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Thermostable Nano Luminophores Composed of Europium Ions and Organic Ligands*

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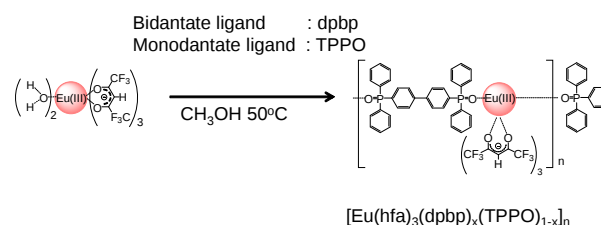
The luminescent nanoparticles with Eu(III) ions are reported. Standard nanoparticles are prepared by the reaction of europium chloride with dpp (diphenylphosphinic acid) joint ligands. The size-controlled nanoparticles are synthesized by the reaction of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (hfa: hexafluoroacetylacetonate) with bidentate dpbp ligands (dpbp: 4,4'-bis(diphenylphosphoryl)biphenyl) and monodentate ligands (TPPO: triphenylphosphine oxide). Their particle sizes were characterized using TEM and dynamic light scattering (DLS) measurements. Their luminescence properties were estimated by the emission spectra and lifetimes. [DOI: 10.1380/ejsnt.2015.219]

Keywords: Lanthanides; Nano-particles; Photoluminescence

I. INTRODUCTION

Lanthanide complexes with narrow emission bands and long emission lifetimes have been regarded as promising luminescent materials for use in luminescent optical materials [1,2], such as organic light-emitting diodes (OLEDs) [3-5] and luminescent bio-sensing applications [6-10]. At the present stage, various types of luminescent lanthanide complexes have been reported [11-25]. Luminescent lanthanide coordination polymers as the thermostable luminescent materials have recently been studied. The lanthanide coordination polymers are composed of lanthanide ions and linker organic coordination parts, periodically. Reddy described thermostable lanthanide coordination polymers with 4-(dipyridine-2-yl)aminobenzoate ligands (decomposition point = 450°C) [26]. Stucchi has demonstrated remarkable thermal stability of luminescent Eu(III) materials composed of Eu(III) ions and diphenylphosphinic acid (Eu-DPP system: decomposition point = 550°C) [27-29]. We have also reported lanthanide coordination polymers with three dimensional tight packing structures [30]. In general, characteristic tight-stacking structures of lanthanide coordination polymers lead to formation of insoluble compounds, micro-sized particles, in water and organic solvents. The insoluble micro-sized particles cause multiple light scattering in UV-Vis region. The nanoparticles of lanthanide coordination polymers without multiple light scattering may increase transmission of optical and luminescent materials. We demonstrated luminescent nanoparticles composed of lanthanide coordination polymers using micelle technique in water media [31]. However, the micelle technique does not provide large amount of luminescent nanoparticles for industrial application. From this reason, improvement of preparation method is required for luminescent nanoparticles composed of Eu(III) ions and organic ligands. We have attempted to control the particle size of lan-

a)



b)

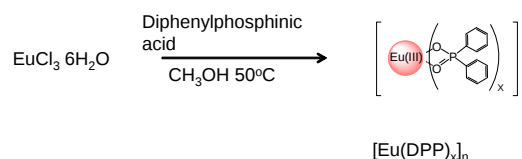


FIG. 1. Synthetic schemes of a) Size-controlled nanoparticles composed of Eu(III) complexes, bidentate ligands and monodentate ligands ($[\text{Eu}(\text{hfa})_3(\text{dpbb})_x(\text{TPPO})_{1-x}]_n$), and b) thermostable luminophores composed of Eu(III) ions and Diphenylphosphinic acid ($[\text{Eu}(\text{DPP})_x]_n$).

