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Luminescent Thin Films Composed of Nano-sized Europium Coordination polymers on Glass Electrodes

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Abstract: Luminescent thin films composed of thermo-stable lanthanide coordination polymers on glass electrodes were successfully prepared using novel combination between micelle reaction and electrochemical deposition techniques. The micelle encapsulated luminescent polymers were obtained by the polymerization of $Eu(hfa)_3$ (hfa: hexafluoroacetylacetonate) with joint phosphine oxide ligands in micelles using redox-active ferrocenyl-derivative surfactant in water. Electrochemical deposition films were prepared on ITO-coated glass electrodes by potentiostatic polarization of micelle encapsulated Eu^{III} coordination polymers. The luminescence properties of the electrochemical deposition films were estimated using the emission spectra, the emission lifetimes and the emission quantum yields. In this study, Preparation and characterization of electrochemical deposition film composed of micelle encapsulated Eu^{III} coordination polymers on the glass electrodes were demonstrated.

Introduction

Lanthanide complexes have been regarded as attractive luminescent materials because of their characteristic narrow emission bands (fwhm < 10 nm), wide emission area (UV-Vis-Near IR) and long emission lifetimes (□ > □s). In general, the luminescence properties of lanthanide complexes derived from 4f–4f transitions. The 4f–4f emission of Eu^{III} and Tb^{III} complexes play an important role of construction of monochromatic red and green luminescence for display devices, respectively.[1-3] The near-IR 4f–4f luminescence of Nd^{III}, Er^{III} and Yb^{III} complexes with long emission lifetimes are useful in bio-imaging applications.[4] At the present stage, various types of luminescent lanthanide complexes have been reported.[5] In this paper, we focus on the luminescent thin films with lanthanide complex on a glass electrode. The luminescent thin films on glass electrode or semiconductor crystals are expected to be useful in application for display device such as organo-electroluminescent (EL), electrochemical luminescent (ECL), LED tip-devices, and photovoltaic polymer memories.[1-3] Bettencourt-Dias provided a review of lanthanide based emitting materials in the field of light-emitting diodes.[2] Luminescent thin films devices containing lanthanide complexes have been also studied, recently.[6] Thin films composed of luminescent lanthanide complexes are expected to open up new field of material science.

According to the industrial applications, the thermal stabilities of lanthanide complexes as an emitting layer are required the stability at temperatures around 250 °C making them useful in molding materials and solder dissolution processes for construction of electronic devices. Industrial molding and soldering processes at high temperature are be used for modern manufacturing process. Based on these points, luminescent lanthanide coordination polymers have recently received focus as thermally stable luminescent materials. Lanthanide coordination polymers are composed of lanthanide complex-bridged organic coordination units periodically.[7] Polymer structures are combined with chemical bonding such as CH/π and CH/F interactions. The periodical structures lead to improvement of thermal stability with suppression of thermal relaxation at high temperatures. We have recently reported thermo-stable lanthanide coordination polymers with high emission quantum yields.[8, 9] The lanthanide coordination polymers are composed of hfa (hexafluoroacetylacetonate) ligands for suppression of vibrational relaxation and bidentate phosphine oxide ligands for formation of asymmetric coordination structures. The emission quantum yield and decomposition point of Eu^{III} coordination polymer appended with dpbp (4,4.-bis(diphenylphosphoryl)biphenyl), $[Eu(hfa)_3(dpbp)]_n$, are found to be > 70% and 308 °C, respectively. The three-dimensional network structure provides thermo-stable and strong-luminescent properties.[8]

Effective luminescent thin films composed of lanthanide coordination polymers on substrates have not yet been prepared, because lanthanide coordination polymers with network structures are not readily dissolved in general organic solvents and polymer matrices, although layer-by-layer fabrication of transition metal-organic frameworks has been reported.[10] In particular, luminescent Eu^{III} coordination polymer thermo-stable $[Eu(hfa)_3(dpbp)]_n$ is not be dissolved in general organic solvents (chloroform, dichloromethane, toluene, acetone, methanol, THF, DMSO, DMF etc.) and water.[8] The key factor for the fabrication of thin film on a substrate is the solubility of lanthanide coordination polymers with network structures. We have here attempted to use luminescent nanoparticles composed of lanthanide coordination polymers for preparation of thin film on a glass electrode. The nanoparticles are dispersed in liquid media, homogeneously. Kimizuka has successfully reported lanthanide

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coordination nanoparticles using supramolecular networks.[11] We have also prepared lanthanide coordination nanoparticles using micelle reaction techniques.[12] The nano-sized lanthanide coordination polymer has been synthesized using micelle reaction techniques in aqueous solution. The micelle reaction techniques lead to automatic polymerization of coordination polymer in micelle capsules. The nanoparticles composed of lanthanide coordination polymers show effective luminescent properties and thermal stability such as bulk powders of lanthanide coordination polymers.

