Organo Lanthanide Metal Complexes for Electroluminescent Materials

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Contents

I. Introduction

Luminescence is the emission of light from an excited molecule. One of the most common forms is photoluminescence in which excitation occurs via the absorption of light by a molecule. In electroluminescence, on the other hand, electrical energy is transformed into light.

Electroluminescence (EL) of organic materials has been known since the 1960s.[1–2] Resulting devices are commonly called "organic light-emitting diodes" (OLED).[3] Intense research activity, however, started in the late 1980s after the development of the multilayered cell structure by Tang and Vanslyke,[4] who demonstrated the bright green emission of aluminum tris(8-hydroxyquinolinate) (Alq$_3$) in thin film organic layers. In their device, the luminance (brightness) exceeds 1000 cd/m^2 below 10 V with a quantum efficiency of 1% photon/electron (i.e., one photon output per 100 electrons injected). Another breakthrough came in 1990 when Burroughes and co-workers reported an EL device using a single layer of a π-conjugated polymer poly(phenylene−vinylene), PPV, between metallic electrodes.[5]

The operating mechanism in OLED is of the so-called injection type in which carriers, such as electrons and holes, are injected into the organic emitter layer to recombine there. We will describe general OLED in below.

II. Organic Electroluminescent Devices

Thin film OLEDs usually consist of multiple organic and metallic layers on an ITO-covered glass
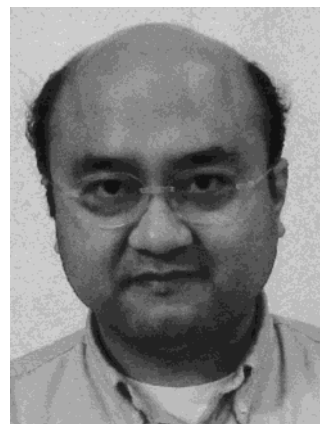
Junji Kido has received his B.S. degree (1984) from Waseda University, Tokyo, Japan, and Ph.D. degree (1989) from Polytechnic University, Brooklyn, NY, respectively. He is now an associate professor at the Graduate School of Science and Engineering, Yamagata University, Yonezawa, Japan. He was associated as a research scientist at Brookhaven National Laboratory (1990−1992). In 1993, he developed the first white color organic electroluminescent devices. He is now investigating extensively organic electroluminescence materials and devices. His work has been recognized by awards from the Society of Polymer Science, Japan and Society for Information Display, U.S.A. (2002).

Yoshi Okamoto received Ph.D. degree from Purdue University in 1957, majoring in physical organic chemistry. He was a research associate at Purdue University (1957) and at the Massachusetts Institute of Technology (1957−1960). From 1960 to 1973, he was a member of the Faculty of Engineering and Science, New York University. Since 1973, he has been on the faculty of the Chemistry and Polymer Research Institute, Polytechnic University. He was associated as a research scientist at Brookhaven National Laboratories (1985−1993) and as a principal investigator of the New York Center for Advanced Technology Ultra-Fast Photonic Materials at City University of New York (1993−1996). His current research interests are design, synthesis, and applications of polymer optical fiber and optoelectronic materials. He has published over 250 articles in the fields of organic and polymer chemistry.
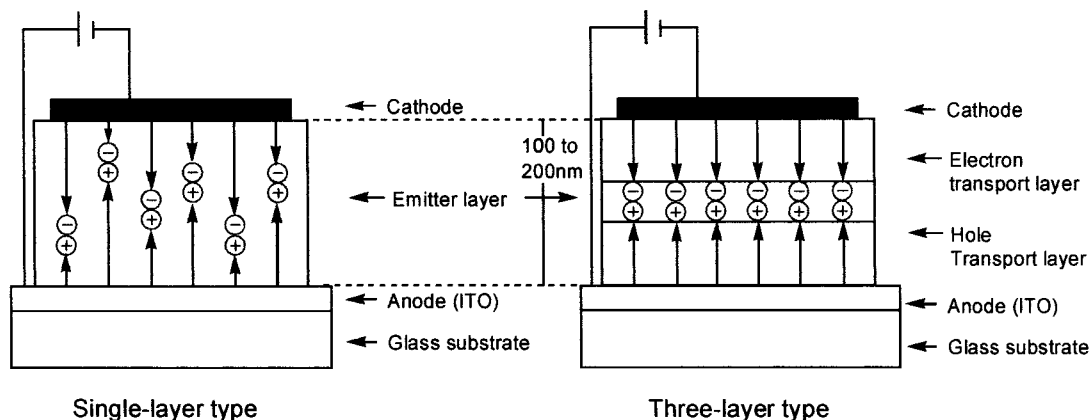
Figure 1. Configurations of typical EL cells. The thickness of the organic layer in each case is typically 100−200 nm.
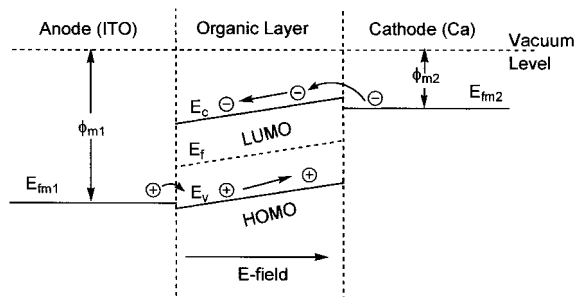

Figure 2. Energy level diagram for a forward-biased single-layer device.

plate. These layers may be deposited by various methods such as plasma deposition, thermal evaporation, Langmuir−Blodget deposition, or spin casting from solutions. All layers should be chemically stable, especially under device operating conditions, and resistant to oxidation or photooxidation.

In addition, the optical properties of each layer should be considered when designing the device structure. For higher efficiency light output, the device layers should be highly transparent to the emitted radiation.

Except for the anode and cathode, electroluminescent devices may contain single-layer or multiple-layer structures (see Figure 1). The single-layer device consists of a single organic layer sandwiched between the anode and cathode. In this case, the organic layer serves as the emitting source for the device and should therefore have a relatively high photoluminescence quantum efficiency. This emissive layer must also have good bipolar charge-transport properties, which are necessary for the transport of holes and electrons through the organic layer. These

holes and electrons, driven into the emitting layer by the applied electric field, will later recombine on the emitter molecules to form singlet and triplet excitons. To forward bias the LED, the anode, usually high-work-function materials such as indium tin oxide (ITO), is connected to a positive potential. Low-work-function metals such as calcium (Ca), magnesium (Mg), or aluminum (Al) and alloys such as Mg: Ag are used as the negative electrode (cathode). Electron transport will occur through the lowest unoccupied molecular orbital (LUMO), which is analogous to the conduction band (E_c) in semiconductors. Holes are transported through the highest occupied molecular orbital (HOMO), which corresponds to the valence band (E_v) in semiconductors. The efficiency of electron and hole transport is determined by the mobilities of both of the charge carriers in the organic layer (Figure 2).

Instead of using single-layer structures, additional layers can be added to the OLED to improve charge transport and injection. In a multilayer device the layers may consist of the anode, hole-transport layer (HTL), emission layer (EML), electron-transport layer (ETL), and cathode (Figure 1).

