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Formation of molecular glasses of (*N*-acylalaninato)europium(III) complexes and the luminescence properties

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Abstract

Tris(*N*-octanoyl-DL-alaninato)europium(III) (Eu(oct-ala)$_3$) was newly prepared and it was found that the complex takes a stable glassy state by an evaporation of methanol from the solution, whereas tris(octanoato)europium(III) (Eu(octnt)$_3$, i.e. europium soap) does not easily take a purely vitrified state. The luminescence intensity was larger and the spectrum was simpler in the glassy state than those in the devitrified state. It is characteristic that an addition of 2,2′-bipyridine (bpy) or 4,4′-dinonyl-2,2′-bipyridine (dnbpy) to Eu(oct-ala)$_3$ increases the luminescence intensity both in solutions and in solids and that Eu(octnt)$_3$ becomes to take a stable glassy state by an addition of bpy.

Keywords: *N*-octanoylalanine; Europium(III) complex; Molecular glass; Luminescence

1. Introduction

In developing a possibility of new materials, it is an important subject to create a glassy state of low molecular weight compounds (i.e. molecular glasses), since the low molecular glasses are more easily designed and characterized in comparison with macromolecular glasses. Stable molecular glasses hitherto reported are almost limited to a series of organic π-electron compounds [1]. Although metal complexes have high and extensive functionalities, most of them are easily crystallized, and thus there have been only a few reports on their stable glassy states at room temperature [2–7]. For metal soaps, phase behavior of tris(alkanoato)lanthanides was recently studied in detail, and it was found that these compounds aggregate more isotropically in comparison with bis(alkanoato)metal complexes. Long-chained tris(octadecanoato)lanthanides take more stable vitreous states than shorter-chained lanthanide soaps do [7]. Most of lanthanide soaps actually form mixed crystalline and glassy states or thermotropic liquid crystals, and thus their glassy states have not been well characterized [7–10].

On the other hand, we have recently reported a synthesis of tris(*N*-octanoyl-DL-alaninato)yttrium(III) (Y(oct-ala)$_3$) and a formation of the stable glass from the methanol solution in a preliminary communication [11]. In the present paper, we report the formation of glassy state and the luminescence properties for the tris(*N*-octanoyl-DL-alaninato)europium(III) (Eu(oct-ala)$_3$) complex (Fig. 1). We expected that the luminescence properties of molecular aggregates would reflect the situation of molecular assemblies. The characteristics of glassy states were observed by using differential scanning calorimeter (DSC), X-ray diffraction (XRD), polarizing microscope (PM) and fluorescence spectroscopy (FS).

2. Experimental

The *N*-octanoylalaninato–europium(III) complex was synthesized as follows: *N*-octanoylalanine was prepared from *N*-octanoylchloride and DL-alanine according to the previously reported method [12]. *N*-octanoyl-DL-alanine (3.2×10^{-3} mol) in methanol was neutralized to pH 7–8 with an addition of potassium hydroxide in methanol. Europium chloride hexahydrate (1.0×10^{-3} mol) in methanol solution

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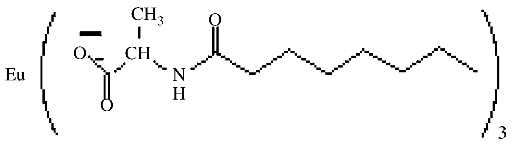

Fig. 1. Eu(oct-ala)$_3$ complex.

was then carefully added. In the reactions, small amounts of white precipitates (the main component was a by-product of europium–octanoate [13]) formed were filtered out. After a complete evaporation of methanol, the glassy solid formed was washed with distilled water and then with acetone, and dried in vacuo at room temperature. In order to compare the physical properties of (Eu(oct-ala)$_3$) with metal soaps, we isolated tris(octanoato)europium(III) (Eu(octnt)$_3$) according to the method for tris(dodecanoato)lanthanide(III) [9]. The Eu(oct-ala)$_3$ glass characterized by DSC was prepared by an annealing treatment as will be described below and contained one water per molecule. Calc. for Eu(oct-ala)$_3$·H_2O: C, 48.81; H, 7.65: N, 5.18. Found: C, 48.97; H, 7.68; N, 5.17%. Calc. for Eu(octnt)$_3$·2.0H_2O: C, 46.64; H, 8.01. Found: C, 46.38; H, 7.98%. The water content was determined by a Karl–Fischer's titration. The vapor pressure depression (VPD) for the Eu(oct-ala)$_3$·H_2O methanol solution was measured with a Knauer Vapor Pressure Osmometer at 37 °C in the concentration range of 0.04–0.4 mol kg^{-1}. The glass transition was observed by DSC in the temperature range of 20–250 °C (with Shimadzu DSC-50 at a constant rate of 10 K min^{-1}).

