AIP | Applied Physics Letters

Efficient red organic light-emitting devices based on a europium complex

Junfeng Fang and Dongge Ma

Citation: Applied Physics Letters **83**, 4041 (2003); doi: 10.1063/1.1626022
View online: http://dx.doi.org/10.1063/1.1626022
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/83/19?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS VOLUME 83, NUMBER 19 10 NOVEMBER 2003

Efficient red organic light-emitting devices based on a europium complex

Junfeng Fang and Dongge Ma[a)]
State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

(Received 21 July 2003; accepted 23 September 2003)

An efficient organic light-emitting device using a trivalent europium (Eu) complex Eu(Tmphen)(TTA)$_3$ (TTA = thenoyltrifluoroacetone, Tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) as the dopant emitter was fabricated. The devices were a multilayer structure of indium tin oxide/N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-biphenyl-4,4-diamine (40 nm)/Eu complex:4,4-N,N-dicarbazole-biphenyl (1%, 30 nm)/2,9-dimethyl,4,7-diphenyl-1,10-phenanthroline (20 nm)/AlQ (30 nm)/LiF (1 nm)/Al (100 nm). A pure red light with a peak of 612 nm and a half bandwidth of 3 nm, which is the characteristic emission of trivalent europium ion, was observed. The devices show the maximum luminance up to 800 cd/m^2, an external quantum efficiency of 4.3%, current efficiency of 4.7 cd/A, and power efficiency of 1.6 lm/W. At the brightness of 100 cd/m^2, the quantum efficiency reaches 2.2% (2.3 cd/A). © *2003 American Institute of Physics.* [DOI: 10.1063/1.1626022]

Organic light-emitting devices (OLEDs) are one of the most promising next generation low cost full color flat panel displays alterative to liquid crystal-based ones. At present, organic materials including fluorescent organic molecules and polymers, and phosphorescent organic molecules with heavy metals have been widely used as active mediums in OLEDs.[1–3] These organic materials show good electroluminescent performance in OLEDs, particularly, the phosphorescent molecules have been demonstrated the prospect of obtaining devices with the internal quantum efficiencies of 100% through radiative recombination of both singlet and triplet excitons.[4] However, the broad nature of the luminescent spectra of these organic molecules leads to the poor luminescent purity, which are dull and, thus, not suited for actual display applications. For OLEDs, the development of high-performance red emission is still much in demand compared with both green and blue emission, which are already available. Therefore, how to obtain red OLEDs with high efficiency as well as good purity of color is necessary.

It is well known that rare-earth complexes emit sharp spectral band due to inner *f* orbitals of the central rare-earth metal ions and are expected to show high luminescence efficiency since both singlet and triplet excitons are involved in the luminescence process.[5] Of rare-earth complexes studied, europium complexes, which exhibit strong photoluminescence corresponding to the $^5D_0-^7F_2$ transition of Eu^{3+} ions, appear most attractive in view of red emission ability. At present, OLEDs based on europium complexes have achieved certain progress in electroluminescent (EL) performance,[6–9] but the EL efficiency, particularly in the case of high brightness such as 100 cd/m^2, is not satisfied compared to the fluorescence organic molecules and electrophosphorescent organic molecules. The design of europium complexes as active medium in OLEDs to further improve EL efficiency is therefore crucial for practical applications.

In this letter, we developed a europium complex and studied its EL properties. The europium complex is Eu(Tmphen)(TTA)$_3$ (TTA = thenoyltrifluoroacetone, Tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline). The Eu(Tmphen)(TTA)$_3$ is synthesized by a conventional method.[10] Europium chloride was prepared by suspend anhydrous europium oxide (99.99% pure) in hydrochloride acid and digesting on a steam bath until completely dissolved. The ligands 3,4,7,8-tetramethyl-1,10-phenanthroline and thenoyltrifluoroacetone were dissolved in 95% hot ethanol, then sodium hydroxide was added. The mixture was stirred while europium chloride solution was added dropwise. The mixture was cooled after 2 h, and washed with water and ethanol, in turn, and finally recrystallized. Figure 1 shows the chemical structure of Eu(Tmphen)(TTA)$_3$.

The EL properties of Eu(Tmphen)(TTA)$_3$ were studied by using multilayer structure of indium-tin-oxide (ITO)/TPD (40 nm)/CBP: Eu(Tmphen)(TTA)$_3$ (30 nm)/BCP (20 nm)/Alq$_3$ (30 nm)/LiF (1 nm)/Al (100 nm) (Fig. 1), where TPD is N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-biphenyl-4,4-diamine as the hole transport layer, CBP is 4,4-N,N-dicarbazole-biphenyl as the host, BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline as the electron transport/hole block layer, and Alq$_3$ is tris(8-hydroxyquinoline) aluminum as the electron transport layer. LiF/Al is as the cathode. All the organics were evaporated with rate in the range 0.1–0.3 nm/s under high vacuum ($\leqslant 3\times10^{-4}$ Pa). The metallic cathode was evaporated at higher rate (0.8–1 nm/s) without opening the vacuum. Current–brightness–voltage characteristics were measured by using a Keithley source measurement unit (Keithley 2400 and Keithley 2000) with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer. All the measurements were carried out in ambient atmosphere at room temperature. The active area of device is 9 mm^2.

