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Short communication

Light-emitting electrochemical cells based on a solution-processed multilayered device and an anionic iridium (III) complex

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ABSTRACT

The optical and electronic properties of a solution-processed light-emitting electrochemical cell (LEC) based on an anionic iridium (III) complex as the emitter material has been designed and investigated. The obtained multi-layered devices emitted light of a light-green color (CIE, $x = 0.29$, $y = 0.45$) at low external applied voltage. The electroluminescent devices fabricated from this anionic iridium complex exhibited a relatively moderate electroluminescent efficiency and a luminance as high as 140 cd/m^2 at 7.2 V.

1. Introduction

During the past decade, intense research efforts have been devoted to the design of new emitters for organic light emitting diode (OLED) and light-emitting electrochemical cells (LECs). Academic and industrial interest for new optoelectronic materials is supported by the potential uses of these materials in lighting and flat panel displays [1–7]. Among the different classes of materials under investigation, transition metal complexes have emerged as some of the most promising candidates as both singlet and triplet excitons of the phosphorescent emitters can be advantageously harvested for light emission [8–11]. In LECs, cyclometalated iridium (III) complexes are without contest the most widely investigated emitters [12,13]. Until recently, LECs were only prepared with cationic complexes as these complexes can be obtained in high yield and exhibit a sufficient solubility to prepare highly concentrated solutions. It is only recently that anionic iridium complexes were incorporated in light-emitting devices, as single emitters for LECs [14] or as co-emitters for OLEDs [15–17]. The major drawback of the anionic complexes is undoubtedly their low solubility in most of the common organic solvents, therefore impeding the deposition of layers with sufficient thickness. Traditionally, LECs are single-layered devices fabricated by sandwiching a thin film of emitters between two metal contacts [18,19]. However, LECs have also been reported as multi-layered devices [20,21] that present the advantages to limit the presence of pinholes if emitters of low solubility are employed. Devices stability is also improved by increasing the thickness of the whole device even if higher driving voltages are therefore required. As underlayer, poly(*N*-vinylcarbazole) (PVK) which is a hole-transport layer is commonly used due to its good solubility in common organic solvents, excellent film-forming properties, high glass-transition-temperature (200 °C), and high triplet energy (3.0 eV) [22]. Herein, we report on a solid-state multilayered LEC prepared with an anionic iridium complex as the emitter. Originality of our work lies in the fact that PVK enabled to bring the sufficient thickness and to avoid the presence of pinholes, thus enhancing the device performance. A luminance as high as 140 cd/m^2 could be obtained at 7.2 V. UV–vis absorption and photoluminescence properties of the anionic complex were also investigated in solution and in the solid state.

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2. Experimental

2.1. General Informations

Mass spectroscopy was performed by the Spectropole of Aix-Marseille Université. ESI mass spectral analyses were recorded with a 3200 QTRAP (Applied Biosystems SCIEX) mass spectrometer. The HRMS mass spectral analysis was performed with a QStar Elite (Applied Biosystems SCIEX) mass spectrometer. Solid state absorption and emission spectra were recorded with a UV MC2 spectrophotometer from the SAFAS Monaco society and a Photon Technology International spectrofluorimeter. Solid state spectroscopic data were obtained on thin films of material deposited by spin-coater. Thickness of approximately 50 nm was controlled by profilometry. ^{1}H and ^{13}C NMR spectra were determined on a Bruker Avance 400 spectrometer of the Spectropole: ^{1}H (400 MHz) and ^{13}C (100 MHz). The ^{1}H chemical shifts were referenced to the solvent peak: $CDCl_3$ (7.26 ppm), and the ^{13}C chemical shifts were referenced to the solvent peak: $CDCl_3$ (77.0 ppm). All starting materials and solvents were purchased from Aldrich and used as supplied commercially. Dimer $Ir_2(ppy)_4\mu\text{-}Cl_2$ (ppy = 2-phenylpyridine) [23,24] was synthesized in an inert atmosphere according to the Nonoyama route by refluxing $IrCl_3.3H_2O$ with 2–2.5 equiv. of cyclometalating ligand in a 3:1 mixture of 2-ethoxyethanol and water. Na[Ir(2-phenylpyridine)$_2$(CN)$_2$] (**Na.1**) was synthesized by following and adapting a literature procedure [25].

2.2. General procedure for the synthesis of the anionic complex *Na.1*

A mixture of dichlorobridged iridium (III) dimer $Ir_2(ppy)_4\mu\text{-}Cl_2$ (536 mg, 0.5 mmol, 1 equiv.) was stirred with sodium cyanide (290 mg, 5.92 mmol, 12 equiv.) in MeOH (60 mL) and the reaction mixture was stirred under reflux for 48 h. After cooling, the solvent was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, DMF) to yield the pure product as a light yellow solid (552 mg, 96% yield) (Scheme 1).

^{1}H NMR (400 MHz, DMSO d_6, ppm): 6.07 (d, 2H, J = 6.8 Hz), 6.59 (t, 2H, J = 7.3 Hz), 6.71 (t, 2H, J = 8.1 Hz), 7.29 (t, 2H, J = 6.0 Hz), 7.65 (d, 2H, J = 7.5 Hz), 7.88 (t, 2H, J = 8.7 Hz), 8.06 (d, 2H, J = 8.0 Hz).

