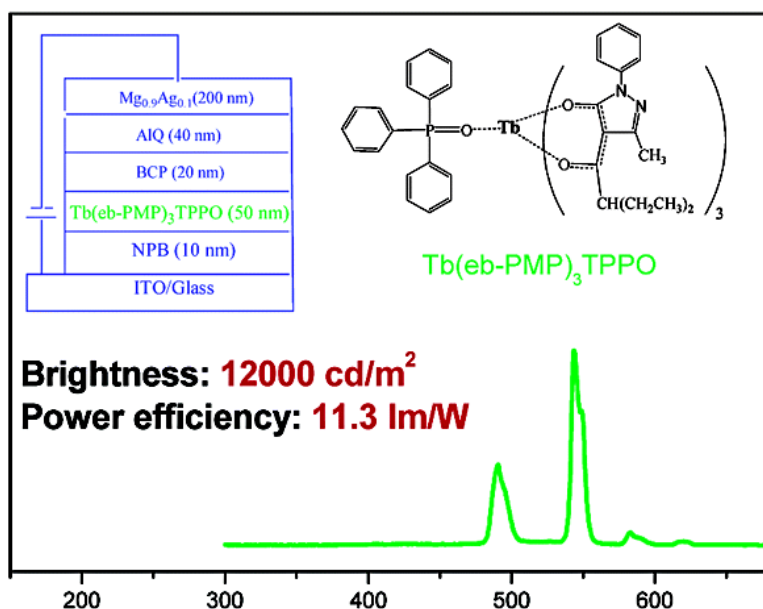


Efficient Electroluminescence from a New Terbium Complex

Hao Xin, Fu You Li, Mei Shi, Zu Qiang Bian, and Chun Hui Huang

J. Am. Chem. Soc., **2003**, 125 (24), 7166-7167 • DOI: 10.1021/ja034087a • Publication Date (Web): 20 May 2003

Downloaded from <http://pubs.acs.org> on March 29, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 18 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

Efficient Electroluminescence from a New Terbium Complex

Hao Xin, Fu You Li, Mei Shi, Zu Qiang Bian, and Chun Hui Huang*

State Key Laboratory of Rare Earth Materials Chemistry and Applications, Peking University, Beijing, 100871, P. R. China

Received January 9, 2003; E-mail: hch@chem.pku.edu.cn

Although the use of tris(8-hydroxyquinoline)aluminum (AlQ) as a green-emitting material has been studied extensively, terbium complexes are still of great interest¹ in the field of electroluminescence (EL), because they offer several distinct advantages,² such as 100% quantum efficiency theoretically, extremely sharp emission bands, and the ability to modify the ligand without affecting the emission characteristics of the central ion. However, the terbium complexes, as EL materials, have not shown their advantages as expected. The highest brightness and power efficiency reported are 2000 cd/m² and 2.6 lm/W, respectively.³ This is believed to be due to the unbalanced carrier injection and transport that would cause recombination at locations other than the emitting layer.⁴

Our previous reports⁵ showed that the complex tris(1-phenyl-3-methyl-4-isobutyl-5-pyrazolone)bis(triphenyl phosphine oxide)terbium, Tb(PMIP)₃(TPPO)₂ (**A**), has very good electron-transport properties, while Tb(PMIP)₃(EtOH)(H₂O) (**B**)⁶ shows only hole-transport properties. In this Communication, aiming at adjusting carrier-transport properties to easily confine the recombination zone in the terbium complex layer, a new terbium complex, tris[1-phenyl-3-methyl-4-(2-ethylbutyryl)-5-pyrazolone](triphenyl phosphine oxide)terbium, Tb(eb-PMP)₃TPPO (**C**), was synthesized by modifying the ligand. As the coordination number of lanthanide complexes is changeable, the goal in making this modification is to enlarge the steric hindrance of the β-diketonate and to make a surrounding which has no room for two TPPOs to coordinate to the central Tb³⁺ ions. Experiments revealed that the hole and electron were more easily confined and balanced in this complex by proper device configuration, and a performance with the peak power efficiency 11.3 lm/W and brightness higher than 12 000 cd/m² was achieved.