The hole-transport layer mainly transports holes within the HOMO level and to a lesser degree may transport electrons within the LUMO level. Therefore, the HTL material should have a high hole mobility. HTL materials should also have a low ionization potential for the efficient injection of holes from the anode. After bipolar charge recombination, the hole-transport layer should help block the migration of excitons from the emitting layer. Therefore, the HTL should have a higher exciton energy level than the emission layer (EML) to help confine excitons within the EML. Finally, the HTL should be
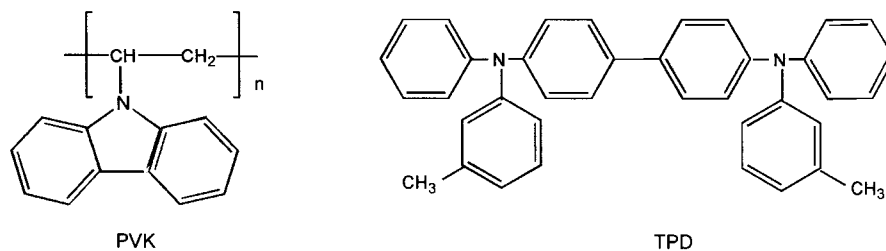

Figure 3. Chemical structures of hole-transporting materials poly(N-vinylcarbazole), PVK, and N,N-diphenyl-N,N-bis-(3-methylphenyl)-1,1′- biphenyl-4,4′-diamine, TPD.
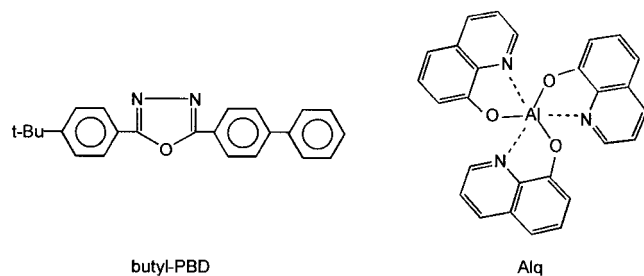
Figure 4. Chemical structure of electron-transporting material 1,3,4-oxadiazole derivative, PBD 8-hydroxyquinoline aluminum, Alq_3.
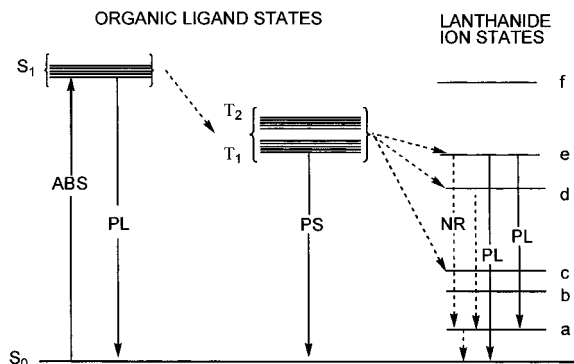

Figure 5. Energy transfer in lanthanide complexes: ABS = absorption; PS = phosphorescence; PL = photoluminescence; NR = nonradiative decay; a, b, c, d, e, and f = lanthanide ion energy levels.

transparent to the radiation emitted from the EL cell to reduce the optical losses within the device.

Many organic materials have hole-transport properties. Poly(N-vinylcarbazole) (PVK) and N,N-diphenyl-N,N-bis(3-methylphenyl)-[1,1′-biphenyl]-4,4′-diamine (TPD) are commonly used hole-transport materials (Figure 3). Several organics have been used as electron-transport layers, such as 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (butyl-PBD). Tris(8-hydroxyquinoline)aluminum complex (ALq_3), a widely studied luminophor, is also commonly used as an electron-transporting agent. The chemical structures of ALq_3 and butyl-PBD are shown in Figure 4.

III. Lanthanide Metal Ions Complexes as the Emitting Layer

Since these developments, numerous investigations on OLEDs using organic dyes, organic metal complexes, and organic polymers as emitting materials have been carried out. Despite such great achievements, obtaining pure and sharp emission from these organic materials is difficult. The emission spectra are generally broad. In addition, it is difficult to fine tune the emission color without affecting the EL material's physical properties.

Lanthanide metal ions, on the other hand, exhibit extremely sharp emission bands due to their 4f electrons which are responsible for their properties. Since 4f orbitals are effectively shielded from the influence of the external forces by the overlying $5s^2$ and $5p^6$ orbitals, the various states arising from the f^n configurations are split by external fields only to the extent of 100 cm^{-1}. Therefore, emission bands as well as absorption bands (f−f transitions) are extremely sharp when electronic transitions occur from one J state of an f^n configuration to another J state of the same configuration.[6]

In addition to the spectral profile of the complexes, the excitation mechanism of the central metal ion also differs widely from that of organic fluorescent compounds. In organic fluorescent compounds, the excited energy of the triplet state will be degraded through thermal deactivation processes without the emission of photons. Thus, the internal quantum efficiencies for devices using organic fluorescent compounds may be limited to approximately 25% by this process. In contrast, for lanthanide complexes with π-conjugated ligands such as β-diketonato, the lanthanide ions are excited via intramolecular energy

transfer from the triplet excited states of the ligands.[7,8] In some cases, higher energy levels may be excited by the ligand but nonradiative relaxations occur from these higher energy levels until the energy has decayed to the emitting levels where visible radiation originates. To improve energy transfer to the lanthanide ions, the triplet states of the ligand must be closely matched to or slightly above the metal ion's emitting resonance levels. Figure 5 shows the excitation and energy transfer mechanisms for the lanthanide chelates. The excitation energy of the ligand's triplet state, which may be directly generated by carrier recombination, can also be utilized to excite the emitting center. Thus, there is no limitation, up to 100%, of the internal quantum efficiencies for devices using lanthanide ion chelates as emitters.

Therefore, in the past decade, much work on OLEDs using lanthanide ion chelates as the emitting layers has been reported. In this review, we focus on the design and selection of lanthanide ions and ligand structures for OLEDs.

IV. Eu (III) and Tb (III) Complexes as Emitting Materials

In 1990, we reported an OLED containing Tb−tris(acetylacetonato), $Tb(acac)_3$, which was made into a double-layer device with a TPD as the hole-transport layer, i.e., ITO/TPD/$Tb(acac)_3$/Al.[9] Figure 6 shows the structures of Eu^{3+} and Tb^{3+} chelates often described in this review. Bright green emission was observed from the OLED when operated in a continuous dc mode (biased Al negative). As shown in Figure 7, the spectrum exhibited the characteristic line luminescence of the Tb^{3+} ion and was found to be identical to the photoluminescence spectrum of the $Tb(acac)_3$. The strongest emission was the 544 nm peak, which corresponds to the $^5D_4 \rightarrow {}^7F_5$ transition of the Tb^{3+} ion. The spectral profile and the relative intensity of the each peak was independent of the current density.

Red electroluminescence from a Eu complex was first observed using a tris(theotyltrifluoroacetonate)-Eu^{3+} ($Eu(TTA)_3$) complex, which was molecularly dispersed in a hole-transporting polysilane in our laboratory.[10,11] The luminance−current−voltage curves for this Eu device are shown in Figure 8. The
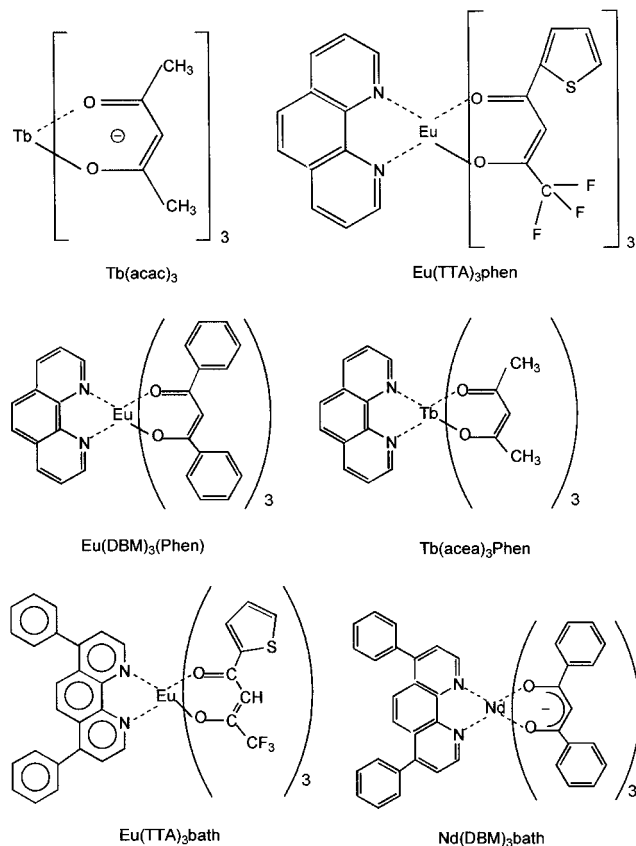
Figure 6. Chemical structures of Eu^{3+}, Tb^{3+}, and Nd^{3+} complexes: (1) Tb tris(acetylacetonate), $Tb(acac)_3$, (2) Eu (1,10-phenanthroline)-tris(4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dionate), $Eu(TTA)_3phen$, (3) Eu tris(dibenzoylmethanato)phenanthoroline, $Eu(DBM)_3(Phen)$, (4) Tb tris(acetyl-acetonate)phenanthhroline, $Tb(acea)_3phen$, (5) Eu (4,7-diphenyl phenanthroline)-tris(4,4,4,-trifluoro)-1-(2-thienyl)-butane-1,3-dionate, $Eu(TTA)_3bath$, and (6) Nd (4,7-diphenylphenanthroline)(dibenzoylmethanato)$_3$, $Nd(DBM)_3bath$.