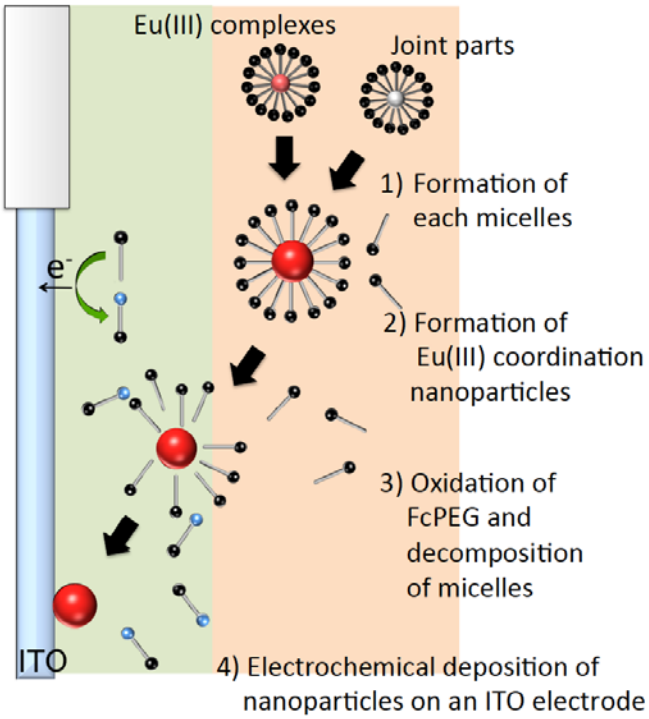


Figure 1. Formation scheme of Eu(III) coordination polymer thin films on the glass electrodes

Based on the micelle reaction and electrochemical deposition techniques, we here successfully prepared of luminescent thin films composed of lanthanide coordination polymer on the glass electrode for the first time. The lanthanide coordination polymers, $[Eu(hfa)_3(dpbp)]_n$ (dpbp: 4,4.-bis(diphenylphosphoryl)biphenyl) and $[Eu(ntfa)_3(dppcz)]_n$ (ntfa: 3-(2-naphtyoyl)-1,1,1-trifluoroacetone, dppcz: 3,6-bis(diphenylphosphoryl)-9-phenylcarbazole), were obtained by the polymerization of Eu^{III} complexes ($[Eu(hfa)_3(H_2O)_2]$ and $[Eu(ntfa)_3(H_2O)_2]$ with joint dpbp and dppcz[13] ligands in micelle capsules under water. Their particle sizes were controlled using ferrocenyl-surfactants (FcPEG: 1,1-ferrocenylundecylpolyoxyethylebe ester[14]) in water (Figure 1 and 2). The sizes of prepared micelles were measured using dynamic light scattering (DLS) measurements. Using the lanthanide coordination polymers covered with ferrocenyl-surfactants, we fabricated nano-sized Eu^{III} coordination polymers on ITO glass electrodes using electrochemical deposition technique. In this study, preparation and characterization of electrochemical deposition films composed of micelle encapsulated Eu^{III} coordination polymers on a glass electrode are demonstrated for the first time.

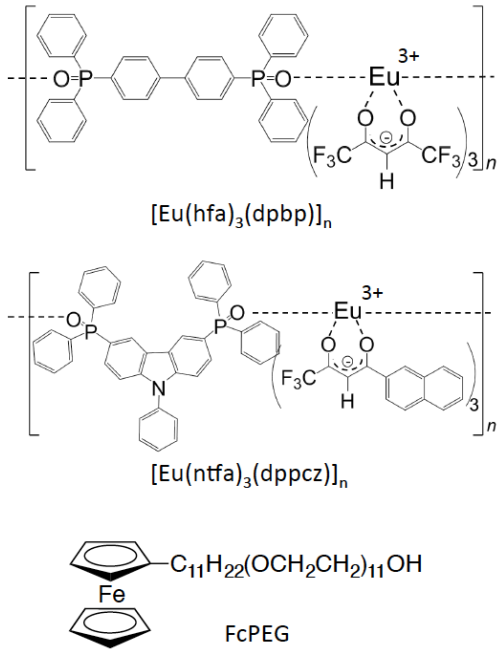


Figure 2. Chemical structures of $[Eu(hfa)_3(dpbp)]_n$, $[Eu(ntfa)_3(dppcz)]_n$and FcPEG.

Results and Discussion

2.1 Size Distributions of Micelle micelle encapsulated Eu^{III} coordination polymers

Bulk powder of lanthanide coordination polymer can not dispersed using various types of surfactants in water. Here, we have attempted to prepare nano-sized Eu^{III} coordination polymer using micelle reaction technique.[12] First, precursor micelles including $Eu(hfa)_3$ and joint dpbp ligand were prepared in water (concentration: 0.04 mmol in 20 mL with FePEG: 1 mM and LiBr: 0.1 M). The precursor micelles were characterized using dynamic light-scattering (DLS) measurements. These size distributions are shown in Figures 3a and 3b. The average number distributions of micelles with Eu^{III} complex and joint ligand were calculated to be 102 and 112 nm, respectively. The particle size are dependent on the concentration of $Eu(hfa)_3$ and joint dpbp ligand. The particle size is independent of the concentration of FePEG. In contrast, the average size depend on concentration of precursor $Eu(hfa)_3$ complex. Smaller concentration of $Eu(hfa)_3$ complex (0.08 mmol) provides larger micelle (ave. size . 300 nm). We also found that higher concentration (> 0.02 mmol) did not lead to formation of micelle in water. The average number distributions are larger than those of previous reported micelles with Eu^{III} complex[12] (SDS: sodium dodecyl sulfate and $[Eu(hfa)_3(H_2O)_2]$, average size = 14 nm) and

