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Thermo-sensitive luminescent materials composed of Tb(III) and Eu(III) complexes

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ABSTRACT

Thermo-stable lanthanide coordination polymers $[Tb,Eu(hfa)_3(dpbp)]_n$ composed of Tb(III) ion, Eu(III) ion, bidentate phosphine oxide (dpbp: 4,4'-bis(diphenylphosphoryl)biphenyl), and low-vibrational frequency hexafluoroacetylacetonate (hfa) ligand are reported. The lanthanide coordination polymers $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=1, 10, 250, 500, and 750) are characterized by XRD, emission spectra and emission lifetime measurements. The energy transfer efficiencies among lanthanide ions are estimated using the emission lifetimes of solid-state coordination polymers. Characteristic emission properties of lanthanide coordination polymers composed of Tb(III) ions and a small amount of Eu(III) ions (Tb/Eu=750) have been observed for the first time. The energy transfer between lanthanide ions in coordination polymers is described in terms of solid-state materials.

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1. Introduction

Lanthanide complexes with characteristic narrow emission bands and long emission lifetimes have been regarded as attractive luminescent materials for use in light-emitting diodes (LEDs), lasers, and optical fibers [1–3]. Various types of luminescent lanthanide complexes have been reported [3,4]. In particular, red-luminescent Eu(III) complexes and green-luminescent Tb(III) complexes with characteristic organic ligands are expected to be useful in application such as chemical and biological sensors [5,6]. These sensors composed of lanthanide complexes provide effective information for detection of proton, metal ions and biological compounds in liquid media [7–9].

Luminescent physical sensors for measurements of temperature and pressure on the material surface are also expected to be useful in applications in the fields of fluid dynamics and aeronautical engineering [10]. Luminescent physical sensors based on lanthanide complexes have been investigated, recently [11,12]. In 2003, Amao and co-workers reported the first temperature sensors based on luminescent Eu(III) complexes [11]. We have also reported lanthanide coordination polymers composed of Tb(III) and Eu(III) complexes, $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=99), for sensing temperature between 200 and 500 K [12]. The remarkable thermo-sensitive properties of $[Tb,Eu(hfa)_3(dpbp)]_n$ are caused by the energy transfer between Tb(III) and Eu(III) ions in coordination polymer matrix. At the present stage, photophysical studies on the energy transfer from Tb(III) ions to Eu(III)

ions have been well-known using mono- and di-nuclear lanthanide complexes in homogeneous organic and aqueous media [13,14]. We consider that the energy transfer mechanisms of $[Tb,Eu(hfa)_3(dpbp)]_n$ might be different from those in previous reported homogeneous systems in solution. Kinetic analysis of the photophysical properties in solid-state coordination polymer is directly linked with not only novel aspects in the fields of solid-state photochemistry but also development of effective thermo-sensors for measurement on the material surface.

Here, we prepared $[Tb,Eu(hfa)_3(dpbp)]_n$ with various Tb/Eu ratios (1, 10, 250, 500, and 750) for analysis of thermosensitive performance and their energy transfer efficiency. The temperature-dependence of the energy transfer efficiency between Tb(III) ions and Eu(III) ions is reported for the first time. Prepared $[Tb,Eu(hfa)_3(dpbp)]_n$ was characterized by IR and XRD measurements. The energy transfer efficiencies between 100 and 350 K were estimated using an optical cryostat for precise photophysical measurements. We found characteristic photophysical properties of lanthanide coordination polymers composed of Tb(III) ions and a small amount of Eu(III) ions (Ln (III) ratio: Tb/Eu=750). In this study, characteristic energy transfer efficiency between lanthanide ions in solid-state coordination polymers is described herein for development of thermo-sensitive luminescent materials.

2. Experimental

Preparation of coordination polymers $[Tb,Eu(hfa)_3(dpbp)]_n$ *(Tb/Eu=1):* All chemicals were of reagent grade and used as received.

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Phosphine oxide ligand (4,4'-bis (diphenylphosphoryl) biphenyl: dpbp) was synthesized as reported [12]. Phosphane oxide ligand (dpbp, 0.44 g), $Tb(hfa)_3(H_2O)_2$ (0.33 g) and $Eu(hfa)_3(H_2O)_2$ (0.32 g) were dissolved in methanol. The solution was refluxed while stirring for 2 h to give white precipitates. The precipitates were filtered, washed with methanol and chloroform several times, and dried in vacuo.

