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NIR-OLED (1.54 µm) emitting electroluminescent diode arrays based on Er-complexes manufactured by cost-effective methods

Matriz de diodos electroluminiscentes orgánicos emisores en el infrarrojo cercano (1.54 µm) basados en complejos de erbio fabricados por métodos de bajo coste

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ABSTRACT:

Solution processed 1.54 µm near infrared organic light-emitting diodes (NIR-OLED) based on novel Er(III) complexes, having the general formula [Er(β-diketonate)$_3$(N,Ndonor)], have been manufactured by cost-effective methods and their properties studied. 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione (Htfnb or Hnta) or 1,1,1-trifuoro-5,5-dimethyl-2,4-hexanedione (Htpm) are the fluorinated β-diketonate primary sensitizers, and 2,2'-bipyridine (bipy) or 5-nitro-1,10-phenanthroline (5NO$_2$phen) act as N,N-donors. The simple structure of the diodes is glass/indium-tin oxide (ITO)/poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)/[Er-complex]/Ca/Al. The resulting electroluminescence corresponds with the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er(III) emission at 1.54 µm and no visible emission is observed. Photophysical characterization proves that, upon organic ligand excitation by UV light, the luminescence from the ligands is totally quenched in favour of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ Er(III) emission, confirming a complete resonant energy transfer from the ligands to the Er(III) ion, analogous to that observed in the electroluminescence emission. We present a fabrication method that avoids any photolithographic or mask step. The reported results show a simple way to obtain large area NIR-OLEDs by cost-effective methods.

Key words: Near-Infrared OLED, Cost-Effective, Arc-Erosion, Erbium(III), β-diketonate, Fluorination.

RESUMEN:

Se han fabricado y caracterizado diodos orgánicos emisores de luz en el infrarrojo cercano (NIR-OLED) procesados desde solución, basados en nuevos complejos de Erbio (III) con fórmula general [Er(β-d)$_3$(N,N-donor)] utilizando métodos de bajo coste. Los ligandos primarios son β-dicetonatos fluorados 4,4,4-trifluoro-1-(2-naftil)-1,3-butanodiona (Htfnb o Hnta) o 1,1,1-trifluoro -5,5-dimetil-2,4-hexanodiona (Htpm) y los ligandos secundarios 2,2'-bipiridina (bipy) o 5-nitro-1,10-fenantrolina (5NO$_2$phen) actúan como bases de Lewis. La estructura del diodo es vidrio/óxido indio-estaño (ITO)/poli (3,4-etilendioxitiofeno)-poli (estireno sulfonato)/complejo de Er(III)/Calcio/Aluminio. La electroluminiscencia resultante corresponde con la emisión de la transición $^4I_{13/2} \rightarrow {}^4I_{15/2}$ del Er(III) a 1.5 µm sin que se observe emisión alguna en el visible. La caracterización fotofísica muestra que, bajo excitación con luz UV, se produce un apagamiento de la emisión de los ligandos acompañado por una

emisión en el NIR del Er(III) análoga a la obtenida por excitación eléctrica, confirmando de este modo la transferencia completa de energía desde los ligandos al ion Er(III). Presentamos un método de fabricación que evita cualquier paso fotolitográfico con máscara. Los resultados reportados muestran un camino sencillo para obtener diodos emisores de luz en el infrarrojo cercano utilizando métodos de bajo coste.

Palabras Clave: OLEDs Infrarrojo Cercano, Bajo Coste, Electroerosión, Erbio (III), β-dicetonato, Fluoración.

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1. Introduction

Organic semiconductors (OS) offer great opportunities in the development of low-cost, flexible and large-area devices (properties difficult to achieve with conventional silicon (Si) based electronics), in addition to the possibility of fine tuning key properties (luminescence, absorption, energy band gaps and charge transport) through a convenient molecular design [1]. Nonetheless, the challenge of organic based devices is enabling the fabrication of certain optoelectronic devices (or part of them) at a significantly lower costs and/or opening the way to new devices functionalities (e.g., flexibility, optical transparency and large area) [2,3]. In this context, it is necessary to act in two complementary aspects in order to increase the fabrication yield so as to achieve a real breakthrough in the market. On the one hand, active research on novel OS with good transport and optical properties is absolutely necessary.