joint ligand (TMOA: trimethyl(octyl)ammonium bromide) and dpbp, average size = 10 nm). The large size-distribution of micelles using FcPEG is due to large hydrophilicity of polyoxyethylene groups. The mixed-micelle for preparation of $[Eu(hfa)_3(dpbp)]_n$ nanoparticles was obtained by addition of solution with Eu^{III} complex micelles into solution with dpbp micelles. The mixed-micelle shows mono dispersed distribution in water (Figure 3c). The average size is observed at around 170 nm (Figure 3c and Table 1). The larger size of mixed-micelle might be caused by reconstruction of micelle shells composed of FcPEG. The reconstruction of micelle shells leads to effective formation of $[Eu(hfa)_3(dpbp)]_n$ in mixed-micelle.

On the other hand, synthesized $[Eu(ntfa)_3(dppcz)]_n$ was dissolved in general organic solvent. We here considered that $[Eu(ntfa)_3(dppcz)]_n$ might be covered with polyoxyethylene units in FcPEG, resulting in formation of micelles including $[Eu(ntfa)_3(dppcz)]_n$ nanoparticles, easily. The micelle with $[Eu(ntfa)_3(dppcz)]_n$ nanoparticles for electrochemical deposition were obtained by just mixing of FcPEG, lithium bromide and $[Eu(ntfa)_3(dppcz)]_n$ powder for 24h, directly. The size distribution of micelles using DLS measurement is shown in Figure 3d and Table 1. The average size is estimated to be 199 nm. The size distribution of $[Eu(ntfa)_3(dppcz)]_n$ micelle is much narrower than that of $[Eu(hfa)_3(dpbp)]_n$ mixed-micelle. The narrow size-distribution of $[Eu(ntfa)_3(dppcz)]_n$ micelle might be caused by removal of larger and smaller micelles using the filtration process.

Prepared solutions with $[Eu(hfa)_3(dpbp)]_n$ mixed-micelle and $[Eu(ntfa)_3(dppcz)]_n$ micelle are including electrolyte (lithium bromide) and redox-active site (ferrocenyl unit in FcPEG). These solutions are made use of the electrochemical deposition for preparation of thin film on a glass electrode, directly.

2.2 Preparation of thin films using electrochemical deposition

Redox-active surfactant in micelle, FcPEG, shows a reversible oxidation peak at $E_{1/2}$ = 0.49 V (SHE) in water solution (see supporting information Figure S1). This indicates that FcPEG is decomposed on electrode surface at potentials higher than $E_{1/2}$. We have attempted to prepare a Eu(III) coordination nanoparticle thin film on ITO-coated glass electrode by potentiostatic polarization at 1.0 V (SHE) which is high enough to oxidize FcPEG. The Ferrocenyl group in FcPEG plays a role in reversible redox unit. The ferocenyl group shows hydrophobic part in FcPEG surfactant. Under potentiostatic polarization at 1.0V, the ferrocenyl group changes to ferrocenyl cation with hydrophilic moiety, resulting in decomposition of micelle composed of FcPEG surfactants. The decomposition of micelles leads to deposition of Eu^{III} coordination nanoparticles on the glass electrode. The time transient of current during polarization is shown in Figures 4a and 4b. A relatively large anodic current flows at the initial stage. However, the current decreases gradually and becomes a constant after 4000 s, indicating that the decomposition of FcPEG on the ITO electrode proceeds in the steady state. The electric charges consumed for 5000 s polarization are ca. 0.1 C (Table 1), suggesting that there is no difference between $[Eu(hfa)_3(dpbp)]_n$ mixed-micelles solution

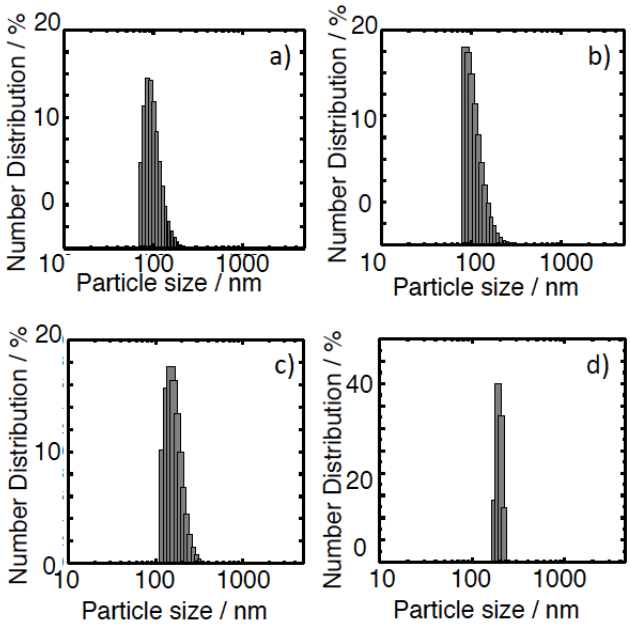


Figure 3. Size number distributions of a) $[Eu(hfa)_3(H_2O)_2]$ micelles, b) dpbp micelles, c) $[Eu(hfa)_3(dpbp)]_n$ micelles, and d) $[Eu(ntfa)_3(dppcz)]_n$ micelles with FcPEG using DLS measurements

