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Size-Control Synthesis and Luminescence Properties of the Eu(III) Coordination Particles

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ABSTRACT

The particle-size control synthesis and photophysical properties of Eu(III) coordination polymers $[Eu(hfa)_3(m\text{-dpb})]_n$ (hfa: hexafluoroacetylacetonato, *m*-dpb: 1,3-

bis(diphenylphosphoryl)benzene) were reported. The Eu(III) coordination polymers were prepared by complexation of $[Eu(hfa)_3(H_2O)_2]$ and linker *m*-dpb ligand in a aqueous micelle solution using cationic CTAB (cetyltrimethylammonium bromide) and anionic SDS (sodium dodecyl sulfate) surfactants. The size of Eu(III) coordination polymers was gradually decreased by increasing CTAB concentrations. The crystal structure formed in a micelle system was different from bulk coordination polymers. The Eu(III) coordination particles showed smaller non-radiative rate constant than bulk coordination polymer. In this study, size-control and luminescence properties of the Eu(III) coordination particles have been demonstrated.

INTRODUCTION

Luminescent lanthanide complexes have attracted much attention as luminescent materials because of their narrow full width of half maximum (FWHM) and long emission lifetimes based on their 4f-4f transitions.[1-3] Their effective luminescence properties are promoted by photo-sensitized energy transfer from π-conjugated organic ligands, called antenna ligands, to lanthanide ions.[3] Luminescent lanthanide complexes have been expected to be applied to future display and imaging materials.[4,5]

Lanthanide coordination polymers composed of lanthanide ions and linker ligands have been recently focused on their three-dimensional structures with dense packing structures[6]. Luminescent lanthanide coordination polymers have characteristic thermo-durability properties. Temperature-dependent color changeable luminescence was also observed in lanthanide coordination polymers with red luminescent Eu(III) and green luminescent Tb(III) ions.[7,8] The luminescent lanthanide coordination polymers have potential applications as luminescent materials with temperature and molecular sensing properties.[2,5,9-12]

The nano- and micro-sized crystals of lanthanide coordination polymers exhibit a large specific surface and high dispersibility in water and organic media.[13,14] The lanthanide coordination polymers are generally prepared by the chemical equilibrium, which is

different from organic polymer preparation. The reaction control of lanthanide coordination polymers is a key factor for the preparation of nano- and micro-sized crystals. Xu et al. demonstrated nanocrystal growth and theoretical calculations of Eu-fumarate coordination polymer with CTAB (cetyltrimethylammonium bromide) using experimental and theoretical approach.[15]

Here, characteristic photophysical properties of the size-controlled Eu(III) coordination particles with high emission quantum yield are reported. The Eu(III) coordination particles are composed of photo-sensitized hfa (hexafluoroacetylacetonate) ligands and *m*-dpb (1,3-bis(diphenylphosphoryl)benzene) linkers. $[Eu(hfa)_3(m\text{-dpb})]_n$ was selected on two perspectives; *m*-dpb is suitable to synthesize coordination polymer in micellar condition on account of their solubility. The other reason is that $[Eu(hfa)_3(m\text{-dpb})]_n$ exhibits high luminescence with a high quantum yield, making it easy to evaluate its photophysical properties[16]. The Eu(III) coordination particles, $[Eu(hfa)_3(m\text{-dpb})]_n$, were synthesized by the reaction of $[Eu(hfa)_3(H_2O)_2]$ with *m*-dpb linkers in micellar solution with cation and anion surfactant, CTAB and SDS (sodium dodecyl sulfate) according to our previous report (Figure 1).[17] CTAB -SDS micelles were chosen because they are easy to adjust micelle size[18] and $[Eu(hfa)_3(H_2O)_2]$ can be dispersed in SDS solution. Their particle size and morphology of $[Eu(hfa)_3(m\text{-dpb})]_n$ were observed using

scanning electron microscopic (SEM) measurements. The coordination structures were analyzed by the single and powder X-ray structural analyses. Their luminescence properties were evaluated using the emission spectra and lifetimes. The bulk crystal structure was hardly formed by micelle method, and size-controlled particles of the Eu(III) coordination polymers showed smaller non-radiative rate constant than bulk coordination polymer. In this study, characteristic luminescent the Eu(III) coordination particles have been demonstrated.

