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Corresponding Author: Dr Luiz Pereira, PhD

Corresponding Author's Institution: University of Aveiro

First Author: Luís Rino, PhD

Order of Authors: Luís Rino, PhD; Wilson Simões, M.D; Gerson Santos, M.D; Fernando Fonseca, Ph.D; Adnei Andrade, Ph.D; Vítor Deichmann, M.D.; Leni Akcelrud, Ph.D; Luiz Pereira, PhD

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Photo and electroluminescence behaviour of Tb(ACAC)₃phen complex used as emissive layer on Organic Light Emitting Diodes

L. Rino¹, W. Simões¹, G. Santos², F.J. Fonseca², A.M. Andrade³, V.A.F. Deichmann⁴, L. Akcelrud⁴, L. Pereira^{1*}

¹*Departamento de Física e I3N – Instituto de Nanoestruturas, Nanofabricação e Nanomodulação, Universidade de Aveiro, 3810-193 Aveiro, Portugal*

²*Laboratório de Microeletrônica, Departamento de Engenharia de Sistemas Eletrônicos, Escola Politécnica da Universidade de São Paulo, Av. Prof. Luciano Gualberto, trav. 3, n° 380, CEP 05508-900, São Paulo – SP, Brasil*

³*Instituto de Eletrotécnica e Energia – Universidade de São Paulo, 05508-900 São Paulo, Brasil*

⁴*Laboratório de Polímeros Paulo Scarpa, Departamento de Química, Centro Politécnico da UFPR – Universidade Federal do Paraná, CP 19081, CEP 81531-900 Curitiba, Paraná – PR, Brasil*

Abstract

This work shows the luminescence properties of a rare-earth organic complex, the Tb(ACAC)₃phen. The results show the $^5D_4 \rightarrow ^7F_{3,4,5,6}$ transitions with no influence of any ligand emission. The photoluminescence excitation spectrum is tentatively interpreted by the ligands absorption. An OLED was made by thermal evaporation (total thickness of 1200 Å) using TPD and Alq₃ as hole and electron transport layers, respectively. The light emission reproduces the photoluminescence spectrum of the terbium complex at room temperature, with CIE (x,y) color coordinates of (0.28, 0.55). No presence of any bands from the ligands was observed. The potential use of this compound in efficient devices is discussed.

PACS codes: 72.80.Le, 78.55.Kz, 78.60.Fi, 85.60.Jb

Keywords: OLED, Rare-Earth complexes, photoluminescence, electroluminescence

1. Introduction

Electroluminescent devices of organic materials are promising candidates for the next generation flat panel displays (OLED's) [1 and references therein].

Although the actual state of the art of organic light emitters based on polymeric materials showed very promising results [2], the absence of colour purity and limited internal efficiency of those materials, open a new OLEDs framework. Rare earth

*Corresponding author: Tel: +351 234370200; fax: +351 234378197. E-mail address: luiz@ua.pt

complexes are actually good candidates, especially those based on europium and terbium [3, 4]. Although some results, was already obtained the device structures still are very complex and need to be addressed when those materials are used to develop electroluminescent devices. In this work, we show some photoluminescence results of an organic luminescent rare-earth complex based on terbium, and the related electroluminescence of an OLED based on that emissive material. The electro-optical discussion will address the further use and improvement of this kind of devices.

2. Experimental

The $\text{Tb}(\text{ACAC})_3\text{phen}$ was obtained by synthesis from $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$, acetylacetonate and 2,2'-phenanthroline. The device was fabricated by thermal deposition of the materials onto a patterned indium – thin – oxide (ITO) substrate (resistivity of $100 \Omega/\square$), with a vacuum of 10^{-6} mBar. The hole transport layer was TPD [N,N' – bis (3 – methylphenyl) – N,N' – diphenylbenzidine] with a thickness of 200 Å; the emissive Tb layer has 500 Å thick and the electron transport layer was Alq3 [aluminium – tris (8 – hydroxyquinoline)] (500 Å thick). The cathode was aluminium and the emitting area is 25 mm². All the materials were evaporated at an average ratio of 2 Å/s. The photoluminescence (PL) and excitation photoluminescence (PLE) was obtained in a Oriel MS-125 and in a Jovin-Ivon Triax 320 spectrometers, respectively. The electroluminescence (EL) data was recorded with a OceanOptics 2000 CCD spectrometer. Electrical measurements were obtained with a Keithley K2410 VoltageSource Meter and optical power data was recorded by a Ophir Optronics PD300-SH PowerMeter.

3. Results and discussion

Figure 1 shows the device scheme and the organic complexes chemical structures.

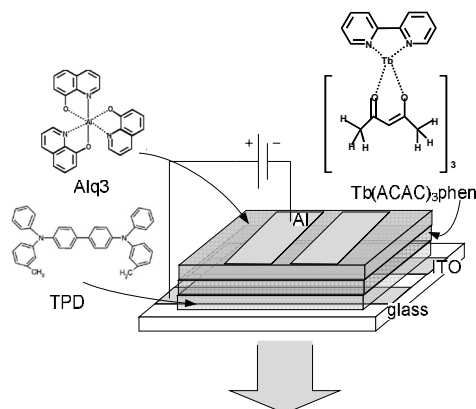


Fig. 1. Device scheme and organic complexes chemical structures.

