

# Lanthanide Coordination Phosphors for Next Generation LED Displays

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## ABSTRACT

Lanthanide coordination phosphors, which are composed of  $\pi$ -conjugated ligands with light absorption ability and rare-earth ions as luminescent centers, are next-generation organic-inorganic phosphors that can simultaneously achieve pure color purity with strong emission. In this paper, we would like to introduce the possibility of designed coordination phosphor series as candidates for LCD backlights and miniLED displays.

## 1 Introduction

Luminescent lanthanide coordination compounds with thermal and chemical stability have attracted attention as an old yet new phosphor system that can be used in a variety of luminescent applications, including light-emitting diode (LED) displays [1], security inks [2], and wavelength conversion materials for solar cells [3]. In particular, europium- and terbium-based coordination compound phosphors, which have visible high color purity and luminosity with strong UV to blue light absorption ability, are expected to play an active role as advanced nanoscale high-brightness phosphors, similar to quantum dots, in next-generation display phosphor applications using micro-LEDs and mini-LEDs as excitation light sources.

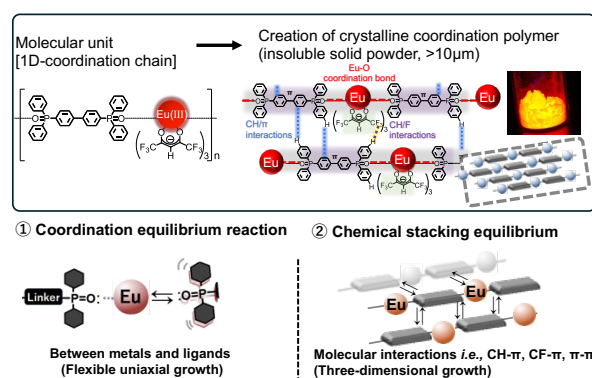
Here, a series of coordination compound phosphors composed of lanthanide and organophosphine oxides-based ligands that combine high luminescence efficiency and chemical stability is described [4, 5]. Among the various coordination phosphor system, crystalline  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$ , (hfa:hexafluoroacetylacetonate and dpbp:4,4'-bis(diphenylphosphoryl)biphenyl) polymers composed of  $\pi$ -conjugated planar bridging ligands are particularly promising LED phosphors that exhibit excellent thermal stability ( $>300^\circ\text{C}$ ) and internal quantum efficiency [6]. However, there are various problems for its application. As an example, these thermally durable coordination phosphors are obtained as large crystalline powders of several tens of micrometers that are insoluble in any organic solvents, making it difficult to use them as the nano-sized phosphors required for next-generation LED-displays. If chemically stable coordination phosphors with morphology controllability including size distribution, could be realized, they are expected to be promising next-generation sub-micro-sized phosphor candidates similar to quantum dot systems. In this paper, we would like to introduce specific examples of lanthanide coordination

compound phosphors for next-generation LED display applications, as well as their characteristics and feasibility. Firstly, we will introduce the shape controllability of polymer crystals of thermally durable coordination phosphors using the above compound examples crystalline  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$  phosphor [7]. We will also introduce its optical properties from the perspective of LED mounting. The obtained results on the structural tunability of these materials can be used for the development of new phosphor techniques for nanoscale materials based on crystalline lanthanide-based coordination phosphors.

## 2 Results and Discussion

### 2.1 Structural tunability of crystalline coordination polymer phosphors and their photophysical properties

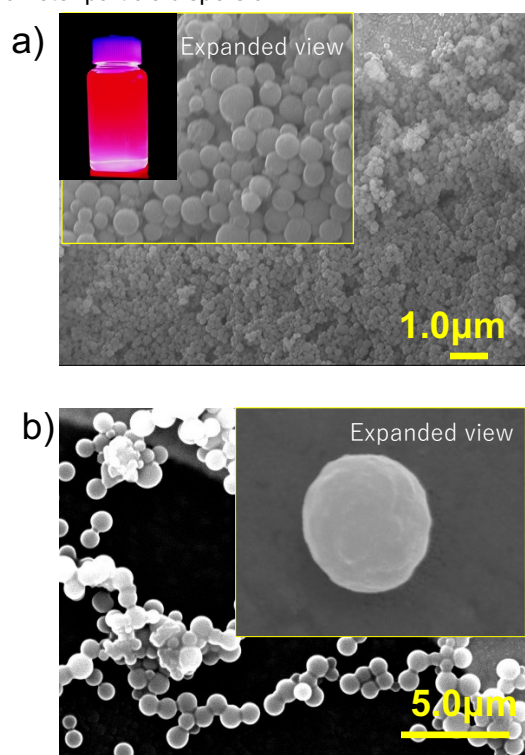
To realize thermostable crystalline coordination phosphors for next-generation LED applications using sub-micro-sized phosphors, it is important to understand the basic morphology controllability including size, and to elucidate their optical properties. Fig. 1 shows the crystallization process of  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$  polymer phosphors.



