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New Narrow-Band Luminescence Using Lanthanide Coordination Compounds for Light-Emitting Diodes

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SUMMARY For ternary system, both anionic carboxylate ligand, namely, 4,4'-oxybis(benzoic acid)(H_2oba) and different auxiliary ligand, namely, 1,10-phenanthroline(Phen), pyrazino[2,3-f][1,10]phenanthroline (dpq) and 1H-imidazole[2,3-f][1,10]phenanthroline(IP) have been designed and employed for the construction of a series of lanthanide compounds (Tb^{3+}, Eu^{3+}). The results of photoluminescence spectra of the compounds show the different optimal excitation spectra that make it closer to UV/Blue range.

key words: *LED, high (wide) color gamut, new phosphor, organic-inorganic hybrid, narrow emission*

1. Introduction

Solid state lighting based on white light emitting diodes (LED) are well known for display devices and the inorganic phosphors have a great attention for their useful advantages in the devices [1]. Inorganic phosphors are exact materials for blue-chip excitation with intensive luminescence and high reliability. However, the conventional phosphors for LEDs have been difficult to make high color gamut because of the limitation to the ability of color reproduction and have re-absorption due to the wide band width [2]. Furthermore, the synthesis conditions of the phosphors need high temperature, pressure, etc [3]. In recent years, great efforts and time have been studying in making the successful devices or materials to overcome these problems. There has been a growing interest in the luminescence properties of lanthanide coordination polymers because of their potential use such as catalysis [4], luminescence [5], magnetism [6] and gas storage [7]. Especially, Eu^{3+}, Tb^{3+} and Sm^{3+} ions have excellent luminescence properties, but their excitation bands are weak and narrow. In order to enhance excitation spectrum, lanthanide (Ln^{3+}) ions are usually coordinated with ligands that have broad intense excitation bands and can red-shift of excitation spectrum to UV/Blue range [8]. In these systems intense ion luminescence originates from the intramolecular energy transfer through the excited state of the ligand to the emitting level of the lanthanide central ions that give a sharp narrow spectral character [9]. In this study, we introduce a new lanthanide coordination compounds composing of lanthanide ions (Ln^{3+} = Eu^{3+}, Tb^{3+}) and specific organic ligands to exhibit sharp and narrow red and green colored emission, respectively, by near UV chip (400nm) for WLEDs. We also demonstrate that this approach showed the possibility to be the ideal phosphors for LEDs.

2. Experimental

Materials. Chemicals were purchased from Sigma Aldrich. All chemicals used without further purification

2.1 Synthesis of [Tb(Phen)(oba)(Hoba)]n

(Compound 1, H_2**oba** = 4,4'-oxybis(benzoic acid))

A mixed solution was prepared by dissolving $Tb(NO_3)_3 \cdot 5H_2O$(0.2mmol), H_2**oba**(0.3mmol) and Phen(0.5mmol) in deionized water and stirred for 20 min in the air. The mixture was transferred into 50mL Teflon-lined reactor and kept at 160°C for 40h, then cooled to room temperature. The product showed light yellow color under natural light was obtain after washed with ethanol and dried at 70°C for 3h in an oven.

2.2 Synthesis of [Tb(dpq)(oba)(Hoba)]n (2)

Compound 2 was prepared in the same way as that of (1) except that adding 0.3mmol of dpq.

2.3 Synthesis of [(Tb)(IP)(oba)(Hoba)]n (3)

Compound 3 was prepared in the same way as that of (1) except that adding 0.3mmol of IP.

2.4 Synthesis of [(Eu)(Phen)(oba)(Hoba)]n (4)

A mixture of $Eu(NO_3)_3 \cdot 5H_2O$(0.5mmol), H_2**oba** (1mmol), Phen(0.5mmol) and water (50ml) was stirred for 20min in the air. The mixture was transferred into 50mL Teflon-lined reactor and kept at 150°C for 50h, then cooled to room temperature. The product showed yellow color under natural light was obtained after washed with ethanol an dried at 70°C for 3h in an oven.

2.5 Synthesis of [Eu(dpq)(oba)(Hoba)]n (5)

Compound 5 was prepared in the same way as that of (1) except that adding 0.5mmol of dpq.