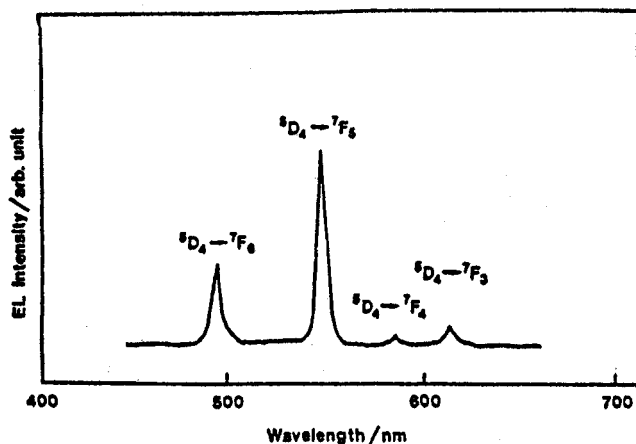**Figure 7.** Electroluminescence spectrum of a $Tb(acac)_3$ cell.

luminance was proportional to the injection current as well as the bias voltage. Luminescence started at 12 V, and a maximum intensity of 0.3 cd/m^2 at 18 V was achieved. More recently, a brighter red electroluminescence has been observed using tris(dibenzoylmethanato)phenanthrolineEu^{3+}, $Eu((DBM)_3(Phen))$, as the emitting material. The second added ligand, phenanthroline, acts to saturate the coordination number of Eu ion and also to improve the fluores-
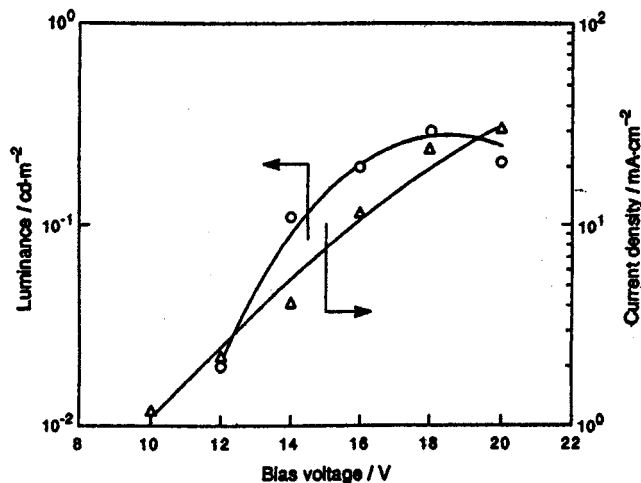

Figure 8. Luminance−current−voltage characteristics for ITO/PMPS−Eu (TTFA)$_3$/PBD/Mg/Ag device.
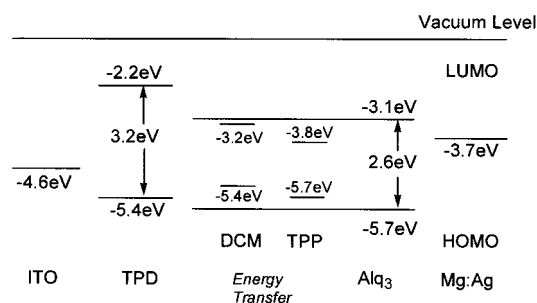

Figure 9. Energy band diagram of a codoped EL device. (Reprinted with permission from ref 15. Copyright 2002 Elsevier Science).

cence intensity, volatility, and stability of the Eu complex.[12] A multilayer device was fabricated using a coevaporated Eu((DBM)$_3$(Phen)) with PBD; ITO/TPD/Eu(DBM)$_3$(Phen):PBD/Alg$_3$/Mg:Ag. The electroluminescence spectrum consists of very sharp emission bands, which is a typical luminescence spectrum of the Eu complex. A luminance of 460 cd/m^2 with an emission peak at 614 nm was observed with a driving voltage of 16 V.

Takada and co-workers also developed a similar OLED based on a sublimable Eu(TTA)$_3$ phenanthroline complex, Eu(TTA)$_3$(Phen).[13] These devices utilized a microcavity design with a cell structure of (SiO$_2$/TiO$_2$ bilayers)/ITO/TPD/Eu complex/Alq$_3$/Mg:Ag. The SiO$_2$/TiO$_2$ bilayers comprised a dielectric quarter wave stack that was used as the output reflector for the microcavity. By adjusting the optical path length of the microcavity, they showed that there was an angular dependence of the spatial emission pattern emitted from the device. Consequently, optical display devices could be designed with an optimized viewing angle by adjusting the cavity length and the reflectivity of the mirrors. Sano et al. observed improved brightness results by modifying the side group of the phenanthroline in the Eu complex.[14] In their devices, they utilized diphenyl-substituted phenanthroline, Eu(TTA)$_3$(diphenylphenanthroline). These devices showed a line emission from the Eu complex with maximum brightness values greater than 100 cd/m^2. Recently, Ohmori and co-workers reported a single-layer OLED based on
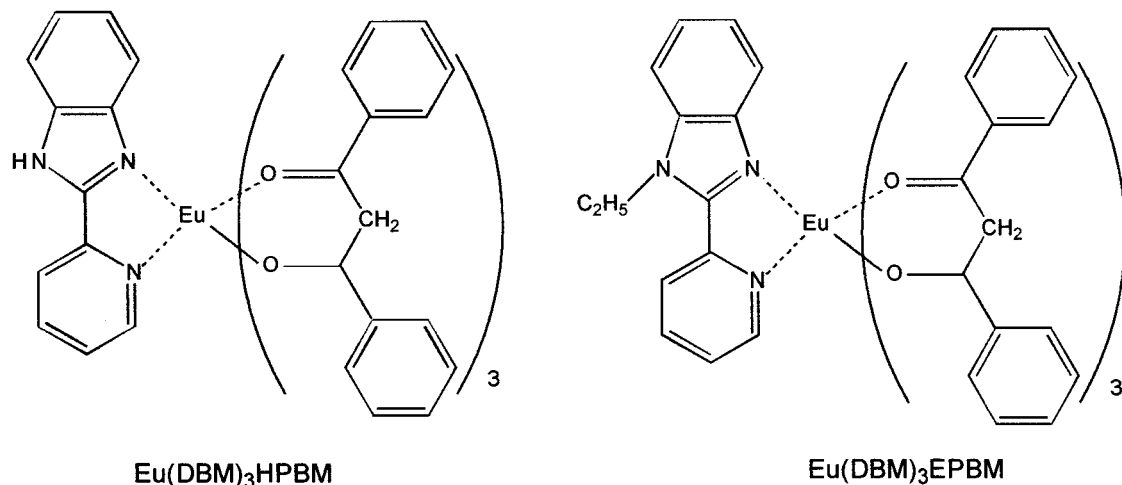
Eu(DBM)₃HPBM   Eu(DBM)₃EPBM