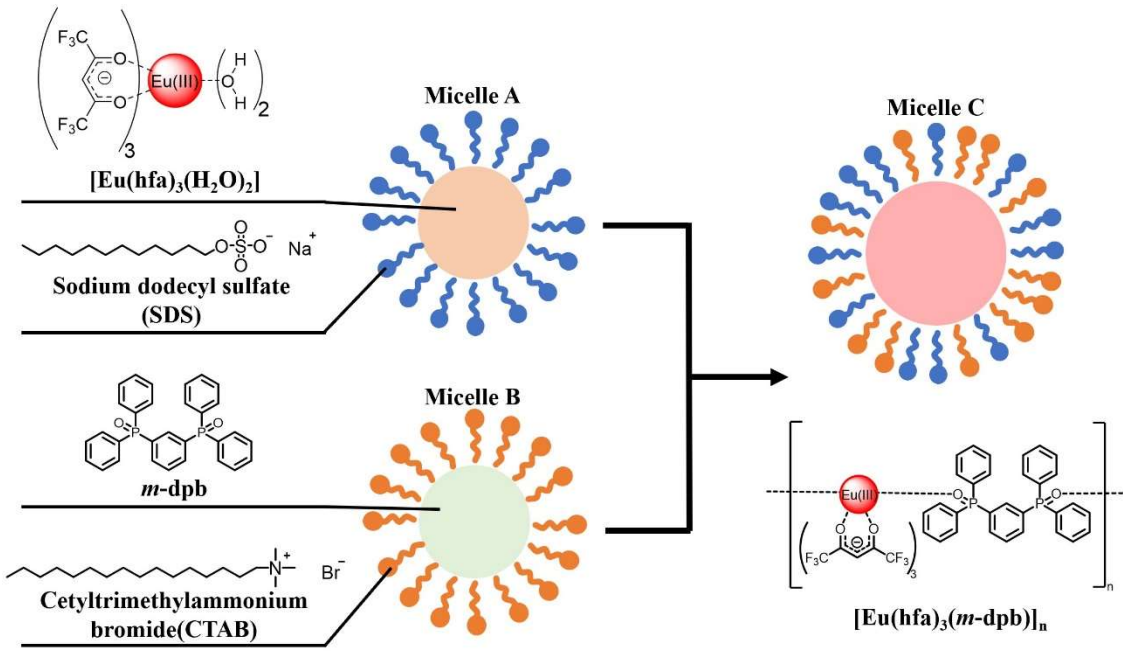

Figure 1. Synthesis of $[Eu(hfa)_3(m\text{-dpb})]_n$ particles using a micelle method.

EXPERIMENTAL METHODS

General Methods: All chemicals were of reagent grade and used without further purification. ^{1}H NMR (400 MHz) spectra were recorded on a JEOL ECS400 at 298 K. Tetramethylsilane (δ_H = 0.00 ppm) was used as an internal reference. Electronic spray ionization mass spectra (ESI-MS) were measured using a JEOL JMS-T100LP. Elemental analysis was performed on an Exeter Analytical CE440. Fourier transforms infrared (FT-IR) spectra were recorded on a JASCO FT/IR-4600 spectrometer. X-ray diffractometry was performed on a Rigaku SmartLab using Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopic (SEM) images were taken with a JEOL JSM-6510LA (acceleration voltage, 10 kV). Single crystals of the $[Eu(hfa)_3(m\text{-dpb})]_n$ was mounted on micromesh (MiTeGen M3-L19–25 L) using paraffin oil. Non-hydrogen atoms were anisotropically refined. All calculations were performed using a crystal-structure crystallographic software package. The CIF data were confirmed by the check CIF/PLATON service. Deposition Number(s) 2298281 (for $[Eu(hfa)_3(m\text{-dpb})]_n$) contain the Supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Preparations of 1,3-bis(diphenylphosphoryl)benzene (*m*-dpb): *m*-dpb linker ligand

