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Communications to the Editor

First Oxadiazole-Functionalized Terbium(III) *β*-Diketonate for Organic Electroluminescence

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Considerable efforts are being devoted to the development of organic light-emitting diodes (OLEDs) for energy efficient, full-color, flat-panel displays.[1] Electroluminescence (EL) across the whole visible spectrum has been demonstrated, and prototype devices meeting realistic specifications for applications have been realized. However, obtaining pure and sharp emission from currently used molecular or polymeric emissive materials is difficult; their emission spectra are generally broad, which would compromise the quality of colors in actual displays.

Luminescent lanthanide complexes are believed to be a promising solution to this problem.[2] Owing to the unique *f*-electronic configurations,[3] lanthanide-based materials can not only generate extremely pure emission, but also offer an unlimited theoretical ceiling for device efficiency. Furthermore, the physical properties pertinent to the processability of these materials can be conveniently altered without affecting the metal-based emission characteristics. Despite these propitious features, only one of the many potential advantages of using lanthanide-based emitting materials, namely the monochromaticity, has been realized. One key issue is that the high photoluminescence (PL) efficiency of lanthanide complexes does not translate into EL efficiency of comparable magnitude.[2] It is agreed upon, although not proven, that this underachievement is due to the poor ability of lanthanide complexes to transport charge carriers (especially electrons); unbalanced injection and transport of charge carriers would cause their recombination at locations other than the emitting layer, leading to low device efficiency and reduced lifetime.[4]

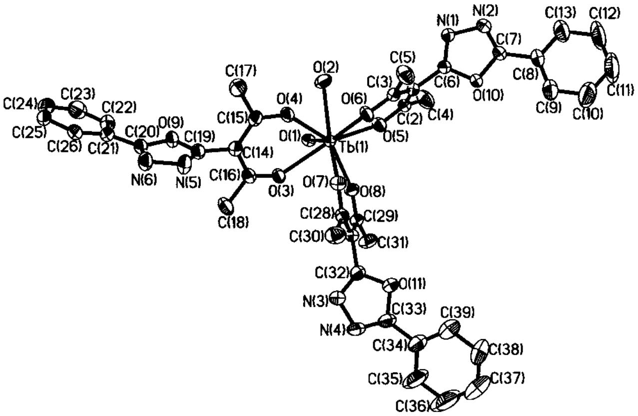
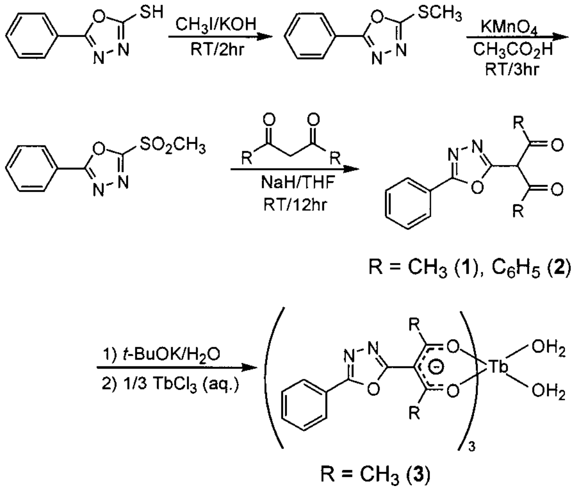


Figure 1. An ORTEP representation of **3** (50% probability ellipsoids). H atoms are omitted for clarity.

Scheme 1



Aiming at actualizing OLEDs of high efficiency, sharp emission, and long lifetime, we sought lanthanide complexes with chelating ligands that would promote balanced injection, transport, and recombination of charge carriers. Our initial efforts have been focused on the design and synthesis of oxadiazole-functionalized *β*-diketone ligands and corresponding lanthanide complexes. The EL applications of lanthanide *β*-diketonates have been well-established,[2,4] while oxadiazole derivatives are among the most widely employed electron-transporting and hole-blocking materials.[5] Extensive work in both areas notwithstanding, 3-(5-phenyl-1,3,4-oxadiazol-2-yl)-2,4-pentanedione[6] (**1**) is the only known oxadiazole-functionalized *β*-diketone, and lanthanide complexes with such ligands have not yet been reported. Herein, we report the high-yield synthesis[7] of two oxadiazole-derivatized *β*-diketones (**1** and **2**). The synthesis, characterization, and structural determination of the first lanthanide complex (**3**) with such ligands, formed by a Tb(III) ion with **1**, are also described.

The syntheses of **1**−**3** are set out in Scheme 1. The compounds were characterized[7] by ^{1}H and ^{13}C NMR, FAB-MS, and microanalysis. The crystal structure of **3** (Figure 1) was established by X-ray diffraction. The Tb(III) ion is surrounded by eight oxygen atoms, six of which are from the bidentate *β*-diketonate

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(6) Yamanaka, H.; Ohba, S.; Sakamoto, T. *Heterocycles* **1990**, *31*, 1115−1127.

(7) Synthetic attempts by following the reported procedure (ref 6) failed to produce any meaningful amount of **1**. See Supporting Information for synthetic details and characterization data.