The emission spectra of lanthanide ions (Ln) arise from $f-f$ transitions. Due to the shield effect, the $f-f$ transitions are extremely narrow, leading to high emission colour purity, and each ion has its own characteristic emission. The direct absorption of Ln(3+) cations is very weak but the population of the Ln emissive state is achieved through sensitization. In this process the metal ion's luminescence is accomplished through excitation of a coordinated ligand and subsequent energy transfer from a triplet state of the ligand to the metal ion by a dipole-dipole exchange mechanism. Figure 2 shows the PL and PLE spectra of the Tb complex.

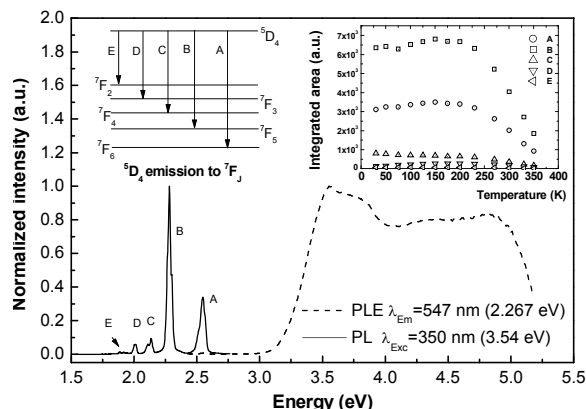


Fig. 2. Room temperature PL ($\lambda_{\text{exc}}=350\text{nm}$) and PLE ($\lambda_{\text{emi}}=547\text{nm}$) of the $\text{Tb}(\text{ACAC})_3\text{phen}$ powder. The features labelled as (A...E) and correspond to emissions from the lowest excited state of the Tb^{3+} ion ($^5\text{D}_4$) to the ground state $^7\text{F}_j$ ($J=2\dots6$). Inset: temperature dependence of the transitions ($\lambda_{\text{exc}}=350\text{nm}$).

The variation with temperature of all transitions show that the main emission $^5D_4 \rightarrow ^7F_5$ is still relatively high at room temperature, which is important for the device operation. The PLE spectrum shows a large band in the UV – blue region that corresponds to the calculated absorption band of the ACAC [5].

Figure 3 shows the OLED EL spectrum and reproduces the PL spectrum from the organic complex. This shows that the simple device structure used is efficient in the carrier confinement inside the emissive layer as no other emissions are observed.

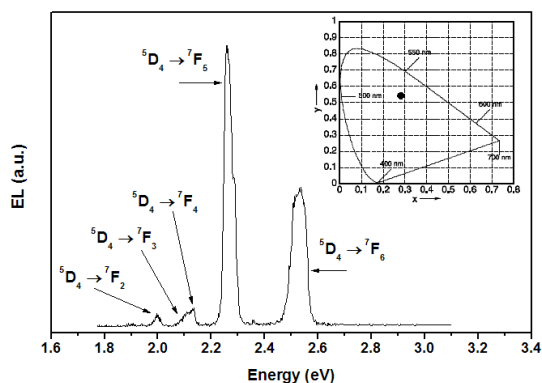


Fig.3 Device EL spectrum at room temperature. Inset: the CIE (x,y) coordinates. Applied voltage of 20 V.

The current – voltage – optical power (@ $^5D_4 \rightarrow ^7F_5$ transition – 547 nm) is shown in figure 4.

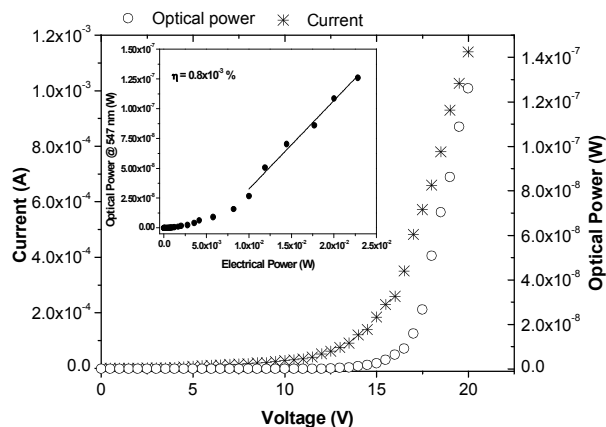


Fig 4 Device electrical current and optical power with applied voltage. Inset: the Optical Power vs. Electrical Power.

From this data we can determine the wall-plug efficiency (η), defined as the optical power over electrical power. In our devices, the best value is of $0.8 \times 10^{-3} \%$ which can be considered a good value for the main transition. One interesting result is that in spite of the relatively high driving voltage (near 17 V), a very small electrical current is needed, resulting thus in an efficient device. Considering the ACAC excited energy level (2.91 eV for the triplet state) [5] an efficient energy transfer to the $^5D_4 \text{ Tb}^{3+}$ level (2.54 eV) occurs. The HOMO level of TPD (5.5 eV) and the Alq3 LUMO level (3.1 eV) allows a good hole / electron density delivery to the emissive layer. The neutral ligand (phenantroline) does not interfere with the process.

Those results are very attractive as clearly proves that this device structure and Tb complex are very promising.

4. Conclusions

In conclusion, we report for a first time an OLED with $\text{Tb}(\text{ACAC})_3\text{phen}$ complex as emissive layer. The PL / EL spectrum shows the pure Tb^{3+} emission without any emission from the organic ligands. The EL spectra and η reveals that the energy transfer from the ACAC is efficient and the charge can be realistically confined into emissive layer. Thus, this simple structure can be usefully applied to build efficient terbium based OLEDs.

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