was prepared with the procedure described in a previous report.[19] 1,3-Dibromobenzene (3.92 g, 16.6 mmol) was dissolved in dry tetrahydrofuran (10 mL) under Ar atmosphere. *n*-BuLi (22 mL, 1.6 M in *n*-hexane) was added dropwise to the solution at −78°C. The mixture was stirred for 2 h at −10°C. Chlorodiphenylphosphine (6.3 mL, 35 mmol) was successively added dropwise to the solution at −78°C. The reaction mixture was gradually warmed to room temperature and stirred for 18 h. The reaction mixture was poured into distilled water and extracted with dichloromethane. The extracts were washed with brine three times and dried over anhydrous sodium sulfate. The solvent was evaporated, and the obtained yellow oil was placed with dichloromethane (30 mL) in a flask. The solution was cooled to 0°C, and then an aqueous 30% hydrogen peroxide solution (10 mL) was added dropwise to the solution. The mixture was stirred for 1 h. The aqueous hydrogen peroxide solution was separated, and organic solution was washed with distilled water. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated. The resultant residue was purified by silica gel column chromatography (methanol/ethyl acetate = 8/92). The obtained powder was recrystallized from ethyl acetate to give the product as a white powder. Yield: 1.55 g (3.2 mmol, 20 %). ^{1}H NMR ($CDCl_3$): δ = 7.98–7.93 (2H, dd, *J* = 7.6, 11.8 Hz), 7.68 (1H, t, *J* = 11.8 Hz), 7.63–7.51 (13H, m), 7.44–7.39 (8H, dt, *J* = 7.6, 2.8 Hz). IR(ATR): ν = 3020−3050 (st, C–H), 1180

cm^{-1} (st, P=O).

Preparation of $[Eu(hfa)_3(m\text{-dpb})]_n$ coordination polymer: $[Eu(hfa)_3(m\text{-dpb})]_n$ was prepared with the procedure described in a previous report.[16] Europium(III) acetate n-hydrate (6.5 g, 20.0 mmol) was dissolved in distilled water (65 mL). Hexafluoroacetylacetone (hfa) (12.8 g, 61.7 mmol) was added to the solution, and the mixture was stirred for 2 h at room temperature. The precipitates were filtered, and the obtained white powder was washed with distilled water and chloroform. The powder was dried in vacuo to give a precursor $[Eu(hfa)_3(H_2O)_2]$ (8.9 g, 11.0mmol). $[Eu(hfa)_3(H_2O)_2]$ (0.32 g, 0.40 mmol) and *m*-dpb (0.19 g, 0.40 mmol) were dissolved in methanol (4 mL) and refluxed for 4 h. The reaction mixture was cooled to room temperature and evaporated to give a light-yellow powder. The obtained powder was washed with dichloromethane and hexane. Recrystallization from methanol gave the product as a white powder. Yield: 0.28 g (0.22 mmol, 56% calculated from monomer unit). IR (ATR): ν = 1652 (st, C=O), 1250 (st, C–F), 1179 cm^{-1} (st, P=O). ESI-MS (*m*/*z*): $[M-(hfa)]^+$ calcd for $C_{40}H_{26}EuF_{12}O_6P_2$, 1045.02; found, 1045.03.

Preparation of Micelle A, Micelle B, Mixed Micelle C, and $[Eu(hfa)_3(m\text{-dpb})]_n$ coordination particles: SDS (300.0 mg, 1.04 mmol) was dissolved in ultrapure water (10 mL). A solution of $[Eu(hfa)_3(H_2O)_2]$ (16.2 mg, 20.0 μmol) in diethyl ether (0.1 mL)

was added dropwise and stirred to give micelle A solution. Micelle B solution was prepared by dissolving CTAB (110 mg, 0.30 mmol) in ultrapure water (10 mL) and added a dichloromethane solution (0.1 mL) of the ligand *m*-dpb (9.6 mg, 20 μmol) dropwise under sonication. Mixed micelle C solution of $[Eu(hfa)_3(m\text{-dpb})]_n$ was obtained by combining solutions of micelle A and micelle B. The mixture was centrifuged at 4000 rpm for 20 min, the supernatant was decanted, washed with water and dichloromethane, and dried in vacuo to afford a white powder of $[Eu(hfa)_3(m\text{-dpb})]_n$ coordination particles (Eu-CP30). IR (ATR): ν = 2918–2848 (st, C–H), 1652 (st, C=O), 1250 (st, C–F), 1179 cm^{-1} (st, P=O). The other $[Eu(hfa)_3(m\text{-dpb})]_n$ particles were similarly synthesized by changing CTAB concentration (CTAB: 11 mg, 55 mg and 218 mg for Eu-CP3, Eu-CP15, and Eu-CP60, respectively).

Optical measurements: Emission and excitation spectra were recorded on a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. Emission decay profiles were measured using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, FWHM = 5 ns, λ = 1064 nm) and a photomultiplier (Hamamatsu Photonics, R5108, response time ≤ 1.1 ns). The Nd:YAG laser response was monitored with a digital oscilloscope (Sony Tektronix, TDS3052, 500 MHz) synchronized to the single-pulse excitation. Emission lifetimes were determined

from the slope of logarithmic plots of the decay profiles.