To determine Eu:Tb ratios of $[Tb,Eu(hfa)_3(dpbp)]_n$, ICP-AES was conducted (Shimadzu ICPE-9000). Concentrations were calculated and averaged from the emission intensities of Eu and Tb ($\lambda = 381.917$ and 350.917 nm, respectively) for each sample using the appropriate calibration curves. These analyses revealed a ratio of Tb:Eu=0.498:0.502 (calcd 1:1). $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=10, 250, 500, 750) were synthesized by the same method.

Tb:Eu=0.908: 9.23×10^{-2} (calcd 10:1), 0.996:3.93×10^{-2} (calcd 250:1), 0.998:2.04×10^{-2} (calcd 500:1), 0.999: 1.30×10^{-2} (calcd 750:1). IR (KBr): 3067 (st, arC–H), 2895 (st, C–H), 1650 (st, C=O), 1493 (arC–C), 1253–1142 (st, C–F), 1125 (st, P=O) cm^{-1} (JASCO FT/IR-420 spectrometer).

Optical measurements: Emission spectra were recorded on a JASCO F-6300-H spectrometer. Emission lifetimes of Tb(III) ions in coordination polymers were measured using the third harmonics (355 nm) of a Q-switched Nd:YAG laser (Spectra Physics, INDI-50, fwhm=5 ns, l=1064 nm), filter transmitting wavelength shorter than 550 nm, and photomultiplier (Hamamatsu photonics R5108, response time $\leq$ 1.1 ns). Emission lifetimes and emission spectra in the range 100–350 K were measured by a cryostat (Thermal Block Company, SA-SB245T) and a temperature controller (Oxford, Instruments, ITC 502S). The emission quantum yields of coordination polymers excited at 380 nm were estimated using JASCO F-6300-H spectrometer attached to JASCO ILF-53 integrating sphere unit ($\phi = 100$ nm).

3. Results and discussion

The structures of lanthanide coordination polymers were analyzed using powder XRD analyses. All signals are calibrated by the signal of silicon powder at 28.4°. Observed signals at 7.5°, 8.8°, 9.4°, 10.3°, 20.1° and 21.5° are attributed to the geometrical structures of $[Tb,Eu(hfa)_3(dpbp)]_n$ (see Supporting information Fig. S1). We found that the signals of $[Tb,Eu(hfa)_3(dpbp)]_n$ agree with those of previously reported $[Eu(hfa)_3(dpbp)]_n$ [12]. These results indicate that the geometrical structures of $[Tb,Eu(hfa)_3(dpbp)]_n$ are the same as those of $[Eu(hfa)_3(dpbp)]_n$. According to our previous data using X-ray single crystal analysis of $[Eu(hfa)_3(dpbp)]_n$, distances between Eu(III) ions inter- and intra-polymer chains have been found to be 11.4 Å and 13.6 Å, respectively. The critical distance for dipole–dipole energy transfer between lanthanide ions has been estimated to be approximately 12 Å [15]. In the solid crystals of $[Tb,Eu(hfa)_3(dpbp)]_n$, positions of lanthanide ions are fixed in the crystal packing structure. The energy transfer is generally dependent on the distance between donor and acceptor. From the point of distance for energy transfer, we propose that inter-polymer chains energy transfer might be dominated because of the shorter distance (11.4 Å). We consider that distances among Ln(III) ions in the solid-state polymer matrix lead to effective energy transfer among Ln(III) ions.

To estimate the energy transfer efficiency between Tb(III) ions and Eu(III) ions in solid-state polymer matrix, we measured temperature-dependent emission spectra of $[Tb,Eu(hfa)_3(dpbp)]_n$. Temperature-dependent emission spectra of $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=10) in the solid state in the temperature range of 100–450 K are shown in Fig. 1(c). The characteristic emission bands at 488 nm, 543 nm and 613 nm are attributed to the 4f–4f transitions of Tb(III) ($^5D_4–^7F_6$, $^5D_4–^7F_5$) and Eu(III) ($^5D_0–^7F_2$), respectively. The emission quantum yield and lifetime at 300 K (excited at $\pi–\pi*$ transition band of hfa ligands) were 59.8% and 0.11 ms, respectively.