The new complex was characterized by element analysis, and its crystal structure (Figure 1) was determined by X-ray diffraction. The Tb(III) ion is surrounded by seven oxygen atoms, six of which are from the β-diketonate ligands and the other from the triphenyl phosphine oxide. The coordination polyhedron can be described as a distorted monocapped trigonal prism with O(6) capping the face O(3)–O(4)–O(5)–O(7). The average Tb–O distance of 2.305(5) Å (range 2.260(2)–2.373(2) Å) is a little smaller than the sum of radii of Tb³⁺ (0.98 Å, seven coordinated) and O²⁻ (1.40 Å).⁷

The photoluminescence (PL) and UV–vis spectra of complex **C**, measured from its 80-nm vacuum-evaporated film on a quartz slide, are shown in Figure 2a. The excitation spectrum overlaid the absorbance wavelength range well, indicating that the emission originated from the energy absorbed by the ligands. The main emission peak at 545 nm split into two peaks at 542 and 548 nm, which may be caused by the asymmetric coordinating environment of the metal ion. Complexes **A** and **B** presented the same PL characteristics as **C**; however, their relative intensity was quite different (for details, see Supporting Information).

The EL of a single-layer device, ITO/complex **C** (80 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm) (device 1, Figure 2a) was identical to its PL, with the main emission peak at 545 nm split into two peaks

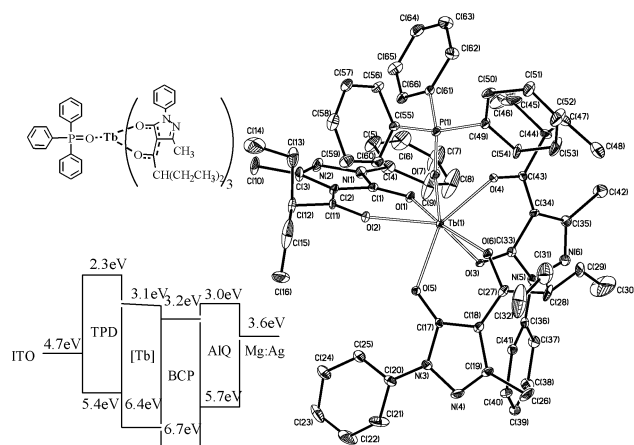


Figure 1. Proposed energy level of the compounds. Chemical and crystal structures of complex **C**. Ellipsoids are drawn at the 30% probability level, and hydrogen atoms were omitted for clarity.

at 542 and 548 nm. A turn-on voltage 11 V, highest brightness 46 cd/m² at 17 V, and peak power efficiency 0.0022 lm/W at 14 V were obtained with this device.

By introducing *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and AIQ as hole- and electron-transport materials, respectively, device 2, with the configuration ITO/TPD (20 nm)/complex **C** (50 nm)/AIQ (30 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm), was fabricated. Compared to device 1, the turn-on voltage decreased to 4 V, attributed to the step injection of the holes due to the introduction of TPD (energy level shown in Figure 1). The highest brightness and power efficiencies obtained from this device were 20 000 cd/m² (20 V) and 3.24 lm/W (10 V, 385 cd/m²). The EL spectrum (Figure 2b) revealed that, despite the major emission originating from complex **C**, a small peak at 520 nm that came from AIQ was detectable, indicating that the charge carriers recombined in both layers.

To prevent hole from entering the AIQ layer, a 20-nm hole-blocking material, 2,9-dimethyl-4,7-diphenyl-1,10-phenylanthroline (BCP), was inserted between complex **C** and AIQ in device 3: ITO/TPD (20 nm)/complex **C** (50 nm)/BCP (20 nm)/AIQ (30 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm). The EL spectrum (Figure 2b) showed that the emission came solely from the Tb³⁺ ion. The Commission Internationale de l'Éclairage (CIE) chromaticity coordinates are *x* = 0.26, *y* = 0.60. Current–voltage (*I*–*V*) and luminance–voltage (*L*–*V*) curves of device 3 are shown in Figure 3; the inset shows the external quantum and power efficiency–voltage curves. At an applied voltage of 18 V, the light output reached 8800 cd/m², and the peak external quantum and power efficiency of 21 cd/A and 9.4 lm/W were achieved at 7 V, 87 cd/m². Compared with device 2, the efficiency was enhanced nearly 3 times and was still larger than 2.1 lm/W at 4300 cd/m², benefiting from the introduction of BCP layer that well confined the exciton in the complex, which is