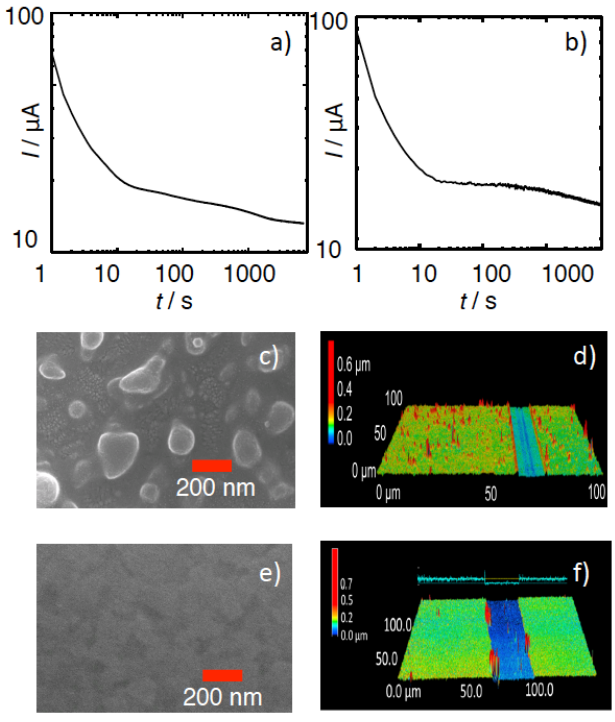


Figure 4. The time transient of current during polarization of a) $[Eu(hfa)_3(dpbp)]_n$ mixed-micelles solution (0.097 C) and b) $[Eu(hfa)_3(dppcz)]_n$ mixed-micelles solution (0.114 C). SEM laser scanning microscopic images of c, d) $[Eu(hfa)_3(dpbp)]_n$ deposition film, e, f) $[Eu(ntfa)_3(dppcz)]_n$ deposition film on the glass electrodes.

Table 1. Thin film performances on glass electrodes

complex	thin film	Size/ nm[a]	electric charge under polarization[b] / C	Film thickness / nm
$[[Eu(hfa)_3(dpbp)]_n$	deposition film	170	0.097	100-600
$[Eu(ntfa)_3(dppcz)]_n$	deposition film	199	0.114	130-150
$[Eu(ntfa)_3(dppcz)]_n$	spin-coat film	-	-	90

[a] micelle size using DLS measurements. [b] WE: ITO-coated glass plat (75mm×25mm, 8-12 Ω) CE: platinum plate RE: platinum wire. Potentiostatic polarization at – 1.0 V (SHE) for 5000 s.

(0.097 C) and $[Eu(hfa)_3(dppcz)]_n$ mixed-micelles solution (0.114 C).

After the potentiostatic polarization, white-colored compounds deposited uniformly on the ITO-coated glass electrodes were observed. SEM and laser scanning microscopic images of the deposition from $[Eu(hfa)_3(dpbp)]_n$ mixed-micelles solution are shown in Figures 4c and 4d, respectively. Rugged surface composed of nanoparticles, the average size of which is approximately 150 nm, was observed on the surface. The size of the nanoparticles is similar to that of $[Eu(hfa)_3(dpbp)]_n$ mixed-micelle (average size = 170 nm), indicating the formation of $[Eu(hfa)_3(dpbp)]_n$ film on the glass electrode. The film thickness measured using a laser scanning microscope is found to be 100-600 nm. Similarly, from SEM and laser scanning microscopy, the formation of $[Eu(ntfa)_3(dppcz)]_n$ deposition film is confirmed as shown in Figures 4e and 4f. However, the deposition film using $[Eu(hfa)_3(dppcz)]_n$ micelle has a smoother surface and the film thickness is found to be 130-150 nm. We consider that the smooth surface of $[Eu(ntfa)_3(dppcz)]_n$ might be caused by the homogenous micelle particles with a narrow size distribution. These film thicknesses were approximately constant at each experiment because of their fixed currents (~0.10 C) under static polarization. Smooth thin film composed of $[Eu(hfa)_3(dppcz)]_n$ on the ITO electrode was successfully prepared using electrochemical deposition technique.

2.3 Emission properties of electrochemical deposition films. The emission spectra of electrochemical deposition films composed of Eu^{III} coordination polymer on glass electrodes are shown in Figures 5a and 5b. Emission bands for the Eu^{III} coordination polymers are observed at 578, 592, 613, 650, and 698 nm and are attributed to the 4f-4f transitions of $^5D_0$-^7F_J with J = 0, 1, 2, 3, and 4, respectively. The spectra are normalized with respect to the magnetic dipole transition intensities at 592 nm (Eu(III): $^5D_0$-$^7F_1$), which is known to be insensitive to the surrounding environment of the lanthanide ions. The branching ratio of the electric dipole transition band, I_{rel} , is given by,

$$I_{rel} = I_{ED} / I_{Md} \quad (1)$$

where I_{ED} and I_{Md} are intensity of the electric dipole transition at around 610 nm and magnetic dipole transition at around 592 nm in emission spectra, respectively. The retiometric analysis of Eu^{III} complexes has been reported by Parker and coworkers.[15] The