Figure 10. Chemical structures of Eu(dibenzolmethanato)₃-2- (2-pyridyl)benzimidazole, Eu(DBM)₃HPBM, and Eu-(dibenzolmethanato)₃-1-ethyl-2-(2 pyridyl)benzimidazole, Eu(DBM)₃EPBM.
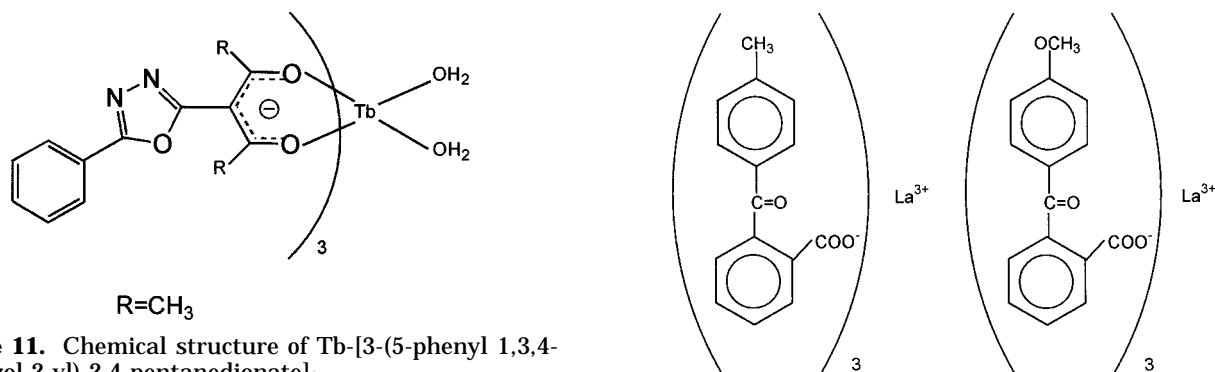

R=CH₃

Figure 11. Chemical structure of Tb-[3-(5-phenyl 1,3,4-oxadiazol-2-yl)-2,4-pentanedionate]₃.

La; Tb and Eu

Figure 12. Chemical structures of lanthanide−tris(4-methybenzoate), La(MeOBB)₃, and lanthanide−tris(4-methoxylbenzoate), La(MeOBB)₃.

Eu(TTA)₃(Phen) which was doped with PVK. The device structure was ITO/Eu(TTA)₃(Phen):PVK/Mg:In. They cited the energy band diagram of the device (Figure 9).[15] The electrons injected from the ITO anode to the lowest unoccupied molecular orbital (HOMO) states of PVK. Excitons were formed at the PVK and were then transferred to the ligand sites of Eu (TTA)₃(Phen). The singlet excitons produced were converted into triplet excitons by intersystem crossing and then transferred to the Eu³⁺. The energy relaxation from ⁵D to ⁷F orbitals in Eu³⁺ resulted in sharp emission at 614 nm. Instead of the phenanthroline ligand described above, 2-(2-pyridyl)benzimidazole (HPBM) and 1-ethyl-2-(2-pyridyl)benzimidazole (EPBM) (Figure 10) were synthesized as the second ligand for the Eu chelate. These ligands may be easily substituted with alkyl chains or other electron-donating groups on the benzimidazole in order to alter chelate properties. The EL luminance of the Eu complex with EPBM ligand was reported to be higher than that with HPBM. The maximum luminance of 180 cd/m² for Eu (DBM)₃EPBM was obtained at 18 V.[16] Oxadiazole derivatives are known as good electron-transporting and hole-blocking materials.[17] Thus, an oxadiazole-functionalized β-diketonate ligand was synthesized and the Tb complex prepared (Figure 11).[18] A light output of 100 cd/m² with an external EL efficiency as high as 1.1% was reported at 15 V. At 20 V, 550 cd/m² with 0.6% efficiency was observed. These investigators claimed

that the oxadiazole ligand played an important role in the high efficiency of the systems. However, in this structure, two water molecules are coordinated to Tb³⁺. It is well-known that the H−O vibration tends to quench the fluorescence intensity.[19] Thus, when these water molecules are replaced with another ligand, such as phenanthroline, the EL efficiency could be greatly increased.

We prepared thermally stable Eu and Tb complexes: Tb tris(4-methylbenzoate), Tb(MeBB)₃), Tb tris(4-methoxybenzoylbenzoate), Tb(MeOBB)₃, and Eu tris(4-methoxybenzoylbenzoate), Eu(MeOBB)₃ (Figure 12).[20] The single-layer light-emitting diodes were fabricated using Tb(MeBB)₃. PVK was selected as a host matrix for the OLEDs because of its good hole-transport and film-forming properties. The cell structure was ITO/Tb(MeBB)₃:PVK/Ca−Al. However, this device showed negligible light output, probably because of the poor electron-transport properties of the doped PVK layer. To improve the electron-transport properties, butyl PBD was added to the layer in the single cells, ITO/Tb(MeBB)₃:PBD:PVK/Ca−Al. The maximum brightness of this device was approximately 0.7 cd/m² for a 2 mol % doping concentration of the Tb complex. When the strong electron-donating
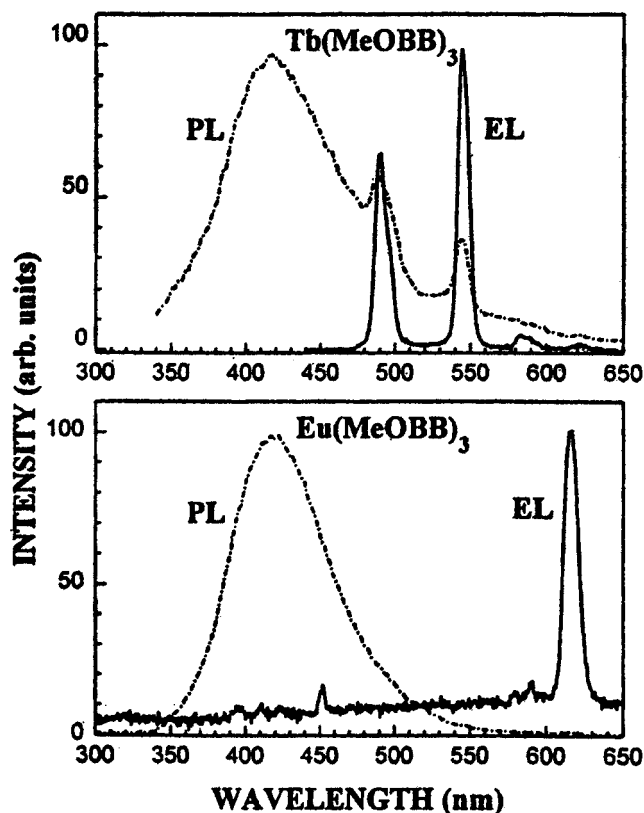
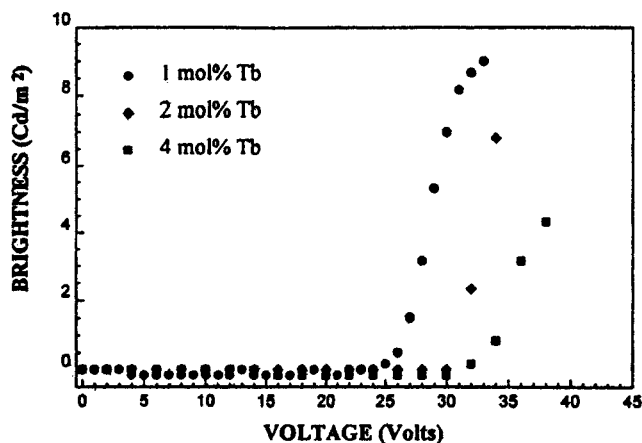**Figure 13.** PL spectra of Tb(MeOBB)$_3$: butyl-PBD:PVK (1:1:1) films and EL spectra of a single layer.

Figure 14. B−V curves for Tb(MeOBB)$_3$ OLEDs.

group methoxy (OCH$_3$) was substituted on the phenyl instead of the methyl group, a brighter electroluminescence was observed. This may be due to the more efficient energy transfer from the excited ligand to the Tb ion. The device structure was ITO/La(MeOBB)$_3$: PBD:PVK/Ca−Al, La = Tb, Eu. When the diodes were forward biased with the ITO electrode at positive polarity, brighter green electroluminescence corresponding to the Tb was observed (Figure 13). There was no observed electroluminescence from the MeOBB ligand, PVK, or butyl PBB. The brightness vs voltage curves for the OLEDs with various Tb-(MeOBB)$_3$ concentrations are shown in Figure 14. A maximum brightness of 45 cd/m^2 was obtained at an operating voltage of 24 V.
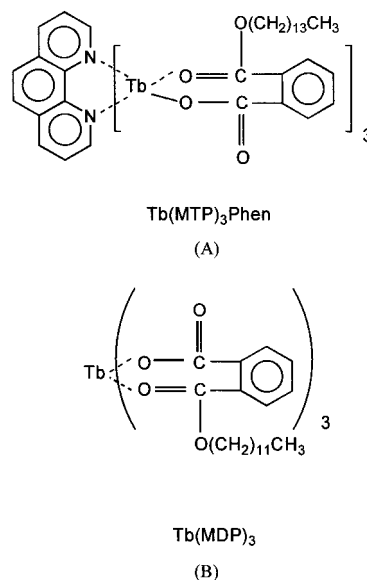

Figure 15. (A) Chemical structure of Tb−tris(tetradecylphethalate)phenanthroline complex Tb(MTP)$_3$(Phen). (B) Chemical structure of alkyl chain-substituted phthalate−Tb complex Tb(MDP)$_3$.