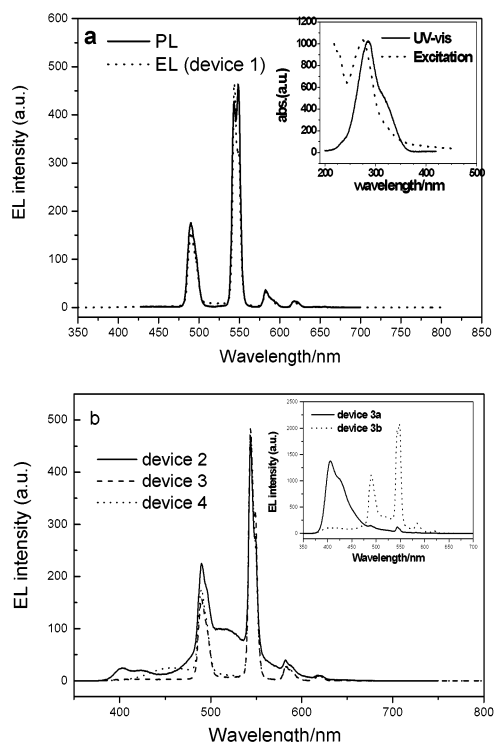


Figure 2. (a) PL and EL of complex **C**. Inset: UV-vis and excitation spectra measured from 80-nm vacuum-evaporated film on the quartz slide. (b) Normalized EL spectra of devices 2, 3, and 4. Inset: Normalized EL of devices 3a and 3b. All the spectra were measured at an applied voltage of 10 V.

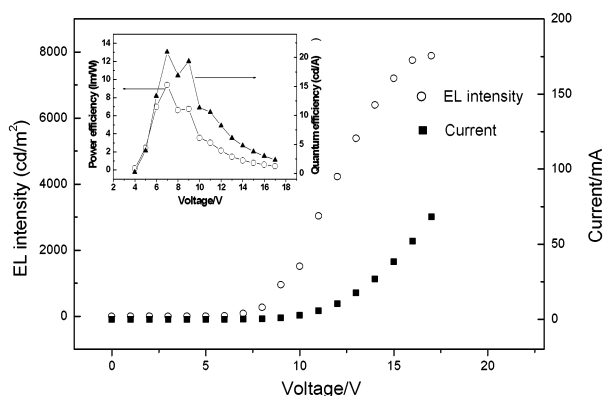


Figure 3. Current–voltage (■), luminance–voltage (○), and external quantum and power efficiency (inset) curves of device 3.

important for phosphorescent OLEDs.⁸ Forrest et al. reported⁹ the external quantum 28 cd/A and power efficiency 31 lm/W obtained from the phosphorescence material *fac*-tris(2-phenylpyridine)iridium [Ir(ppy)₃]; however, that result was obtained from a doped device, while in undoped condition the efficiency decreased by 1 order of magnitude. When *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl)-1,1'-diphenyl-4,4'-diamine (NPB) (whose HOMO level was 5.2 eV) was used as hole-transporting material in device 4, ITO/NPB (10 nm)/ complex

C (50 nm)/BCP (20 nm)/AIQ (40 nm)/Mg_{0.9}Ag_{0.1} (200 nm)/Ag (80 nm) (EL shown in Figure 2b), the performance increased to 12 000 cd/m² at 18 V and 11.3 lm/W at 7 V.