Table 2. Photophysical properties of bulk Eu(III) coordination polymers, nanoparticle deposition films and spin-coat film at room temperature

complex	shape	I_{rel}[a]	τ_{obsd}[b] / ms	Φ[c] / %
$[[Eu(hfa)_3(dpbp)]_n$	bulk powder	18.3	0.85	72
$[[Eu(hfa)_3(dpbp)]_n$	deposition film	18.2	0.85	72
$[Eu(ntfa)_3(dppcz)]_n$	bulk powder	15.4	0.37	32
$[Eu(ntfa)_3(dppcz)]_n$	deposition film	15.0	0.34 0.09	30[d]
$[Eu(ntfa)_3(dppcz)]_n$	spin-coat film	9.3	0.46 0.12	25[d]

[a] Branching ratio of the electric dipole transition in emission spectra (I_{rel} = I_{ED} / I_{Md}: equation 1 in manuscript). [b] Emission lifetime (τ_{obsd}) of the lanthanide compounds were measured by excitation at 355 nm (Nd:YAG 3w). [c] Emission quantum yields for Eu(III) complexes were determined by comparison with the integrated emission signal (550–750 nm) of [Eu(hfa)$_3$(biphepo)] as = 0.60. Excitation at 465 nm. [d] Collected emission quantum yields were estimated using calculation based on the emission lifetimes (longer lifetime components) and radiative rate constants from branching ratio of the electric dipole transition.

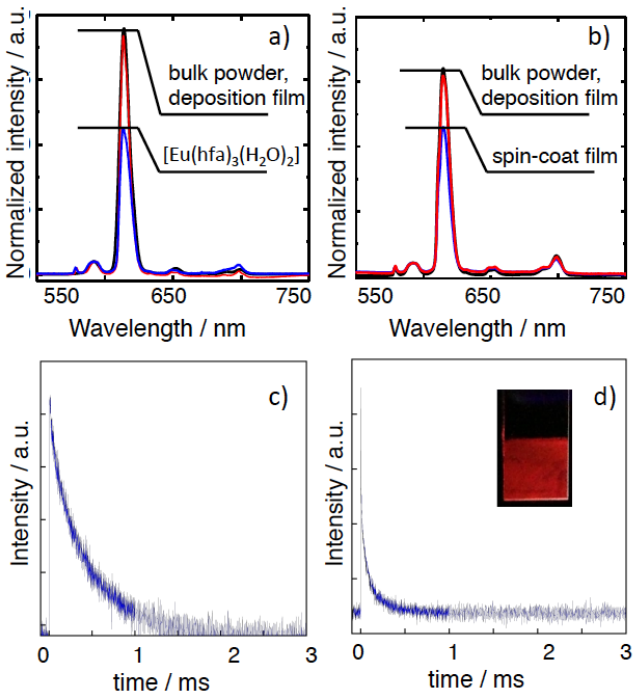


Figure 5. Emission spectra of thin films composed of Eu(III) coordination nanoparticles on a glass electrodes. a) $[Eu(hfa)_3(dpbp)]_n$ bulk powder, $[Eu(hfa)_3(dpbp)]_n$ deposition film, and $[Eu(hfa)_3(H_2O)_2]$ bulk powder. b) $[Eu(ntfa)_3(dppcz)]_n$ bulk powder, $[Eu(ntfa)_3(dppcz)]_n$ deposition film, and $[Eu(ntfa)_3(dppcz)]_n$ spin-coat film. c) Emission decay profiles of $[Eu(hfa)_3(dpbp)]_n$ and $[Eu(hfa)_3(dppcz)]_n$ thin films on a glass electrode. Inset picture in Figure 5d is photoluminescence image of $[Eu(hfa)_3(dppcz)]_n$ thin films on a glass electrode.

I_{rel} values are summarized in Table 2. The I_{rel} values for $[Eu(hfa)_3(dpbp)]_n$ on the electrode is found to be 18.2, which is the same as that of $[Eu(hfa)_3(dpbp)]_n$ bulk powders (I_{rel} = 18.3). This result indicates that the coordination geometry of lanthanide coordination nanoparticles agrees well with that of bulk lanthanide coordination polymers. We also found that the branching ratio for $[Eu(hfa)_3(dppcz)]_n$ thin film on electrode is the

same as that of bulk $[Eu(hfa)_3(dppcz)]_n$ powder. However, the I_{rel} value of $[Eu(hfa)_3(dppcz)]_n$ spin-coat thin film is smaller than those of bulk $[Eu(hfa)_3(dppcz)]_n$ powder. Note that $[Eu(hfa)_3(dppcz)]_n$ spin-coat thin film was prepared from chloroform solution with $[Eu(hfa)_3(dppcz)]_n$. Network structure of $[Eu(hfa)_3(dppcz)]_n$ might be decomposed by dissolving in chloroform for preparation of spin-coat thin film. These results suggest that electrochemical deposition method of Eu^{III} coordination nanoparticle micelles provides a stable and effective thin film on a glass electrode.

