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Temperature-dependent electroluminescence from (Eu, Gd) coordination complexes

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Light emission from single-layered electroluminescent devices is described in which (Eu, Gd) coordination complexes, $(\text{Eu}_{0.1}\text{Gd}_{0.9})(\text{TTA})_3(\text{TPPO})_2$, and electron transport material oxadiazole derivative, 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole, are dispersed in a hole-transporting host polymer poly(*N*-vinylcarbazole) film. The color of the emitted electroluminescence changes smoothly from green-white to red with temperature varying from 77 to 300 K. This phenomenon is discussed in terms of temperature dependent yields of phosphorescence from the triplet state of the Gd and Eu chelates and the intermolecular energy transfer from Gd-chelate to Eu-chelate cages. © 1997 American Institute of Physics. [S0003-6951(97)04944-9]

Organic electroluminescent (EL) devices are of great interest because of their efficient emission in the visible region and for promising applications to a variety of devices such as backlights and flat-panel displays.¹⁻⁶ The clear advantages of organic EL devices are the ease of fabrication, low operating voltages, and possibility of a wide selection of emission colors through the molecular design of organic materials. Great effort so far has been concentrated on the construction of bright and stable organic EL cells with different emission colors. On the other hand, optical and electric properties of some organic molecules can be strongly influenced by the environmental condition. Such organic systems have been used as active materials in various sensors for practical applications. By introducing this kind of organic materials to the EL diode fabrication, it is possible to develop a novel type of EL device in which the emissive characteristics can reflect the variation of environmental parameters. This type of device might be used as an indicator in various possible applications. For example, the environmental temperature can be estimated from the emitted color of the EL device which is dependent on temperature. Recently, thermal control of near-infrared and visible electroluminescence was reported in alkylphenyl substituted polythiophenes.⁷ The polymer film exists in two forms, giving widely different electroluminescence spectra. In the narrow band gap form, the maximum of emission intensity is at 800 nm, while the wide band gap form gives a maximum at 670 nm. The phase change from the wide band gap phase to narrow band gap phase is induced by thermal treatment of the polymers. Since this process is irreversible, the EL devices based on these polymers cannot be used as a variable temperature indicator.

In this letter, the electrophosphorescence from the triplet state of the (Eu, Gd) coordination complexes, $\text{Eu}_{0.1}\text{Gd}_{0.9}(\text{TTA})_3(\text{TPPO})_2$, is demonstrated. Spin-orbit inter-

action between the ligand and the paramagnetic Gd^{3+} ion leads to intense ligand molecular phosphorescence from the complexes. Study of electrophosphorescence from the triplet states of organic materials will be useful for improving the quantum efficiency of organic EL devices, since for EL devices using organic fluorescent dyes the internal quantum efficiencies are in principle limited to 25%, because the triplet excited state can possibly be generated three times more efficiently than the singlet excited state due to the spin multiplicity. There may be even more contributions to the triplet state formation than the direct generation by injection, since the triplet state can be formed via intersystem crossing from the singlet state.⁸⁻¹⁰ By dispersing the (Eu, Gd) complexes and electron-transporting material, oxadiazole derivative, 2-(4-biphenyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD), in a hole-transporting host polymer poly(*N*-vinylcarbazole) (PVK), a single-layered EL device was fabricated. The EL color from the device changes smoothly from green-white to red with temperatures varying from 77 to 300 K.

The chemical structures of the materials used are shown in Fig. 1. The emissive material is

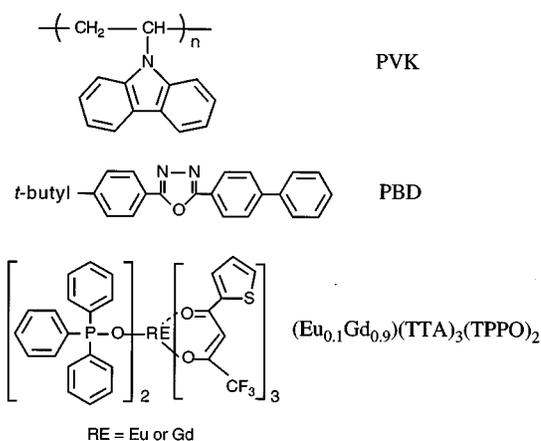


FIG. 1. Molecular structures of the materials used.

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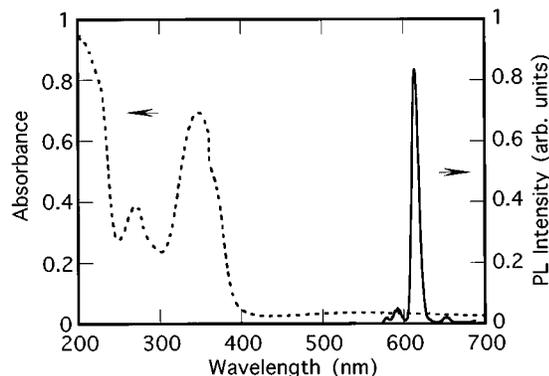


FIG. 2. PL spectrum excited at 350 nm line and absorption spectrum of the sublimed film of the (Eu, Gd) complex on a quartz substrate at room temperature.

