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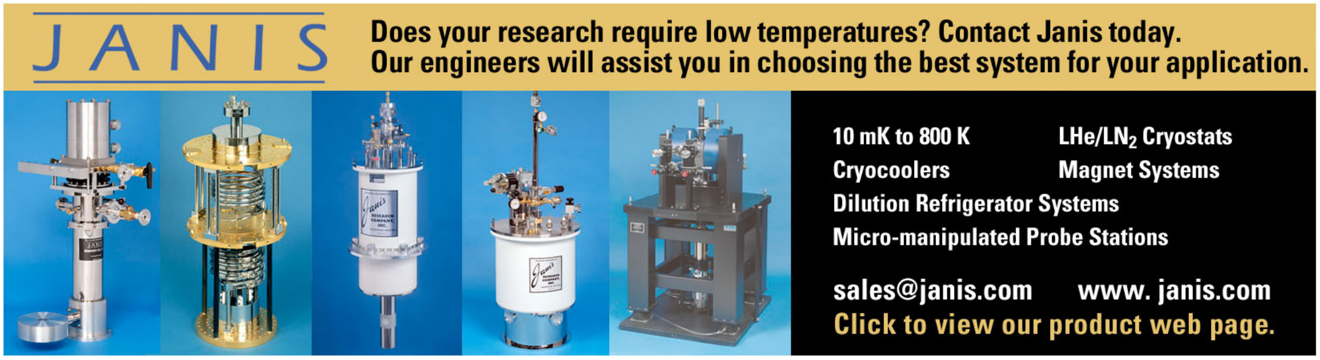

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# Organic light-emitting diodes using 3- or 5-hydroxyflavone–metal complexes

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3- or 5-hydroxyflavone-metal complexes were synthesized and applied to organic light-emitting diodes (OLEDs) as an emitting material and an electron transport material. When *bis*(5-hydroxyflavonato)beryllium [Be(5Fla)$_2$] was used as an emitting material, the OLED showed a luminance of 1900 cd/m$^2$ with yellow. On the other hand, when used as an electron transport material in an organic three-layer cell, a high luminance of more than 10 000 cd/m$^2$ was obtained. Furthermore, the turn-on voltage of the OLED could be lowered to 2.4 V and its lifetime was more than 1300 h. Be(5Fla)$_2$ was found to have a good electron transporting capability and good stability. © *1997 American Institute of Physics.* [S0003-6951(97)00349-5]

Organic light-emitting diodes (OLEDs) have been expected to find application as a new type of display since Tang and co-workers reported on high-performance OLEDs.[1] Chelate–metal complexes are often used as a carrier transport material, an emitting material, and a host material in the OLEDs because they have a good carrier transporting capability and strong fluorescence. They also exhibit good stability in films (no crystal deposition with time), and offer heat resistance because of their high melting points. *Tris*(8-hydroxyquinolinato)aluminum (Alq$_3$) and *bis*(8-hydroxyquinolinato)zinc (Znq$_2$) are well-known materials and exhibit good properties for OLEDs.[1,2] We showed the molecular design of a chelate–metal complex in a previous article.[3] Since the film of a chelate–metal complex is ordinarily deposited by vacuum vapor deposition, the chelate–metal complex must be easily sublimed. It was found that an inner complex salt offers good sublimation in a vacuum and its film was deposited successfully. The complexes mentioned above, such as Alq$_3$ and Znq$_2$, have a structure with an inner complex salt. We have developed various chelate–metal complexes. *Bis*(10-hydroxybenzo[h]quinolinato)beryllium (BeBq$_2$)[4] showed a higher performance than Alq$_3$ when used as an electron transport material. A cell using BeBq$_2$ showed a long lifetime of 3500 h at an initial luminance of 500 cd/m$^2$ and more than 15 000 h at 100 cd/m$^2$.[5,6] The chelate–metal complexes show various emitting colors. For example, azomethine–zinc complexes showed blue or violet,[3] and 5,10,15,20-tetraphenylporphrinato zinc (ZnTPP) and *bis*(4-hydroxyacridinato)zinc (ZnAc$_2$) showed a red emission.[7] *Bis*(2-(2-hydroxyphenyl)benzothiazolato)zinc [Zn(BTZ)$_2$] showed a whitish emission, having a spectrum with a wide half band of more than 150 nm.[8] White emission is important if OLEDs are applied to the backlights or full-color displays with color filters.