In order to analyze their quantitative photophysical properties, we carried out the emission lifetime measurements. The emission decay profiles of $[Eu(hfa)_3(dpbp)]_n$ and $[Eu(hfa)_3(dppcz)]_n$ thin films on a glass electrode are shown in Figures 5c and 5d. The emission lifetimes were determined from the slopes of the logarithmic plots of the decay profiles. The emission lifetimes of bulk powder of $[Eu(hfa)_3(dpbp)]_n$ were found to be 0.85 ms. The emission lifetime in nano-sized $[Eu(hfa)_3(dpbp)]_n$ on a glass electrode agree with those of bulk $[Eu(hfa)_3(dpbp)]_n$ (0.85 ms). These results indicate that the $[Eu(hfa)_3(dpbp)]_n$ on the electrode is composed of $[Eu(hfa)_3(dpbp)]_n$ nanoparticles. Calculated emission quantum yield of electrochemical deposition film of $[Eu(hfa)_3(dpbp)]_n$ on the electrode was found to be 72 %. The emission lifetime of nano-sized $[Eu(ntfa)_3(dppcz)]_n$ on glass electrode were composed of 0.34 ms (longer component: 35 %) and 0.09 ms (shorter component: 65%). The longer component of $[Eu(ntfa)_3(dppcz)]_n$ on electrode is similar to that of bulk $[Eu(ntfa)_3(dppcz)]_n$ powder (0.37 ms). The calculated emission quantum yield based on the longer emission lifetime component and radiative rate constant[16] was estimated to be 30%, which is similar to that of bulk $[Eu(ntfa)_3(dppcz)]_n$ powder (32 %). Origin of the shorter component of the emission lifetime is not clear at the present stage. In contrast, the emission lifetime of $Eu(hfa)_3(dppcz)]_n$ spin-coat thin film (longer component: 0.46 ms) was different from that of $[Eu(ntfa)_3(dppcz)]_n$ powder and nano-sized $[Eu(ntfa)_3(dppcz)]_n$ on glass electrode. Generally, decomposition of asymmetric eight coordination structure of lanthanide coordination compound leads to decrease of 1) the I_{rel} value, 2) the radiative rate constant, and 3) increase the emission lifetimes.[17] The larger emission lifetime of $Eu(hfa)_3(dppcz)]_n$ spin-coat thin film might be due to decomposition of the coordination structure. Calculated emission quantum yield of $Eu(hfa)_3(dppcz)]_n$ spin-coat thin film was estimated to be 25%, which is smaller than those of bulk and thin films of $Eu(hfa)_3(dppcz)]_n$. These results indicate that electrochemical deposition films are the same as those of bulk lanthanide coordination polymers.

Conclusions

Luminescent thin films composed of thermo-stable lanthanide coordination polymer on a glass electrode were successfully prepared using novel combination between micelle reaction and electrochemical deposition techniques. Electrochemical deposition of $[Eu(ntfa)_3(dppcz)]_n$ micelle provides homogenous and smooth thin film on a glass electrode. We also demonstrated that simple thin film device composed of Al/$[Eu(ntfa)_3(dppcz)]_n$/ITO/glass multi-layers was fabricated for evaluation of *I-V* performance (see supporting information Figure S2). Drastic increase in current at around 6 V, which is not ohmic response for short current circuit. The network structure of $[Eu(ntfa)_3(dppcz)]_n$ coordination nanoparticles thin film also provides thermo-stable properties with high decomposition temperature (decomposition point > 280 °C), which is higher than those of previous Eu(III) complexes (decomposition point □ 220 °C).[18] Now, we are trying to fabricate and evaluate a sandwich-typed EL device composed of lanthanide coordination nanoparticle thin film attached with hole and electron transport layers. The optimum ligands for the EL device are also being studied, continuously. Thermo-stable Eu(III) coordination polymer thin film on electrode is expected to open-up a new field of inorganic, material, electrochemical, and colloid science and technology.

Experimental Section

Materials: Europium acetate monohydrate (99.9%) was purchased from Wako Pure Chemical Industries Ltd. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione was obtained from Tokyo Kasei Organic Chemicals and Aldrich Chemical Company Inc. All other chemicals and solvents were reagent grade and were used without further purification.

Apparatus: Infrared spectra were recorded on a JASCO FT/IR–350 spectrometer. ^{1}H NMR (270 and 400MHz) spectra were recorded on a JEOL ECS400. Chemical shifts are reported in □ ppm, referenced to an internal tetramethylsilane standard for ^{1}H NMR. IR spectra were measured using a JASCO FT/IR-350. Elemental analyses were performed using a Yanaco CNH corder MT-6. Mass spectrometry was performed with a JEOL JMS-T100LP. Size-distribution was measured with a BECKMAN COULTER DelsaNanoHC. The thickness of the EuS nanoparticle thin films was measured by a color 3D laser scanning microscope KEYENCE VK-8710. Thermogravimetric analysis (TGA) was performed on an SII EXSTAR-6000 analyzer. Scanning electron microscopy (SEM) was performed with a JEOL JSM-6500F (acceleration voltage, 10 kV).