Because the doping concentration of Eu(Tmphen)(TTA)$_3$ in CBP significantly affects the luminescence efficiency, we first optimized the doping concentration. A 1% Eu(Tmphen)(TTA)$_3$ doped CBP device exhibits

---

[a)] Electronic mail: mdg1014@ciac.jl.cn

0003-6951/2003/83(19)/4041/3/$20.00

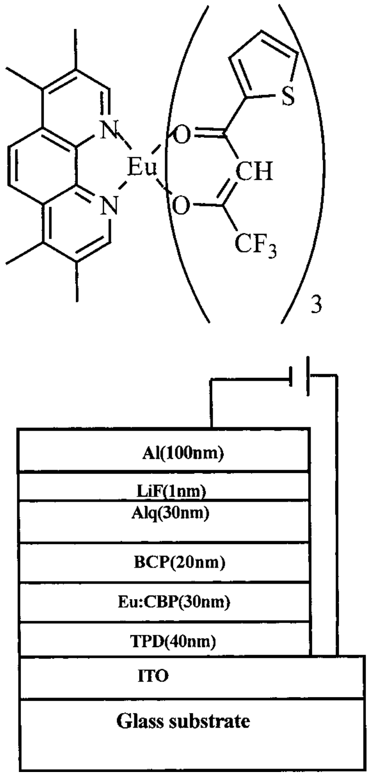

FIG. 1. Chemical structure of Eu(Tmphen)(TTA)$_3$ and structure of the electroluminescence device.

the best efficiency and luminance. Figure 2 shows the current–brightness–voltage characteristics of a 1% Eu(Tmphen)(TTA)$_3$ doped CBP device. The turn-on voltage was 7 V. The maximum brightness of 800 cd/m^2 was obtained at drive voltage of 24.5 V. The EL quantum efficiency–current characteristic of the same device was also measured, as shown in Fig. 3. A maximum current efficiency of 4.7 cd/A, corresponding to an EL quantum efficiency of 4.3%, was obtained at current density of 0.1 mA/cm^2. The maximum power efficiency reached 1.6 lm/W. At the brightness of 100 cd/m^2, the quantum efficiency yet reaches 2.2% (2.3 cd/A) at current density of 4.3 mA/cm^2. Note, as seen in Fig. 3, that the EL quantum efficiency also decreases with increasing current, typical of luminescence originating from recombination of long-lived triplet excitons, which has been explained as triplet–triplet annihilation on CBP molecules following back transfer from TTA due to the near resonance of TTA and CBP triplet states.[6]

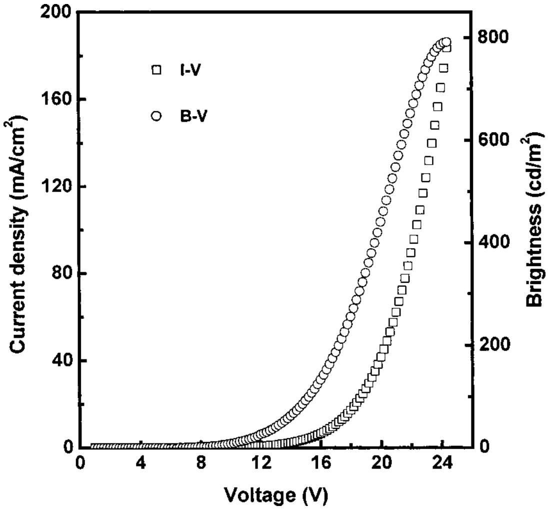

FIG. 2. Current density–brightness–voltage characteristics of the 1% Eu(Tmphen)(TTA)$_3$ doped CBP device.

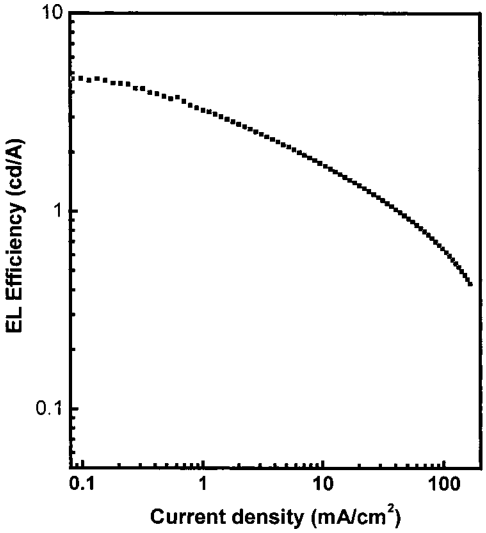

FIG. 3. EL efficiency as a function of current density of the 1% Eu(Tmphen)(TTA)$_3$ doped CBP device.