These complexes almost always have an oxygen, nitrogen-coordinate bond in relation to bonding between ligands and metal ions. For example, the ligands were coordinated with metal ions on oxygen and nitrogen in Alq$_3$, BeBq$_2$. However, complexes which have an oxygen, oxygen-coordinate bond have seldom been reported as materials for OLEDs. A complex with an oxygen, oxygen coordinate bond (o, o-complex) is expected to be useful for OLEDs because the o, o-complex, such as the morin–metal complex, is known to have fluorescence in analytical chemistry. In this letter we report on new o, o-complexes, which were constructed with 3- or 5-hydroxyflavone and metal ions. These complexes showed high performance in OLEDs as an electron transport material or an emitting material.

The four complexes of *tris*(5-hydroxyflavonato) aluminum [Al(5Fla)$_3$], *bis*(5-hydroxyflavonato)zinc [Zn(5Fla)$_2$], *bis*(5-hydroxyflavonato)beryllium [Be(5Fla)$_2$], and *bis*(3-hydroxyflavonato)zinc [Zn(3Fla)$_2$], were newly synthesized. The molecular structure of these complexes are shown in Fig. 1. For example Al(5Fla)$_3$ was prepared

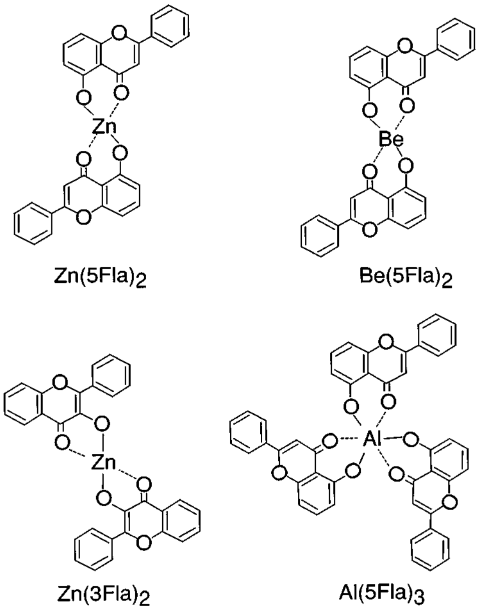

FIG. 1. The molecular structures of 3- or 5-hydroxyflavone-metal complexes.

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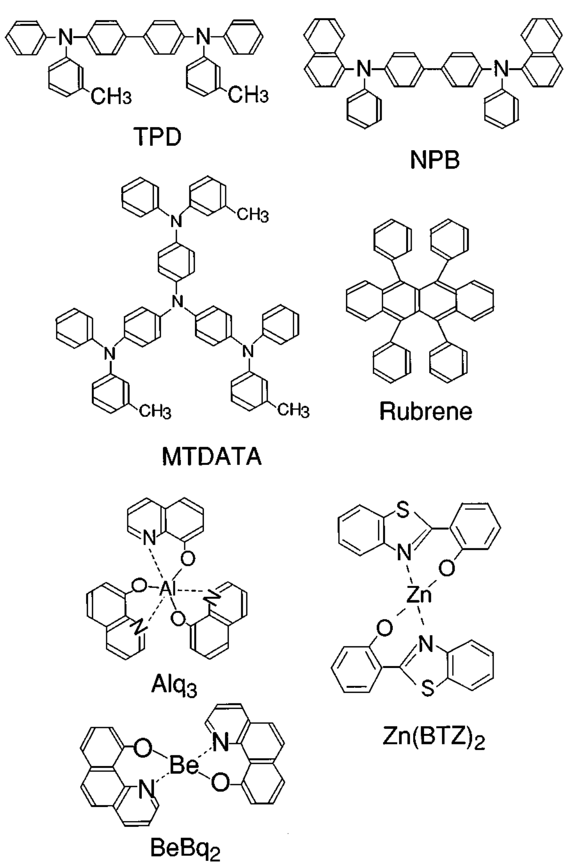

FIG. 2. The molecular structures of the hole transport materials and host material.

through the reaction of 5-hydroxyflavone and aluminum isopropoxide in methanol with reflux, and purified by train sublimation.[9] These complexes are an inner complex salt and are easily sublimed in a vacuum.

