

## Short Communication

Sky-blue OLED through PVK:[Ir(Fppy)<sub>2</sub>(Mepic)] active layer

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## ABSTRACT

The heteroleptic [Ir(Fppy)<sub>2</sub>(Mepic)] complex exhibits an intense sky-blue phosphorescence ( $\lambda_{\max} = 474$  nm; CIE color coordinates:  $x = 0.14$  and  $y = 0.29$ ) and a unitary quantum yield ( $\phi = 0.98$ ) in acetonitrile from a distinct triplet excited state of mixed <sup>3</sup>MLCT/LLCT characters. [Ir(Fppy)<sub>2</sub>(Mepic)] as a guest in a poly-(9-vinylcarbazole) (PVK) host matrix leads to energy transfer from the polymer to the complex, resulting in the complex's blue emission with quenching of the PVK fluorescence. The active layer of an operational organic light-emitting diode (OLED) with PVK:[Ir(Fppy)<sub>2</sub>(Mepic)] film had its optoelectronic properties characterized by current-voltage curve and electroluminescent spectrum. The device exhibits a space-charge limited current and its illumination occurs after reaching the trap-filled limit at 35 V. This work is a successful proof of concept for a feasible low-cost sky-blue OLED with a simple architecture and fabrication methods that require non-specific instruments.

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## 1. Introduction

The smart use of lighting technologies aiming to a sustainable development is at the forefront of the global agenda [1–8]. Light-emitting devices (LEDs) are alternatives to conventional incandescent and fluorescent lamps due to their lower power consumption, faster response time, and longer durability with a facile maintenance [1,3,8]. Organic semiconductors, such as unsaturated polymers and crystals, can be employed in LEDs as the electroluminescent layer in a sandwich type architecture consisted of a metallic cathode and a transparent conductive oxide anode [7–13]. In the active layer of these so-called organic light-emitting diodes (OLEDs), electrons and holes interact to produce excitons, which recombine with light emission [7–13]. Additional contact and blocking multilayers can promote a more efficient charge transfer to the electroluminescent thin film and further enhancements are achieved by doping the active layer with phosphorescent metal complexes, fully using both singlet and triplet excitons [10,14–21]. Following this strategy, several triplet emitters were engineered to be employed in the active emissive layer, aiming to high emission quantum yields and diverse emission colors, with special emphasis to blue [3,7,8,10,12,22–31].

Our focus lies on different classes of emissive compounds [32–36], in special highly emissive heteroleptic Ir(III) complexes

[8,37–39]. The sky-blue emissive [Ir(Fppy)<sub>2</sub>(Mepic)] complex (FIrMepic) was molecular-engineered to achieve a more-efficient blue emitter [39] (with photophysical characteristics summarized in Section 3) and, in this work, an operational OLED was fabricated with FIrMepic and poly-(9-vinylcarbazole) semiconductor (PVK) in a very simple device architecture.

## 2. Experimental

The FIrMepic complex was synthesized and characterized in our previous work [39]. Aluminum (Kurt J. Lesker), PEDOT:PSS (Aldrich) and PVK (Aldrich) were used without additional purification. HPLC grade solvents (Aldrich) were employed in the preparation of thin films and in photophysical measurements.

Thin films were deposited by spin-coating using a Laurell Technologies' WS-6S0SZ-6NPP/LITE/IND spinner. For the deposition of the emissive layer, a viscous chloroform solution of 20 mg mL<sup>-1</sup> PVK and 2 mg mL<sup>-1</sup> FIrMepic was employed and, after deposition, films were dried under vacuum (10<sup>-3</sup> mbar) for at least 10 h. Aluminum was deposited by thermal evaporation under vacuum (10<sup>-6</sup> mbar) using a homemade evaporator at Sala Limpa from Escola Politécnica – USP.

Surface parameters were obtained employing a KLA Tencor P6 profilometer. Waviness deviations were factored out of the raw profile data in a Profiler 7.35 software by employing a 0.14 μm low pass algorithmic filter that best fitted to the investigated sample.

Device optoelectronic studies were performed with the instruments available in our laboratory, carried out in air under standard

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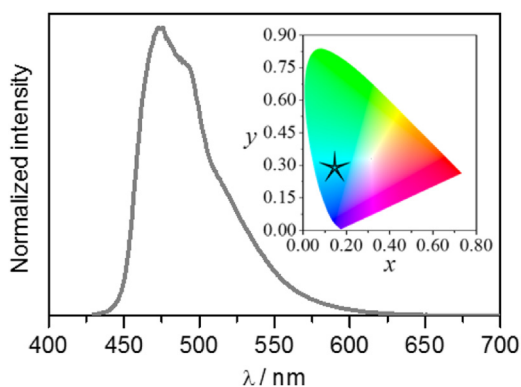
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atmosphere, temperature and pressure conditions [38,40]. A Keithley 2410-c source meter was employed to measure its current density–voltage characteristics. Photo- and electroluminescence measurements were performed using an ISS PC1 photon counting spectrofluorometer coupled with a Keithley 2410-c source meter.

### 3. Results and discussion

The electronic absorption of FlrMepic in acetonitrile shows a major band around 253 nm ascribed to a ligand-centered (LC)  $\pi\pi^*$  transition in the Fppy ligand(s) and weak broad absorptions in the longer wavelength region related to an overlap of LC, ligand-to-ligand charge transfer (LLCT) and metal-to-ligand charge transfer (MLCT) transitions [39]. Excitation of FlrMepic in acetonitrile results in an intense sky-blue emission (CIE color coordinates:  $x = 0.14$  and  $y = 0.29$ ) from the lowest-energy triplet excited state ( $T_1$ ) ascribed to a mixing [16,41,42] between  ${}^3\text{MLCT}_{\text{Ir}(\text{Fppy})-\text{Fppy}}$  (87%) and  ${}^3\text{LLCT}_{\text{Fppy}\rightarrow\text{Mepic}}$  (13%) states [39]. Such  $T_1$  nature leads to a vibronically-resolved spectrum ( $\lambda_{\text{max}} = 474$  nm), Fig. 1, with an impressively high emission quantum yield ( $\phi = 0.98$ ) and a short-lived emission ( $\tau = 0.77$   $\mu\text{s}$ ); check reference 39 for a more detailed, comprehensive elucidation of FlrMepic's photophysics.