A thermally stable Tb carboxylate and phenanthroline complex (Figure 15A) was also prepared and used as an emitting layer.[21] The EL device structure was multilayered consisting of ITO/poly(p-phenylenevinylene) (PPV) as a hole transfer layer/PVK doped with the Tb complex, Tb (MTP)$_3$(Phen)/Alg$_3$/Al. The sharp green emission was observed with 152 cd/m^2 at 24 V, and the external quantum efficiency was as low as 0.017%. A long alkyl-chain-substituted phthalate Tb complex (Figure 15B), which is soluble in chloroform, was prepared. The Tb complex was doped with PBD and PVK, and a double-device structure, ITO/PVK:PBD:Tb(MDP)$_3$/Alg$_3$/Al, was fabricated. However, these devices did not show a sharp characteristic Tb^{3+} emission but exhibited an emission due to Alg$_3$.[22] Recently, Ling and co-workers investigated a OLED based on Eu(BA)$_3$(Phen) as an emitting layer.[23] Eu(BA)$_3$(Phen) was sandwiched between bis(2-[2-hydroxyphenyl]pyridinato)beryllium (BePP$_2$) (energy gap 3.1ev) as the barrier layers. The OLED structure, ITO/TPD/BePP$_2$/Al:Li/Eu(BA)$_3$(Phen), may act as the multiquantum well. The terminology multiquantum well (MQW) is often used in inorganic semiconductor devices. The well structure limits the separation between the electron and hole, and the confinement enhances the efficiency of light generation. MQW structures have been used in OLEDs in order to improve device performance.[24,25] Thus, at a low bias applied to this device, carriers cross the barrier layers through thermal activation and may be confined within the emitting layer; Eu(BA)$_3$(Phen) and Eu emission at 612 nm was observed. However, when the bias was increased, EL emission from the barrier layer, BePP$_2$, mixes with the emission of the Eu ion and exhibits a white color.[23] Huang and co-workers prepared various Tb complexes (Figure 16).[26] The R and R′ were different substituents, such as hydrogen, alkyl, alkylamine, and acryl groups. They constructed OLEDs using these Tb complexes. The photoluminescence and electroluminescence of the systems
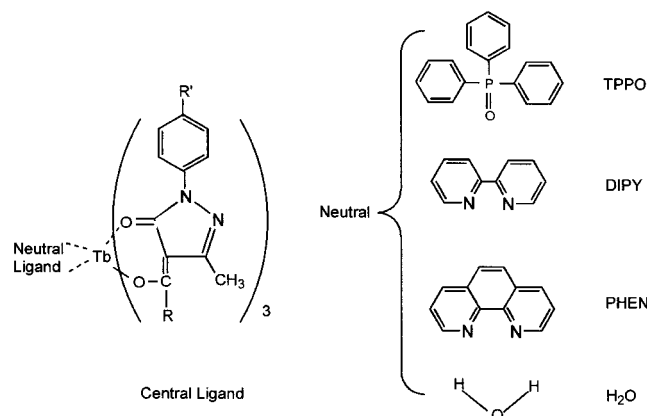
Figure 16. Chemical structures of the terbium complexes with various neutral ligands. (Reprinted with permission from ref 26. Copyright 2002 Elsevier Science).
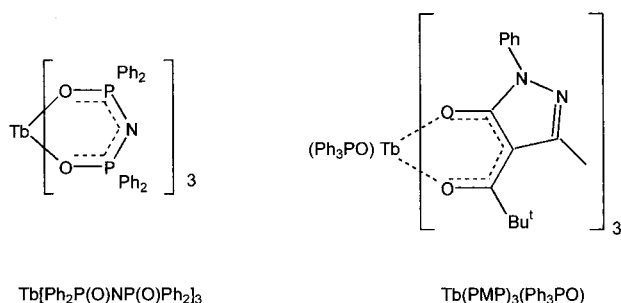

Tb[Ph₂P(O)NP(O)Ph₂]₃

Tb(PMP)₃(Ph₃PO)

Figure 17. Chemical structure of Tb−imidodiphosphinate and 1-phenyl-3-methyl-4-(trimethylacetyl)pyrazol-4-one complexes, Tb(PMP)₃(Ph₃PO) and Tb[Ph₂P(O)NP(O)Ph₂]₃.

were affected by the substituents R and R′. Among these devices, R = *tert*-butyl, R′ = H-substituted ligand, tris(1-phenyl-3-methyl-4-isobutyryl-5-phrazolone) (PMIP), triphenylphosphine oxide (TPPO), (PMIP)₃−Tb-TPPO showed the highest electroluminescence efficiency.

Lin et al. fabricated OLEDs based on Eu complexes such as Eu(DBM)₃(Phen) using oxadiazole derivatives as hole-transport materials.[27] Zhang and co-workers also prepared OLEDs using Eu chelates with PVK and Alq₃ used as the hole and electron-transport layers, respectively.[28] Other Eu complexes such as LiEu(TTA)₄, NaEu(TTA)₄, and KEu(TTA)₄ were doped into PVK films and fabricated into OLEDs. The nature of the cations in the Eu complexes were found to have no effect on the luminescence performance.[29] Wang et al. constructed sharp red OLEDs with enhanced efficiency using Eu complexes.[30] Christou and co-worker prepared OLEDs using unusual Tb complexes such as the Tb−imidodiphosphinato ligand, tris(1-phenyl-3-methyl-4-(trimethylacetyl)pyrazol-4-one) (PMP), and triphenylphosphine oxide, [(PMP)₃Tb-(Ph₃PO)]. These structures are shown in Figure 17.[31,32] By controlling the OLED structure using suitable hole- and electron-transporting layers and utilizing [(PMP)₃Tb(Ph₃PO)] as the emitting material, the device efficiency was improved from 0.05 lm/W in a single-layer structure to 2.63 lm/W in a multi-layer structure.

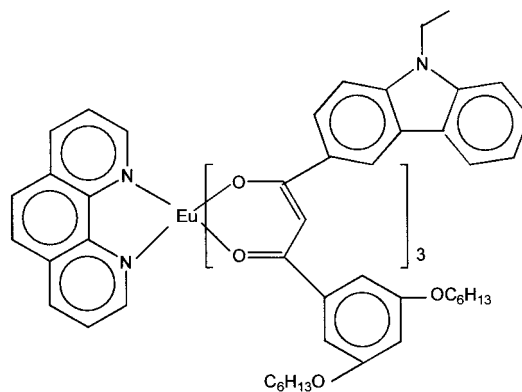Recently, Kido and co-workers constructed a white-light-emitting electroluminescent device using Eu-

Figure 18. Structure of the single component of OLED.

