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Thermo-Sensitive Eu^{III} Coordination Polymers with Amorphous Networks

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Abstract: Luminescent Eu^{III} coordination polymer with amorphous transformation and thermo-sensing abilities under higher temperature, $[Eu(hfa)_3(tppa)_n]_m$ (hfa: hexafluoroacetylacetonate, tppa: tri-diphenylphosphoryl-4,4,4-triphenylamine) is reported. The glass transition and decomposition temperatures are found to be 142°C and 270°C, respectively. The intrinsic emission quantum yield Φ_{4f-4f} of $[Eu(hfa)_3(tppa)_n]_m$ was estimated to be 69% in solid state. $[Eu(hfa)_3(tppa)_n]_m$ shows effective decrease in the emission lifetime upon increasing the temperature from 320 to 400 K. The temperature-depended emission lifetime is caused by the back energy transfer from emitting level of Eu^{III} ion ($^5D_0$) to the LLCT band (tppa ligand to hfa ligand) in $[Eu(hfa)_3(tppa)_n]_m$. Thermo-sensitive lanthanide luminophore with stable glass formation in higher temperature (> 100°C) is useful for surface temperature detection in the field of high-speed wind tunnel experiments such as aircraft and automobile designs.

Introduction

Luminescent thermo-sensors composed of lanthanide complexes have attracted attention owing to their precise temperature imaging with narrow emission bands (full-width at half maximum (FWHM) < 10 nm) and long emission lifetimes (> 1 ms), which are based on the 4f–4f transitions.[1-4] In 2003, Amao and co-workers reported a luminescent thermosensitive paint that used the vibrational relaxation process of a red luminescent Eu^{III} complex.[5] In 2004, we described the temperature-sensing ability of a green luminescent Tb(III) complex that was based on the back energy transfer.[6] The temperature-depended energy transfer process from Tb^{III} to Eu^{III} in a lanthanide coordination polymer has also been used for a ratiometric luminescent thermo-sensor.[5] Thermosensitive paints containing luminescent lanthanide complexes have been widely investigated.[7-11]
Thermo-sensitive luminescent lanthanide complexes and coordination polymers are usually dissolved or homogenous-dispersed in polymer matrices such as polymethyl methacrylate for transparent luminescent materials to avoid light scattering from crystal grain boundary of the compounds.[12,13] The low-concentration of lanthanide luminophore in polymer films (thickness < 1 mm, concentration < 1 w%), however, leads to decrease of the photon-absorption and luminescence intensities as a thermo-sensing paint. Thermo-sensitive lanthanide luminophores with transparent glass formation is expected to be useful in application for strong luminescent paint. The phase-transition behavior of molecular materials is based on their steric structures in the molecular crystals.[14] According to the molecular glass formation, Nakano and Shirota have reported that a series of C_3-symmetric triphenylamine derivatives (bond-angle 120°) exhibits glass transition and electrical conductivity.[15, 16] We also succeeded in synthesizing luminescent and amorphous Eu^{III} complexes, light-harvesting hexafluoroacetylacetonate (hfa) ligands, and 120°-angled bridging ligands with ethynyl groups.[17] Their glass transition behaviors are observed under 90°C. Thermo-sensitive lanthanide luminophore with stable glass formation in a higher temperature range (> 100°C) is required for surface temperature detection in the field of high-speed wind tunnel experiments such as aircraft and automobile designs.[18]
In this study, novel thermo-sensitive and amorphous Eu^{III} coordination polymer in a higher temperature range is reported. The Eu^{III} coordination polymer with amorphous transformaion, Eu^{III} coordination-glass, is composed of $Eu(hfa)_3$ and tridentate phosphine oxide ligands with triphenylamine units (tppa: tri-diphenylphosphoryl-4,4,4-triphenylamine) ($[Eu(hfa)_3(tppa)_n]_m$, Fig. 1a).