thanide coordination polymers using monodentate ligand such as a polymerization terminator. The size-controlled nanoparticles are obtained by reaction of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (hfa: hexafluoroacetylacetonate) with bidentate ligands (dpbp: 4,4'-bis(diphenylphosphoryl)biphenyl) and monodentate ligands (TPPO: triphenylphosphine oxide) ($[\text{Eu}(\text{hfa})_3(\text{dpbb})_x(\text{TPPO})_{1-x}]_n$: Fig. 1a). Previous thermo-stable nanoparticles, Eu-DPP system, are also prepared by the reaction of europium chloride with dpp (diphenylphosphinic acid) joint ligands as a reference ($[\text{Eu}(\text{DPP})_x]_n$: Fig. 1b) [32]. The particle size of previous reported $[\text{Eu}(\text{DPP})_x]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dpbb})_x(\text{TPPO})_{1-x}]_n$ were measured using TEM and dynamic light scattering (DLS) measurements, respectively. Their emission properties were estimated using emission spectra and emission lifetimes. In this study, size-controlled nanoparticles composed of luminescent Eu(III) ions and organic ligands are performed.

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II. EXPERIMENTAL MATERIALS

Europium acetate monohydrate (99.9%) and europium chloride hexahydrate (99.9%) were purchased from Wako Pure Chemical Industries Ltd. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione, 4,4'-dibromobiphenyl (> 98%), diphenylphosphinic acid and triphenylphosphine oxide (99.9%) were obtained from Tokyo Kasei Organic Chemicals. All other chemicals and solvents were reagent grade and were used without further purification.

A. Apparatus

Infrared spectra were recorded with a JASCO FTIR-350 spectrometer. ^1H NMR (400 MHz) spectra were recorded with a JEOL ECS-400 spectrometer. Chemical shifts are reported in ppm and are referenced to an internal tetramethylsilane standard for ^1H NMR spectroscopy. Elemental analyses were performed with a Yanaco CNH MT-6 analyzer. Thermogravimetric analysis (TGA) was performed on a Seiko EXSTAR 6000 (TG-DTA 6300) analyzer. Size-distributions were measured with a BECKMAN COULTER Delsa Nano HC. High-resolution images of luminophore were obtained with a JEOL 2010 FASTEM (200 kV) TEM.

B. Preparation of

Tris(hexafluoroacetylacetonato)europium Dihydrate $[\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2]$

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 white-yellow precipitate after stirring for 3 h at room temperature. The powder was collected by filtration and recrystallized from methanol/water to afford colorless needle crystals of the title compound, yield 9.6 g (95%). IR (KBr): 1650 (s, C=O), 1145-1258 (s, C-F) cm^{-1} . $\text{C}_{15}\text{H}_7\text{EuF}_{18}\text{O}_8$ (809.91): calcd. C 22.48, H 0.88; found C 22.12, H 1.01.

C. Preparation of

4,4'-bis(diphenylphosphoryl)biphenyl [dpbp]

4,4'-bis(diphenylphosphoryl)-biphenyl was synthesized according to the published procedure[30]. A solution of *n*-BuLi (9.3 mL, 1.6 M hexane, 15mmol), was added dropwise to a solution of 4,4'-dibromobiphenyl (1.9 g, 6.0 mmol) 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 allowed to stir for 3h at -10°C , after which a PPh_2Cl (2.7 mL, 15 mmol) 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 for three times and dried over anhydrous MgSO_4 . The solvent was evaporated, and resulting residue was washed with acetone

and ethanol for 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 for 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 (st, P=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3 , 25°C) δ 7.67-7.80 (m, 16H; P - C_6H_5 , C_6H_4), 7.45-7.60 (m, 12H; P - C_6H_5 , C_6H_4) ppm. ESI-Mass (m/z) = 555.2 $[\text{M} + \text{H}]^+$. Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{O}_2\text{P}_2$: C, 77.97; H, 5.09%. Found: C, 77.49; H, 5.20%.

D. Preparation of $[\text{Eu}(\text{DPP})_x]_n$

Diphenylphosphinic acid (20 mg, 90 μmol) was dissolved in methanol (5 mL) in a 30 mL flask. Methanol solution (0.2 mL) of $\text{Eu}(\text{Cl})_3(\text{H}_2\text{O})_6$ (10 mg, 27 μmol) was added at 50°C . Reaction mixture was centrifuged at 4000 rpm for 20 minutes and the white powder of nanoparticles composed of $[\text{Eu}(\text{DPP})_x]_n$ were prepared. Nanoparticles composed of $[\text{Eu}(\text{DPP})_x]_n$ were washed twice with methanol, and then dried.