(DBM)₃(Phen) with Tb(DBM)₃(Phen) and a TPD. TPD has relatively sharp emission peaks at around 410−420 nm, blue-violet, and also good hole-transport properties.[33] Alq₃ was used as the electron-transporting layer. The organic layers were successively deposited onto a precleaned ITO-coated glass plate, and the Mg:Ag electrode was finally co-deposited on the organic layer. The device structure was ITO/TPD/Tb(acea)₃(Phen)/Eu(DBM)₃(Phen)/Alq₃/Mg:Ag. White OLEDs were also fabricated by Pyo and co-workers.[34] They also used TPD as a blue-light-emitting and hole-transporting material and Tb(acea)₃(Cl(Phen)) as a green-light-emitting material. Cl(Phen) is monochloride-substituted phenanthroline. Eu(TTA)₃(Phen) was a red emitter. The device structure was ITO/TPD/Tb(acea)₃(Cl(Phen)/Eu(TTA)₃(Phen)/Alq₃/L:Al; alternately, bis(10-hydroxybenzo[*h*]quinolinato)beryllium-(Bebq₂) could be used instead of Alq₃. The white-light-emitting characteristics of these device structures were discussed by considering the energy band diagrams of the various materials used. White-light-emitting OLEDs were also reported using Eu$_x$Tb$_{1-x}$(acac)₃-(Phen) dinuclear complex as the emitting layer.[35] It consists of two active organic layers sandwiched between an electron-injecting (Al) and a hole-injecting (ITO) layer. The TPD layer doped with PVK was fabricated by spin coating on ITO, and then Eu$_x$Tb$_{1-x}$-(acac)₃(Phen) doped with PVK was deposited by evaporation on the TPO layer. Its luminescence consists of three parts: red color from Eu³⁺, green from Tb³⁺, and blue from TPD. When the compositions of the three color sources were adjusted and operated under proper voltage (7−10 V), white light was observed.

Recently, Bazan and co-workers reported polymeric OLEDs based on Eu complexes.[36,37] Eu complexes with β-diketonate and phenanthroline were incorporated in the polymer matrix, poly[2-(6′cyano-6″-methylheptyloxy)-1,4-phenylene. The thin film was obtained by spin casting. The efficient energy transfer from the polymer to the Eu complex resulted in complete quenching of the broad emission of the polymer, and a pure red Eu-based emission was observed. They also fabricated a single-component OLED using a polymeric Eu complex, tris[1-(*N*-ethyl-carbazolyl)(3′,5′-dihexyloxybenzoyl)methane](phenanthroline) (Figure 18). The phenanthroline ligand
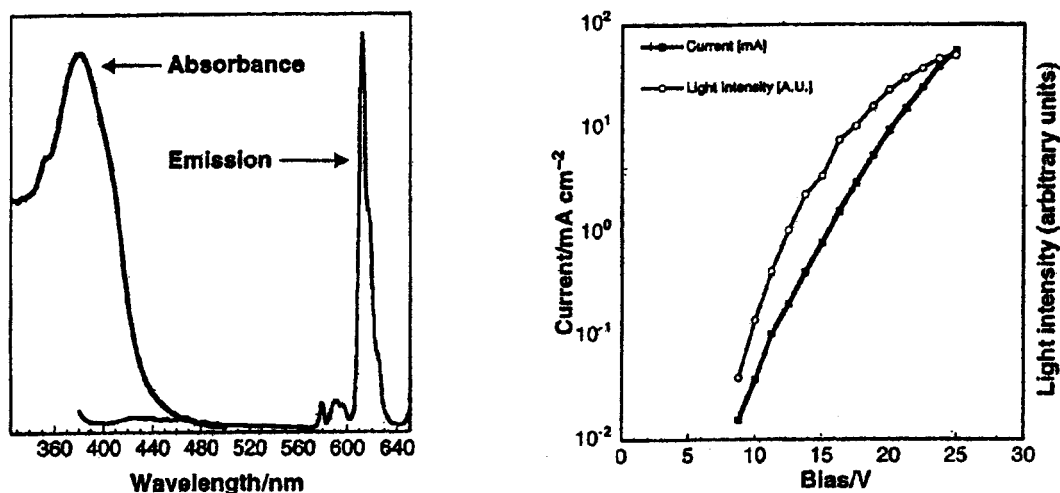
Figure 19. Absorption and emission spectra of a thin film of the emitting component and current−voltage curve of the device with configuration ITO/PVK/Eu complex/Ca. (Reprinted with permission from ref 37. Copyright 2002 The Royal Society of Chemistry).
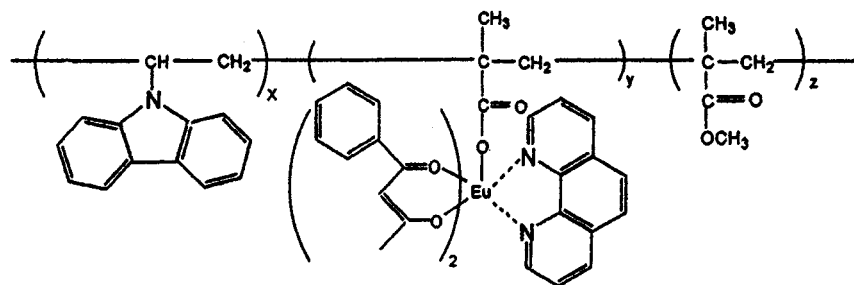

Figure 20. Structure of Eu^{3+} complex containing copolymer $x = 3$, $y = 0.1$, $z = 1.9$, Eu content about 1.8% (wt).

acted as the electron-transport medium, and an attached carbazole was used for the hole transport. The hexyloxyl groups substituted on the phenyl prevented crystallization, and a transparent clear film was obtained by directly spin casting onto an ITO anode from a toluene solution. The absorption and emission spectra of the thin film of the Eu complex and the current−voltage curves of the ITO/PVK/Eu complex/Ca device are shown in Figure 19. A red single-layer type of EL device based on a copolymer containing carbazole, Eu complex, and methyl methacrylate (Figure 20) was fabricated by Ling and co-workers.[38] A sharp red EL from the single-layer ITO/carbozale−Eu complex/Al:Li was observed under a drive bias over 6 V. However, the EL intensity reached 3 cd/m² at 10 V drive bias, and the EL efficiency was only 0.1%.

As discussed in the Introduction, lanthanide ion complexes can achieve very high lanthanide ion excitation efficiency by the optimization of the energy transfer in the solid state system. However, the maximum external EL quantum efficiencies using lanthanide ion chelates as an emitting layer have typically exhibited values less than 1%. Forrest and co-workers investigated in detail the cause of the inefficiency in the lanthanide ion chelate OLED system.[39,40] They utilized $Eu(TTA)_3(Phen)$ as an emitting source guest material, and the chelate was doped into 4,4′-*N,N*-dicarbazolebiphenyl (CBP) as a host compound. CBP has a wide energy gap which sup-
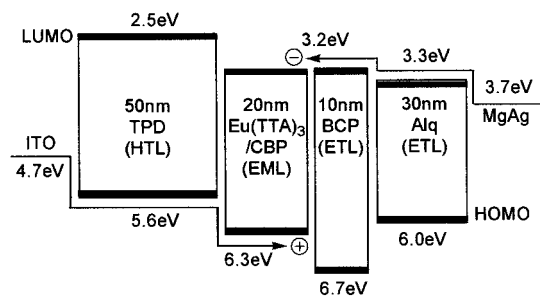

Figure 21. Proposed energy level diagram of the OLEDs used in this study. The HOMO and LUMO are also shown. The HOMO and LUMO levels of $Eu(TTA)_3$phen are unknown. (Reprinted with permission from ref 40. Copyright 2002 American Institute of Physics).

ports bipolar carrier transport. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline was used as an electron-transporting layer, and Alq_3 is used to confine holes within the EML. The proposed energy levels and each organic layer of the device are shown in Figure 21. First TPD was deposited by high vacuum: thermal evaporation onto ITO (a sheet resistance of 20 Ω/sq), followed by deposition of $Eu(TTA)_3(Phen)(1\%)$−CBP mixture, and then BCP and Alq_3. The cathode consisted of Mg:Ag (10:1). They have observed a maximum external EL quantum efficiency of 1.4% at a current density of 0.4 mA/cm² for the system. However, the quantum efficiency was significantly decreased at high current (1−100 mA/cm²). From the
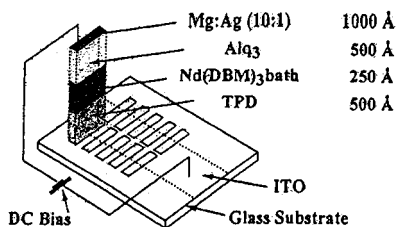
Figure 22. Configuration of Nd(DBM)$_3$bath of OLED. (Reprinted with permission from ref 45. Copyright 2002 American Institute of Physics).

