Soluble Europium Complexes for Light-Emitting Diodes

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Soluble rare-earth complexes $LiEu(TTA)_4$, $NaEu(TTA)_4$, and $KEu(TTA)_4$ [TTA = 2-thenoyl-trifluoroacetonato] were synthesized, and their luminescence properties doped in poly(*N*-vinylcarbazole) (PVK) thin films and in different solvents were observed. The results indicate that the emission comes from the Eu^{3+} ion. The photoluminescence spectra of $NaEu(TTA)_4$ are independent of the solvent, with the exception of the luminescence intensity. When $NaEu$-$(TTA)_4$ is doped into PVK films, the luminescence intensity of the Eu^{3+} ion is enhanced with increasing $NaEu(TTA)_4$ concentration in the PVK film. The nature of the cations in the Eu^{3+} complexes does not affect the luminescence performance and processability of the complexes. Single-, double-, and three-layer light-emitting diodes based on PVK doped with $LiEu(TTA)_4$, $NaEu(TTA)_4$, and $KEu(TTA)_4$ as an active layer were fabricated and investigated.

Introduction

High-performance light-emitting diodes (LEDs) that use small organic molecules and polymers as the emissive layer were reported by C. W. Tang[1] and J. H. Burroughes,[2] respectively. Such organic and polymer LEDs have received considerable attention because of their potential application in various displays.[3–8] The organic and polymer devices have shown several advantages over inorganic ones, such as low cost, high luminous efficiency, wide selection of emission colors through the molecular design of organic and polymer materials, and easy processing. Organic and polymer electroluminescence across the whole visible spectrum from blue to red has been demonstrated, and the efficiencies, brightnesses, and device lifetimes are rapidly approaching commercial target figures.[9–17] How-ever, obtaining pure emission colors from conjugated polymers or small organic molecules is difficult because their emission spectra typically have a full width at half-maximum of 100–200 nm, which is not well-suited for actual display applications. On the other hand, in an organic or polymer LED, electrons are injected into the emitting layer from the cathode, and holes are injected from the anode. The recombination of the injected holes with the injected electrons allows the formation of singlet and triplet excitons, the singlet excitons radiatively decaying to produce electroluminescence (EL). Conventional wisdom holds that 75% of recombination events give rise to the triplet excitons, which probably decay nonradiatively with the emission of photons or relax into traps and do not yield any light in organic media. As a result, the maximum internal quantum efficiency for organic or polymer LEDs employing the fluorescence materials is limited to 25%. Recent successful demonstrations of luminescence from organic triplet states has opened a way to very high-efficiency organic LEDs. The red phosphor 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine platinum and the green phosphor tris(2-phenylpyridine) iridium have been used in these LEDs with 4% and 8% external quantum efficiencies, respectively.[18,19]

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Rare-earth complex materials have been widely used in cathodoluminescent display phosphor screens, liquid lasers, and lamps because their photoluminescence exhibits high quantum yields and very sharp spectral bands.[20] These complexes have sharp photoluminescence (PL) spectra that are characterized by the absorption of light energy by the ligand and emission spectra originating from the rare-earth ion.[21] In this case, the ligand absorbs energy, is excited to its singlet state, and, through intersystem crossing, is transformed to the triplet state. Then, the energy is intramolecularly transferred to the energy levels of the central ion, and luminescence is emitted when a transition to the ground state occurs. Recently, to realize an applicable sharp red emission from organic LEDs, some LEDs have been fabricated by using europium (Eu) complexes as an emissive layer because the Eu complexes are known as excellent red phosphors that exhibit intense sharp red emission at around 613 nm.[22-26] However, there are some problems with organic LEDs containing these Eu complexes. The Eu complexes reported so far exhibit poor carrier-transporting ability and film formability, are not volatile enough, and are easily decomposed during vacuum vapor deposition, which is a common technique for fabricating organic electroluminescence (EL) devices. Therefore, in general, conventional rare-earth complexes, such as $Eu(TTA)_3$ (TTA = 2-thenoyl-trifluoroacetonato) and $Eu(TTA)_3(phen)$ (phen = 1,10-phenanthroline) showed quite high photoluminescence efficiency but very low electroluminescence efficiency when they were incorporated into LEDs.[27] Kido and co-workers reported the fabrication of an EL device with Eu complexes as the dopant by spin coating from a solution containing a transporting polymer.[28,29] However, in their case, the solubility of these Eu complexes was poor, and the luminance of the EL devices was low. On the other hand, doping the Eu complexes in a polymer film with good carrier-transporting abilities can improve the carrier-transporting ability and enhance the film formability. Therefore, soluble europium complexes were designed and synthesized to improve the efficiency of red light organic EL devices.