^{13}C NMR (100 MHz, DMSO d_6, ppm): 119.1, 120.1, 122.65, 123.7, 128.4, 130.8, 131.5, 136.4, 144.5, 153.3, 163.6, 165.8, 168.0.

HRMS (TOF-MS ES$^-$) m/z: theor: 553.1011, exp: 553.1026 (M$^-$ detected).

2.3. LEC fabrication and measurements

LECs were fabricated onto cleaned indium tin oxide (ITO) glass substrates with sheet resistance of 10–12 Ω/cm^2. Prior to organic layer deposition, the ITO substrates were successively washed with acetone, ethanol and isopropanol under ultrasonic for 15 min, and finally exposed to UV-ozone for 20 min. The poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) layer was spin-coated in ambient atmosphere at a rate of 3000 rpm for 90 s and then dried by baking in air at 120 °C for 1 h. A filtered solution of poly(vinylcarbazole) (PVK, average M_n = 25,000–50,000, 20 mg/mL in 1,2-dichlorobenzene) was spin-coated at a rate of 3000 rpm for 40 s on top of the PEDOT:PSS layer to form a PVK-coating of 60 nm-thick. The light-emitting layers were then spin-coated from a filtered 1,2-dichlorobenzene solution (solution of 30 mg/mL) of complex **Na.1** The Ca/Al bilayer cathode (device A) was formed with a shadow mask by the successive thermal evaporation of Ca (300 nm) and Al (60 nm) under secondary vacuum. The Al cathode (device B) was formed with a shadow mask by evaporation of Al (60 nm) under secondary vacuum. Current density–voltage–luminescence (*J*–*V*–*L*) characteristics of LECs were measured with a Keithley 4200 semiconductor analyser coupled with a Hamamatsu Light sensor calibrated with a Minolta CS-100 luminancemeter. The EL spectra were collected with an Ocean Optics HR2000 Spectrometer. Chromatic Coordinates were calculated from the EL spectra and reported following the CIE-1964 chromaticity diagram. From the electrode deposition step, devices are stored and characterized in nitrogen filled gloveboxes (O_2 and H_2O < 0.1 ppm) without encapsulation.

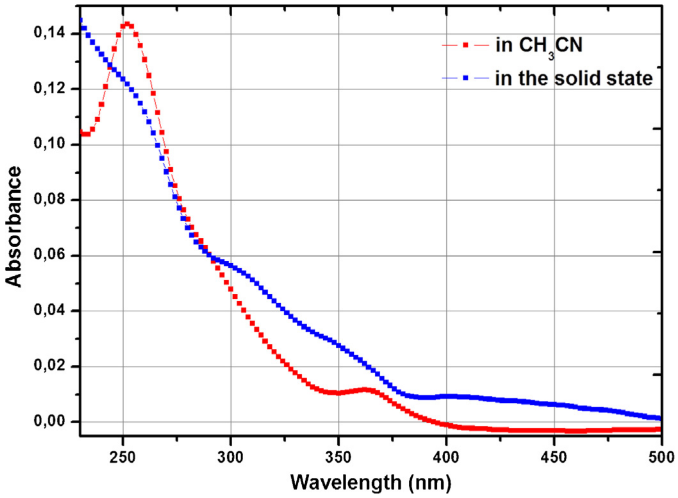

Fig. 1. UV–vis absorption spectra of **Na.1** in solution (CH_3CN) and in the solid state.

3. Results and discussion

3.1. Synthesis of *Na.1*

Anion **Na.1** was conveniently synthesized by reaction of the corresponding dichloro-bridged iridium (III) dimer $[Ir(ppy)_2\mu\text{-}(Cl)]_2$ with 12 equiv. of sodium cyanide in refluxing methanol. Purification by column chromatography using DMF as the eluent provided the salt in 96% yield.

3.2. Photophysical properties

The absorption and photoluminescence (PL) spectra of the complex, recorded in the solid state and in solution, are shown in Figs. 1 and 2 respectively. Intense absorption bands were observed in the ultraviolet region between 200 and 300 nm and assigned to transitions of ligand-centered states with mostly spin-allowed $^{1}\pi\text{–}\pi^*$ character from the cyclometalated C$\hat{N}$ ligand. The weaker and well-resolved absorption bands extending from 300 to 450 nm were attributed to both spin-allowed and spin-forbidden metal-to-ligand charge transfer (MLCT) transitions [26,27]. Similar absorption spectra were obtained in solution and in the solid state.

Fig. 2 shows the photoluminescence spectra of **Na.1** in the solid state and in a CH_3CN solution at 298 K. When excited within the $\pi\text{–}\pi^*$ and MLCT absorption band, the PL spectrum recorded in solution showed two peaks, the main one centered at 450 nm and a less intense one at 478 nm with a shoulder at 510 nm. With reference to previous work on heteroleptic iridium (III) complexes [28,29], the ^{3}MLCT peak is usually observed at high energy without vibronic replica whereas the $\pi\text{–}\pi^*$ emission is observed at lower energy under the form of a broad peak with vibronic replicas. Therefore, from these results, the first peak can be confidently assign to arise from a predominantly ^{3}MLCT state, whereas the second peak that presents a vibronic replica at 510 nm arises from mainly $\pi\text{–}\pi^*$ ligand states. When studied in the solid state, a completely different