Control of Peak Wavelength of Organic Electro Luminescence Device using Ru Complex

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Fabrication of organic electro luminescence device using wet process is required in the viewpoint of the process simplification and the reduction of the production cost. In this study, several ruthenium complex monomers were synthesized. Their energy band gaps were measured by using photo-acoustic spectroscopy and the luminescence spectra were measured by photoluminescence spectroscopy. It was found that the peak wavelength can be control from 630nm to 720nm by adding the functional group to the ruthenium complex monomer. It was also found that by adding polyethylene oxide and LiCF$_3$SO$_4$ and sodium hydroxide into the ruthenium complex, the light intensity of the organic light emitting device was increased from 1500cd/m$^2$ to 2000cd/m$^2$ and the response delay which is the characteristic of the electro chemical luminescence is drastically improved.

Key Words: organic electro luminescence, ruthenium complex, wet process, EL, photo acoustic spectroscopy, electro chemical luminescence

1. Introduction
Recent progress in the development of organic electro luminescence (EL) devices is extremely remarkable and the development of the devices with high luminance, full color and large area are strongly enforced. Most of the devices that have been put into practice as EL devices are using Alq$_3$ as the materials and they are fabricated by the dry process such as vacuum evaporation. These materials require a refined packaging because of the rapid degradation in air.

In the point of cost reduction and the process simplification, however, fabrication of organic EL devices by wet process is strongly required. For the fabrication of large light emitting area devices to realize the cost reduction, the film fabrication at room temperature and at normal pressure has much advantages compared with the dry process, vacuum evaporation.

The light emitting device using $\pi$ conjugated polymer reported by Friend’s group at Cambridge in 1990 for the first time[1]. After that the devices and the materials had a big attention not only from science but also from industry. Recently new approaching methods for the construction of the light emitting materials using the electrochemical doping of the $\pi$ conjugated polymers have been reported[2]. In these electrochemical light emitting materials, the ion conductivity has been improved by mixing polymers and solid electrolytes or by modify the chemical structure of the polymers. To control the morphology of the materials is very important for the device performance and the response improvement of the devices.
Electrochemical light emitting cells are promising for their high quantum efficiency and low driving voltage required for the light emission. The electrochemical light-emitting cell using ruthenium (Ru(II)) complex materials is one of the promising materials to utilize the advantages of the electrochemical reaction.

Ru(II) complexes are well known for their high efficiency liquid state electro generated chemiluminescence (ECL). Indeed, values up to 24% at room temperature have been previously reported. The creation of light in such cells is related to the electrochemical processes of the Ru(II) complex, the electron hopping or self-exchange between Ru(II) complex sites and the bimolecular reaction of neighboring Ru(III) and Ru(I) redox state to create an excited Ru(II) state. Recently, Murray’s group was successful at fabricating a solid-state ECL device by placing a Ru(II) complex on an interdigitated array (IDA) of platinum electrodes. However, this kind of device could only be operated under certain conditions. Unlike the liquid state ECL, such solid state devices exhibited diode-like characteristics and relatively low quantum efficiency (about 0.3%).

On the other hand, Handy and Rubner et al. reported a very simple EL devices using Ru complex by spin casting method. In this study, we synthesized several types of the Ru complex materials with different functional groups and investigated the device performance fabricated by using the materials. First, we investigated the change of the peak wavelength of the light emission from the several Ru complex materials. Next, we tried to improve the device performance using the ion conducting materials, poly ethylene oxide (PEO).

2. Experimental

2.1 Materials preparation

We synthesized the five ruthenium monomers and one ruthenium polymer. The synthesized materials are (a)tris(2,2'-bipyridineruthenium)dihexafluorophosphate, (b)bis(2,2'-bipyridine)-4,4'-dimethyl-2,2'-bipyridine ruthenium dihexafluorophosphate, (c)bis(2,2'-bipyridine)-4,4'-dicarboxy-2,2'-bipyridine ruthenium dihexafluorophosphate, (d)bis(2,2'-bipyridine)-4,4'-dicarboxy-2,2'-bipyridine ruthenium dihexafluorophosphate sodium salt, and (e)tris(4,4'-dimethyl-2,2'-bipyridine)ruthenium dihexafluorophosphate. The chemical structures are shown in Fig.1.