Preparation of Tris(hexafluoroacetylacetonato)europium Dihydrates $[Eu(hfa)_3(H_2O)_2]$: Europium acetate monohydrate (5.0 g, 13 mmol) was dissolved in distilled water (20 mL) in a 100 mL flask. A solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7.0 g, 34 mmol) was added dropwise to the solution. The reaction mixture produced a precipitation of white yellow powder after stirring for 3 h at room temperature. The reaction mixture was filtered, and the resulting powder was recrystallized from methanol/water to afford colorless needle crystals of the titled compound. Yield: 9.6 g (95%); IR (KBr): □ = 1650 (st, C=O), 1145□1258 (st, C–F) cm^{-1}; elemental analysis calcd (%) for $C_{15}H_7EuF_{18}O_8$ (809.91): C 22.27, H 0.87; found: C 22.12, H 1.01.

Preparation of 4,4.-Bis(diphenylphosphoryl)biphenyl (dpbp). 4,4.-Bis-(diphenylphosphoryl)biphenyl was synthesized

according to a published procedure[8, 9]. A solution of n-BuLi (9.3 mL, 1.6M hexane, 15mmol) was added dropwise to a solution of 4,4.-dibromobiphenyl (1.9 g, 6.0mmol) in dry THF (30 mL) at -80 °C. The addition was completed in ca. 15 min during which time a yellow precipitate was formed. The mixture was stirred for 3 h at -1 °C, after which a PPh2Cl (2.7 mL, 15mmol) was added dropwise at -80 °C. The mixture was gradually brought to room temperature, and stirred for 14 h. The product was extracted with ethyl acetate, the extracts washed with brine three times and dried over anhydrous $MgSO_4$. The solvent was evaporated, and resulting residue was washed with acetone and ethanol several times. The obtained white solid and dichloromethane (ca. 40 mL) were placed in a flask. The solution was cooled to 0 °C and then 30% H_2O_2 aqueous solution (5 mL) was added to it. The reaction mixture was stirred for 2 h. The product was extracted with dichloromethane, the extracts washed with brine three times and dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a white powder. Recrystallization from dichloromethane gave white crystals of the titled compound. Yield: 1.1 g (33%). IR(KBr): 1120 cm^{-1} (st, P=O). ^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C): □/ppm = 7.66-7.81 (m, 16H), 7.45-7.60 (m, 12H). ESI-Mass (m/z) = 555.2 $[M + H]^+$. Anal. Calcd for $C_{36}H_{28}O_2P_2$: C, 77.97; H, 5.09%. Found: C, 77.49; H, 5.20%.

Preparation of 3,6-Bis(diphenylphosphoryl)-9-phenylcarbazole (dppcz). 3,6-Bis(diphenylphosphoryl)-9-phenylcarbazole was synthesized according to a published procedure[8]. A solution of n-BuLi (8.8 mL, 1.6 M hexane, 14 mmol) was added dropwise to a solution of 3,6-dibromo-9-phenylcarbazole (2.4 g, 6.0 mmol) in dry THF (30 mL) at –80°C. The addition was completed in ca. 10 min during which time a white yellow precipitate was formed. The mixture was stirred for 2 h at –10 °C, after which a PPh_2Cl (2.6 mL, 14 mmol) was added dropwise at –80 °C. The mixture was gradually brought to room temperature, and stirred for 18 h to give a white precipitate. The precipitate was filtered, washed with methanol for several times, and dried in vacuo. The obtained white powder and dichloromethane (ca. 40 mL) were placed in a flask. The solution was cooled to 0 °C and then 30% H_2O_2 aqueous solution (8 mL) was added to it. The reaction mixture was stirred for 2 h. The product was extracted with dichloromethane, the extracts washed with brine for three times and dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a white powder. Recrystallization from dichloromethane/hexane gave colorless crystals of the titled compound. Yield: 2.0 g (53%). IR (KBr): 1122 (st, P=O) cm–1. ^{1}H-NMR (400 MHz, $CDCl_3$, 25°C) δ/ppm = 8.43–8.47 (d, *J* = 12.0 Hz, 2H), 7.63–7.76 (m, 11H), 7.43–7.60 (m, 18H). ESI–Mass (m/z) = 644.2 $[M+H]^+$. Anal. Calcd for $C_{42}H_{31}NO_2P_2$: C, 78.37; H, 4.85; N, 2.18%. Found: C, 78.42; H, 5.00; N, 2.18%.

Preparations of $[Eu(hfa)_3(dpbp)]_n$ Coordination Polymer. The dpbp ligand (1 equiv.) and $[Eu(hfa)_3(H_2O)_2]$ (1 equiv.) were dissolved in chloroform (20 mL). The solution was refluxed while stirring for 8 h, and the reaction mixture was concentrated to dryness. A single crystal suitable for X-ray structural determination of Eu(III) coordination polymer was obtained by the diffusion method of methanol–chloroform solution at room temperature. $[Eu(hfa)_3(dpbp)]_n$. Yield: 98 mg (67%; for monomer). IR (KBr): 1653 (st, C=O), 1255–1145 (st, C–F), 1127 (st, P=O) cm^{-1}. ESI–Mass (m/z) = 1120.08 $[Eu(hfa)_2(dpbp)]^+$, 2447.15 $[Eu_2(hfa)_5(dpbp)_2]^+$. Anal. Calcd for $[C_{51}H_{31}EuF_{18}O_8P_2]_n$: C, 46.14; H, 2.35%. Found: C, 45.59; H, 2.49%. Decomposition temperature = 308 °C.