RESULTS AND DISCUSSION

Structural Analysis: The Eu(III) coordination particles of $[Eu(hfa)_3(m\text{-dpb})]_n$ in micelle C were prepared by mixing of $[Eu(hfa)_3(H_2O)_2]$ in micelle A (SDS 100 mM) with *m*-dpb in micelle B (CTAB; 3 mM (Eu-CP3), 15 mM (Eu-CP15), 30 mM (Eu-CP30) and 60 mM (Eu-CP60)) at room temperature. The bulk coordination polymer $[Eu(hfa)_3(m\text{-dpb})]_n$ (Eu-bulk) was obtained by mixing $[Eu(hfa)_3(H_2O)_2]$ and *m*-dpb in methanol. The Eu(III) coordination particles and Eu-bulk were identified by the FT-IR and the ESI-MS. In the IR spectrum of Eu-CP30, vibrational signals of the $Eu(hfa)_3$ and *m*-dpb parts were observed, which was similar to that of Eu-bulk (Figure S2). The ESI-MS and calculated mass patterns of the Eu-bulk are shown in Figure S3. The peaks observed at mass number (*m*/*z*) 1045.0, 2295.0 and 3547.0 were assigned to be fragments of $[Eu(hfa)_2(m\text{-dpb})]^+$, $[Eu_2(hfa)_5(m\text{-dpb})_2]^+$ and $[Eu_3(hfa)_8(m\text{-dpb})_3]^+$, respectively. Additionally, the isotopic distribution of $[Eu_n(hfa)_{3n-1}(m\text{-dpb})_n]^+$ was also identical to the calculated data. (*m*/*z* 1045.0, 2295.0 and 3547.0).

The crystal structure of the $[Eu(hfa)_3(m\text{-dpb})]_n$ is shown in Figure 2a (see also Table S1). The obtained crystal structure (space group; $P12_1/n1$) is different from that of

previous report (space group; $P2_1/n$).[16] The coordination sites of the Eu(III) polymer units consist of three hfa ligands and two *m*-dpb ligand. Intermolecular CH···F interactions between the hfa ligand and the phosphine oxide ligand were observed. The coordination geometry was categorized to be eight-coordinated trigonal dodecahedron (TDH) structure (Table S2). The PXRD patterns of the Eu-bulk and the Eu(III) coordination particles are shown in Figure 2b–d. The characteristic peaks for the Eu-bulk were observed at 2θ = 8.0, 9.1, 11.5, 12.8, 14.5, 15.0, 16.1, 16.8, 18.2, 20.1, 20.9, 21.6, and 22.9 degree. These peaks were also observed in the PXRD patterns for Eu-CP30. The other peaks were found at 2θ = 8.5, 9.4, and 12.7 degree in the PXRD data for Eu-CP3, Eu-CP15, Eu-CP30 and Eu-CP60. These results suggested that the crystal structure of Eu-bulk is different from those of Eu(III) coordination particles.