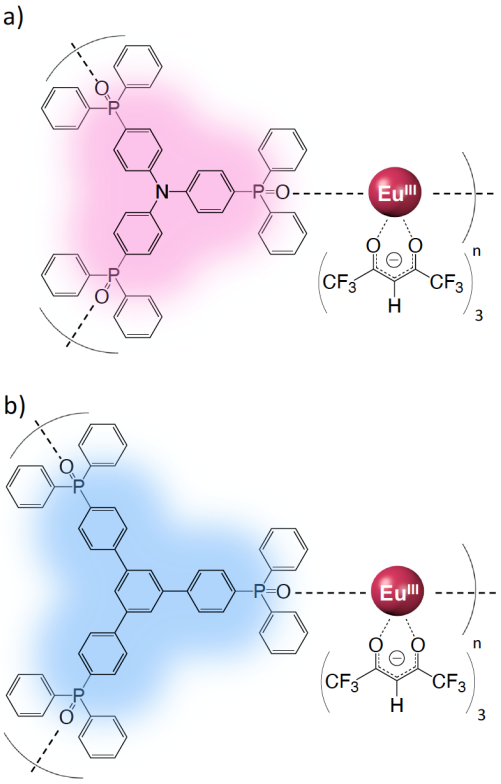

Figure 1. Molecular structures of a) $[Eu(hfa)_3(tppa)_n]_m$ and b) $[Eu(hfa)_3(tppb)_n]_m$.

The triphenylamine units in tppa ligands promote amorphous formation of transparent glass material. The typical phosphorescence band edge of the triphenylamine derivatives is shown at around 500 nm (~20,000 cm^{-1}), which is close to the energy gap of Eu^{III} ($^7F_0$-$^5D_0$: 578 nm, ~17,200 cm^{-1}).[19] The lower-lying triplet band of triphenylamine exhibits the temperature-depended luminescence based on the back energy transfer process. The Eu^{III} coordination polymer connected with tridentate phosphine oxide units is also expected to provide three-dimensional networks, resulting in increase of glass transition temperature and enhancement of the emission quantum yield.[20] Their glass transition behavior of $[Eu(hfa)_3(tppa)_n]_m$ was characterized using DSC and TGA measurements. The glass transition and decomposition temperatures were found to be 142ºC and 270ºC, respectively. The intrinsic emission quantum yield Φ_{4f-4f} of $[Eu(hfa)_3(tppa)_n]_m$ at room temperature (293K) was estimated to be 69%, which is similar to those of previous luminescent Eu^{III} coordination polymers.[7] The triphenyl-benzene-linked Eu^{III} coordination polymers $[Eu(hfa)_3(tppb)_n]_m$ (tppb: tris(4-diphenylphosphorylphenyl)ben-zene) was also prepared as a reference (Fig. 1b).[22] We observed that $[Eu(hfa)_3(tppa)_n]_m$ showed an effective decrease in the emission lifetime upon increasing the temperature from 320 to 400 K.

Results and Discussion

The Eu^{III} coordination polymers, $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$, were prepared by the complexations of $Eu(hfa)_3(H_2O)_2$ with the corresponding tridentate phosphine oxide ligands. The polymeric structure of $[Eu(hfa)_3(tppa)_n]_m$ was characterized using ESI-MS. The observed ESI-MS signals of $[Eu(hfa)_3(tppa)_n]_m$ are shown in Figure 2. The observed signals with mass numbers (m/z) of 1412.22, 2186.30, 2257.31 2959.91, 3030.44 and 3805.14 were assigned to fragments $[Eu(hfa)_2(tppa)]^+$, $[Eu_2(hfa)_5(tppa)]^+$, $[Eu(hfa)_2(tppa)_2]^+$, $[Eu_3(hfa)_8(tppa)]^+$, $[Eu_2(hfa)_5(tppa)_2]^+$ and $[Eu_3(hfa)_8(tppa)_2]^+$ respectively. The assignments were made by comparing the observed isotope distribution of $[Eu(hfa)_3(tppa)_n]_m$ (m/z at around 1412.22, 2186.30, 2959.91 and 3805.14) with the calculated data. The polymeric structure of $[Eu(hfa)_3(tppb)_n]_m$ was also identified using ESI-MS according to our previous report. [20] Estimated Eu/P atomic ratio using CIP-OES of $[Eu(hfa)_3(tppa)_n]_m$ was found to be 2.07. Prepared $[Eu(hfa)_3(tppa)_n]_m$ is amorphous material, which is difficult for coordination structural analysis. Based on our previous paper, [20] Eu(III) ion might be coordinated by three hfa ligands.

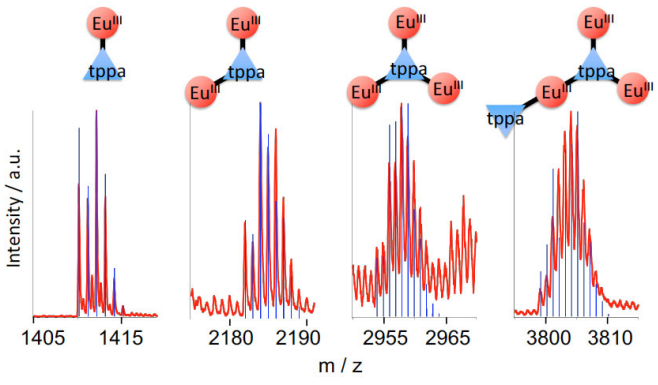

Figure 2. ESI-MS spectrum of $[Eu(hfa)_3(tppa)_n]_m$ using methanol.