These novel OS must be suitable for being processed by solution methods which afford their compatibility with profitable manufacturing techniques for large area production, such as roll-to-roll (R2R) techniques. In this sense, wet processing OS emitting in the near infrared (NIR) region (900-2000 nm) could offer added value applications beyond optical communications, such as health care applications, clothing, night vision equipment, irregular surfaces signalization, greenhouse lighting or environmental heating. On the other hand, if we combine these novel materials with low cost fabrication procedures, for instance avoiding photolithographic steps for large-area patterning of thin film semi-conductors, then the way is paved for large area and low-cost active optical and electronic devices.

For these purposes, lanthanide complexes which emit in the NIR region are amongst the most promising approaches. It is known that the optical population of their emitting levels can be achieved by employing organic ligands as chromophores, with strong absorption in the UV spectral region, avoiding the fact that direct optical excitation of the lanthanides is a low efficient process due to their weak optical absorption. These ligands can sensitize the central lanthanide by intramolecular energy transfer, a process known as "antenna effect" [4,5]. This motivated our interest in developing lanthanide complexes that could combine good film forming properties by cost-effective methods, good thermal stability and NIR emission capability [6]. Among lanthanides, Er(III) ion is particularly interesting because its 1.54 µm emission matches the spectral region used in long distance optical fibre telecommunications.

In this contribution, we report NIR solution processed OLEDs based on Er-complexes having the general formula, [Er(β-diketonate)$_3$(N,N−donor)]. The fluorinated β-diketonate ligands, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione and 4,4,4-trifluoro-1-(2-naphthyl)-1,3-butanedione, combine a good absorption cross-section in the ultraviolet region with a significant reduction of non-radiative quenching of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er(III) emission at 1.54 µm, while the rigidity and bulkiness of the

N,N-donors (2,2'-bipyridine and 5-nitro-1,10-phenanthroline) have a pronounced impact on the emission intensity of luminescence [7,8]. These materials, [Er(tpm)$_3$(5NO$_2$phen)] and [Er(tfnb)$_3$(bipy)], have been selected due to their good structural data and film forming properties. The simple structure of the OLEDs is: ITO/PEDOT:PSS/[Er-complex]/Ca/Al. We report the NIR electroluminescence and current-voltage characteristics of the devices. The resulting 1.54 µm electroluminescent emission is studied, in order to investigate the energy transfer from the organic ligands to the central lanthanide(III) ion, by means of pholuminescence (PL) studies. A tentative mechanism for the indirect excitation process of Er(III) from the singlet excited state S_1 of the ligand is proposed. Finally, to illustrate the capabilities of the proposed cost-effective technique, a 3×3 display based on a commercial OS, Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), with visible emission, has been fabricated avoiding any photolithographic step, using electrical arc erosion to pattern the successive electrodes of the devices [9]. Thus, the way for manufacturing infrared emission displays in large area format has been paved. Further work is currently in progress.

2. Experimental

The synthesis and structural data of the materials, together with their optical characterization have been reported elsewhere [7,8]. The crystallographic structure of the Er-complexes are shown in Fig. 1.