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2.6 Fabrication of a Simple LED Assembly

A red LED was prepared by dripping the compound **5** of 5wt% with silicon encapsulment on a commercially available LED chip (λex = 400nm). The LEDs were evaluated at 3.0V with currents of 60mA.

2.7 Characterization

The solid-state luminescent spectra were obtained with a DARSA PRO-5200 SYSTEM (Xe lamp, 500W).

3. Result and Discussion

3.1 Photophysical Properties of Green Compounds 1-3

The luminescence excitation and emission spectra of compounds 1-3 that are solid powder samples are shown in Fig. 1. Figure 1 (a) shows that the emission spectra of compound 1-3 upon excitation at 400 nm consist of sharp lines within the 450-700 nm range. These spectra are composed of the typical Tb^{3+} green emission, corresponding to $^5D_4 \rightarrow {}^7F_J$ (J = 0-6) levels of Tb^{3+} ions [10]. The main emission peak at 545nm is due to the $^5D_4 \rightarrow {}^7F_5$ transitions of Tb^{3+}; the peak at 487 nm is attributed to $^5D_4 \rightarrow {}^7F_6$ transitions; and the peaks at 580 and 620 nm are due to the $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions of Tb^{3+}. Figure 1 (b) shows the excitation spectrum of the compound 1-3 recorded at 298K in the 300–450nm range by monitoring the Tb^{3+} emission from the $^5D_4 \rightarrow {}^7F_5$ transition at around 545nm, which matches well with near UV chip of the 400 nm. Interestingly, the excitation spectra of the compounds 1-3 have an obvious red-shift. The excitation spectra of compound 1-3 exhibit a broad band between 300 and 400nm which is definitely originated from the different coordination environments caused by the different auxiliary ligand of compounds. The compounds 1-2 have weak luminescence upon excitation at 400nm because of barely excitation spectra around near UV range, but the compound 3 exhibits an intense, characteristic green Tb^{3+} emission. General phosphors with lanthanide ions formed small absorption regions because of forbidden character of f-f transition. However, a slight red shift is discernible in the optimal excitation of the compound 1-3 that is from 300 to 400nm, which could be ascribed to the perturbation induced by Ln^{3+} coordination.

For ternary systems, both anionic and neutral ligands can serve as the antenna effect to harvest and transfer energy to Ln^{3+}. They contain two distinct coordination domains, one from anionic carboxyl group which is called main ligand and another from neutral phen-based ligands domain which is called auxiliary ligand.

Commonly, an anionic ligand have to suitable triplet energy to meet Latvia's empirical rule that is an optimal ligand-to-metal energy transfer process for Tb^{3+} and Eu^{3+} about $\Delta E(T\text{-}{}^5D_j)$ in gate 2100-4500 cm^{-1} [11], and an auxiliary ligand should have suitable excited levels to support energy transfer to anionic ligand and Ln^{3+}. The singlet energy($^1\pi\pi^*$) levels of phen(29,000 cm^{-1}), dpq(28,000 cm^{-1}), and triplet energy($^3\pi\pi^*$) levels of phen (22,100 cm^{-1}), dpq(24,000cm^{-1}) were found from the literatures. Based on this experimental results, it is suggested that the red shifted excitation of compound 1-3 originated from the π-π^* electronic transition of auxiliary ligand that can easily be extended conjugated system. The different auxiliary ligands can make it to relocate the energy from organic linkers to metals and the triplet energy level of auxiliary ligands are obviously higher than the $^5D_4$ level (21000 cm^{-1}) of Tb^{3+}, and its energy gap $\Delta E({}^3\pi\pi^* - {}^5D_4)$ between ligand and metal-centered levels is too high to allow an effective back energy transfer. In this case, the ligand in coordination polymers absorbs the light and transfers the energy to the lanthanide ions. Therefore, the compounds have wide excitation bands with sharp emission. This optical property in the compounds is so-called antenna effect. Both emission spectra show enhanced bright and narrow green light at the same wavelength at about 545 nm, but both bands can be distinguished in the intensity of luminescence and excitation spectra of the materials, 1 which contains Phen described the excitation band with a maximum at about 340nm and the main excitation peak of 2 is about 365 nm and of 3 is about 400 nm (Fig. 1 (b)). The different excitation spectra are attributed to the energy differences from the auxiliary ligands. High conjugated ligands such as dpq, IP make the main peak of excitation shift to the longer