In this paper, as a route to pure red-emitting organic EL devices and the use triplet excited states, we present the synthesis and characterization of Eu complexes and their application in LEDs. These complexes not only display a high luminescent efficiency but also are quite soluble in common organic solvents. The effects of the concentration of $NaEu(TTA)_4$ in poly(*N*-vinylcarbazole) (PVK) films on the photoluminescence (PL) and elec-

troluminescence (EL) properties of $LiEu(TTA)_4$, $NaEu(TTA)_4$, and $KEu(TTA)_4$ are also discussed.

Experimental Section

General Information. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer for C, H, and S determinations. FT-IR spectra of the complexes dispersed in KBr disks were recorded on a Bio-Rad TFs156 spectrometer. The EL spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer with the LED devices forward biased. The ultraviolet−visible absorption spectra were recorded with a General TU-1201 UV−vis recording spectrophotometer. The luminance was measured with an LS-1 portable luminance meter. The current−voltage characteristics were measured with a programmable Solartron 7081 precision voltmeter interfaced to a personal computer through an IEEE488 interface board. Scanning electron microscopy (SEM) was performed with a Hitachi S-530 scanning electron microscope. All measurements were performed under ambient atmosphere at room temperature.

Synthesis: $NaEu(TTA)_4$. HTTA (2-thenoyltrifluoroacetone) (8 mmol) was dissolved in 20 mL of 95% ethanol in a flask and converted to its salt with NaOH. $EuCl_3\cdot6H_2O$ (2.0 mmol) was dissolved in 10 mL of 95% ethanol in another flask. The $EuCl_3\cdot6H_2O$ solution was poured into the HTTA solution with heating, and the mixture was allowed to settle at 60 °C and then stirred for 1h. After being allowed to cool, the precipitate was washed with water. $NaEu(TTA)_4$ was recrystallized from petroleum ether and ethyl acetate (1:1 v/v) to give a yellowish pink powder. The solid product was dried under reduced pressure at 40 °C for 5h.[30] Anal. Calcd for $C_{32}H_{16}F_{12}O_8S_4EuNa$ (%): C, 36.27; H, 1.52; S, 12.10. Found: C, 36.03; H, 1.57; S, 12.44. FT-IR (KBr): 1610, 1358, 860, 723, 425 cm^{-1}.

A similar synthetic procedure was performed for the syntheses of $LiEu(TTA)_4$ and $KEu(TTA)_4$.

$LiEu(TTA)_4$. Anal. Calcd for $C_{32}H_{16}F_{12}O_8S_4EuLi$ (%): C, 36.83; H, 1.55; S, 12.29. Found: C, 36.03; H, 1.57; S, 12.44.

$KEu(TTA)_4$. Anal. Calcd for $C_{32}H_{16}F_{12}O_8S_4EuK$ (%): C, 35.73; H, 1.50; S, 11.92. Found: C, 36.03; H, 1.57; S, 12.44.

Device Preparation. To study the EL behavior of $NaEu(TTA)_4$, LEDs were fabricated by spin coating PVK doped with 1, 3, and 5 wt % of $NaEu(TTA)_4$ from a chloroform solution onto the indium−tin oxide (ITO) glass substrates as an emissive layer, and then layers of an oxadiazole derivative (OXD-7) and aluminum tris(8-hydroxyquinoline) (Alq_3) were grown by means of conventional vacuum deposition. Finally, aluminum was evaporated at 2×10^{-3} Pa as a cathode. The active area of the EL device was 14 mm^2. The absorption and photoluminescence (PL) spectra of $NaEu(TTA)_4$ in PVK thin films were studied using quartz substrates. The structures of the LEDs and the molecular structures used in this study are shown in Figure 1.

