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## Efficient EL Emission from Eu Complex Doped Poly(vinyl carbazole) for Sharp Red Light Source

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Recently, organic electroluminescent (EL) diodes have been studied for various types of emission characteristics, for example, sharp spectrum emission<sup>1-4)</sup>. There are some requirements for sharp light emission from the light sources used for printing equipments or optical communication. Sharp emission is obtained from transition element metal complexes. For example, europium (Eu) complex is one of the promising candidate for sharp emission source in organic light emitting diodes. However, since it lacks carrier transporting ability for electroluminescence, it requires carrier injection to form excitons. In order to inject carrier to organic layer, we have examined some quantum-well structures of (1,10-phenanthroline)-tris(4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate) europium (III) ( $\text{Eu}(\text{TTA})_3\text{phen}$ ) sandwiched between barrier layer fabricated using the organic molecular beam deposition, and observed enhanced emission from  $\text{Eu}(\text{TTA})_3\text{phen}$ <sup>5)</sup>.

In this study, we report a sharp red emission from  $\text{Eu}(\text{TTA})_3\text{phen}$  doped in poly(N-vinyl carbazole) (PVK). Dye-doped polymer EL devices<sup>6)</sup> have advantages in terms of simple fabrication process by using spin-casting method and thermal stability in operation. The mechanism of enhanced sharp red emission from  $\text{Eu}(\text{TTA})_3\text{phen}$  doped in a polymer system is discussed.

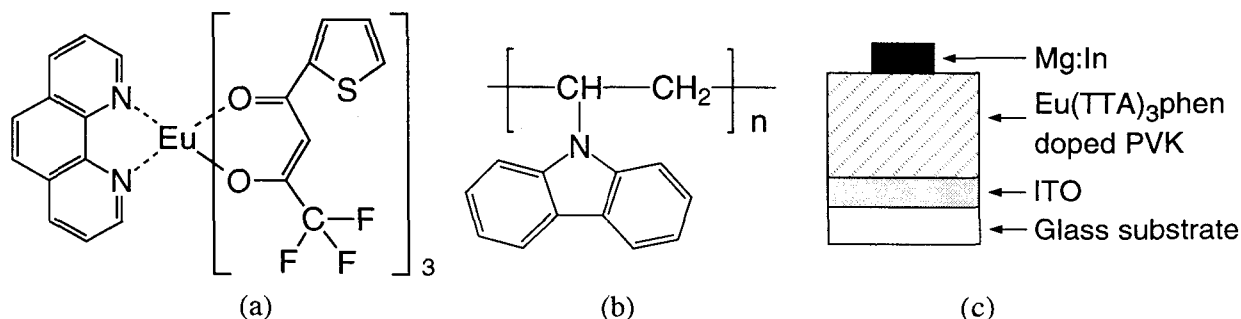


Fig. 1 Molecular structures of organic materials used in this experiment and schematic description of EL diode. (a) (1,10-phenanthroline)-tris(4,4,4-trifluoro-1-(2-thienyl)-butane-1,3-dionate) europium (III) ( $\text{Eu}(\text{TTA})_3\text{phen}$ ). (b) poly(N-vinylcarbazole) (PVK). (c) Schematic description of dye-doped EL diode.

Figure 1 shows the molecular structures of the host polymer material of PVK and dopant dye molecules of  $\text{Eu}(\text{TTA})_3\text{phen}$  used in this study. As shown schematically in Fig. 1, the EL diodes consist of an indium-tin-oxide (ITO)-coated glass substrate, an emissive layer of  $\text{Eu}(\text{TTA})_3\text{phen}$  doped PVK and an indium-containing magnesium (Mg:In) electrode.  $\text{Eu}(\text{TTA})_3\text{phen}$  and PVK of appropriate molar ratio were dissolved in chloroform, and thin films were fabricated by spin-casting the solution onto a sufficiently cleaned ITO-coated glass substrate. The molar ratio was determined from the molecular weight of a monomer unit of PVK and that of  $\text{Eu}(\text{TTA})_3\text{phen}$ . The layer thickness of spin-casted polymer was measured by X-ray diffraction pattern and optical absorption to be in the range of 90-120nm. An electrode of a mixture of Mg and In metals was coevaporated at a high vacuum of under  $10^{-4}\text{Pa}$  onto the spin-casted film. After deposition, the device was covered with a glass plate and encapsulated by epoxy resin in argon gas atmosphere to prevent oxidation of the Mg:In electrode. The active area of the EL diodes was 2mm square. Forward bias condition is defined as the case in which the ITO electrode is positively biased against the Mg:In electrode, and negative bias, *vice versa*. All of the measurements were carried out at room temperature.