(Eu_{0.1}Gd_{0.9})(TTA)₃(TPPO)₂, which was prepared following the method reported previously.^{11,12} The optical absorption and photoluminescence (PL) spectrum of the sublimed film on a quartz plate at room temperature are shown in Fig. 2. In order to fabricate a single-layered EL device, PVK is used as hole-transporting host material,¹³ which emits around 420 nm, and PBD is doped to improve the electron-transport ability in the EL device.¹⁴ The sharp intense PL peak at 612 nm originates from the $^5D_0 \rightarrow ^7F_2$ transition of trivalent europium ion. From the absorption spectrum, it is seen that the efficient excitation is in the ultraviolet region. In the complexes, because of the intermediate role of Gd³⁺ ion, the energy transfer to Eu³⁺ can be completed at fairly low Eu content, and the PL intensity reaches about 90% of that of simple Eu complex fluorescent materials at room temperature. This offers a great advantage for (Eu, Gd) complexes since Eu is the most expensive among the materials used in the device.

Phosphorescence of the sublimed film of the (Eu, Gd) complexes on a quartz substrate was measured at 77 K with a fluorescence spectrophotometer (Hitachi, F-4500) as shown in Fig. 3. A strong phosphorescent band is observed around 500 nm which originates from the radiative transition of the triplet state of the ligand. The effects of different metal-ion substitution on luminescence of complexes have been studied by Yuster and Weissman.¹⁵ It is found that the spin-orbit perturbation of the levels of the ligand electronic states, pre-

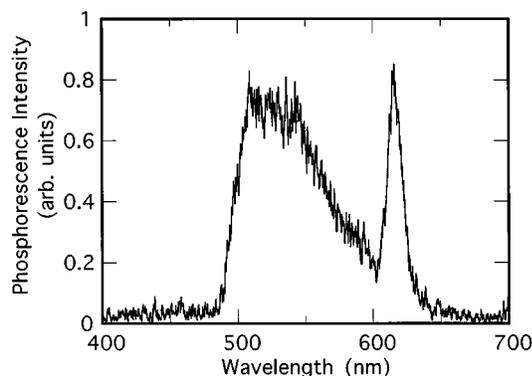


FIG. 3. Phosphorescence spectrum of the sublimed film of the (Eu, Gd) complex on a quartz substrate with 350 nm excitation at 77 K.

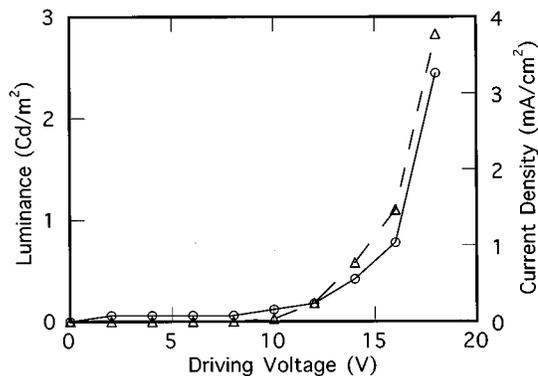


FIG. 4. Luminance-voltage (circles) and current-voltage (triangles) characteristics of an ITO/PVK:(Eu, Gd) complexes:PBD/Mg(Al) cell.

dominantly induced by the paramagnetic Gd³⁺ ion, gives rise to intense ligand-molecule phosphorescence in the metal-organic complex.

The thin film for EL cells was prepared by spin coating on an indium tin oxide (ITO) coated glass substrate with a sheet resistance of 20 Ω/\square from PVK:(Eu, Gd) complexes:PBD dichloroethane solution with a concentration of 15 mg/ml. The concentrations of the (Eu, Gd) complexes and PBD were prepared to be 15 and 30 wt. %, respectively, with respect to PVK. The thickness of the luminescent layer is about 100 nm. Then the sample was vacuum deposited with 20 nm Mg and 150 nm Al films in 4×10^{-3} Pa at a rate of about 1 nm/s. The electroluminescent area is 12 mm². The PL and EL spectra were measured with a spectrophotometer (Shimadzu, RF 5000). The EL brightness was measured with a luminance meter (Minolta, LS-110).

Figure 4 shows the luminance-current-voltage curves for ITO/PVK:(Eu, Gd) complexes:PBD/Mg(Al) cells. Electroluminescence started at a drive voltage of 10 V, and the external efficiency of the devices was about 0.1%. The EL device was quite stable in measurement. When the temperature was varied from 77 to 300 K, the emitted color from the EL cell smoothly changed from green-white to red. The emission spectra are converted to the *x, y* chromaticity diagram coordinates of Commission Internationale De L'Eclairage (CIE) as shown in Fig. 5. At 77 K, the emissive color at the CIE coordinates of *X*=0.35, *Y*=0.49 exhibits green-white, and at 300 K, the CIE coordinates are *X*=0.55, *Y*=0.36 and the color becomes red.