Results and Discussion

The complexes $NaEu(TTA)_4$, $LiEu(TTA)_4$, and $KEu(TTA)_4$ are all soluble in common organic solvents, such as chloroform, ethanol, acetonitrile, and acetone.

Optical Properties in Solution. Either in chloroform solution or in the solid state, $LiEu(TTA)_4$, $NaEu(TTA)_4$, and $KEu(TTA)_4$ emit strong red fluorescence under ultraviolet irradiation. Figure 2 shows the absorption and luminescence spectra of $LiEu(TTA)_4$, $NaEu(TTA)_4$, and $KEu(TTA)_4$ in chloroform. The absorption spectrum of $NaEu(TTA)_4$ in chloroform has a maximum at 340 nm with a shoulder at 272 nm, which is similar to the corresponding spectrum of the ligand

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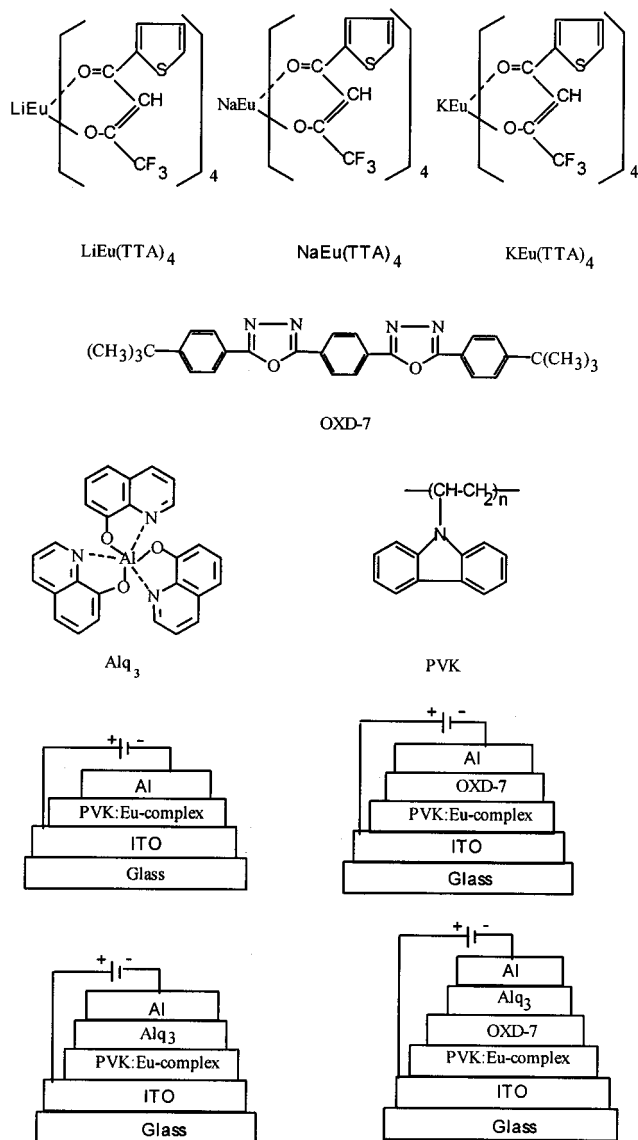(25) Takada, N.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1994**, *33*, 863.
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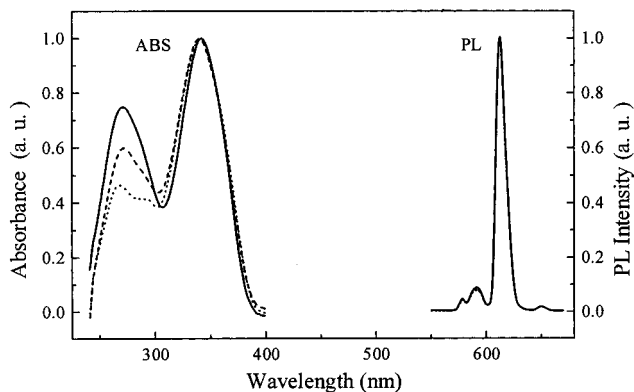(29) Kido, J.; Nagai, K.; Okamoto, Y. *J. Alloys Compd.* **1993**, *192*, 30.