Figure 2 shows the normalized emission spectra of the EL diodes with  $\text{Eu}(\text{TTA})_3\text{phen}$  of different concentration, which are driven with the same applied voltage of 30V. An emission peak from  $\text{Eu}(\text{TTA})_3\text{phen}$  and PVK is observed at 610nm and 420nm, respectively. The emission peak intensity ratio of PVK to  $\text{Eu}(\text{TTA})_3\text{phen}$  dramatically decreases with increase in the  $\text{Eu}(\text{TTA})_3\text{phen}$  concentration, as shown in Fig. 3. Sharp red emission from  $\text{Eu}(\text{TTA})_3\text{phen}$  was obtained above the concentration of  $\text{Eu}(\text{TTA})_3\text{phen}$  of more than 0.01 mol %.

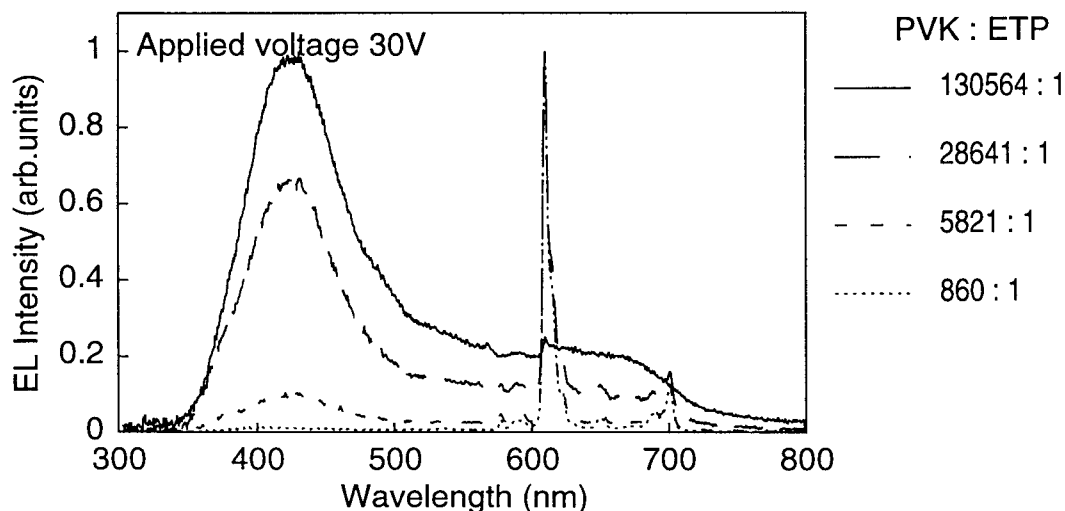


Fig. 2 Emission spectra of  $\text{Eu}(\text{TTA})_3\text{phen}$  doped PVK diodes as a function of molar ratio of PVK to  $\text{Eu}(\text{TTA})_3\text{phen}$ .