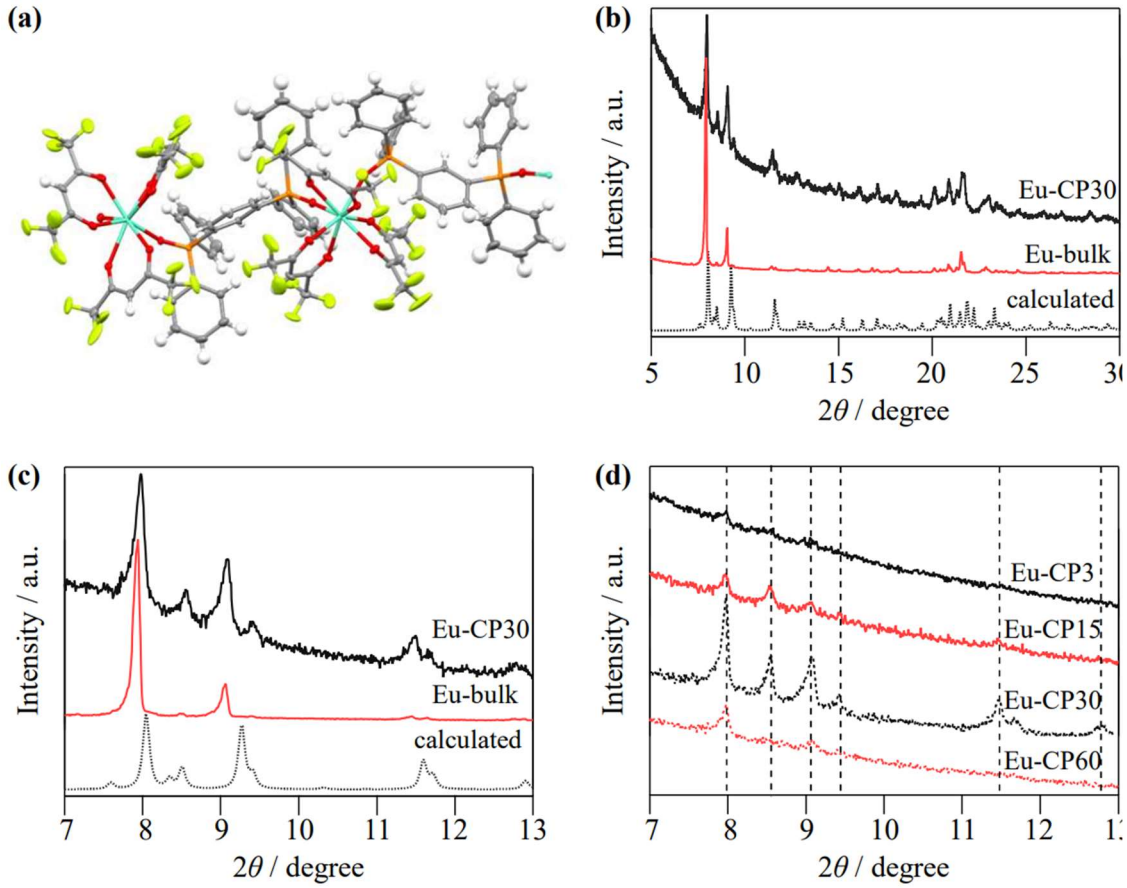

Figure 2. (a) ORTEP drawings (ellipsoids set at 50% probability) of Eu-bulk. (b) PXRD patterns of Eu-CP30 (solid black line), Eu-bulk (solid red line) and calculated data from the SCXRD result (dashed black line). (c) PXRD patterns in the region of 2θ = 7–13 degree (Eu-CP30 (solid black line), Eu-bulk (solid red line) and calculated data from the SCXRD result (dashed black line)). (d) PXRD patterns of the Eu(III) coordination particles in the region of 2θ = 7–13 degree (Eu-CP3 (solid black line), Eu-CP15 (solid red line), Eu-CP30 (dashed black line) and Eu-CP60 (dashed red line).

The SEM images of the Eu(III) coordination particles are shown in Figure 3a, c, e, g.

The morphological shapes of Eu-CP3, Eu-CP15, Eu-CP30 and Eu-CP60 were observed to be spherical aggregates, plates, large-column and short-column, respectively. The particle size distributions for each the Eu(III) coordination particles were obtained by analyzing 200 particles from the SEM images. The average diameters of Eu-CP3, Eu-CP15, Eu-CP30, and Eu-CP60 were found to be 3.3, 1.3, 0.62, and 0.46 μm, respectively (Figure 3b, d, f, h), indicating that the size of coordination particles gradually decreased at higher CTAB concentration. The synthetic condition with large amount of surfactants promots formation smaller micelles in water media. We considered that particle sizes were depended on the difference of synthesis scale delimited by micelle. These results revealed that crystal size and shape were depended on the CTAB concentration in preparation process. And we thought that the crystallinity of Eu(III) coordination polymer is also depended on the concentration of CTAB on the results of the PXRD.

