outcoupling factor is not accurate or that not all charge carriers recombine. In particular, the LECs using **1** have a significantly lower experimental EQE, whereas for those using **3** the error between the predicted and observed EQE is not that large, indicating that the latter represents a rather optimized device configuration.

The highest current densities are observed for the devices making use of complex **1** and are approximately twice as high as those for the devices making use of complex **2** or **3**. However, due to the increased device efficiencies, the maximum luminances obtained for the devices using **2** and **3** are significantly higher than that found for the reference device, reaching 183 and 284 cd/m², respectively, at only 3 V bias.

The lifetime, when expressed as the time to reach half of the maximum brightness ($t_{1/2}$) decreases with faster t_{on} . This trend, although not understood, has been observed for many LECs.[1] However, as mentioned in the work by Kalyuzhny et al., $t_{1/2}$ is not a good value to compare the lifetime of LECs: $t_{1/2}$ can only be used when the maximum luminances of the different devices are similar.[8] It is known that in electroluminescent devices the time to reach the half of the initial luminance depends strongly on the initial luminance chosen. Since the devices described in this work have very different maximum luminances at the same driving voltages, the device lifetimes cannot be compared using the $t_{1/2}$ values. In their work, Kalyuzhny et al. proposed an alternative method, where the lifetime is expressed as the total emitted energy ($E_{1/5}$) up to the time the luminance reaches 1/5th of the maximum value ($t_{1/5}$) for a cell area of 3 mm². [8] When the devices are compared in this way, we obtain the surprising result that the devices using **2** or **3** show higher values of the total emitted energy (17.2 and 17.4 J, respectively) than the reference device (13.6 J). Hence, the introduction of the bulky side groups not only increases the device efficiency but also increases the device stability.

4 CONCLUSION

In conclusion, three new ionic iridium(III) complexes were prepared that contain bulky groups of increasing size

and have the ability to form intramolecular cages through π - π^* interactions between the pendant phenyl ring of a 6-phenyl-2,2'-bipyridine bpy ligand and one of the phenyl rings of the ppy ligands. With increasing size of the bulky side groups the photoluminescence quantum efficiency of the complexes increases. When used to prepare simple LECs, complexes **2** and **3** resulted in very efficient devices with high luminances. Additionally, the total emitted energy during the lifetime of the devices was larger than the device based on the unsubstituted reference complex. Hence, substituting the complex on the periphery with large (electronically inactive) groups greatly improves the efficiency, the luminance, and the stability of the LECs employing them. It appears that this strategy can-not be extended indefinitely, as we observed no electroluminescence from the device employing the complex with the largest side group. The reason for that inability is unclear but might be related to a too-large intersite distance between the cations.

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