What needs to be noted is that complexes **A** and **B** presented much lower EL performance than complex **C**, due to the unbalanced carrier injection (for details, see Supporting Information). The performance obtained from devices 3a and 3b (EL spectrum shown in Figure 2b, inset), having configuration similar to device 3, respectively using complexes **A** and **B** as emitter, was 3100 cd/m², 3.61 lm/W and 2400 cd/m², 2.60 lm/W, respectively. For device 2a, the recombination zone was mainly located in the TPD layer, caused by the overly strong electron-transport feature of complex **A**. For device 2b, in contrast, hole could not be completely prevented from entering the AIQ layer, although BCP was used.

In summary, we report the synthesis and EL application of a new terbium complex, Tb(eb-PMP)₃TPPO. Remarkable EL performance (12 000 cd/m², 11.4 lm/W) was obtained from this new complex. This EL performance was a result of the relatively balanced carrier-transport properties of this new complex, which led to the recombination zone being easily confined in the emitting layer. Our results revealed that higher efficiency EL performance could be obtained from undoped lanthanide complex if carrier injection was well balanced and the recombination was well confined in the emitting layer. Modifying ligands to alter the complex carrier-transport properties may provide a useful clue to this requirement. It is reasonably expected that lanthanide complexes can show their advantages as phosphorescent materials in OLEDs.

Acknowledgment. The authors thank the State Key Program of Fundamental Research on Rare Earth Functional Materials (G 1998061308, 2001CCD04300) and NHTRDP (863 Program No. 2002AA324080) for financial support.

Supporting Information Available: X-ray crystallographic data (CIF); synthesis, device fabrication, and PL, EL details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (a) Kido, J.; Nagai, K.; Ohashi, Y. *Chem. Lett.* **1990**, 657. (b) Kido, J.; Nagai, K.; Okamoto, Y. *J. Alloys Compd.* **1993**, 192, 30. (c) Kido, J.; Hayase, H.; Hongawa, K.; Nagai, K.; Okuyama, K. *Appl. Phys. Lett.* **1994**, 65, 2124. (d) Christou, V.; Salata, O. V.; Ly, T. Q.; Capecchi, S.; Bailey, N. J.; Cowley, A.; Chippindale, A. M. *Synth. Met.* **2000**, 111–113, 7. (e) Zheng, Y. X.; Liang, J. L.; Lin, Q.; Yu, Y. N.; Meng, Q. G.; Zhou, Y. H.; Wang, S. B.; Wang, H. A.; Zhang, H. J. *J. Mater. Chem.* **2001**, 11, 2615. (f) Zheng, Y. X.; Lin, J.; Liang, Y. J.; Lin, Q.; Yu, Y. N.; Guo, C.; Wang, S. B.; Zhang, H. J. *Synth. Met.* **2002**, 54, 424.
- For details, see: Kido, J.; Okamoto, Y. *Chem. Rev.* **2002**, 102, 2357.
- Capecchi, S.; Renault, O.; Moon, D.-G.; Halim, M.; Etschells, M.; Dobson, P. J.; Salata, O. V.; Christou, V. *Adv. Mater.* **2000**, 12, 1591.
- (a) Wang, J. F.; Wang, R. Y.; Yang, J.; Zheng, Z. P. *J. Am. Chem. Soc.* **2001**, 123, 6179. (b) Adachi, C.; Baldo, M. A.; Forrest, S. R. *J. Appl. Phys.* **2000**, 87, 8049.
- (a) Gao, X. C.; Cao, H.; Huang, C. H.; Li, B. G.; Umitani, S. *Appl. Phys. Lett.* **1998**, 72, 2217. (b) Gao, X. C.; Cao, H.; Huang, C. H.; Umitani, S.; Chen, G. Q.; Jiang, P. *Synth. Met.* **1999**, 99, 127.
- It is Tb(PMIP)₃ as the emitting material, as it lost its small molecules during evaporation; see Supporting Information.
- Huang, C. H. *Coordination Chemistry of Rare Earths*; China Science Press: Beijing, 1997; Vol. 16.
- Chen, F. C.; He, G. F.; Yang, Y. *Appl. Phys. Lett.* **2003**, 82, 1006.
- Baldo, M. A.; Lamansky, S.; Thompson, M. E.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, 75, 4.

JA034087A