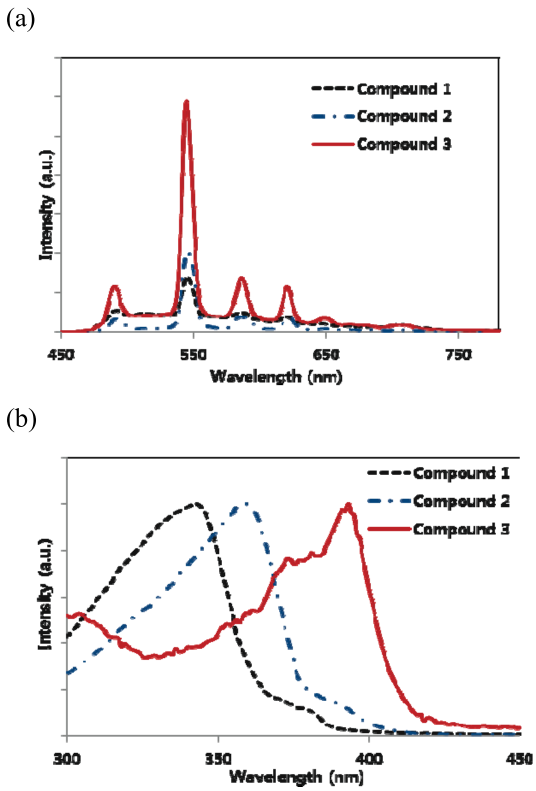

Fig. 1 Compounds 1-3 of emission spectra (excited at 400 nm) for (a) and normalized excitation spectra for (b) (both monitored at 545 nm)

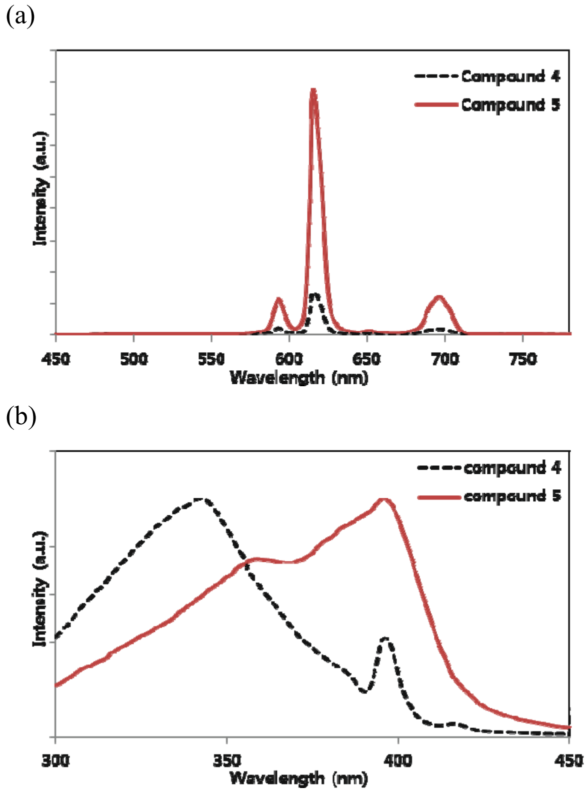

Fig. 2 Compounds 4-5 of emission spectra (excited at 400 nm) for (a) and normalized excitation spectra (both monitored at 615 nm) for (b)

wavelength.