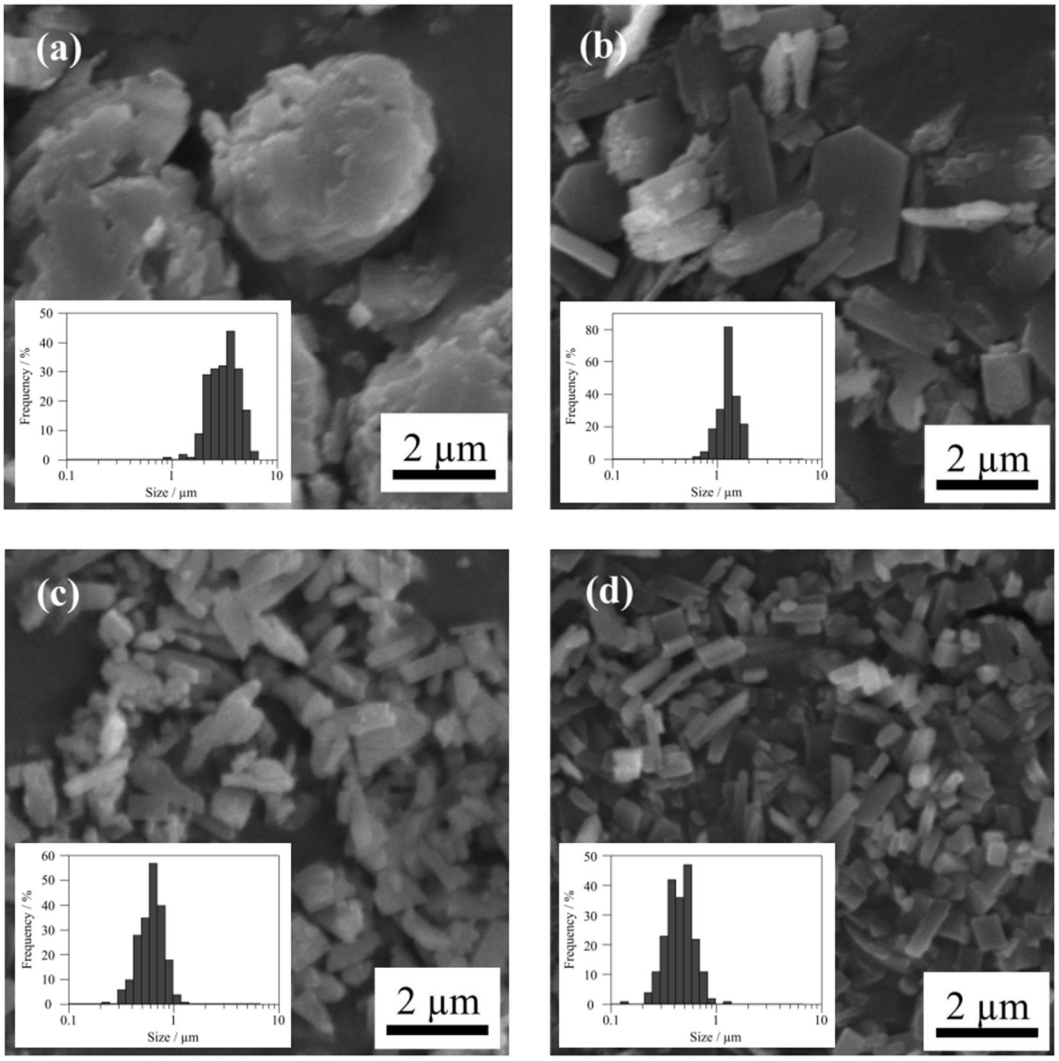

Figure 3. SEM images and particle size distributions obtained from SEM images ((a) Eu-CP3, (b) Eu-CP15, (c) Eu-CP30 and (d) Eu-CP60).

Photophysical Properties: The photophysical properties were demonstrated in solid state. The diffuse reflectance spectra of the Eu-bulk and Eu-CP30 were measured (Figure S5). In the Eu-bulk, a strong broad peak at around 330 nm and a weak sharp peak at 465 nm were observed, which were attributed to the π-π* transition of the hfa ligand and the 4f-4f transition ($^5D_2 \leftarrow ^7F_0$) of the Eu(III) ion, respectively. The diffuse reflectance spectrum of Eu-CP30 also showed similar peaks at around 330 nm and at 465 nm.

The Eu(III) coordination particles and Eu-bulk showed red luminescence under the UV irradiation. The excitation and emission spectra of Eu-CP30 were shown in Figure 4a. The broad excitation band at around UV region is attributed to the π-π* transition of the hfa ligand. The emission bands were observed at 578, 590, 612, 650 and 700 nm by photosensitization of hfa, which originate from 4f-4f transitions of Eu(III) ions ($^5D_0 \rightarrow ^7F_J$: J = 0, 1, 2, 3 and 4). The stark splitting of the $^5D_0 \rightarrow ^7F_2$ transition band for the Eu-bulk and the Eu(III) coordination particles are shown in Figure 4b (see also Figure S6). These spectral shape of luminescence suggests that the coordination geometrical structures around Eu(III) ions of the Eu(III) coordination particles are the same as that of Eu-bulk. The phenomena was reported that some different crystal structure showed the same coordination geometry near the Eu(III) ions and the same stark splitting shape in emission spectra.[20]