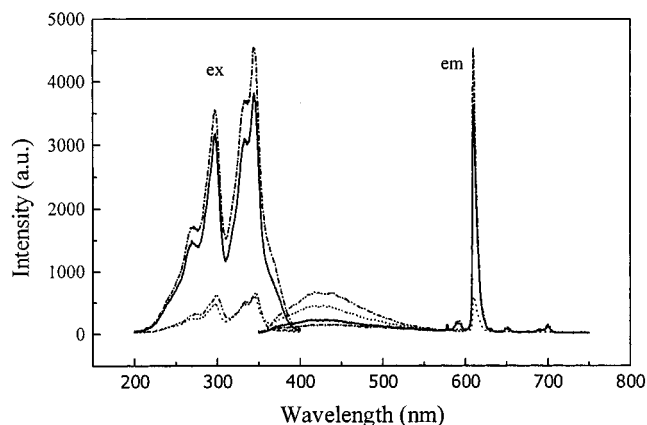(30) Wagner, H. J.; Loutfy, R. O.; Hsiao, C. K. *J. Mater. Sci.* **1982**, *17*, 2781.

Figure 1. Molecular structures of the materials used and LED structures.

Figure 2. Absorption and photoluminescence spectra of LiEu-(TTA)$_4$ (—), NaEu(TTA)$_4$ (– – –), and KEu(TTA)$_4$ (· · ·) in chloroform (10^{-5} M).

Figure 3. PL spectra of PVK thin films doped with NaEu-(TTA)$_4$ (·····, 0; · · ·, 1; —, 3; and –·–·–·, 5 wt %).

TTA. Thus, the absorption spectrum is caused by the $\pi-\pi^*$ transition of TTA. The emission spectrum from the NaEu(TTA)$_4$ complex shows sharp emission peaks due to the electronic energy transitions of Eu^{3+} ion [$^5D_0\rightarrow^7F_0$ (578.4 nm), $^5D_0\rightarrow^7F_1$ (591.4 nm), $^5D_0\rightarrow^7F_2$ (612.8 nm),$^5D_0\rightarrow^7F_3$ (650.4 nm)].[31] The PL spectra for NaEu(TTA)$_4$ (10^{-5} M) were measured in chloroform, ethanol, acetonitrile, and acetone. The PL spectra are similar to the corresponding spectra of the Eu^{3+} ion, but the fluorescent intensities vary with the solvent used [chloroform (25.92), ethanol (34.94), acetonitrile (94.92), and acetone (101.1)]. The higher-dielectric-constant solvent and the coordinating solvent tend to better solvate Na$^+$ ions and prevent aggregation of the europium species, which will produce quenching.

Optical Properties in the PVK Film. To fabricate LEDs by using LiEu(TTA)$_4$, NaEu(TTA)$_4$, and KEu-(TTA)$_4$ as the active emitting layer, we deposited a PVK thin film doped with the Eu complexes from a chloroform solution on an indium–tin oxide (ITO) glass sub-

strate. Therefore, the study of the photoluminescence properties of NaEu(TTA)$_4$ in PVK thin films is useful to understand the electroluminescence mechanism of NaEu(TTA)$_4$. The PL spectra of the PVK thin films doped with NaEu(TTA)$_4$ (1, 3, and 5 wt %) were measured to determine the influence of the NaEu(TTA)$_4$ concentration on the EL spectra (Figure 3). The emission color is pink when the concentrations of NaEu-(TTA)$_4$ are 1 wt % and 3 wt %, because blue emission from PVK is observed in addition to the red emission from NaEu(TTA)$_4$. The PL intensity of the Eu^{3+} ion is enhanced with increasing NaEu(TTA)$_4$ dopant concentration in the PVK thin film with a concomitant reduction of the PL intensity of the PVK thin film, indicating that the degree of energy transfer from PVK to NaEu-(TTA)$_4$ increases with the NaEu(TTA)$_4$ concentration. When the concentration of NaEu(TTA)$_4$ is 5 wt %, only the PL emission from NaEu(TTA)$_4$ is observed, and the PL intensity of the Eu^{3+} ion is the highest. The excitation spectra of the different NaEu(TTA)$_4$ dopant concentrations in the PVK are almost identical to that of PVK. These results indicate that the excitation energy of PVK is transferred to NaEu(TTA)$_4$. To enhance the luminescence efficiency, it is necessary that the excitation energy is transferred from the host molecule to NaEu(TTA)$_4$. The absorption peak of NaEu(TTA)$_4$ is situated at around 250–400 nm, which slightly overlaps with the PL peak (420 nm) of PVK. Therefore, energy transfer from PVK to the complex is possible. The degree of energy transfer depends on the concentration of