3.2 Photophysical Properties of Red Compounds 4-5

Compound 4 composed of 4,4'-oxybis(benzoic acid), Eu^{3+} ion and 1,10-phenanthroline by method reported previously and Compound 5 are easily synthesized by modified the method of compound 4 [12]. The photoluminescence properties of the solid powder samples of compound 4-5 were investigated by the condition with compound 1-3 but the results are not the same as that of green compounds. The materials show various luminescent phenomena derived from chemical building blocks such as ligands and metals or interactions between components [13]. Figure 2 (a) shows that the emission spectra of compound 4-5 upon excitation at 400nm appear in the range of 570-705 nm with sharp lines. It displays intensity red luminescence and the characteristic f-f transition of Eu(III) ions that have the $^5D_0 \rightarrow {}^7F_J (J = 0\text{-}4)$ transitions. The sharp emission at 613nm of the Eu^{3+} ion from $^5D_0 \rightarrow {}^7F_2$ was observed accompanied by weak emission corresponding to emissions at 579, 594, and 643 nm that are attributed to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ respectively [14]. According to the above experimental results, the auxiliary ligands of phen and dpq have higher triplet energy level that is over $22000 cm^{-1}$ than the $^5D_0$ level($17000 cm^{-1}$) of Eu^{3+}, which is in the range proposed for optical ligand-to-Eu^{3+} energy transfer. The quantum yield of the compound, evaluated under 400nm at room temperature, was 22%, which is lower than inorganic phosphors, but our group has found that quantum yield can be improved by using modified ligands [11].

Table 1 Important optical parameters of compound **5**

	Excitation main peak	Emission main peak	QuantumYield
Compound 5	400nm	613nm	22%

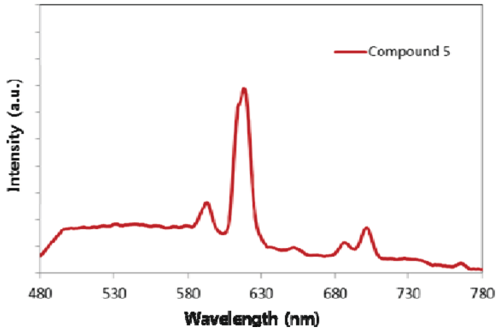

Fig. 3 Emission spectrum of compound **5** (excited at 450nm)

Figure 2 (b) shows that the excitation spectra of compound 4-5 exhibit broad bands from 300 to 450 nm which is attributable to the auxiliary ligands of aromatic moiety. Compared to compound 4 under 300-400nm excitation, compound 5 has the broad band with a maximum at 400nm. (Fig. 2 (b)). Obviously, the spectrum of coumpound 5 is more red-shifted due to the energy level of auxiliary ligands.

The different singlet energy level of auxiliary ligands between phen($29{,}000 cm^{-1}$) and dpq($28{,}000 cm^{-1}$) made it near-UV excitation and it can become a good candidate for blue LED. Figure 3 shows that the emission spectra of compound 5 upon excitation at 450 nm. The research is still continued to shift the excitation range from near UV region to 450 nm used in blue LEDs.

3.3 Fabrication and Performance of LED of Compounds 5

To evaluate the PKG device fabrication of LEDs of compound 5, we made red LEDs by combining UV chips (400nm) and Compound 5. The PL spectrum of compound exhibits emission maxima at 613nm. When we collected the brightness and PL spectra of the LEDs under multiple weights(%) of 5wt%, 10wt% and 15wt%, the compound had (0.262, 0.088), (0.405, 0.188) and (0.485, 0.250), representatively, marked in CIE 1931. The color of packages shifts to red when changing weights of compound. However, at Cx of compound, the color shifts less towards red, because the portion of UV chip light is dominant. Photographs and spectrum of the fabricated LED, which are 5wt% compound, are shown in Fig. 4.

4. Conclusion

We have developed Organic-inorganic hybrid materials

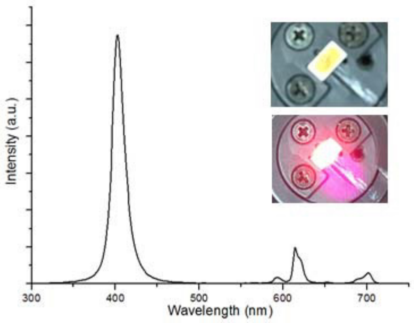

Fig. 4 Photoluminescent (PL) spectrum of 5wt% compound under 60mA drive current a.u., arbitrary units

from metal nitrates, auxiliary ligands and main ligands by hydrothermal methods. The Materials have narrow photoluminescence to protect re-absorption. Furthermore, Preparing the LEDs with purchasable UVLED chips and silicon encapsulant showed its potential for use as luminescent display material. We are certain that we can also fabricate the white LEDs with the developed red and green compounds in a well-controlled manner. We found that we can shift the excitation spectrum. We are under study about shifting the excitation from near UV region to blue (450 nm) by changing the ligands or metals.

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