2.a. Optical measurements

Photoluminescence spectra of the materials were measured at room temperature. The NIR PL emission at 1.54 µm was excited at the ligand absorption, λ_{exc} =337 nm (N$_2$ laser), or at the Er: $^4I_{11/2}$ absorption level, λ_{exc} =980 nm (MOPO laser system). The emitted light was dispersed by a Spex model 340E (f=34 cm) spectrometer and detected with a Peltier-cooled NIR Hamamatsu photomultiplier and a lock-in amplifier. All the emission spectra have been corrected by the spectral response of the experimental setups.
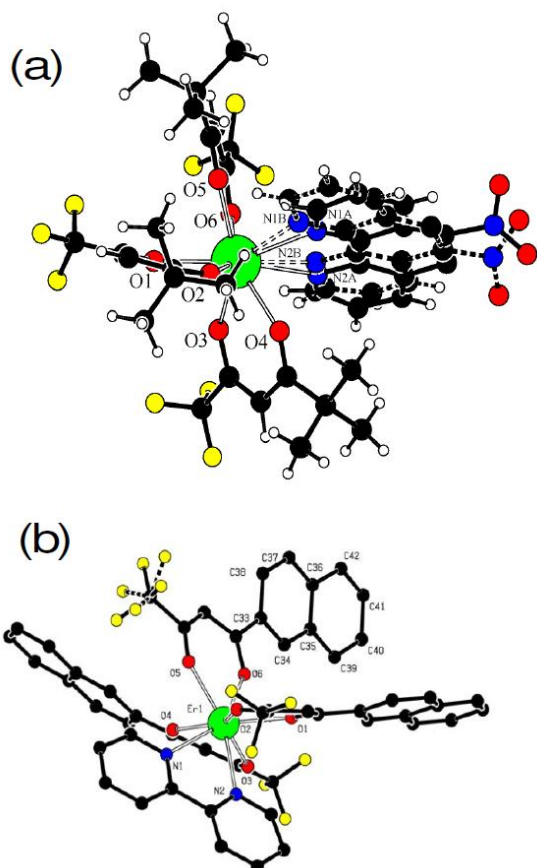
Fig. 1: Crystallographic structure of (a) [Er(tpm)₃(5NO₂phen)] and (b) [Er(tfnb)₃(bipy)] complexes. In (b) the H atoms were omitted for clarity. Er (green), O (red), F (yellow) and N (blue).

2.b. OLED fabrication procedure

For NIR-OLEDs, pre-patterned ITO glass plates with four circular diodes (1 mm and 1.5 mm radii) were extensively cleaned, using chemical and UV–ozone methods, just before the deposition of the organic layers. PEDOT:PSS (CLEVIOS P VP AI 4083) was deposited by spin coating (30 s @ 2000 RPM) and cured (15 min @ 140ºC). 4%wt methanol precursor solutions of [Er(tpm)₃(5NO₂phen)] and [Er(tfnb)₃(bipy)] were kept in an ultrasonic bath for 45 min and filtered through a 0.2 μm polytetra-fluoroethylene (PTFE) syringe filter, prior to being spin coated. The active layer were then deposited (30 s @ 1500 RPM) and cured (10 min @ 90ºC, 10 min @ 120ºC) to achieve complete solvent removal. The thickness of the layers was measured using an Alpha Step D120 profilometer (KLA-Tenkor Instruments),
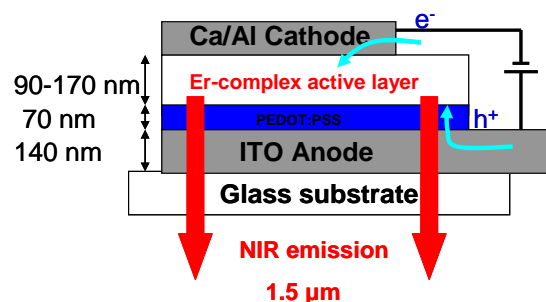

Fig. 2. Structure of the manufactured NIR organic light emitting diodes (OLEDs).

obtaining 70 nm for PEDOT:PSS layer and 97 nm and 170 nm for [Er(tfnb)₃(bipy)] and [Er(tpm)₃(5NO₂phen)] active layers, respectively. The Ca/Al cathode was thermally evaporated (8×10^{-6} Torr) on top of the organic layer surface and the device was finally encapsulated using a glass cover attached by a bead of thermally cured epoxy adhesive. The layers structure is shown in Fig. 2.