FlrMepic OLEDs were assembled using TEC 8 fluorine-doped tin oxide (FTO,  $8 \Omega/\square$ , Pilkington, thickness of 702 nm). A thin layer (82 nm) of the hole-conductor poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) was deposited on the conducting surface of TEC 8 by spin-coating (3000 RPM, 20 s) followed by heating at 110 °C for 1 h aiming to smooth occasional FTO surface imperfections. As summarized in Table 1, the waviness and roughness of this PEDOT:PSS film (14.2 and 5.9 nm, respectively) resemble those of the TEC 8 FTO substrate (15.2 and 5.2 nm). Similarly, the morphological parameters of the PEDOT:PSS film deposited on glass without FTO (7.6 and 3.4 nm) are comparable to those of the glass itself (9.8 and 3.7 nm). Therefore, since the PEDOT:PSS film is very thin, its waviness and roughness



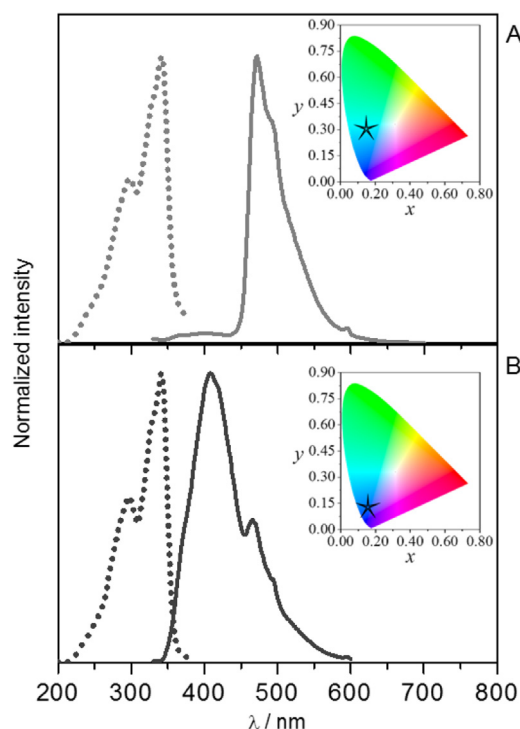
**Fig. 1.** Photoluminescence spectrum ( $\lambda_{\text{exc}} = 370$  nm) of FlrMepic in acetonitrile at 298 K (inset: CIE color coordinates of the photoluminescence) [39].

characteristics depend exclusively on the characteristics of the surface on which the film is deposited.

A PVK:FlrMepic (10% w:w) film was deposited by spin-coating (3000 RPM, 60 s) as the subsequent emissive layer with  $\sim 2270$  nm thickness and invariable waviness and roughness independent on the substrate surface. Such a thick layer leads to lower currents due to a high electrical resistance, which was required in order to fit the measured current under the upper detection limit of the picoamperimeter available in our laboratory.

Independently of the excitation wavelength, the photoluminescence spectrum of the PVK:FlrMepic film (Fig. 2A) refers mainly to the emission of the FlrMepic complex ( $\lambda_{\text{max}} \sim 475$  nm, Fig. 1), with a negligible contribution of the typical PVK fluorescence ( $\lambda_{\text{max}} \sim 405$  nm, Fig. 2B). On the other hand, the excitation spectrum of the PVK:FlrMepic film is ascribed solely to the excitation of the polymer, being identical to the spectrum of a pure PVK film, with no participation of FlrMepic. These results indicate that the emission of this PVK:FlrMepic film arises from an efficient energy transfer from the polymer to the complex, which is a desired characteristic for OLED emissive layers on the strategic harvesting of both singlet and triplet generated excitons [34].

A thin film ( $\sim 100$  nm) of aluminum was deposited on top of the PVK:FlrMepic film by thermic evaporation under vacuum to act as



**Fig. 2.** Photoluminescence (—,  $\lambda_{\text{exc}} = 320$  nm) and excitation spectra (•••,  $\lambda_{\text{em}} = 470$  nm) of doped PVK:FlrMepic films (A) or pure PVK films (B) (insets: CIE color coordinates of the photoluminescence).

**Table 1**

Surface characteristics of the FTO/PEDOT:PSS/PVK:FlrMepic/Al device.

Sample	Thickness/nm <sup>a</sup>	Roughness/nm <sup>a</sup>	Waviness/nm <sup>a</sup>
Glass without FTO	–	9.8 ± 0.9	3.7 ± 0.7
FTO on top of glass	702 ± 19	15.2 ± 0.8	5.2 ± 1.2
PEDOT:PSS (measured on glass without FTO)	82.0 ± 9.2	7.6 ± 1.1	3.4 ± 0.5
PEDOT:PSS (measured on FTO)	–	14.2 ± 0.1	5.9 ± 0.8
PVK:Ir (measured on glass without FTO)	2270 ± 330	3.0 ± 0.8	4.0 ± 0.8
PVK:Ir (measured on PEDOT:PSS on FTO)	–	4.7 ± 1.6	5.4 ± 2.1

<sup>a</sup> values are averages of, at least, three individual films.

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