The emission decay profiles of Eu-CP30 and Eu-bulk are shown in Figure 4c. Single-exponential decay for bulk sample and Eu-CP3, and double-exponential decay for Eu-CP15, Eu-CP30 and Eu-CP60 with sub-millisecond-scale lifetimes were observed. The multiexponential decay might arise from the Eu(III) ions in the crystal structure. These results indicate that the concentration of CTAB in synthesis contribute to form the crystal structure observed rarely in Eu-bulk. The 4f-4f emission quantum yield ($\Phi_{f\text{-}f}$), radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) were estimated based on the emission lifetime and spectra using the following equations,

$$k_r = \frac{1}{\tau_{rad}} = A_{MD,0} n^3 \frac{I_{tot}}{I_{MD}} \quad (1)$$

$$\Phi_{f-f} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \quad (2)$$

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \quad (3)$$

where τ_{obs} and τ_{rad} are the observed and radiative emission lifetimes, respectively; τ_{rad} is defined as the ideal emission lifetime without a non-radiative process. In these calculations, we used the τ_{ave} value as the τ_{obs} unit. The parameter $A_{MD,0}$, n, and the calculated I_{tot}/I_{MD} are the spontaneous emission probability for the $^5D_0 \rightarrow {}^7F_1$ transition in vacuo (14.65 s^{-1}), the refractive index of the medium (n = 1.5)[21], and the ratio of the total area of the corrected Eu(III) emission spectrum to the area of the $^5D_0 \rightarrow {}^7F_1$ band, respectively. The calculated k_r, k_{nr} and $\Phi_{f\text{-}f}$ values are summarized in Table 1.

The k_r values of Eu(III) coordination particles were almost the same as that of Eu-bulk. On the other hand, The k_{nr} value of Eu-CP30 (1.0×10^2 s^{-1}) was much smaller than that of Eu-bulk (3.2×10^2 s^{-1}) resulting in large emission quantum yield ($\Phi_{f\text{-}f} = 91\%$ for Eu-CP30). The k_{nr} of Eu-CP30 was different from those of Eu-CP3 (3.4×10^2 s^{-1}) and Eu-CP60 (1.8×10^2 s^{-1}). These results indicate that k_{nr} value of the crystal structure formed in micelle system was smaller than that of the other crystal structure observed in Eu-bulk. We considered that drastic change of emission lifetime is cause by crystal structure, such as anisotropic crystal shape[22].