Preparations of $[Eu(ntfa)_3(dppcz)]_n$ Coordination Polymer. Europium chloride hexahydrate (0.54 g, 1.5 mmol) was dissolved in ethanol (10mL) in a 100 mL flask. A solution of 3-(2-naphtyoyl)-1,1,1-trifluoroacetone (ntfa) (1.2 g, 4.5 mmol) in ethanol (40mL) and triethylamine (0.6 mL, 4.5 mmol) were added dropwise to the solution. The reaction mixture produced a precipitation of white yellow powder after stirring for 2 h at room temperature. The reaction mixture was filtered, and the resulting powder was recrystallized from methanol/water. Phosphine oxide ligand (dppcz, 0.2g, 0.31 mmol) in chloroform 3 mL were added into the 5 mL ethanol solution with prepared $Eu(ntfa)_3(H_2O)_2$ (0.34 g, 34 mmol). The solution was mixed at room temperature while stirring for 4h to give white precipitates. The precipitates were filtered, washed with ethanol and hexane several times, and dried in vacuo. Yield: 0.34 g (63%). ESI–Mass (m/z) = 1326.2 $[Eu(ntfa)_2(dppcz)]^+$, 1969.38 $[Eu(ntfa)_2(dppcz)_2]^+$, 2917.4 $[Eu_2(ntfa)_2(dppcz)]^+$. Anal. Calcd for $C_{84}H_{55}EuF_9NO_8P_2$: C, 63.40; H, 3.48; N, 0.88%. Found: C, 64.64; H, 3.67; N, 1.05%. Decomposition temperature = 280 ^{0}C.

Preparations of Micelles with Eu^{III} complexes, joint ligands and micIIIe encapsulated Eu^{III} coordination polymers. FcPEG (1,1-ferrocenylundecylpolyoxyethylebe ester: 1 mM) and lithium bromide (0.1 M) was dissolved in distilled water (20 mL) in a 100 mL flask. Diethyl ether solution (2 mL) of $[Eu(hfa)_3(H_2O)_2]$ (32.4 mg, 0.04 mmol) was added at room temperature, resulting in formation of micelle composed of FCPEG, lithium bromide and $[Eu(hfa)_3(H_2O)_2]$ in water. In contrast, Dichloromethane solution (2 mL) of dpbp (22.2 mg, 0.04 mmol) was added into water solution (20 mL) including FcPEG (1 mM) and lithium bromide (0.1 M) at room temperature, resulting in formation of micelle composed of FcPEG, lithium bromide and dpbp in water. The mixed-micelle for preparation of $[Eu(hfa)_3(dpbp)]_n$ nanoparticles was obtained by addition of solution with Eu^{III} complex micelles (1 mL) into solution with dpbp micelles (20 mL). The micelle with $[Eu(ntfa)_3(dppcz)]_n$ nanoparticles is obtained by mixture of FcPEG (1 mM), lithium bromide (0.1 M) and $[Eu(ntfa)_3(dppcz)]_n$ powder (2 mg) in water (20 mL) for 24 h under room temperature. The water solution including micelles was filtrated using micro-filter (CS080AS ADVANTEC).

Electrochemical measurement and preparation of deposition thin film on a glass electrode. The water solution including micelle encapsulated Eu^{III} coordination polymers prepared above was located in a three-electrode electrochemical cell and bubbled with pure argon gas to remove dissolving oxygen. An ITO-coated glass plate (sheet resistance: 8-12 Ω) with an area of 75 mm×25 mm was used as working electrode while a platinum plate and a platinum wire were used as counter electrode and quasi-reference electrode, respectively. The quasi-reference electrode potential was calibrated into the standard hydrogen electrode potential (SHE) by measuring a redox potential of ferrocene (E^0 = 0.554 V vs SHE) before and after the polarization. A potentiostat (Hokuto HA-151) and a function generator (Hokuto HB-104) were used for the following two modes of polarization. Cyclic voltammetry in the potential region between 0 and 1.3 V (SHE) at a scan rate of 5 mV s^{-1} was carried out to survey the electroactivity of FcPEG. Potentiostatic polarization at 1.0 V (SHE) for 5000 s was also conducted to electrodeposite nanoparticles on the electrode surface. .

Preparation of Spin-coat Thin Film on the Glass Electrode. Spin-coat thin film as a reference was prepared using a spin coater NANBU Mechatro Co. ltd (2000 rpm, 60 s) with chloroform solution including bulk $[Eu(ntfa)_3(dppcz)]_n$ powder (1 mM). After spin-coating, thin film was sintered at 60 °C for 30 min for evaporation of chloroform.

Optical Measurements: Absorption and emission spectra of the lanthanide complexes were measured with a JASCO V-670 spectrophotometor, JASCO F-6300-H and Horiba FluoroLog spectrometers which corrected for the response of the lamp, mirrors, gratings, and photomultiplier detector system. The emission quantum yields of lanthanide complex solutions degassed with argon (10 mM in acetone-d_6) were obtained by comparison with the integrated emission signal (550–750 nm) of $Eu(hfa)_3(TPPO)_2$ as a reference (= 0.60: 50 mM in acetone-d_6) with an excitation wavelength of 465 nm (direct excitation of Eu(III) ions) for Eu(III) complexes.Emission lifetimes of lanthanide complexes (10 mM in acetone-d_6) were measured using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm = 5 ns, =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.

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