Figure 6 shows the EL spectra at 77, 180, and 300 K. The spectra are composed of three components, the origins of which can be assigned with the aid of the emission spectra shown in Figs. 2 and 3. The emission band around 420 nm originates from PVK, while that around 500 nm corresponds to the electrophosphorescence from the triplet states of the ligands and the sharp line at 612 nm with a side peak around 592 nm results from the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transition of the Eu³⁺ ion. The latter two spectral components from the complexes are sensitive to the temperature changes, and the color-variation mechanism can be explained in terms of intermolecular energy transfer from Gd-chelate to Eu-chelate cages.

The energy transfer process in chelates has been studied for many years.¹⁶ Generally, the ligands absorb the ultraviolet

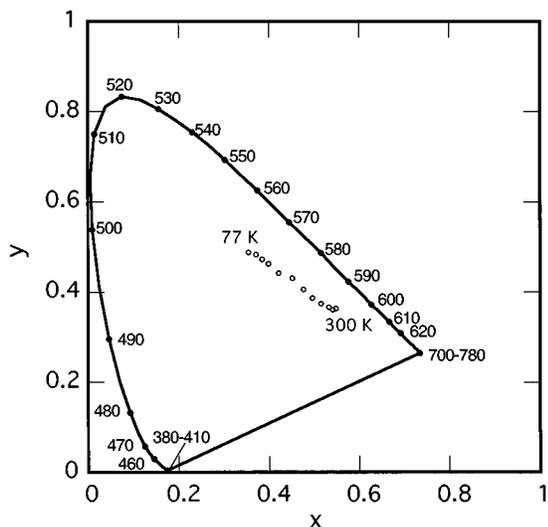


FIG. 5. The CIE x, y chromaticity diagram showing the changes of the color of the emitted light as temperature varied between 77 and 300 K. The mark following 77 K is 100 K and the temperature interval of each mark between 100 and 300 K is 20 K.

let energy and transit to the excited singlet (S_1) state. The dissipation of the absorbed energy may take place in two ways. The excited singlet state may combine with the S_0 ground state through radiative transition, $S_1 \rightarrow S_0$, giving rise to molecular fluorescence; or, the energy migration may take place via nonradiative intersystem crossing from the S_1 state to the triplet (T_1) state. At this stage molecular phosphores-

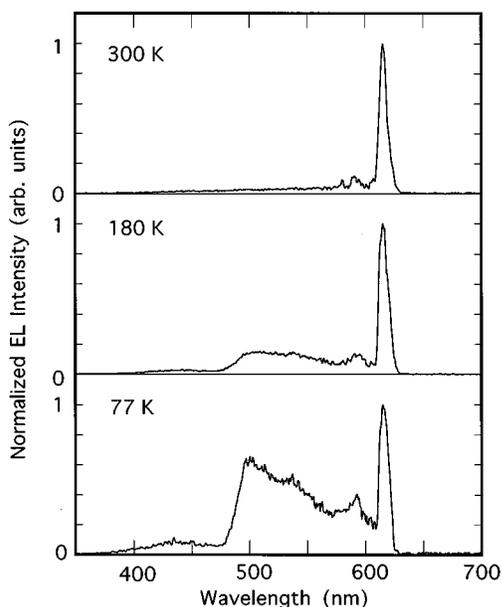


FIG. 6. EL spectra for ITO/PVK:(Eu, Gd) complexes:PBD/Mg(Al) cells at 77, 180, and 300 K.

cence ($T_1 \rightarrow S_0$) may occur due to the combination of the trivalent state with the ground state or intramolecular transfer of energy from triplet state to a resonance level of the coordinated rare earth ion may take place. However, since the excited ligand part of the Gd compound molecule is perturbed by the paramagnetic Gd ion and the excited level, ${}^6P_{3/2}$, of the Gd^{3+} ion lies higher than the lowest excited triplet state by about 1.5 eV,^{12,15} the molecular phosphorescence becomes the main route for the energy dissipation. As expected there was no observable fluorescence from the Gd complex. On the other hand, in the (Eu, Gd) complexes studied in the present letter, intermolecular energy transfer from Gd-chelate cages to Eu-chelate cages occurs. The peculiar characteristics of the Gd chelate then can be utilized to enhance the efficiency of the ligand-to- Eu^{3+} energy transfer in the (Eu, Gd) complexes at relatively low Eu content, and it is also this involvement of the Gd chelate in the energy transfer that leads to the temperature-dependent electroluminescence from the fabricated devices.

In conclusion, temperature-dependent electroluminescence was achieved using (Eu, Gd) complexes. The color-variation mechanism is discussed in terms of the electrophosphorescence from the triplet state of the Gd chelate and intermolecular energy transfer from Gd-chelate cages to Eu-chelate cages. This type of EL device might offer potential for temperature indicator applications.

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