The cells were fabricated on indium-tin-oxide (ITO, anode) substrates which were cleaned by an ultraviolet ozone cleaner immediately before use. Organic layers and a cathode layer (Mg$_{0.9}$In$_{0.1}$) were deposited by conventional vapor vacuum deposition in $5\times10^{-6}$ Torr. The emitting area was $2\times2$ mm$^2$. The cell structures used in this experiment are shown as follows: A two organic layer type of [ITO/hole transport layer (500 Å)/emitting layer (500 Å)/MgIn] was employed when the chelate–metal complexes were examined as an emitting material. The hole transport layer was composed of N,N′-diphenyl-N,N′-di(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine. A three organic layer type of [ITO/hole transport layer (500 Å)/emitting layer (200 Å)/electron transport layer (400 Å)/MgIn] was employed when the complexes were examined as an electron transport material. The emitting layer was composed of N,N′-diphenyl-N,N′-di(1-napthyl)-1,1′-biphenyl-4,4′-diamine (Ref. 10) (host material) and rubrene (dopant, 5 wt % against NPB). The rubrene doped system was used in this cell because this system showed high luminance and high stability.[5] 4,4′,4″-tris(3-methylphenylphenylamino)triphenylamine was used in the hole transport layer.[11] The molecular structures mentioned above are shown in Fig. 2.

The photoluminescence (PL) spectra of the organic films (1000 Å) were measured with a fluorescence spectrophotometer. The ionization potential of these films was measured by atmosphere ultraviolet photoelectron analysis using a Riken Keiki AC-1 under ambient atmosphere.

These complexes were examined first as an emitting material. Their films were easily deposited and were uniform. The PL peak wavelengths are shown in Table I. These PL intensities are very weak compared with Alq$_3$. Three 5-hydroxyflavone-metal complexes had almost the same PL peaks of around 560 nm. The PL of the 3-hydroxyflavone-metal complex, Zn(3Fla)$_2$, could not be measured because of its weak intensity. The electroluminescence (EL) results are shown in Table I. The OLEDs which used these complexes showed yellow–orange emissions. The luminance of these complexes was not relatively high. Although the Be(5Fla)$_2$ cell showed the highest luminance of all at 1900 cd/m$^2$, the Al(5Fla)$_3$ cell and Zn(5Fla)$_2$ cell showed luminance of around 1000 cd/m$^2$ and the Zn(3Fla)$_2$ cell showed luminance of only 186 cd/m$^2$. The reason for this low luminance is that these complexes had a weak PL intensity. The turn-on voltage, which was defined as the voltage when the luminance was 1 cd/m$^2$, was also measured. The turn-on voltage of the Be(5Fla)$_2$ cell was 2.4 V, which was the lowest voltage of all. The Be(5Fla)$_2$ cell had the highest luminance and the lowest turn-on voltage although Be(5Fla)$_2$ had a weak PL. It seems that Be(5Fla)$_2$ has a good electron transporting capability.

Be(5Fla)$_2$ was examined as an electron transport material. Simultaneously, conventional electron transport materials such as Alq$_3$, BeBq$_2$, and Zn(BTZ)$_2$, were also examined for comparison with Be(5Fla)$_2$. The cell structure in this experiment was the organic three-layer structure mentioned above. The results are shown in Table II. All cells showed a yellow emission which originated in rubrene because each EL peak was almost identical to the PL peak of rubrene (560 nm). The luminance-voltage characteristics of these cells are shown in Fig. 3. The Be(5Fla)$_2$, BeBq$_2$, and Zn(BTZ)$_2$ cells showed better luminance-voltage properties than the Alq$_3$ cell. The BeBq$_2$ cell showed the highest maximum luminance of all at 44 000 cd/m$^2$. However, the turn-on voltage of the Be(5Fla)$_2$ cell was 2.4 V, which was the lowest of all, although the Be(5Fla)$_2$ cell had a low maximum luminance