Figure 4 shows the EL spectra of the 1% Eu(Tmphen)(TTA)$_3$ doped CBP device at different voltages. It can be seen that a pure red Eu^{3+} ion emission based on $^5D_0 \rightarrow {}^7F_2$ transition with a peak of 612 nm and a full width at half maximum of 3 nm was observed at a wide voltage range. In the case of a doped organic system, carrier trapping and Förster energy transfer are thought of as two main luminescent mechanisms.[11] The two mechanisms may simultaneously exist in the luminescence process, or one of them is dominant, which depends on the used dopant and organic host. For the case of europium complex doped in CBP, generally considered that the energy transfer between CBP and europium complexes is incomplete.[6] The fact that no emission from CBP in an Eu(Tmphen)(TTA)$_3$ doped CBP device was observed demonstrates that the carrier trapping is the main luminescence process. In this case, the injected electrons and holes through CBP are first trapped by Eu(Tmphen)(TTA)$_3$, and then form excitons on Eu(Tmphen)(TTA)$_3$. However, the Förster energy transfer

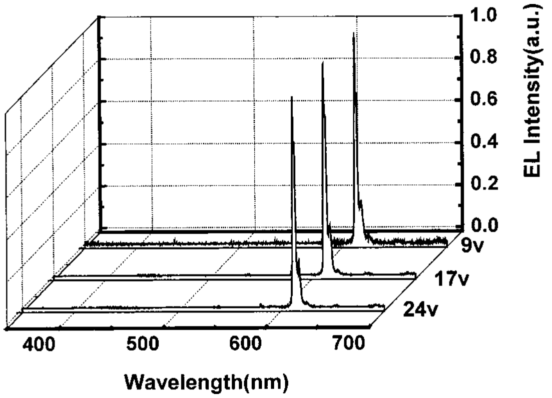

FIG. 4. Electroluminescence spectra of the 1% Eu(Tmphen)(TTA)$_3$ doped CBP device at different voltage.

from excited CBP singlet energies to $\mathrm{Eu(Tmphen)(TTA)_3}$ singlet states, which is partial, cannot also be completely excluded in the EL process.

$\mathrm{Eu(Tmphen)(TTA)_3}$ exhibits high EL efficiency, even at higher brightness. We attribute the high EL efficiency to the excellent planar structure of Tmphen ligand due to the introduction of four methyl groups. Our results demonstrate that it is possible to achieve high emission efficiency in the lanthanide complexes by optimized design of molecular structures as well as reasonable device structures.

In conclusion, we developed an europium complex $\mathrm{Eu(Tmphen)(TTA)_3}$, and studied its EL characteristics using structure ITO/TPD/$\mathrm{Eu(Tmphen)(TTA)_3}$:CBP/BCP/$\mathrm{Alq_3}$/LiF/Al. A pure red light with a peak of 612 nm and a half bandwidth of 3 nm at a wide voltage range was observed. The device shows a luminance up to 800 cd/$\mathrm{m^2}$, an external quantum efficiency of 4.3%, current efficiency of 4.7 cd/A. At the brightness of 100 cd/$\mathrm{m^2}$, the quantum efficiency yet remains 2.2%, which is a better result reported so far using europium complexes as active medium in OLEDs. Our results indicate that the lanthanide complexes showing their advantages as phosphorescent materials to achieve high EL performance in OLEDs are worth anticipating.

One of the authors (Dr. D.M.) is grateful to Hundreds Talents program of Chinese Academy of Sciences, Outstanding Youth Foundation of Jilin Research Council and Ministry of Science and Technology of China (973 Program No. 2002CB613403) for financial support.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, Nature (London) **347**, 539 (1990).
[3] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[4] C. Adachi, M. C. Baldo, M. E. Thompson, and S. R. Forrest, Appl. Phys. Lett. **90**, 5048 (2001).
[5] J. Kido and Y. Okamoto, Chem. Rev. (Washington, D.C.) **102**, 2357 (2002).
[6] C. Adachi, M. Baldo, and S. R. Forrest, J. Appl. Phys. **87**, 8049 (2000).
[7] P. P. Sun, J. P. Duan, H. T. Shih, and C. H. Cheng, Appl. Phys. Lett. **81**, 792 (2002).
[8] M. Sun, H. Xin, K. Z. Wang, Y. A. Zhang, L. P. Jin, and C. H. Huang, Chem. Commun. (Cambridge) **2003**, 702.
[9] F. S. Liang, Q. G. Zhou, Y. X. Cheng, L. X. Wang, D. G. Ma, X. B. Jing, and F. S. Wang, Chem. Mater. **15**, 1935 (2003).
[10] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, J. Am. Chem. Soc. **86**, 5117 (1964).
[11] M. Uchida, C. Adachi, T. Koyama, and Y. Taniguchi, J. Appl. Phys. **86**, 1680 (1999).