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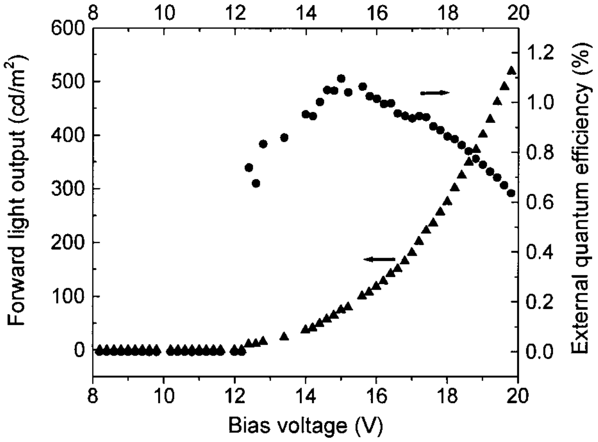

Figure 2. Luminance–voltage characteristics of the device with the configuration ITO/PVK:PBD:**3**/Alpop/CsF/Al.

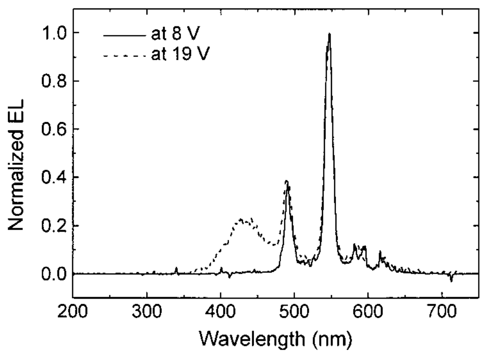

Figure 3. The EL spectra of the device ITO/PVK:PBD:**3**/Alpop/CsF/Al at 8 (solid line) and 19 V (broken line) of driving voltage.

ligands and the other two from the coordinated water molecules. The coordination polyhedron can be best described as square antiprismatic. The Tb–O bond distances, ranging from 2.310(2) to 2.466(3) Å (average 2.360(7) Å), are comparable with those observed in other complexes of terbium with analogous ligands.[8]

Using **3** as the emitting material, a bright and highly efficient green-emitting LED was fabricated. The device was constructed on a glass slide precoated with indium–tin oxide (ITO). The first layer was formed by spin casting a chloroform solution of hole-transporting poly(*N*-vinylcarbazole) (PVK) and electron-transporting 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (1:1 weight) containing 5 wt % of **3**. A thin layer of hole-blocking and electron-transporting tris(2-(5-phenyl-1,3,4-oxadiazolyl)phenonate) aluminum (Alpop)[5b] was then grown by means of vacuum vapor deposition on top of the spin-coated layer. Finally, a thin layer of electron injection-facilitating CsF (0.6 nm) was introduced, followed by the deposition of 200 nm of aluminum as the cathode. Doping of **3** is expected to further balance the injection and transport of charges due to the electron transport-facilitating oxadiazole substituent. Putative recombination of charge carriers within the PVK:PBD:**3** composite layer generates excitons that effectively transfer their energy to the emission-responsible Tb(III) center, thereby yielding bright luminance with high efficiency.

The forward light output–voltage (EL-V) characteristics for the device are presented in Figure 2. Green light emitted was visible at as low as 8 V. The emission comes solely from the Tb(III) ion, as the EL spectrum is identical to that of the PL of **3**. The brightness of the device increases with the current density. At 15 V, the light output reaches 100 cd/m^2 with an external EL efficiency as high as 1.1% (0.4 cd/A), and 550 cd/m^2 with an efficiency of 0.6% (0.2 cd/A) at 20 V. It is worth noting that starting from 19 V a broad peak appears at about 430 nm in the EL spectrum (Figure 3). This appreciable blue emission is attributable to exciplex formation between PVK and **3**, as similar observations are well documented[9] for devices fabricated by spin casting using Tb(III) complexes doped in PVK matrix.

The favorable role played by the oxadiazole ligand of facilitating charge transport is clearly established when the parameters characterizing the performance of the present device are compared with those of an otherwise identical device employing the unsubstituted terbium tris(acetylacetonate) (Supporting Information). Although green light was clearly visible with the control device, the emission was too weak to be measured with the experimental setup. Moreover, the current density of this device is 0.6 and 1.3 mA/cm^2 at driving voltages of 15 and 20 V, respectively. The corresponding current density is 25 and 275 mA/cm^2, respectively, when compound **3** was used. Such drastic increases in current density strongly suggest that charge transport across the thin-film structure can be significantly improved by the introduction of the oxadiazolyl group and that the ligand design approach elaborated in this work to improve OLED performance is feasible.

In summary, we report for the first time the design, synthesis, and EL application of a terbium(III) complex with oxadiazole-functionalized β-diketonate ligands. Although neither the configurational nor the compositional structure of the present device is optimized, it is, to the best of our knowledge, the brightest and the most efficient EL device fabricated by *spin casting* a Tb(III) complex-doped polymer.[10] Our results suggest that incorporating oxadiazole moiety into the β-diketone platform is a viable strategy for modifying the physical properties and electronic structure of the corresponding lanthanide complex. This in turn may lead to more stable devices with brighter and more efficient emission due to more balanced injection, transport, and recombination of charge carriers in an appropriately configured device. Efforts are being directed toward increasing the volatility of the complexes and further enhancing their electron transport ability.

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Supporting Information Available: Synthetic details, characterization data (**1**–**3**), crystallographic data (**3**), and control experiment results using terbium tris(acetylacetonate) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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