The emission intensities of Tb(III) ions in $[Tb,Eu(hfa)_3(dpbp)]_n$ decrease with increasing temperature. We also observed that the emission intensities of Eu(III) ions in $[Tb,Eu(hfa)_3(dpbp)]_n$ increase with rise of temperature. The ratio of the luminescent intensities of Tb(III) and Eu(III) ions (I_{Eu}/I_{Tb}) in $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=10, 250, 500, and 750) is shown in Fig. 2(a). The luminescent intensity ratio (I_{Eu}/I_{Tb}) depends on the concentration of Tb(III) and Eu(III) ions. We think that the emission spectral ratios in various concentrations of $[Tb,Eu(hfa)_3(dpbp)]_n$ are directly linked to the energy transfer process between Tb(III) and Eu(III) ions.

The temperature-dependence of emission spectra in $[Tb,Eu(hfa)_3(dpbp)]_n$ are attributed to the energy transfer between Tb(III) and Eu(III) ions. The energy transfer efficiency from the Tb(III) to Eu(III) ion (η_{Tb-Eu}) is estimated by the following equation [16]:

$$n_{Tb-Eu} = 1 - \left(\frac{\tau_{obs}}{\tau_{Tb}} \right) \quad (1)$$

in which τ_{obs} and τ_{Tb} are the emission lifetimes of $[Tb,Eu(hfa)_3(dpbp)]_n$ and $[Tb(hfa)_3(dpbp)]_n$, respectively. The lifetime measurements were monitored at the 4f–4f transition bands of Tb(III) ion, $^5D_4–^7F_6$ (545 nm) and $^5D_4–^7F_5$ (488 nm).

The temperature dependence of the energy transfer efficiency η_{Tb-Eu} of $[Tb,Eu(hfa)_3(dpbp)]_n$ are shown in Fig. 2(b). We observed the energy transfer efficiencies between Tb(III) and Eu(III) ions at 100 K were equal to approximately zero. The photophysical phenomena is similar to that in previous study on energy transfer between Tb(III) and Eu(III) ions in solid state [17]. According to the
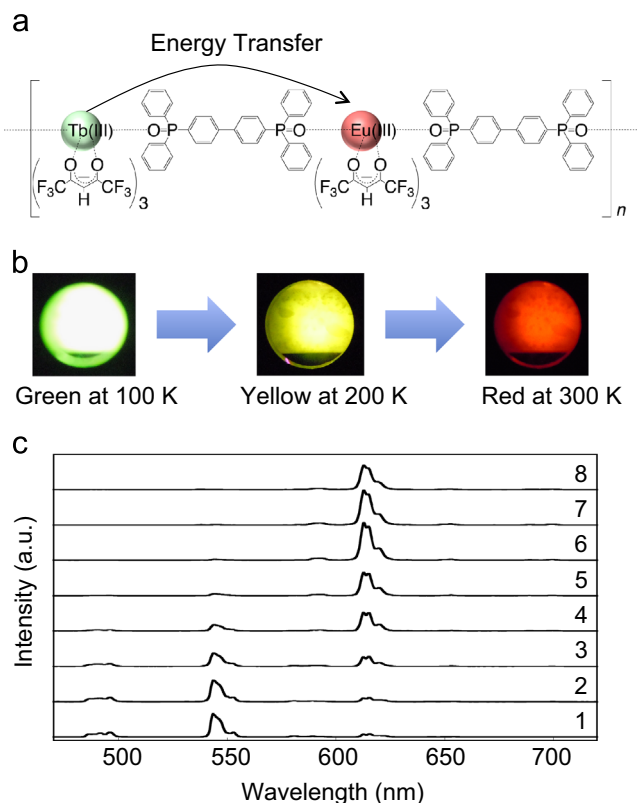