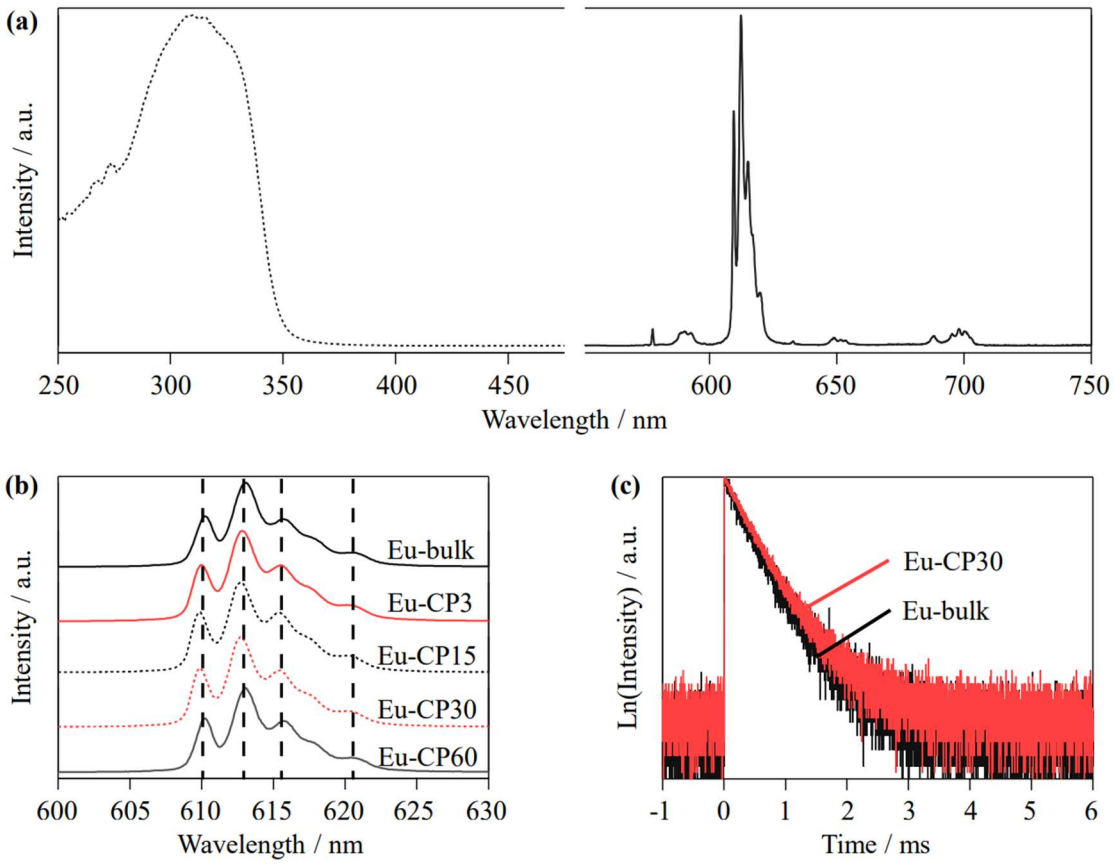

Figure 4. (a) Excitation (dashed line, λ_{em} = 612 nm) and emission spectra (solid line, λ_{ex} = 350 nm) of Eu-CP30. (b) Emission spectra (λ_{ex} = 350 nm) of Eu-bulk (solid black line), Eu-CP3 (solid red line), Eu-CP15 (dashed black line), Eu-CP30 (dashed red line) and Eu-CP60 (solid gray line) in the region of $^5D_0 \rightarrow {}^7F_2$ transition. (c) Emission decay curve of Eu-CP30 (red line) and Eu-bulk (black line).

Table 1. Photophysical parameters of Eu(III) coordination particles and Eu-bulk.

Sample	τ_1 / ms	τ_2 / ms	k_r/ 10^3 s^{-1}	k_{nr}/ 10^2 s^{-1}	$\Phi_{f\text{-}f}$/ %

Eu-CP3	0.73 (±0.02)	---	1.0 (±0.1)	3.4 (±1.1)	75 (±7)
Eu-CP15	0.72 (±0.07) (38%±2)	0.93(±0.04) (62%±2)	1.0 (±0.0)[a]	1.6 (±0.8)	86 (±4)
Eu-CP30	0.71(±0.07) (43%±4)	1.00(±0.10) (57%±4)	1.1 (±0.0)[a]	1.0 (±0.0)[b]	91 (±0)[c]
Eu-CP60	0.73(±0.08) (40%±4)	1.00(±0.08) (60%±4)	1.1 (±0.0)[a]	1.8 (±0.7)	86 (±5)
Eu-bulk	0.73(±0.01)	---	1.0 (±0.0)[a]	3.2 (±0.3)	77 (±3)

[a] $k_r < 0.1\times10^3$ s^{-1}. [b]$k_{nr} < 0.1\times10^2$ s^{-1}. [c]$\Phi_{f\text{-}f} < 1\%$.

CONCLUSIONS

Size-control synthesis of Eu(III) coordination particles were achieved by varying the surfactant concentration through the micelle method. The higher CTAB concentration in a micelle system, the smaller particle sizes of the Eu(III) coordination particles were obtained. Through the micelle synthesis, the crystal structure observed rarely in synthesis by methanol was obtained and showed smaller non-radiative rate than the other crystal structure observed in synthesis by methanol. We considered the crystal structure affected the emission lifetime of Eu(III) coordination particles. The detail of this characteristic photophysical phenomena will be elucidated through future study on synthetic conditions such as surfactant species, reaction times, and ratio of surfactants and Eu(III) coordination particles. The link between crystal structure and luminescence lifetime has the potential to open up the future of coordination chemistry, crystal science, and luminescent materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.xxxxxxx

Schematic reaction of Eu(III) coordination polymers and particles; ^{1}H NMR spectrum;

FT-IR spectra; ESI-MS spectra; X-single crystal data of $[Eu(hfa)_3(m\text{-dpb})]_n$ Eu-bulk; PXRD patterns of $[Eu(hfa)_3(m\text{-dpb})]_n$ coordination particles; Particle size distribution in micellar solution; absorption spectra, emission spectra and excitation spectra of $[Eu(hfa)_3(m\text{-dpb})]_n$ Eu-bulk and coordination particles (PDF)

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Notes

The authors declare no competing financial interest.

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