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NaEu(TTA)$_4$. At lower concentrations, the energy transfer from PVK to NaEu(TTA)$_4$ is incomplete because the average distance from a photoexcited polymer chain to the complex is too large. At higher concentrations, the energy is effectively transferred to NaEu(TTA)$_4$, but concentration quenching reduces the fluorescence intensity. Thus, a dopant concentration of about 5% is necessary to observe only the luminescence of the complex. Therefore, emission of NaEu(TTA)$_4$ can also be observed from the LED using PVK as a host.

LED Devices. NaEu(TTA)$_4$ was applied as the active material by spin coating in four different types of devices: a single-layer device with ITO/PVK:NaEu-(TTA)$_4$(100 nm)/Al (I); two double-layer devices with ITO/PVK:NaEu(TTA)$_4$(50 nm)/OXD-7(50 nm)/Al (II) and ITO/PVK:NaEu(TTA)$_4$(50 nm)/Alq$_3$(30 nm)/Al (III), and a three-layer device with ITO/PVK:NaEu(TTA)$_4$(50 nm)/OXD-7(50 nm)/Alq$_3$(30 nm)/Al (IV). The doping concentrations of NaEu(TTA)$_4$ are 1, 3, and 5 wt % vs the host material.

When the single-layer LED is forward biased with the ITO electrode at positive polarity, EL emission is observed. When the concentration of NaEu(TTA)$_4$ is 1 or 3 wt %, a pink EL is obtained with maxima at 420 and 613 nm; the blue and red emissions come from PVK (420 nm) and NaEu(TTA)$_4$ (613 nm), respectively. However, a red emission was observed from the single-layer device with a 5 wt % concentration of NaEu(TTA)$_4$. The EL spectrum of PVK disappears, leaving only the EL spectrum of NaEu(TTA)$_4$. The brightness of these diodes is, however, very low, and the EL is barely visible in a dimly lighted room. To improve the diode performance, electron-transporting materials were introduced as PVK is a hole-transporting material. The emission color from the double-layer device using Alq$_3$ is green, and the EL spectrum resembles the PL spectrum of the Alq$_3$ film. Thus, we conclude that the emission originated only from Alq$_3$, and recombination of electrons and holes eventually leads to the formation of Alq$_3$ singlet excited states that then undergo radiative deactivation. For the devices ITO/PVK:NaEu(TTA)$_4$/OXD-7/Al with different concentrations of NaEu(TTA)$_4$, the emission colors are similar to those of the corresponding single-layer devices, i.e., a pink emission is observed when the concentrations of NaEu(TTA)$_4$ are 1 and 3 wt %, and an red emission is observed for 5 wt %. These results indicate that the OXD-7 layer serves as the electron-transporting layer and confines holes and excitons within the PVK layer.