The wide angle X-ray scattering (WAXS) ($2\theta = 5°–60°$) and small angle X-ray scattering (SAXS) ($2\theta = 0.5°–5°$) experiments were performed with an X'pert Pro of PANAtycal (operated at 20 mA and 40 kV) and with a Rigaku RDA (150 mA and 40 kV), respectively, at room temperature. The Cu Kα X-ray source ($\lambda = 1.54$ Å) was monochromatized with a plate-like graphite monochrometer. The WAXS and SAXS intensity distributions were detected with an X'Celerator (diode array) and a position sensitive proportional counter (PSPC), respectively.

The ^{2}H and ^{13}C NMR spectra were obtained on a JEOL EX-270 spectrometer operating at 41.5 and 67.9 MHz, respectively. The ^{2}H longitudinal relaxation times (T_1) for CH_3OH-d_4 were obtained by the inversion-recovery method. Self-diffusion coefficients were measured by the ^{1}H NMR PGSE (Fourier Transform Pulsed Field Gradient Spin-Echo) technique with a JEOL FX-90 spectrometer.

The photoluminescence spectra of the europium complexes in solutions and solids were measured with a JASCO FP-6300 spectrofluorometer.

3. Results and discussion

The solubilities of Eu(oct-ala)$_3$ were more than 10 wt% in methanol, ethanol and 1,4-dioxane. The vitreous solid of Eu(oct-ala)$_3$ was isolated by a solvent-evaporation from the concentrated methanol solution. The Eu(oct-ala)$_3$·2H_2O, thus obtained was furthermore changed to a stable glassy state of Eu(oct-ala)$_3$·H_2O by annealing at 110 °C for 1 day and then by cooling down gradually in a desiccator [14].

The ^{13}C NMR spectrum and CHN elemental analysis also gave a confidence that any chemical change does not occur by the annealing. All the glasses obtained were not hygroscopic but stable for at least half a year on exposure to air.

The VPD measurement revealed that this complex is present almost as a monomer in methanol at concentrations below 0.4 mol kg^{-1} and the possibility of the formation of polymerized glassy state by the annealing is excluded.

The PM observation revealed that the glassy Eu(oct-ala)$_3$ complex is completely isotropic and transparent and the isotropy of the aggregates was similarly confirmed both in the Eu(oct-ala)$_3$–methanol gel and in the concentrated methanol solutions.

3.1. DSC curves

As the Eu(oct-ala)$_3$ glass formed from the methanol solution contains two waters per molecule, the DSC curve did not show a clear glass-transition point but large endothermic curve at around 90 °C due to the contained waters. When we kept the solid at 110 °C for 1 day, and then in a desiccator for another day, the water in the molecule was reduced to unity and the DSC curve gave a clear glass transition, as shown in Fig. 2. The glass transition point is close to that for the yttrium complex. The Eu(octnt)$_3$ complex did not give any glass transition point on DSC curve but gave endothermic peak at around 90 and 150 °C. The former peak can be assigned to the dehydration one and the latter to the melting.

3.2. WAXS and SAXS profiles

The WAXS and SAXS measurements were carried out in comparing the degrees of amorphous structures between the Eu(octnt)$_3$·2H_2O and Eu(oct-ala)$_3$·H_2O solids. Both WAXS and SAXS results showed that the Eu(octnt)$_3$·2H_2O complex gives many sharp diffraction peaks, while the Eu(oct-ala)$_3$·H_2O complex provides only two broad peaks

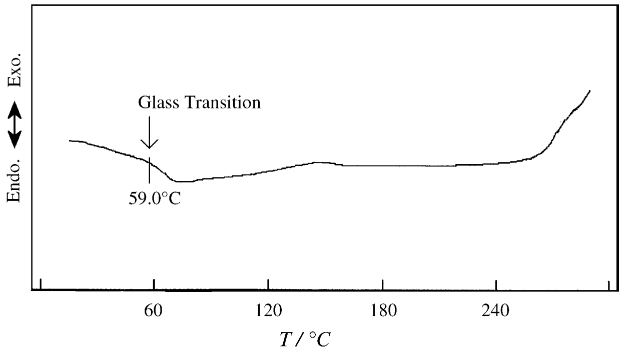

Fig. 2. DSC curve for the Eu(oct-ala)$_3$·H_2O complex in the glassy state.