The DSC measurements were conducted to evaluate the thermophysical properties of tppa ligands, $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$ (Figure 3: argon atmosphere, heating rate = 5 ºC, min^{-1}). We successfully observed that their thermograms of tppa and $[Eu(hfa)_3(tppa)_n]_m$ show endothermic peaks based on the glass transition of amorphous molecules at 121 ºC (range: 102-143 ºC) and 142 ºC (range 129-178 ºC), respectively (Fig. 3a-i and 3a-ii). The glass-transition point for $[Eu(hfa)_3(tppb)_n]_m$ was not observed (Fig. 3a-iii). The characteristic glass transition phenomena exhibited by tppa and $[Eu(hfa)_3(tppa)_n]_m$ are very similar to those shown by previous amorphous triphenylamine molecules.[21] Introduction of triphenylamine in Eu^{III} coordination polymer provides characteristic formation of amorphous structure. The glass transition temperature (142ºC) of $[Eu(hfa)_3(tppa)_n]_m$ is much higher than those of previous reported Eu^{III} coordination polymers with ethynyl groups (< 100ºC). The decomposition temperature of tppa and $[Eu(hfa)_3(tppa)_n]_m$ using TGA analysis were estimated to be 510ºC and 270ºC, respectively (Fig. 3b-i and 3b-ii). From these results, $[Eu(hfa)_3(tppa)_n]_m$ has kept a stable amorphous structure for effective monogenous thermo-sensor in the range of higher temperature (under 400 K).

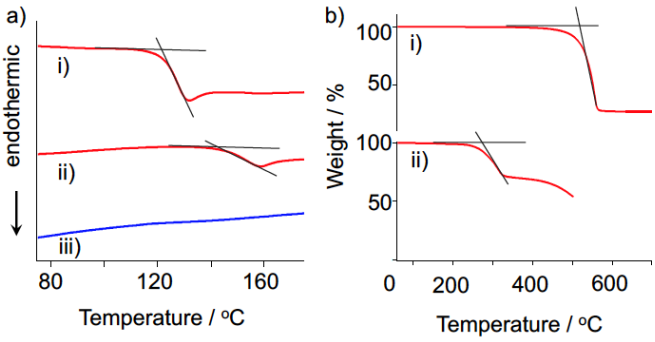

Figure 3. a) DSC profiles for tppa ligand (i: red line), $[Eu(hfa)_3(tppa)_n]_m$ (ii: red line) and $[Eu(hfa)_3(tppb)_n]_m$ (iii: blue line). Heating rate = 5 ºC, min^{-1}. b) TGA profiles for tppa ligand (i: red line), $[Eu(hfa)_3(tppa)_n]_m$ (ii: red line). Heating rate = 5 ºC min^{-1}.

The diffuse reflectance spectra of tppa ligand, $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$ in solid are shown in Fig. 4a. The absorption shoulder bands at 300 nm are attributed to π–π^* transitions of the tppa and hfa ligands in $[Eu(hfa)_3(tppb)_n]_m$, which agree with the absorption band of $[Eu(hfa)_3(H_2O)_2]$ at around 300 nm. The characteristic absorption shoulder bands of solid state $[Eu(hfa)_3(tppb)_n]_m$ at around 400 nm could be assigned to the interligand charge transfer (ILCT) via charge re-distribution of the hfa ligands.[22] The ILCT state via charge redistribution is formed in close packing crystals.[23] We also found that the remarkable absorption shoulder band of $[Eu(hfa)_3(tppa)_n]_m$ was observed at around 425 nm (red line, arrow symbol, band edge ~ 450 nm), which is different from those of corresponding tppa ligands (black line) and $[Eu(hfa)_3(tppb)_n]_m$ (blue line). This red-shift of absorption shoulder band is caused by complexation of Eu^{III} coordination polymer, $[Eu(hfa)_3(tppa)_n]_m$. In order to identify the absorption shoulder band, TD-DFT calculation (B3LYP, 6-31G(d)) of excited $[Eu(hfa)_3(tppa)_n]_m$ using Al^{III} ions instead of Eu^{III} ions was carried out. Their molecular orbital representations by Natural Transition Orbitals (NTO) are shown in Figure 4b. The electron densities in ground and excited states for S_0–T_1 transition of $[Eu(hfa)_3(tppa)_n]_m$ units are localized in π orbitals of tppa and hfa ligands,