The 3×3 MDMO-PPV based OLED display manufacturing procedure was conducted as follows. The ITO anode was patterned by electric arc ablation [9] according to a column design. Next, the glass/ITO substrate was etched by a pre-heated diluted 6M hydrochloric solution, in order to remove any waste that may have remained after the arc erosion procedure. With this step we guaranteed the full isolation of the pad previously patterned and avoided any possibility of short circuits. After a second careful washing and drying stage, we proceeded to deposit by spin coating layers of the device in inert atmosphere. First, PEDOT:PSS (30 s @ 2000 RPM) plus solvent evaporation (30 min @ 150ºC). Then, the MDMO-PPV active layer (diluted in THF 1.8 wt %) was deposited (30 s @ 4000 RPM) and annealed (15 min @ 100ºC). A commercial polymer, instead of an Er-complex, is used here to avoid material wasting in case of failure. Furthermore, an orange-emitter was chosen since readers can easily perceive a visible-range device working in Fig. 4. The Ca/Al cathode was then evaporated and the whole sample (glass/ITO/PEDOT:PSS/OSC/Ca/Al) was taken from the glove box and re-aligned in our arc erosion facility, using a home-made software for this purpose. We then proceed to erode the
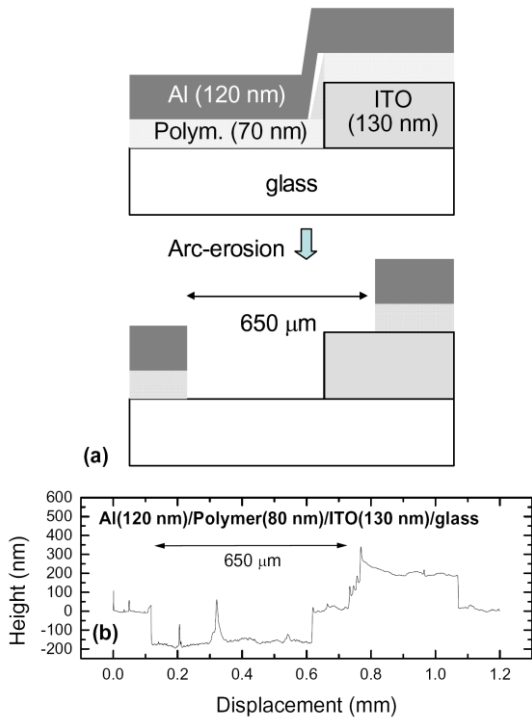
Fig. 3. Erosion performed on a glass/ITO/polymer/Al structure @ 3 V, on a 3×0.65 mm area (line plus line, steps=20 μm, tip diameter f =40 μm).

Fig. 4. 3×3 orange-emitting display based in MDMO-PPV, 9 mm^2 per pixel.

adequate grooves for the cathode rows conformation. In Fig. 3 we can observe the resulting profile of the erosion performed on a glass/ITO/OSC/Al structure @ 3 V, on a 3×3 mm area, (line plus line, steps=20 μm, tip diameter F=40 μm). Finally, back in an inert atmosphere, the device is encapsulated for subsequent characterization. Figure 4 shows the resulting display based on commercial MDMO-PPV red-
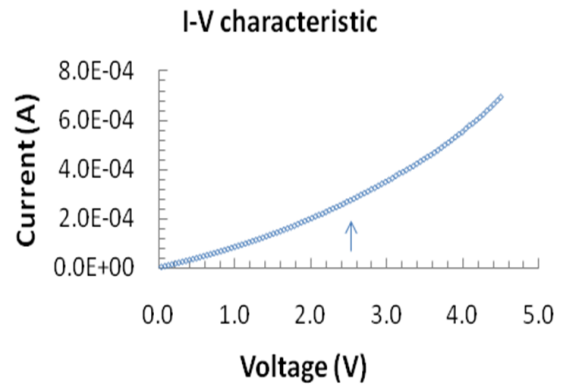

Fig. 5. Current-voltage response of one pixel from display of Fig. 4. Arrow marks the onset for electroluminescence.

emitter under operation. Fig. 5 shows the current-voltage response of one pixel from this display. Arrow marks the onset for electroluminescence. The significant leakage current at low voltages arises from a crossover effect to neighboring pixels.