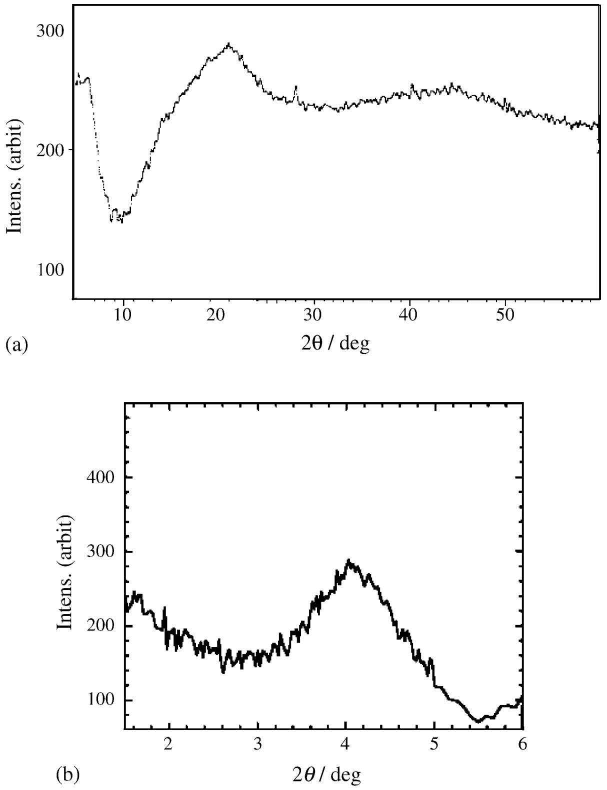

Fig. 3. (a) WAXS and (b) SAXS profiles for the Eu(oct-ala)$_3$·H_2O complex in the glassy state.

at $2\theta = 4.1°$ and 21°. Fig. 3 shows the profiles for Eu(oct-ala)$_3$·H_2O. The broad single peak in the small angle region corresponds to the nanostructure of the aggregates ($d = 2.2$ nm for the Eu(oct-ala)$_3$ glasses) due to the alkyl chains while the peak in the wide-angle region ($2\theta = 21°$) is specific to the disordered alkyl chains. The peak positions in the X-ray scatterings are very close to those for the Y(oct-ala)$_3$ complex in the glassy state, which have been previously reported [11]. The formation of similar aggregates is presumed for the europium and yttrium complexes in the glassy states.

3.3. Luminescence properties

The emission spectrum of Eu(oct-ala)$_3$ in the glassy state is shown in Fig. 4. The profile of the spectrum in the glassy state is similar to that in the methanol solution. The difference in the luminescence intensity was followed for the peak at 616 nm, corresponding to $^7F_0 \rightarrow {}^5D_0$ transmission.

It is characteristic that the emission intensity significantly increases with an addition of 2,2′-bipyridine (bpy) or of 4,4′-dinonyl-2,2′-bipyridine (dnbpy) both in the methanol solution and the glassy state. The increase in the intensity by an addition of bpy in methanol is shown in Fig. 5. In the present stage of the study, the coordination arrangement around the europium(III) center is not clear; however, the bpy ligand may additively coordinate to the europium(III) center. Furthermore, the luminescence intensity for the Eu(oct-ala)$_3$ glassy state at [dnbpy]/[Eu-complex] = 0.3 was about 4 times larger than that in the absence of dnbpy; the larger content of dnbpy made the complex devitrified.

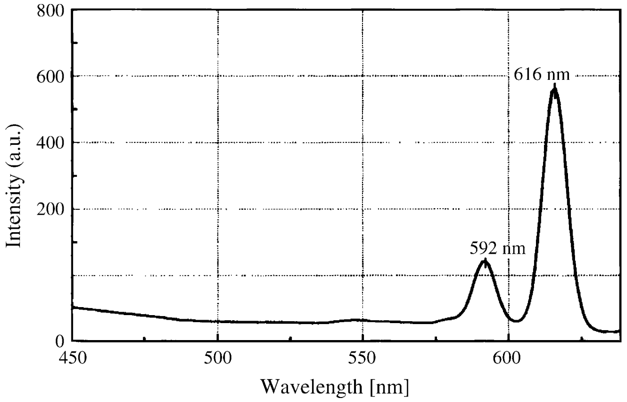

Fig. 4. Emission spectrum of the Eu(oct-ala)$_3$·H_2O complex in the glassy state. The excitation wavelength is 330 nm.

The emission spectrum of the devitrified Eu(octnt)$_3$ is more complicated and the intensity was about one-half compared to that for the Eu(oct-ala)$_3$ glass. This result indicates that in the former system different europium sites due to the heterogeneous states may be reflected in the emission spectra. It is remarkable that the Eu(octnt)$_3$ complex also tends to take a stable glassy state with an addition of dnbpy (0.3 molar ratio to the Eu-complex) as well as an increase in the emission intensities.