analysis of the electroluminescent and photoluminescent spectra and the current density characteristics, they concluded that direct trapping of holes and electrons and subsequent formation of the excitons occurs on the dopant, leading to high quantum efficiencies at low current densities. However, at high current densities, triplet–triplet annihilation on CBP molecules following back transfer from TTA is due to the near resonance of TTA and CBP triplet states. Liang and co-workers also reported the efficiency–current characteristics in an OLED. They investigated the luminance–current relationship of a simple double-layer Eu(DBM)$_3$bath complex and showed that the quantum efficiency of the device rapidly decreased with increasing current density, due to biexcitonic quenching among the excited Eu^{3+} ions.[41] Takada et al. also investigated recently the factors that influence the EL efficiency of Eu complex devices. They examined exciton relaxation processes as well as the mechanisms of carrier transport and recombination.[42]

V. Nd(III), Er(III), and Yb(III) Complexes as Emitting Materials

Neodymium (Nd^{3+}) and erbium (Er^{3+}) are used as the active elements in optoelectronic devices due to their intra-4f transitions at 1340 nm (Nd^{3+}, $^4F_{3/2} \rightarrow {}^4I_{11/2}$) and 1530 nm (Eu^{3+}, $^4I_{13/2} \rightarrow {}^4I_{15/2}$). The infrared emission at 1530 nm of Er ion is particularly highly interesting for fiber-optic communication, because of the narrow line width of the emission at room temperature and the high bandwidth capacity.[43] Recently, several investigators have fabricated near-infrared and infrared OLRDs containing Nd, Er, and Yb ions.

A neodymium-ion-doped inorganic semiconductor EL diode was reported several years ago.[44] Yanagida et al. reported a OLED based on a Nd organic complex; Nd(DBM)$_3$ bath was the emitting material; TPD and Alq$_3$ were used as the hole- and electron-transport materials.[45] All of the organic layers and the cathode (Mg:Ag (10:1)) were fabricated by vacuum deposition. The device structure is shown in Figure 22. Sharp near-infrared emission bands corresponding to f–f transitions of the Nd ion were obtained (Figure 23). However, the device was found to be degradated during the measurement.

Klink and co-workers synthesized a lissamine-functionalized Nd complex (Figure 24).[46] Triphenylene was incorporated into the ligand, because it allows excitation up to 350 nm and has a high
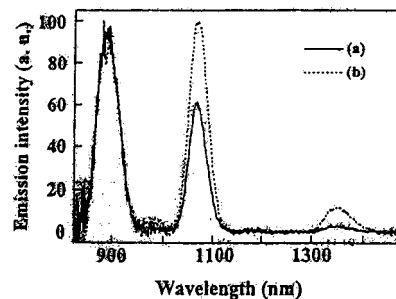

Figure 23. Emission spectra in the near-infrared region; (a) EL spectrum of ITO/TPD/Nd(DBM)$_3$bath/Alq$_3$/Mg:Ag device at the applied voltage of 19 V, (b) PL spectrum of deposited film of Nd(DBM)$_3$bath. Thickness of deposited film for PL was 2000 Å and excited by 390 nm light. (Reprinted with permission from ref 45. Copyright 2002 American Institute of Physics).
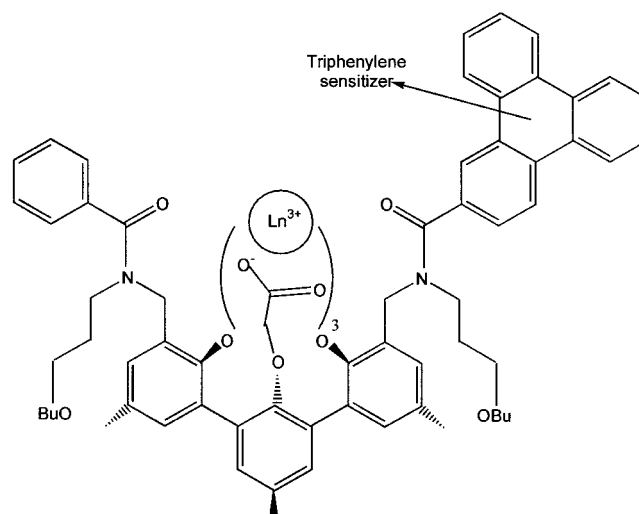

Figure 24. Chemical structure of Nd^{3+} lissamine complex, triphenylene-functionalized derivative. (Reprinted with permission from ref 45. Copyright 2002 American Institute of Physics).

intersystem crossing quantum yield.[47] Sloott and co-workers synthesized a similar lissamine-functionalized Nd complex as an 890 nm emitter (Figure 25).[48] The complex was blended with poly(dioctylfluorene-*co*-benzothiadiazole). This polymer was chosen as the host material because it has a very high photoluminescent efficiency in the solid state ($\sim$0.6) along with good solubility in common organic solvents and a high electron affinity ($\sim$ 2.9 eV), which facilitates electron injection from cathodes such as Ca. The quantum efficiency of the Nd OLED device was estimated as $\sim$1%.

Gillin and Curry fabricated an Er-containing OLED. An Er–tris(8-hydroxyquinoline) complex was the emitting material. They observed 1540 nm sharp emission due to the Er^{3+} ion the 4f transition at room temperature.[49,50] Sun and co-workers also prepared an Er(acea)$_3$(Phen) complex as the infrared emitter. The device structure was ITO/PVK/Er(acea)$_3$(Phen)/Al:Li/Ag. They suggested that these devices provided a simple and cheap light source at 1540 nm wavelength.[51] Recently, Schauze et al. synthesized a tetraphenylporphyrin (TPP) Er complex which was
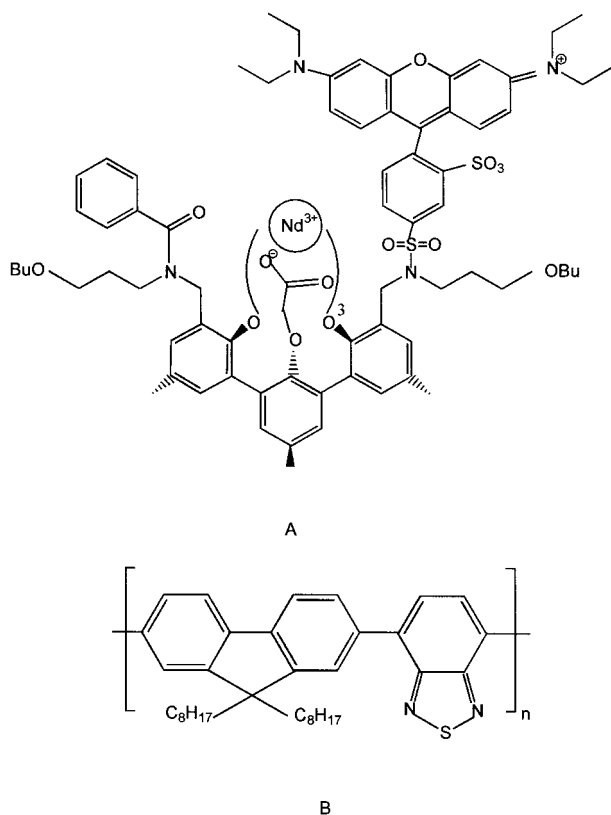
Figure 25. (A) Chemical structure of lissamine-functionalized Nd complex. (B) Chemical structure of poly(dioctylfluorene-*co*-benzothiadiazole). (Reprinted with permission from ref 48. Copyright 2002 American Institute of Physics).

blended with conjugated poly(*p*-phenylene) or poly-(*p*-phenylene–vinylene) (Figure 26).[52] They showed that the TPP ligand and the conjugated polymers provide effective energy transfer to Er and lead to a high efficiency for OLED. Similarly, a Yb ion complex was prepared. The OLED was based on Yb(TPP)acea blended with these conjugated polymers. The EL of the PPP–OR11:Yb(TPP)acea device was dominated by the 977 nm Yb emission, and an external quantum efficiency of 1.0×10^{-3} at 7 V was observed. The efficiency was about five times higher compared to the MEH–PPV:Yb(TPP)acea device.