**Fig. 1 Formation process for  $[\text{Eu}(\text{hfa})_3(\text{dpbb})]_n$  polymer**

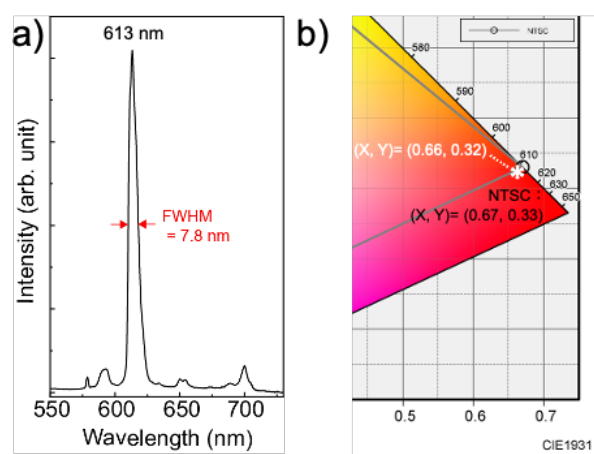
The formation process consists mainly of two equilibrium reactions: 1. Coordination equilibrium reaction between the metal and the ligand, and 2. Chemical stacking equilibrium due to CH- $\pi$  and CF- $\pi$  interactions acting between molecules (polymer chains). Such complicated crystal growth mechanisms in crystalline coordination polymers offer new possibilities

in materials chemistry. Mirkin and coworkers reviewed the structural tailorability and functionality of coordination polymers with transition metals and revealed the freedom in material design of coordination compounds [8]. We have also shown that a simple and effective way to control their morphology is by changing the chemicals and organic solvent conditions used during the coordination reaction [7, 9]. Fig. 2a) shows a spherical phosphor with an average particle size of  $\sim 200$  nm as a typical example [7]. It has been found that by utilizing the difference in the two equilibrium reaction rates of lanthanide coordination polymer formation shown in Fig. 1, the solid form of the resulting molecule can be significantly changed. These spherical phosphors are microscopic, ranging from a few 10 nm to sub-micrometers, and their average size varies with reaction time. Fig. 2 shows a SEM image to show the change in the average particle diameter as the reaction time increases. Under these conditions, spherical particles with a size distribution of 0.8-1.0  $\mu\text{m}$  can be obtained. These are consisted of the aggregations of nanosized coordination polymer crystal grains, and their chemical durability and optical properties are equivalent to the insoluble large crystalline state of several 10 micrometers. In addition, they are highly dispersible in many solvents due to their surface activity and the spherical form and shows a high optical transparency even in the sub-micrometer particle dispersion.



**Fig. 2** FE-SEM images of representative samples, which prepared under dilute solvent, 250 mL MeOH, a) reaction time 6 h, and b) 10 h

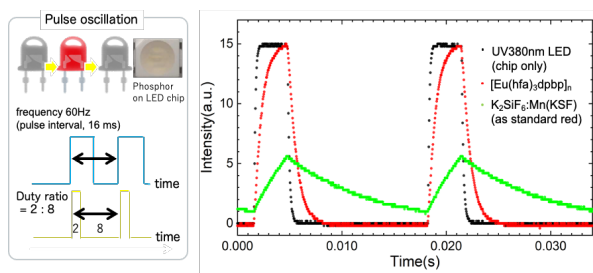
In general,  $\text{Eu}^{3+}$ -activated phosphors are known to exhibit sharp luminescence based on 4f-4f electronic transitions with a closed shell structure. However, in the case of Eu, since there is selectivity for electronic transition from the starting level of light emission  $^5\text{D}_0$  to  $^7\text{F}_j$  ( $j = 0, 1, 2, \dots$ ), it exhibits multiple sideband emissions, which is a factor that reduces color purity and output efficiency. A feature of the Eu coordination compound shown here is that the coordination structure around europium is asymmetric because bulky three-dimensional organic molecules such as  $\beta$ -diketones and phosphine oxide coordinate to the lanthanide ion. As a one of the photophysical properties [7], the photoluminescence spectrum and local CIE 1931 chromaticity coordinates is shown in Fig. 3. Line emission peaked at 613 nm was observed, and the FWHM of the spectrum was 7.8 nm. The internal quantum efficiency ( $\Phi_{\text{Ln}}$ ) of spherical form  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$  was estimated to 75%. The red coordinate point (x, y) calculated from the spectrum is (0.66, 0.32), which is comparable to the NTSC standard (0.67, 0.33). We believed that this feature, which shows a single, sharpened spectrum, is a feature not seen in other inorganic Eu-phosphors.