E. Preparations of nanoparticles composed of lanthanide coordination polymers

Amount of Bidantate dpbp ligands in $[\text{Eu}(\text{hfa})_3(\text{dpbp})_x(\text{TPPO})_{1-x}]_n$ (x : molecular ratio of dpbp) were controlled under 0.20(20%), 0.40(40%), 0.60(60%), 0.80(80%) and 1.00 (100%), respectively. In the molecular ratio of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$, bidantate dpbp ligands (7 mg, 12 μmol) and monodantate TPPO ligands (14 mg, 50 μmol) were dissolved in methanol (10 mL) in a 50 mL flask. Methanol solution (10 mL) of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (50 mg, 62 μmol) was added at 50°C . The reaction mixture was stirred for 6 h. The product was centrifuged at 4000 rpm for 20 minutes and the white powder of nanoparticles composed of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$, dpbp and TPPO were prepared. Nanoparticles composed of lanthanide coordination polymers were washed twice with methanol, and then dried. Nanoparticles characterized using DLS measurements.

F. Optical Measurements

The emission spectra of the lanthanide coordination polymers were measured with a JASCO F-6300-H spectrometer and corrected for the response of the detector system. The emission lifetimes of the lanthanide coordination polymers (solid state) were measured by using the third harmonic (355 nm) of a Q-switched Nd:YAG laser [Spectra Physics, INDI-50, full width at half maximum (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)

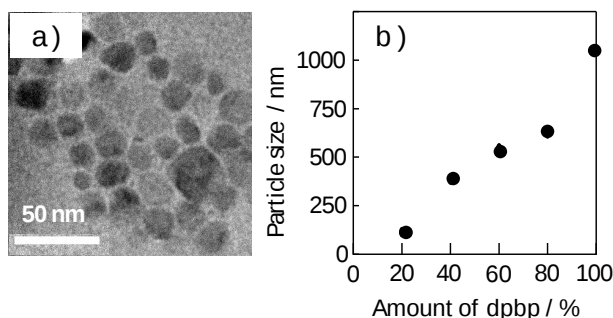


FIG. 2. a) TEM image of $[\text{Eu}(\text{DPP})_x]_n$. b) Particle size dependence of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_x(\text{TPPO})_{1-x}]_n$ under addition of monodentate TPPO ligand. Molecular ratio of dpbe (%): $x = 0.20, 0.40, 0.60, 0.80$ and 1.00 .

synchronized to the single pulse excitation. The emission lifetimes were determined from the slope of logarithmic plots of the decay profiles.

III. RESULTS AND DISCUSSIONS

A. Structural characterizations

TEM image of standard $[\text{Eu}(\text{DPP})_x]_n$ is shown in Fig. 2a). We observed various size of $[\text{Eu}(\text{DPP})_x]_n$ nanoparticles. The average particle size was estimated to be 30 nm with large size distribution. The particle size of $[\text{Eu}(\text{DPP})_x]_n$ was not controlled under reaction temperature and time. We have also attempted to control the particle size of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_x]$ using addition of monodentate TPPO ligand as a polymerization terminator. Size distribution of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_x(\text{TPPO})_{1-x}]_n$ (x : molecular ratio of dpbp) using DLS measurement is shown in Fig. 2b). The size distribution is dependent of the molecular ratio of bidantate dpbp ligands in $[\text{Eu}(\text{hfa})_3(\text{dpbp})_x(\text{TPPO})_{1-x}]_n$. We also observed mono size-distribution of the particles using DLS measurements. Particle size of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ was found to be 115 nm. These results indicate that particle size is controlled using monodentate TPPO ligands as a polymerization terminator. The thermal stabilities of size-controlled nanoparticles were characterized using thermogravimetric analyses (Fig. 3). The decomposition temperatures of $[\text{Eu}(\text{DPP})_x]_n$ and $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ were estimated to be 560°C and 263°C , respectively. Unfortunately, we found that the decomposition temperature of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ nanoparticles is lower than that of corresponding bulk $[\text{Eu}(\text{hfa})_3(\text{dpbp})]_n$ polymer (decomposition temperature = 308°C). The decomposition temperature of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ might be caused by the elimination of monodentate TPPO ligands in nanoparticles.