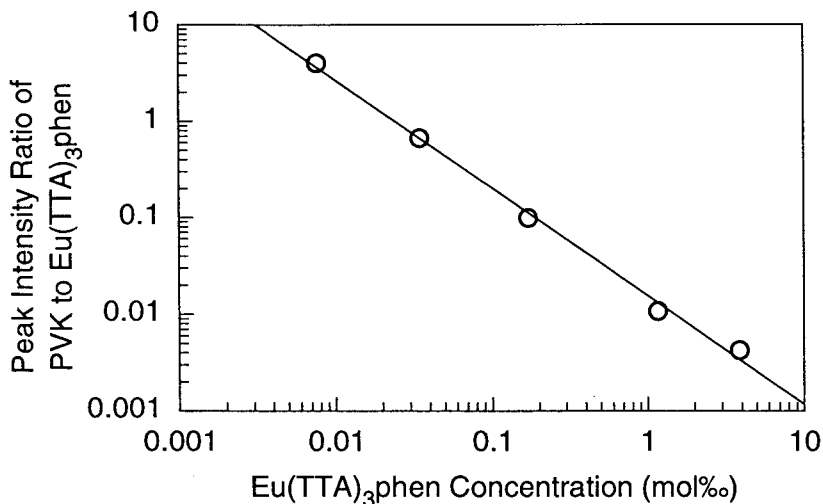


Fig. 3 Emission peak intensity ratio of PVK to Eu(TTA)<sub>3</sub>phen as a function of Eu(TTA)<sub>3</sub>phen concentration.

The energy band diagram is estimated from the optical absorption edges and the highest occupied molecular orbital (HOMO) states by photoelectron spectroscopy. However, the HOMO states of Eu(TTA)<sub>3</sub>phen could not be determined accurately by the measuring system, because it is considered to exist at levels which are more than 6eV below the vacuum level, which are beyond the upper detection limit of the measuring system.

The energy band diagram of the device used in this study is schematically shown in Fig. 4. In the positive biased condition, the electrons injected from the Mg:In cathode and the holes injected

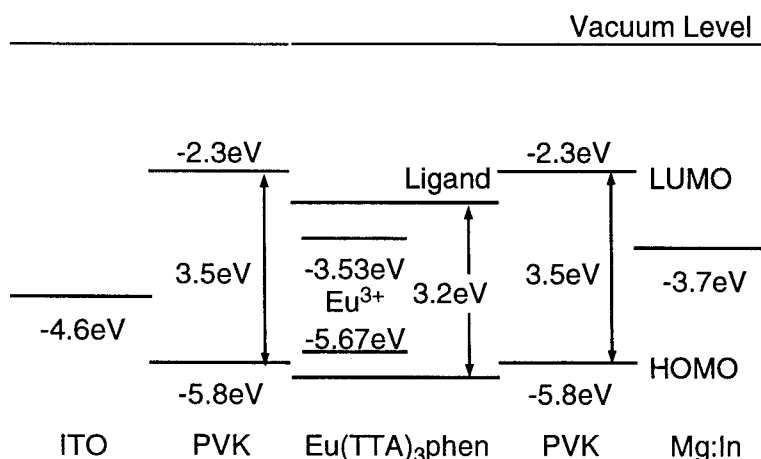


Fig. 4 Schematic description of energy band diagram of Eu(TTA)<sub>3</sub>phen doped PVK EL device

from the ITO anode move to the lowest unoccupied molecular orbitals (LUMO) and HOMO states of PVK, respectively. Excitons are formed at the PVK and are transferred to the ligands sites of  $\text{Eu}(\text{TTA})_3\text{phen}$ . The singlet excitons are converted into the triplet excitons by inter system crossing, then transferred to the  $\text{Eu}^{3+}$  sites of  $\text{Eu}(\text{TTA})_3\text{phen}$ . The energy relaxation from  $^5\text{D}$  to  $^7\text{F}$  orbits in  $\text{Eu}^{3+}$  sites results in sharp emission at 614nm.

In conclusions, EL diodes with  $\text{Eu}(\text{TTA})_3\text{phen}$  doped PVK fabricated, and their EL characteristics were studied. Enhanced sharp red emission from  $\text{Eu}(\text{TTA})_3\text{phen}$  at 610nm was obtained with dye-doped EL diodes structure, which has the advantage of very simple fabrication process. With increasing concentration of  $\text{Eu}(\text{TTA})_3\text{phen}$ , efficient carrier transport from the host material of PVK to the ligand of  $\text{Eu}(\text{TTA})_3\text{phen}$  occurs, and results in efficient emissive relaxation in  $\text{Eu}^{3+}$  sites. The application of such a sharp red emission to various light source is expected.

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