respectively. This transition in $[Eu(hfa)_3(tppa)_n]_m$ units are interpreted to be ligand-to-ligand charge transfer (LLCT) transitions.[24] The energy gap between the lowest excited singlet (S_0) and triplet (T_1) states in $[Eu(hfa)_3(tppa)_n]_m$ was estimated to be 20,200 cm^{-1}. The low-lying energy level of the photosensitization ligand is higher than that of the emitting level of the Eu^{III} ion ($^7F_0$-$^5D_0$: 17,200 cm^{-1}). The energy back transfer from the lanthanide ion to the ligands is enhanced at room temperature, when the energy gap is around 1,850 cm^{-1}.[25] The excited $[Eu(hfa)_3(tppa)_n]_m$ is expected to promote the back energy transfer with activation energy from the excited Eu^{III} to LLCT state at higher temperature.

The steady-state emission spectra of $[Eu(hfa)_3(tppa)_n]_m$ and $Eu(hfa)_3(tppb)_n]_m$ in the solid are shown in Figure 4c. The wavelength dependence of the detector response and the beam intensity of the Xe light source for each emission spectrum are calibrated using a standard light source. The emission bands for the Eu^{III} coordination polymers are observed at around 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. Their spectra are normalized with respect to the magnetic dipole transition intensities at 592 nm (Eu: $^5D_0$-$^7F_1$), which is known to be insensitive to the surrounding environment of the lanthanide ions.[29] The excitation bands at around 425 nm in $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$ (arrow symbol) might be originated from LLCT and ILCT bands, respectively. The sharp excitation bands at 465 and 532 nm are contributed by the 4f-4f transitions of Eu^{III} ions.

The time-resolved emission profiles of $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$ revealed single-exponential decays with lifetimes in the millisecond time scale Figure 4d. The emission lifetimes were determined from the slopes of logarithmic plots of the decay profiles. The observed emission lifetimes (τ_{obs}) of $[Eu(hfa)_3(tppa)_n]_m$ and $[Eu(hfa)_3(tppb)_n]_m$ at 20 °C were found to be 0.70 and 0.87 ms, respectively. The notable amorphous form of luminescent $[Eu(hfa)_3(tppa)_n]_m$ is shown in Figure 4e. We observed transparent glass with red-luminescence of $[Eu(hfa)_3(tppa)_n]_m$, which is produced by rapid cooling after heat-treatment at 200°C. On the other hand, $[Eu(hfa)_3(tppb)_n]_m$ cannot be transformed. The amorphous Eu^{III} coordination polymer with triphenylamine units would be useful for new application such as strong luminescent lanthanide glass.

The emission quantum yields (Φ_{4f-4f}), radiative (k_r) and nonradiative (k_{nr}) rate constants for the Eu^{III} coordination polymers are shown in Table 1. The Φ_{4f-4f} of $[Eu(hfa)_3(tppa)_n]_m$ was estimated to be 69% in solid state, which is smaller than that of $[Eu(hfa)_3(tppb)_n]_m$.[20] The smaller Φ_{4f-4f} of $[Eu(hfa)_3(tppa)_n]_m$ is based on the large k_{nr}. The non-radiative rate constant k_{nr} is generally related to the thermal relaxation from the excited state, which is dependent on the vibrational structure of the luminescent materials. The characteristic three-dimensional structure of $[Eu(hfa)_3(tppa)_n]_m$ might also produce an asymmetric coordination structure at around the Eu^{III} ions with molecular strain, which provides larger k_r. The Φ_{4f-4f} of $[Eu(hfa)_3(tppa)_n]_m$ is similar to those of corresponding previous one-dimensional Eu^{III} coordination polymer with remarkable luminescence performance.[7]

The photosensitized emission efficiency ($\Phi_{\pi-\pi^*}$) of $[Eu(hfa)_3(tppa)_n]_m$ excited at 370 nm at 20°C using an integrating sphere (ϕ= 100 mm) was estimated to be 18%, which are smaller than that of $[Eu(hfa)_3(tppa)_n]_m$ ($\Phi_{\pi-\pi^*}$ = 78%).[22] The smaller efficiency of $[Eu(hfa)_3(tppa)_n]_m$ should be caused by lower energy level of the T_1 state of LLCT band. The lower energy level of LLCT band in $[Eu(hfa)_3(tppa)_n]_m$ promotes the energy back transfer from excited Eu^{III} ion to the T_1 state, resulting in thermo-sensing properties.