TABLE I. PL and EL results of 3-, or 5-hydroxyflavone-metal complexes used as an emitting material.

| Emitting materials | PL (nm) | EL (nm) | Chromaticity coordinates | Turn-on voltage (V) | Maximum luminance (cd/m$^2$) |
|---|---|---|---|---|---|
| Al(5Fla)$_3$ | 563 | 598 | $x=0.467$, $y=0.511$ | 4.0 | 1276 (10 V) |
| Zn(5Fla)$_2$ | 568 | 591 | $x=0.472$, $y=0.516$ | 4.2 | 878 (9 V) |
| Be(5Fla)$_2$ | 554 | 559 | $x=0.460$, $y=0.524$ | 2.4 | 1900 (7 V) |
| Zn(3Fla)$_2$ | weak | 607 | $x=0.474$, $y=0.476$ | 6.2 | 186 (12 V) |

TABLE II. EL results of $Be(5Fla)_2$ used as an electron transport material and comparison with other materials.

| Electron transport materials | EL (nm) | Chromaticity coordinates | Turn-on voltage (V) | Maximum luminance ($cd/m^2$) |
|---|---|---|---|---|
| $Be(5Fla)_2$ | 559 | $x=0.484, y=0.513$ | 2.4 | 10 670 (10 V) |
| $BeBq_2$ | 553 | $x=0.467, y=0.518$ | 2.8 | 44 000 (10 V) |
| $Alq_3$ | 556 | $x=0.445, y=0.552$ | 3.6 | 29 200 (14 V) |
| $Zn(BTZ)_2$ | 559 | $x=0.490, y=0.498$ | 3.5 | 10 090 (12 V) |

of 10 670 $cd/m^2$ as compared with the $BeBq_2$ cell. Incidentally, the turn-on voltage of the $BeBq_2$ cell was 2.7 V, and that of the $Alq_3$ cell was 3.6 V. The current of the $Be(5Fla)_2$ cell was stable and no noisy current was observed in the low voltage region (1–3 V). It seems that $Be(5Fla)_2$ plays a role as the good electron transport layer in the low voltage region.

The reason for the low turn-on voltage of the $Be(5Fla)_2$ cell is that the electron injection barrier between $Be(5Fla)_2$ and MgIn (0.5 eV) is smaller than that of $Alq_3$/MgIn (0.8 eV) and $BeBq_2$/MgIn(0.8 eV). [Ionization potential: $Be(5Fla)_2$ (5.7 eV), $BeBq_2$ (5.5 eV), $Alq_3$ (5.6 eV), electron affinity: $Be(5Fla)_2$ (3.2 eV), $BeBq_2$ (2.9 eV), $Alq_3$ (2.9 eV), work function: MgIn (3.7 eV).] Electron affinity was calculated to subtract the optical band gap from the ionization potential. Furthermore, it seems that the electron transporting of $Be(5Fla)_2$ and $BeBq_2$ is better than that of $Alq_3$ because their luminance-voltage curves are located in a lower voltage region compared with the $Alq_3$ cell in Fig. 3.

The reason for the low maximum luminance of the $Be(5Fla)_2$ cell is that the melting point of $Be(5Fla)_2$ (272 °C) is lower than that of $BeBq_2$ (368 °C). When the cells showed the maximum luminance, the heat was generated in the cells because the large current flowed. Therefore, the $Be(5Fla)_2$ cell was broken in low luminance compared with the $BeBq_2$ cell.