2.c. OLED characterization

Current density–voltage (J–V) characteristics were measured using a semiconductor parameter analyzer Agilent 4155C and a SMU pulse generator Agilent 41501B. A pulse train was used as the input signal. The duty cycle was set to be 0.2%. The refresh time between two consecutive pulses ensures long time operation without significant device degradation. Furthermore, the J–V curve stability was achieved by gradually increasing the pulse amplitude up to the point where reproducible measurements were observed.

NIR EL spectra from the OLED devices were analysed using a SPEX 1702/04 (f=1 m) monochromator and detected with a 77 K cooled Ge detector connected to a Stanford Research system SR530 locking amplifier, using 50% duty cycle waveform from a TTi40 MHz arbitrary waveform generator and a TREK-601C amplifier.

3. Results and discussion

Figure 6 shows the recorded NIR EL of [Er(tfnb)$_3$(bipy)] and [Er(tpm)$_3$(5NO$_2$phen)] OLEDs measured at 0.5 mA and 2 mA driving current respectively (6.5 V and 15 V). The
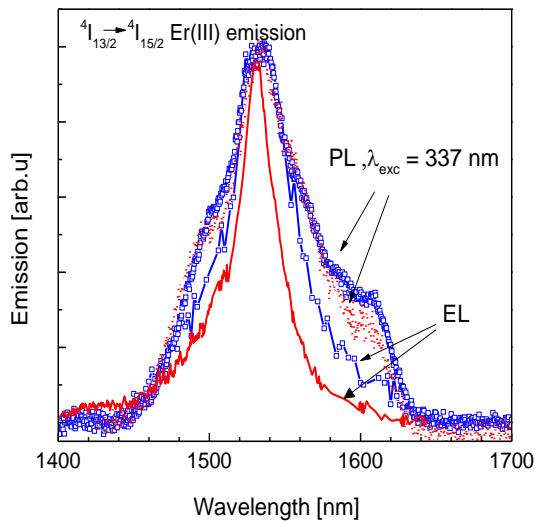
Fig. 6. Normalized EL spectra of the Er-complexes based OLEDs: [Er(tmp)$_3$(5NO$_2$phen)] based device (red solid line) and [Er(tfnb)$_3$(bipy)] based device (blue open squares). The normalized photoluminescence emission obtained upon excitation of the organic ligands at λ = 337 nm is included for comparison purposes.

emission is assigned to Er(III):^{4}I$_{13/2}$→^{4}I$_{15/2}$ transition at 1.54 μm [10]. This NIR emission can be attributed to the exciton-harvesting processes from the ligands, as no visible emission from the latter is observed. In the same figure, we have included the photoluminescence emission of the material upon excitation of the organic ligands at 337 nm. We can observe that the EL spectra match very well the photoluminescence spectra, except for a narrowing at the low energy wing of the band. This is most likely related to the increase in the material temperature and consequently to the redistribution of the electronic population in the excited ^{4}I$_{13/2}$ multiplet. The charge carrier transfer process that takes place resulting in the Er(III) 1.54 μm EL emission has to be very similar to that of the PL indirect excitation of Er(III) via the organic ligand, since no visible emission from the ligand is observed in both cases.

The indirect electrical excitation of the Er(III) NIR EL process could be explained as follows: electrons and holes are respectively injected from the low and the high work function electrode into the lowest unoccupied and the highest occupied electronic levels of the organic
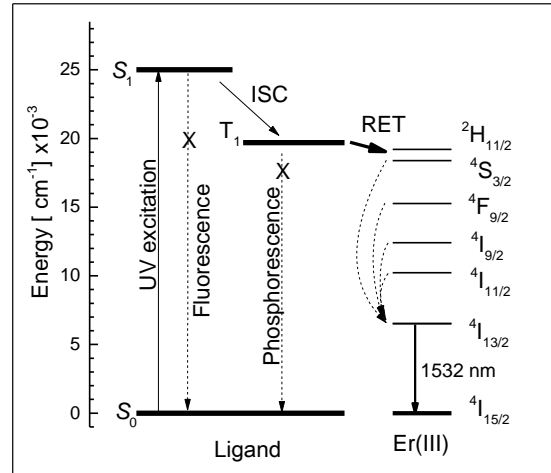