B. Emission properties

The size-controlled nanoparticles are dispersed in organic solvent, homogeneously. The emission spectrum of

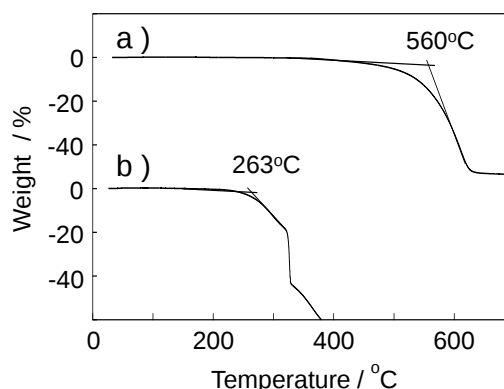


FIG. 3. TGA thermograms of a) $[\text{Eu}(\text{DPP})_x]_n$ and b) $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$.

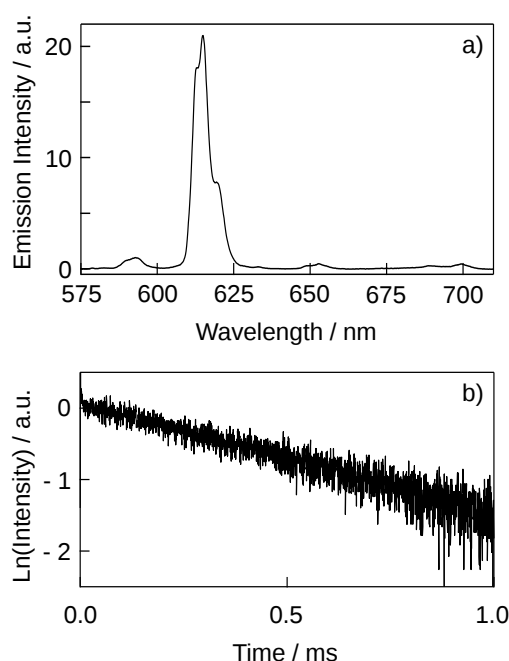


FIG. 4. a) Emission spectra of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ in methanol at room temperature. Excited at 380 nm. b) Emission decay of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ in the solid state at room temperature.

$[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ in methanol is shown in Fig. 4a). Emission bands excited at $\pi-\pi^*$ transition band of organic hfa ligand ($\lambda = 380$ nm) are observed at 578, 592, 613, 650 and 698 nm are attributed to the $4f-4f$ transitions of $^5\text{D}_0-^7\text{F}_J$ with $J = 0, 1, 2, 3$ and 4 , respectively. We successfully observed photo-sensitized luminescence of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ nanoparticles under excitation at 380 nm. In contrast, we could not observe the emission of $[\text{Eu}(\text{DPP})_x]_n$ under excitation at 380 nm because of the absence of $\pi-\pi^*$ transition band at around 380 nm (transition band of DPP = 273 nm) [32]. The time-resolved emission decay profiles of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ in the solid state is shown in Fig. 4b). The emission lifetime was determined from the slopes of the logarithmic

mic plots of the decay profiles. Emission decay was found to be 0.66 ± 0.01 ms. The emission life time is smaller than that of bulk $[\text{Eu}(\text{hfa})_3(\text{dpbp})_2]_n$ ($\tau = 0.85 \pm 0.01$ ms)[30]. The smaller emission lifetime of $[\text{Eu}(\text{hfa})_3(\text{dpbp})_{0.20}(\text{TPPO})_{0.80}]_n$ may be due to presence of vibrational relaxation on the nanoparticle surface covered with monodentate TPPO ligands.

IV. CONCLUSIONS

The nanoparticles including Eu(III) ions were successfully prepared by addition of monodentate TPPO lig-

ands as the polymerization terminator. The particle size is controlled using the molecular ratio of the bidentate dpbp ligands and the monodentate TPPO ligands. In this study, we successfully observed photo-sensitized luminescence of Eu(III) nanoparticles excited at 380 nm. However, their thermal stability and emission properties are dominated by monodentate TPPO ligands on the nanoparticles surface. In order to prepare thermo-stable luminescent Eu(III) nanoparticles, improvement of the polymerization terminator on the particle surface may be required. The size-controlled nanoparticles expected to open up the new application of future optical materials.

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