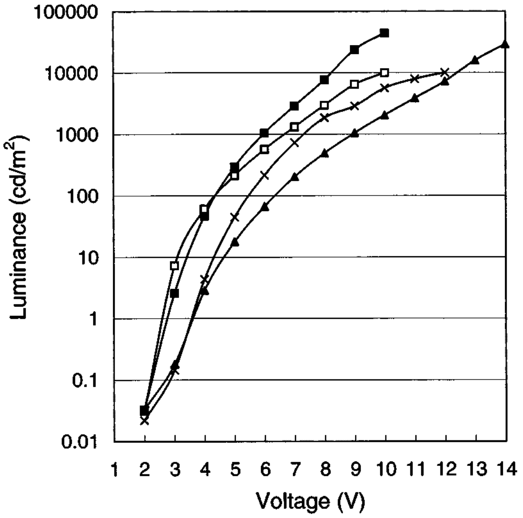

FIG. 3. The luminance-voltage characteristics of organic three-layer cells. (■) $BeBq_2$, (□) $Be(5Fla)_2$, (×) $Zn(BTZ)_2$, (▲) $Alq_3$.

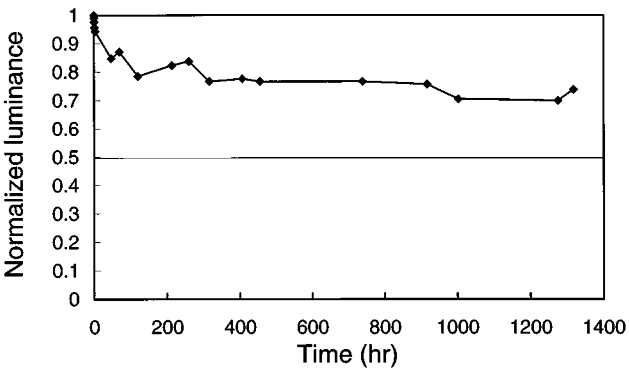

FIG. 4. The life test of the $Be(5Fla)_2$ cell.

The life test of the $Be(5Fla)_2$ cell was examined at room temperature when the cell structure of [ITO/MTDATA/TPD +rubrene 5 wt %/$Be(5Fla)_2$/MgIn] was employed. The luminous efficiency of this cell was 2.3 lm/W at 547 $cd/m^2$. The life test was carried out at an initial luminance of 210 $cd/m^2$ under a constant current density of 6 $mA/cm^2$. The result of the life test is shown in Fig. 4. The life was defined as the half decay time of initial luminance. The luminance of the $Be(5Fla)_2$ cell maintained 74% of the initial luminance after 1300 h passed. $Be(5Fla)_2$ was chemically stable and no crystal deposition of $Be(5Fla)_2$ was observed on the film.

$Be(5Fla)_2$ was found to be an excellent electron transport material, equal to $BeBq_2$. This is the first time that $Be(5Fla)_2$ has been found to be useful as an oxygen, oxygen-coordinate complex.

[1] C. W. Tang and S. A. VanSlyke, Appl. Phys. Lett. **51**, 913 (1987).
[2] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, and K. Shibata, Jpn. J. Appl. Phys., Part 2 **32**, L514 (1993).
[3] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, and K. Shibata, Jpn. J. Appl. Phys., Part 2 **32**, L511 (1993).
[4] Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, and K. Shibata, Chem. Lett., 905 (1993).
[5] Y. Hamada, T. Sano, K. Shibata, and K. Kuroki, Jpn. J. Appl. Phys., Part 2 **34**, L824 (1995).
[6] T. Sano, Y. Hamada, and K. Shibata, Extended Abstracts of Inorganic and Organic Electroluminescence, Berlin, Germany, 1996, Vol. EL96, p. 249.
[7] Y. Hamada, IEEE Trans. Electron Devices **44**, 1208 (1997).
[8] Y. Hamada, T. Sano, H. Fujii, Y. Nishio, H. Takahashi, and K. Shibata, Jpn. J. Appl. Phys., Part 2 **35**, L1339 (1996).
[9] J. Wagner, R. O. Loutfy, and C. K. Hsiao, J. Mater. Sci. **17**, 2781 (1982).
[10] S. A. VanSlyke, C. H. Chen, and C. W. Tang, Appl. Phys. Lett. **69**, 2160 (1996).
[11] Y. Shirota, Y. Kuwabara, H. Inaba, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, and K. Imai, Appl. Phys. Lett. **65**, 807 (1994).