Lee and co-worker prepared Y, La, and Gd ion complexes with M(acea)$_3$(Phen).[53] However, these complexes were used as electron-transporting mate-

rials for the organic emitter, *N,N*-bis(1-naphthyl-1,1′-biphenyl-4,4′-diamine) (NPB). The OLED structure was ITO/NPB/M(acea)$_3$(Phen)/Mg:Ag. For the device using the Gd chelate, a bright and sharp blue emission of 1000 cd/m^2 at 20 V was observed.

VI. Tm(III) and Eu(II) Complexes as Emitting Materials

Tm^{3+} exhibits a spectrally narrow light emission at about 480 nm. The spectroscopic properties of Tm^{3+} have mostly been studied in inorganic crystals and glasses as laser media. The blue luminescence of Tm ions in ZnS:Tm^{3+} inorganic thin film[49] electroluminescent devices based on the 4f($^1G_4$) → 4f($^3H_6$) transition has also been investigated.[54,55] However, Li and co-worker were the first to use Tm^{3+} ion in OLEDs.[56] They prepared a tris(acetylacetonato)-monophenanthroline Tm complex. Double-layer cells, ITO/PVK/Tm complex/Al, were constructed. The electroluminescence spectrum of the OLED with a drive voltage of 10 V and the photoluminescence spectrum under an excitation wavelength at 350 nm are shown in Figure 27. The emitting intensity of 6.0 cd/m^2 was achieved when a 16 V forward bias voltage was applied.

Unlike the optical spectra of trivalent europium ions which are dominated by parity forbidden f–f transitions, the spectra of the divalent europium may arise both from interconfigurational transitions between the states of 4f^{6}5d and the states of the lowest energy configuration 4f^7 and from charge-transfer transitions, both of which are parity allowed and therefore potentially efficient.[57] Thus, Christou et al. fabricated OLEDs based on a Eu^{2+} complex.[58] They prepared bis[tris(dimethylpyrazol)borate]Eu^{2+}, Tp$_2$-Eu^{2+} as an emitting layer (Figure 28). The multilayer structure consists of TPD, the Eu^{2+} complex, and 3-(4-biphenylyl)-4-phenyl-5-(4-*tert*-butylphenyl)-1,2,4-triazole (TAZ) as the hole-transfer, emitting, and electron-transfer layers, respectively: ITO/TPD/Eu^{2+} complex/TAZ/Al. The Eu^{2+} complex was coated onto ITO by evaporation, and the other layers were also coated by evaporation. The device exhibited an orange-colored electroluminescence with a maximum luminance of 10 cd/m^2 at a current density of 20 mA/cm^2.
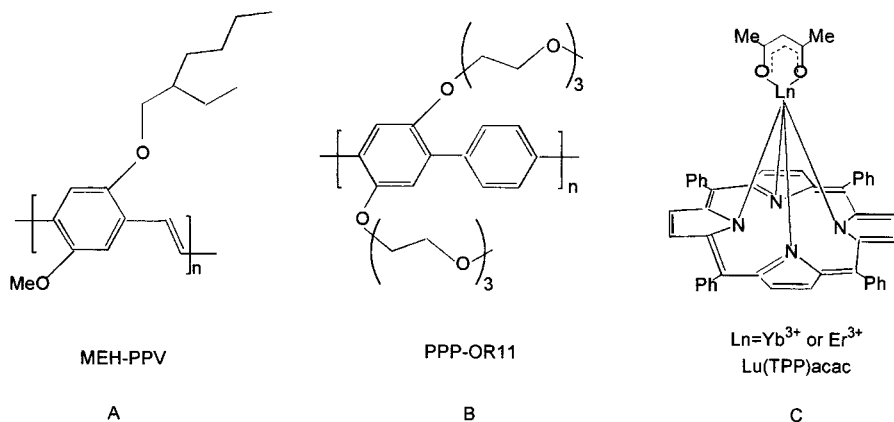

Figure 26. (A) Poly(oligoethylene oxide substituted *p*-phenylene vinylene). (B) Poly(substituted *p*-phenylene). (C) Er–tetraphenylporphyrin complex. (Reprinted with permission from ref 52. Copyright 2002 American Institute of Physics).
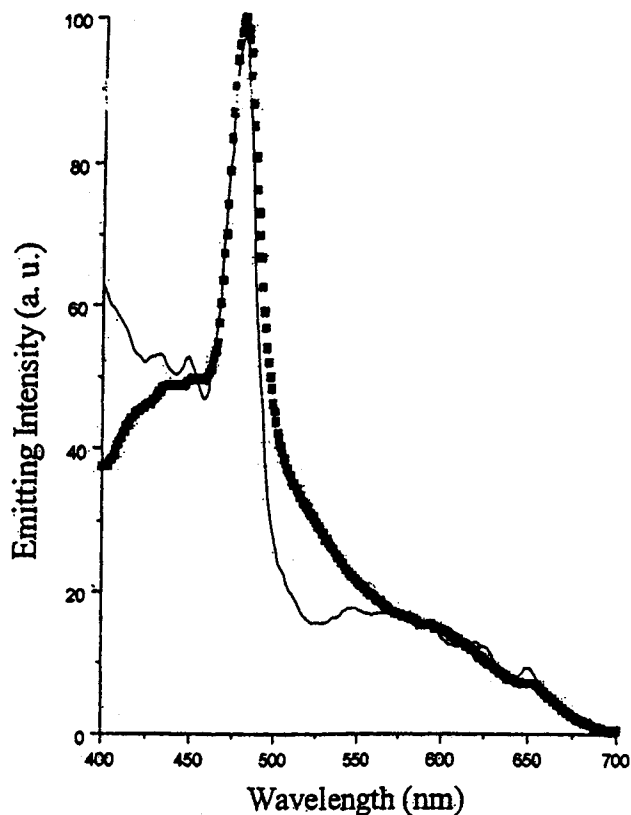
Figure 27. (■ ■ ■) the EL spectrum of the devices at a drive voltage of 10 V. (—) PL spectrum of the Tm-(AcAc)₃phen powder (excitation wavelength 350 nm). (Reprinted with permission from ref 56. Copyright 2002 Elsevier Science).
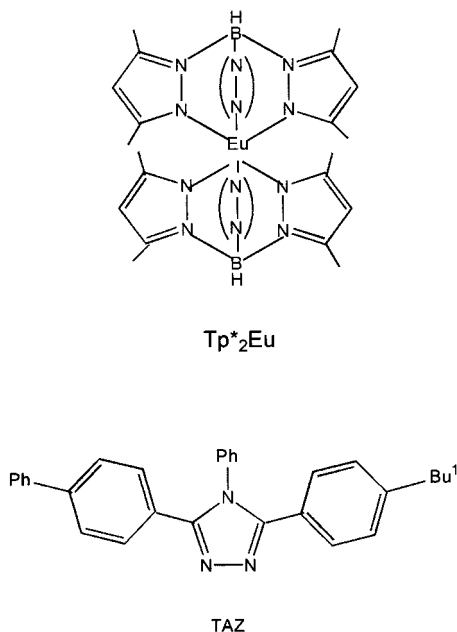

Tp*₂Eu

TAZ

Figure 28. Chemical structures of Tp₂ Eu²⁺ and TAZ. (Reprinted with permission from ref 58. Copyright 2002 Wiley VCH).

VII. Conclusion

Recently, considerable progress has been achieved with OLEDs by utilizing lanthanide metal ions such as Eu and Tb as the emitting layer. However, the quantum efficiency of most of these lanthanide com-plexes is unfortunately still low. This may be mostly due to inefficiency of the energy transfer, particu-larly, triplet−triplet transfer in these lanthanide complexes. Thus, in order to obtain effective and useful OLEDs using lanthanide-based compounds, we must further design ligands which have better energy transfer property to the lanthanide metal ion. Furthermore, the host materials should have effec-tive energy transfer to the lanthanide complexes. For the practical application of the lanthanide metal complexes in OLEDs, further development should be also focused on obtaining lower cost, easier fabrica-tion, and better mechanical and thermal stability of the lanthanide metal complexes.

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