Fig. 7. Mechanism for the main intra-molecular energy transfer between the ligands and the 4f levels of Er(III). Dashed lines correspond with non-radiative transitions. ISC = intersystem crossing, RET = resonant energy transfer.
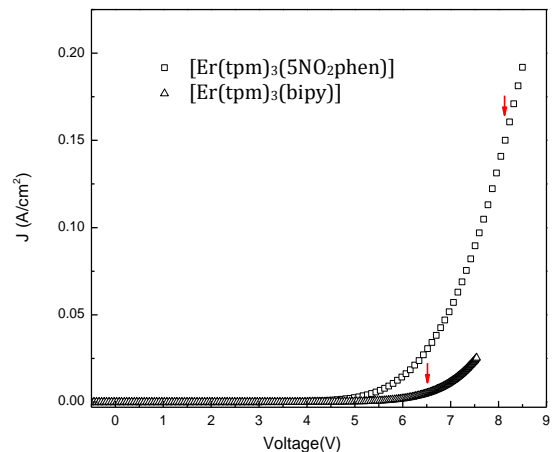

Fig. 8. $J - V$ response of the solution processed OLEDs based on [Er(tmp)$_3$(5NO$_2$phen)] (open squares) and [Er(tfnb)$_3$(bipy)] (open triangles). The red arrows indicate the EL onset voltage.

material present at the metal–organic interface, and are respectively transported from the electron transport layer and the hole transport layer to the emission layer. Then, electrons and holes recombine, leading to the formation of excitons, which will excite the electrons from the ground 4f state to the higher 4f excited states of Er(III) ion. Finally, the NIR-EL emission results from the electrons in the excited 4f state (^{4}I$_{13/2}$) of the Er(III) ion relaxing radiatively to the 4f ground state (^{4}I$_{15/2}$), according to the scheme presented in Fig. 7.

Figure 8 shows the J-V response measured from ITO/PEDOT:PSS(70 nm)/active layer (170 nm or 97 nm)/Ca/Al. The diodes exhibit a good electrical performance, with a threshold voltage of a few volts, 8 V for [Er(tpm)$_3$(5NO$_2$phen)] and 6.5 V for [Er(tfnb)$_3$(bipy)], similar to that reported by Wei *et al* [11] for a multilayer vacuum-deposited device and further lower than that reported for ErQ-based devices. Moreover, the very low noise level is indicative of the quality of the layer. Red arrows indicate the onset voltage for EL. The fact that the EL onset is lower in the thicker sample may be attributed to a more balanced electron-hole injection in the [Er(tfnb)$_3$(bipy)] based device, as a result of a better energetic level alignment.

4. Conclusion

Novel Er(III) complexes with fluorinated β-diketonate and 2,2'-bipyridine/5-nitro-1,10-phenanthroline ligands have been successfully used as an active layer for solution-processed organic light-emitting diodes (OLEDs) in the 1.54 µm near infrared (NIR) band. A complete energy transfer from the organic ligand (excited in the UV region) to Er(III) ion is observed: under UV excitation, the luminescence from the ligands is totally quenched in favour of $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er(III) emission. A tentative mechanism for the indirect excitation process of Er(III) from the singlet excited state S_1 of the ligand has been proposed. This property is retained when the complexes are incorporated in solution-processed OLEDs with structure ITO/PEDOT:PSS/[Er-complex]/Ca/Al and the emission is excited via an electrical field. As a whole, the excellent properties of these novel Er-complexes and the mask-free, photolitographic patterning-free method, pave the way for the manufacturing of large area NIR-OLED displays by cost-effective methods.