2.2 Measurement of materials characteristics

Photo acoustic spectra (PAS) and photo luminescence (PL) spectra were measured for synthesized materials and compared. PAS spectrum was used to measure the energy band gap of the materials in the powder condition. Each ruthenium complex was dissolved in pyridine. By using the solution, 200nm thin film of ruthenium complex were spin-cast onto ITO-patterned glass substrate. The films were annealed at 100 °C under vacuum, and an aluminum cathode was thermally-evaporated on
top to complete the device. Device testing was computer-automated using a LABVIEW and performed in air at room temperature. Power was supplied by a Keithley programmable voltage source.

3. Results and discussions

Each PAS spectrum of the materials was shown in Fig.2. And EL spectra were shown in Fig.3(a)-(e). As shown in Fig.2, the energy band gap of the materials are the following: (a) 2.1eV (b) 1.95ev (c) 1.75eV (d) 1.7eV. On the other hand, as shown in Fig.3, the peak wavelength of the PL spectrum was the following: (a) 630nm (b) 640nm (c) 695nm (d) 720nm.

As is clearly shown in these values, the order of the peak wavelength is quite consistent with the order of the energy band gap obtained from the PAS measurement. Therefore, we can predict the peak wave-length of the light emission by using the photo acoustic spectroscopy in the powder condition before fabricating the devices.

On the other hand, it was found that there were two peaks of the PL spectrum in the Ru complex polymer: 660nm and 770nm. We consider that this was caused by the mixture of two kinds of substance originated from Ru complex monomer and Ru complex polymer.

The applying voltage – current (I-V) characteristic of each material is shown in Fig.4. As shown in the figure, there was no big difference in the I-V characteristics.

The applying voltage – light intensity (L-V) characteristics when using each material is shown in Fig.5. As shown in this figure, generally, the threshold voltage of the light emission from the materials were increased and at the same time, the light emitting intensity were decreased by adding the methyl group or carboxylic group to the Ru complex monomer.

The only the exception was Ru(bpy)3(COONa) formed with polyethylene oxide containg PSSLi and NaOH. It’s threshold voltage of the light emission was as low as 3.6V. Maximum light emitting intensity of Ru(bpy)3(COONa) was as high as 2000cd/m² (28•W), however, that of Ru(bpy), was 1500cd/m²(22•W).

Comparing the results shown in Fig.4 and Fig.5, there were big differences in the threshold voltage, however, the I-V characteristics are almost the same. Therefore, we can easily estimate the order of the external quantum efficiency : (e)≥(a)> (b) > (c) > (d).

And the order was the same order with the threshold voltage.

Next, the difference of the response between Ru(bpy)3 and Ru(bpy)3(COONa) after applying the step voltage to the device was measured and compared in Fig.6. For the latter, the response time to reach the maximum intensity was within the 10msec, however, that of the former was more than 300sec. As shown in the figure, response velocity of the latter was drastically improved compared with the former. We consider that the electron hopping in the Ru(bpy)3(COONa) was much improved than that of Ru(bpy3), by combining the solid polyelectrolyte and the dopant into the material..

It is noteworthy that these characteristics are obtained in air at room temperature.

![Fig.2 Photo acoustic spectroscopy of the light emitting materilas](image-url)
Fig. 3 PL spectra of ruthenium complex materials
4. Conclusions

Ruthenium complex monomers with different functional groups were synthesized. Their energy band gaps were measured by using photo-acoustic spectroscopy and the luminescence spectra were measured by photoluminescence spectroscopy. It was found that the peak wavelength can be control from 30nm to 720nm by adding the functional group to the ruthenium complex monomer.

It was also found that by adding polyethylene oxide and LiCF₃SO₄ and sodium hydroxide into the ruthenium complex, the light intensity of the organic light emitting device was increased from 1500cd/m² to 2000cd/m² and the response delay which is the characteristic of the electrochemical luminescence is drastically improved.

Fabrication of the EL devices using layer-by-layer sequential adsorption process is now undergoing. [7,16]
Acknowledgements

A part of this work was supported by TEPCO science foundation from 1999 to 2001.
The authors acknowledge Dr. Handy Erik and M. F. Rubner of Massachusetts Institute of Technology, USA for their precious advice on this study.

References

(15) Seimei Shiratori, Japanese PAT Application,
(16) Japanese PAT Application, H 10-267286/ PCT/JP 99/04432, WO 00/13806