Fig. 1. (a) Chemical structures of energy transfer process between Tb(III) and Eu(III) ions in lanthanide coordination polymer $[Tb,Eu(hfa)_3(dpbp)]_n$. (b) Luminescence images of $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=10) in cryostat at 100, 200 and 300 K. (c) Temperature-dependence of emission spectra of $[Tb,Eu(hfa)_3(dpbp)]_n$ (Tb/Eu=10) in the solid state (1:100 K, 2:150 K, 3:200 K, 4:250 K, 5:300 K, 6:350 K, 7:400 K, 8:450 K), excited at 380 nm.
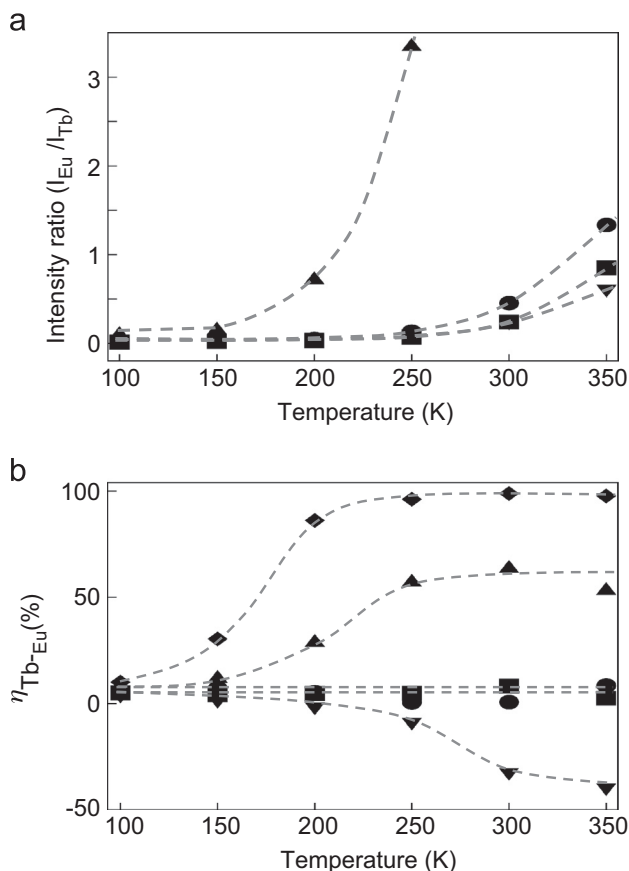
a

b

Fig. 2. (a) Temperature dependence of relative emission intensities (I_{Eu}/I_{Tb}, ▲: Tb/Eu=10, ●: Tb/Eu=250, ■: Tb/Eu=500 and ▼: Tb/Eu=750). (b) The temperature dependence of energy transfer efficiencies of [Tb,Eu(hfa)$_3$(dpbp)]$_n$ (η_{Tb-Eu}, ◆: Tb/Eu=1, ▲: Tb/Eu=10, ●: Tb/Eu=250, ■: Tb/Eu=500 and ▼: Tb/Eu=750).

measurements at 300 K, the energy transfer efficiencies η_{Tb-Eu} are found to be 99%, 65%, 7.4% and 8.2% for Tb/Eu=1, 10, 250 and 500, respectively. These results indicate that the energy transfer efficiency η_{Tb-Eu} depends on the concentration of the energy transfer acceptor, Eu(III) ions. We also found that the energy transfer efficiency η_{Tb-Eu} of [Tb,Eu(hfa)$_3$(dpbp)]$_n$ (Tb/Eu=750) showed negative value (-33%), which indicates that emission lifetime of Tb(III) ions in [Tb,Eu(hfa)$_3$(dpbp)]$_n$ (Tb/Eu=750) is larger than that of [Tb(hfa)$_3$(dpbp)]$_n$ (see Supporting information Table S1). The energy transfer mechanisms in solid-state of these polymers might be different from general Forster mechanism in liquid media.

4. Conclusion

We synthesized lanthanide coordination polymers with various ionic ratios [Tb,Eu(hfa)$_3$(dpbp)]$_n$ (Tb/Eu=1, 10, 250, 500, and 750) and measured the temperature-dependent emission spectra and lifetimes. We found that the thermo-sensitive performance and energy transfer efficiency from Tb(III) ions to Eu(III) ions are dependent on Tb/Eu ratios in lanthanide coordination polymers. In particular, characteristic energy transfer properties of lanthanide coordination polymers composed of Tb(III) ions and a small amount of Eu(III) ions (Tb/Eu=750) have been observed for the first time. We are now trying to analyze the unusual

photophysical properties using opto-magnetic measurements of [Tb,Ln(hfa)$_3$(dpbp)]$_n$ (Ln=Nd, Sm, Eu, Gd, Dy, and Yb). In the solid-state polymers, we also think that the π-orbital in ligands also affects the thermo-sensing properties. Those studies will provide novel aspects of the energy transfer mechanisms in solid-state lanthanide coordination polymers.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.05.074.

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