3.4. Aggregations of Eu(oct-ala)$_3$ in methanol

In order to speculate the formation processes of glassy states from methanol solution, we measured the dynamic behavior of the concentrated methanol solutions of Eu(oct-ala)$_3$. As stated above, this complex was revealed to be present almost as monomers at concentrations below

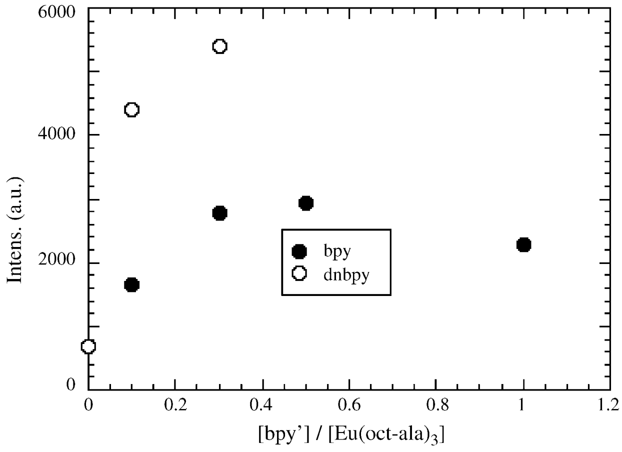

Fig. 5. Increase in the luminescence intensities as functions of the [bpy]/[Eu-complex] and [dnbpy]/[Eu-complex] molar ratios in the methanol solutions. The bpy' signifies bpy or dnbpy. The concentration of the Eu-complex is 0.2 mol dm^{-3}.

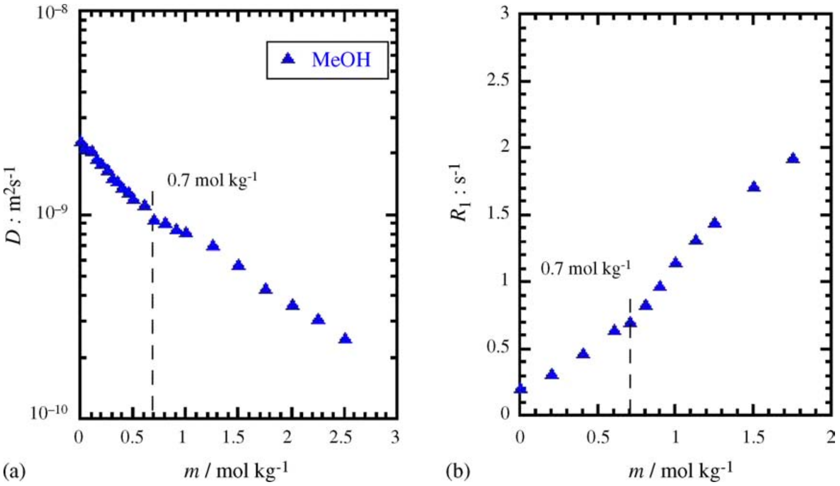

Fig. 6. (a) Diffusion coefficients of MeOH and (b) ^{2}H-relaxation rates of MeOH-d_4 as functions of the Eu-complex concentrations.

0.4 mol kg^{-1} by the VPD measurement. The extent of the aggregation at higher concentrations is expected to be more properly followed by the measurements of dynamic behavior of methanol solutions by NMR spectroscopies [15]. In the high concentration region, however, the NMR signals of the Eu(oct-ala)$_3$ complex were too broad to be monitored for the dynamic properties, and thus we followed only the signal for the methanol solvent. Fig. 6 shows the change in the diffusion coefficients (D) of CH_3OH and in the CH_3OH-d_4 relaxation rates (R_1) as functions of the complex concentrations. In both cases there are slight break points at around 0.7 mol kg^{-1}. Above this concentration, the broad peak also appears at around $2\theta = 4.1°$ in the SAXS observation and the peak position was almost unmoved with an increase in the complex concentrations. This peak is ascribed to the formation of molecular aggregates as described above. Therefore, we can consider that the formation of glassy state is a result of the isotropic aggregation of Eu(oct-ala)$_3$ in methanol, since the formation of lyotropic liquid crystal was not detected in the concentrated solutions by the PM observation.

In conclusion, the Eu(oct-ala)$_3$ complex takes a glassy state more easily than Eu(octnt)$_3$ does. It is a rare case for C8-chained metal complexes that the stable glassy states are easily formed at room temperature even by the solvent-evaporation method, in contrast to the metal alkanoates where the stable glassy state was formed only in the case of long-chained tris(octadecanoato)lanthanides by super cooling. It is characteristic that the luminescence properties of both Eu(oct-ala)$_3$ and Eu(octnt)$_3$ complexes are enhanced with an addition of bpy or dnbpy, and furthermore Eu(octnt)$_3$ also becomes to form a transparent glass in the presence of bpy or dnbpy.

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