The best results so far are obtained for the following device structure: ITO/PVK:NaEu(TTA)$_4$ (5 wt %)/OXD-7/Alq$_3$/Al. PVK is a hole-transporting material with low electron mobility, and its PL spectrum overlaps with the absorption spectrum of NaEu(TTA)$_4$, enabling efficient energy transfer from the transport material, PVK, to the emitter, NaEu(TTA)$_4$. OXD-7 is a hole-blocking material, and Alq$_3$ is an electron-transporting material. Red electroluminescence was observed from the three-layer devices with 5 wt % concentration of NaEu(TTA)$_4$. Figure 4 shows the EL spectrum of a three-layer LED with a 5 wt % concentration of NaEu-(TTA)$_4$. The EL spectrum is similar to the PL spectrum of NaEu(TTA)$_4$, indicating that the emission originated from NaEu(TTA)$_4$. The excitation mechanism can be
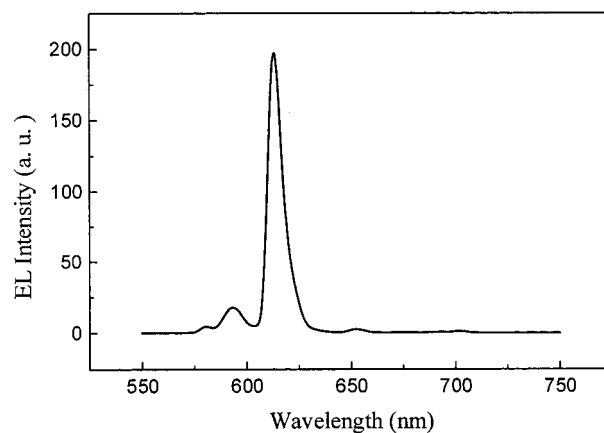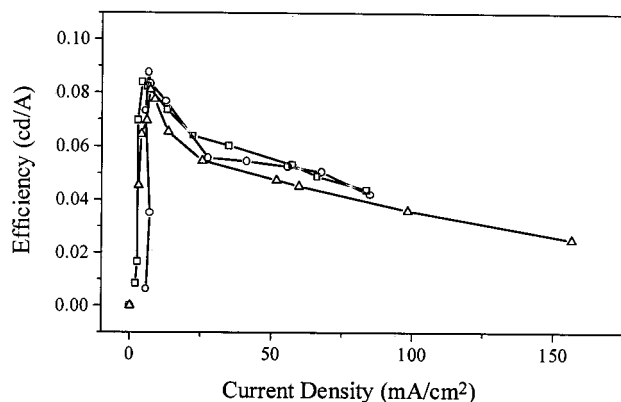

Figure 4. EL spectrum of the three-layer LEDs with 5 wt % concentration of NaEu(TTA)$_4$.
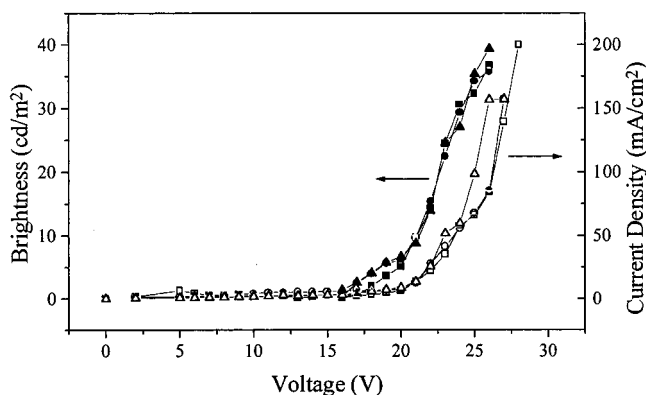
Figure 5. Current density−brightness−voltage characteristics of the three-layer LED with a 5 wt % concentration of LiEu(TTA)$_4$ (○, ●), NaEu(TTA)$_4$ (□, ■), and KEu(TTA)$_4$ (△, ▲).

explained in terms of energy transfer from the host PVK to the complex. It can be assumed that carrier recombination takes place in the hole-transporting PVK layer. As mentioned above, in the photoluminescence of NaEu-(TTA)$_4$ in the PVK films, the luminescence of the complex was observed through the excitation of PVK by energy transfer from PVK to NaEu(TTA)$_4$. Therefore, under EL operation, PVK is first excited by the recombination of the carriers, which are injected from the anode and the cathode, and then the excited-state energy is transferred to NaEu(TTA)$_4$. Singlets and triplets that form on the ligand can be transferred to the Eu^{3+} ion to generate red light. Thus, the color of electroluminescence varies with the doping concentration of NaEu(TTA)$_4$, which affects the degree of the energy transfer from the host PVK to NaEu(TTA)$_4$.

The current density−voltage and brightness−voltage characteristics are shown in Figure 5. It is found that the luminance increases with increasing injection current as well as bias voltage. Luminescence starts at a drive voltage of 12 V, and a bright red light with a maximum luminance of 36.7 cd/m^2 was achieved at 26 V. Compared with the previously reported luminance (0.3 cd/m^2) of a Eu(TTA)$_3$ device,[29] the luminance intensity is drastically enhanced. Such an improvement is due to the employment of PVK as the host, which can enhance the carrier-transporting ability and improve the film formability, because conventional europium complexes show a poor carrier-transporting ability and film formability.