**Fig. 3** PL spectrum and CIE 1931 chromaticity coordinates for spherical  $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$  polymer with crystallinity

## 2.2 LED drive properties using Eu-coordination compound phosphor

For the display standard using next-generation Mini LEDs and  $\mu\text{LEDs}$ , the afterglow luminescence under pulse drive is an important issue. For conventional backlight for LCD (liquid crystal display)-applications, only the achievements of color gamut and emission efficiency were important. However, in recent years, phosphor-LEDs have been operated in pulses with high refresh rates ( $>80\text{Hz}$ ) to make high-speed images look clear and local dimming to achieve vivid blacks. In the



**Fig. 4 Photo emission intensity-time change behavior due to pulse oscillation drive, 60 Hz of prepared red-LED using  $[\text{Eu}(\text{hfa})_3\text{dppp}]_n$  phosphor and standard red phosphor, KSF:Mn for LCD displays**

use of phosphor LEDs using quantum dots which have been put into practical use in recent years, the above problems do not arise because the phosphors have essentially short fluorescence lifetimes under nano second order. In contrast, KSF:Mn phosphor, which conventionally used for the red color component of white LEDs in LCD backlights, showed a suitable color gamut for human eyes and emission efficiency, however, it has a long fluorescence decay lifetime,  $>5$  ms, making it difficult to use LED pulses driven. Therefore, when using europium coordination compound phosphors as a next-generation nanophosphors, to evaluate the pulse drive properties became important. Fig.4 shows the pulse drive properties of the red LEDs composed of KSF red phosphor, and the obtained  $[\text{Eu}(\text{hfa})_3\text{dppp}]_n$ . As the experimental conditions, a frequency, 60-120 Hz was selected, which is a typical LCD refresh rate, and the changes in the afterglow intensity were observed over time. Wavelength selection was performed using a bandpass filter. It can be seen that the light intensity changes of KSF:Mn, which has a long fluorescence decay lifetime, are not able to follow the ON/OFF pulse of the LED drive 60Hz. When  $[\text{Eu}(\text{hfa})_3\text{dppp}]_n$  was used as a phosphor, the fluorescence lifetime was at around 700  $\mu\text{s}$ . A slight afterglow was observed in the intensity change over time. Estimating from the specific fluorescence decay lifetime, it was found that the emission intensity can follow changes in the excitation LED up to a frequency of about 100-120Hz, which is approximately twice as high. Here,  $[\text{Eu}(\text{hfa})_3\text{dppp}]_n$  spherical phosphors are shown as an example of coordination compound phosphors for LEDs. This example shows that a series of molecular lanthanide coordination compound phosphors have a narrow line width  $<8$  nm, monochromatic emission, and optical functionality not found in conventional inorganic phosphors, making them, like quantum dots, useful candidates for next-generation phosphors. In addition, the knowledge obtained regarding the structural tunability of  $[\text{Eu}(\text{hfa})_3\text{dppp}]_n$  are expected to be widely used for the development of synthesis techniques for nanoscale materials for crystalline lanthanide coordination phosphors.

### 3 Conclusion

In conclusion, we have introduced the tunability of the morphology of  $[\text{Eu}(\text{hfa})_3(\text{dppp})]_n$  with high thermal stability and obtained nano- and micro-sized spheres. The formation of spherical particles composed of nano-sized crystalline polymers showed size tunability through a simple reaction time dependence. In addition, excellent photophysical properties were achieved. We believe that morphology-controllable lanthanide coordination compound phosphors are promising materials for next-generation nanophosphors such as mini-LEDs and micro-LEDs.

### References

- [1] L. Shuaibing, L. Zhou, H. Zhang, "Investigation progresses of rare earth complexes as emitters or sensitizers in organic light-emitting diodes," *NPG Light. Sci. Appl.*, 11, 177 (2022).
- [2] V. V. Utochnikova, et al., "Lanthanide Tetrafluoro terephthalates for Luminescent Ink-Jet Printing," *Eur. J. Inorg. Chem.*, 48, pp.5635-5639 (2017).
- [3] B. McKenna, R. C. Evans, "Towards efficient spectral converters through materials design for luminescent solar devices," *Adv. Mater.*, 29, 1606491 (2017).
- [4] Y. Hasegawa, Y. Kitagawa, T. Nakanishi, "Effective photosensitized, electrosensitized, and mechano-sensitized luminescence of lanthanide complexes," *NPG Asia Mater.*, 10, pp.52-70 (2018).
- [5] Y. Hasegawa, T. Nakanishi, "Luminescent lanthanide coordination polymers for photonic applications," *RSC Adv.*, 5(1), pp.338-353 (2015).
- [6] K. Miyata, T. Kobayashi, Y. Hasegawa, et al., "Thermostable organo-phosphor: low-vibrational coordination polymers that exhibit different intermolecular interactions," *ChemPlusChem.*, 77, pp.277-280 (2012).
- [7] T. Nakanishi, Y. Hirai, T. Takeda, et al., "Structural metamorphosis and photophysical properties of thermostable nano- and microcrystalline lanthanide polymer with flexible coordination chains," *Sci. Technol. Adv. Mater.*, 24, 2183711 (2023).
- [8] M.S.Alexander, C.A.Mirkin et al., "Infinite coordination polymer nano- and microparticle structures," *Chem Soc Rev.*, 38, pp.1218-1227 (2009).
- [9] H. Onodera, Y. Kitagawa, T. Nakanishi, et al., "Acid-protected Eu (iii) coordination nanoparticles covered with polystyrene," *J Mater Chem C*, 4, pp.75-81(2016)