Figure 6. Efficiency−current density characteristics of the three-layer LED with a 5 wt % concentration of LiEu(TTA)$_4$ (○), NaEu(TTA)$_4$ (□), and KEu(TTA)$_4$ (△).

Figure 6 shows the efficiency−current density characteristic of the three-layer LED with a 5 wt % concentration of NaEu(TTA)$_4$. The maximum efficiency of 0.084 cd/A (external quantum efficiency = 0.04%) was observed at 4.3 mA/cm^2. In the low-current-density region, the efficiency increases with an increase in the current density. In this region, the number of holes and electrons and the recombination efficiency increase as the current density increases. After reaching its maximum value, the efficiency decreases with an increase in the current density in the high-current-density region.

The above-described results indicate that PVK serves as a good hole-transporting and host material, and the doping concentration of NaEu(TTA)$_4$ determines the emission color of the LEDs with NaEu(TTA)$_4$ as the emitting material. However, the effective injection of electrons into the PVK layer, by selecting a suitable structure for the device so as to cause the effective coupling of holes and electrons in the PVK layer, is crucial for development of efficient NaEu(TTA)$_4$-based LEDs.

Effect of the Nature of the Cation. Uniform PVK thin films doped with LiEu(TTA)$_4$, NaEu(TTA)$_4$, and KEu(TTA)$_4$ were verified by SEM images. Obviously, the inorganic salts should be substantially incompatible in polymer films, and this raises the question of phase separation in the preparation of the films. However, the organic ligand in the complexes has a good compatibility in the polymer films and leads to the formation of uniform PVK films doped with LiEu(TTA)$_4$, NaEu-(TTA)$_4$, and KEu(TTA)$_4$. The complexes LiEu(TTA)$_4$ and KEu(TTA)$_4$ in organic solvent or in PVK films have a strong red luminescence under ultraviolet irradiation. The absorption spectra of the complexes (Figure 2) have

typical characteristics, with two absorption peaks at 340 and 272 nm, which originate from the absorption of the ligand. For the three complexes, the PL spectra are very similar with four peaks at 578.4 nm, 591.4 nm, 612.8 nm, and 650.4 nm; the luminescent intensities are also the same. Therefore, the nature of the cation does not affect the luminescence performance and processability of the complexes.

To study the effects of the cations on the EL characteristics of the Eu^{3+} complexes, multilayer organic light-emitting diodes using either LiEu(TTA)$_4$ or KEu(TTA)$_4$ as an emission layer, namely, ITO/PVK:LiEu(TTA)$_4$ (5 wt %)/OXD-7/Alq$_3$/Al and ITO/PVK:KEu(TTA)$_4$ (5 wt %)/OXD-7/Alq$_3$/Al, were also fabricated. The results are shown in Figures 5 and 6. All of the complexes have similar EL properties. The EL efficiencies of the devices with LiEu(TTA)$_4$ and KEu(TTA)$_4$ are 0.087 and 0.081 cd/A, respectively, which are the same as that of NaEu-(TTA)$_4$.

Conclusions

Soluble luminescent rare-earth complexes NaEu-(TTA)$_4$, LiEu(TTA)$_4$, and KEu(TTA)$_4$ with narrow emission bands were synthesized, and the luminescence properties of these complexes in PVK thin films and in different solvents were studied. The emission is generated from the Eu^{3+} ion. The use of different solvents does not affect the photoluminescence spectra of NaEu-(TTA)$_4$, but the fluorescence intensities change with the solvent polarity. When NaEu(TTA)$_4$ is doped into a PVK thin film, the luminescence intensities of the Eu^{3+} ion are enhanced with increasing NaEu(TTA)$_4$ concentration. The electroluminescent properties of NaEu(TTA)$_4$ were studied in single-, double-, and three-layer light-emitting diodes. A red LED has been successfully fabricated utilizing the emitter material NaEu(TTA)$_4$, and a maximum luminance of 36.7 cd/m^2 was achieved. NaEu(TTA)$_4$, LiEu(TTA)$_4$, and KEu(TTA)$_4$ give similar luminescence performance, EL results, and processability.

Supporting Information Available: SEM images of (a) PVK thin films doped with (b) LiEu(TTA)$_4$, (c) NaEu(TTA)$_4$, and (d) KEu(TTA)$_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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