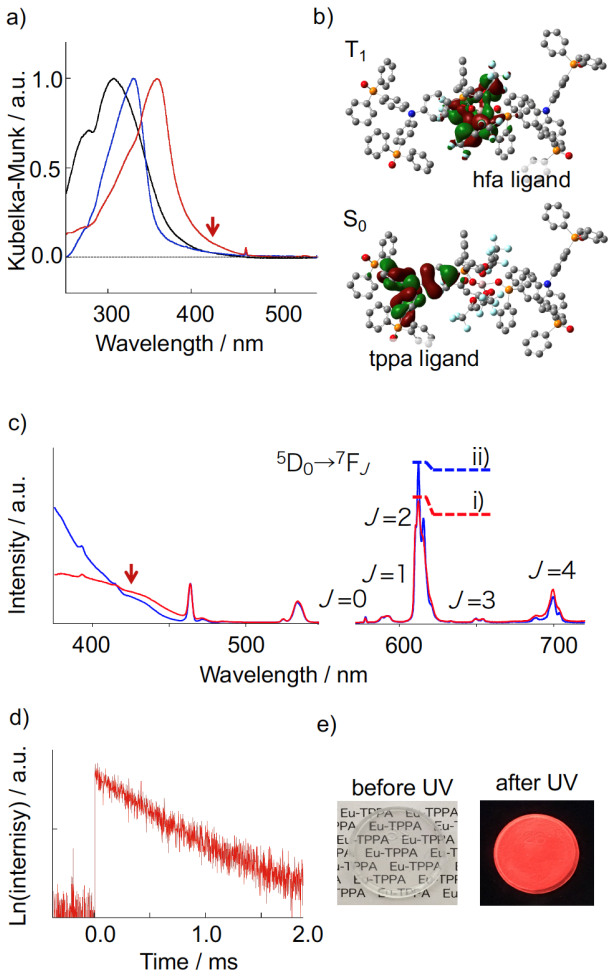

Figure 4. a) Diffuse reflectance spectra of tppa ligand (black line) $[Eu(hfa)_3(tppa)_n]_m$ (red line) and $[Eu(hfa)_3(tppb)_n]_m$ (blue line) in solid. b) Molecular orbital representations of the lowest triplet and ground states of $[Eu(hfa)_3(tppa)_n]_m$ simplified by NTO showing the highest transition probability. DFT calculations were performed using Al^{III} ions instead of Tb^{III} ions for all complexes. c) Emission and excitation spectra of $[Eu(hfa)_3(tppa)_n]_m$ (i: red line) and $[Eu(hfa)_3(tppb)_n]_m$ (ii: blue line). Excited and emission wavelength were 370 nm and 612 nm, respectively. d) Emission decay profile $[Eu(hfa)_3(tppa)_n]_m$. Excitation wavelength 355 nm (third harmonics of Q-switched Nd: YAG laser. fwhm = 5 ns, λ = 1064 nm). e) Photographs of amorphous $[Eu(hfa)_3(tppa)_n]_m$ before and after UV irradiation.

Table 1. Photophysical properties of Eu^{III} coordination polymers at 294 K.

compound	Φ_{4f-4f} / % [a]	τ_{obs} / ms [b]	k_r / s^{-1}	k_{nr} / s^{-1}
$[Eu(hfa)_3(tppa)_n]_m$	68 ± 2	0.70 ± 0.01	9.9×10^2	$(4.4 \pm 0.2) \times 10^2$
$[Eu(hfa)_3(tppb)_n]_m$[c]	83 ± 1	0.87 ± 0.01	9.5×10^2	$(2.0 \pm 0.1) \times 10^2$

[a] Emission quantum yields Φ_{4f-4f} were estimated using emission lifetimes τ_{obs} and calculated radiative rate constants from emission spectra. [b] Emission lifetime were measured by excitation at 355 nm (Nd: YAG, λ = 355 nm). [c] Data for $[Eu(hfa)_3(tppb)_n]_m$: Y. Hasegawa et al, *Chem. Eur. J.* 23, 2666 (2017).

Thermosensitive measurements through change in emission lifetime have been reported as a precise and reliable evaluation for estimation of performance in thermo-sensors.[26–30] Temperature-dependent emission lifetimes were measured to investigate the temperature sensitivity of the Eu^{III} coordination polymer. $[Eu(hfa)_3(tppb)_n]_m$ did not show any change in the emission lifetime from 100 to 400 K. We found that $[Eu(hfa)_3(tppa)_n]_m$ showed decrease in the emission lifetime upon increasing the temperature from 320 to 500 K (Figure 5a). These emission lifetimes changes are caused by the back energy transfer to the LLCT transitions in $[Eu(hfa)_3(tppa)_n]_m$.

To analyze the back energy transfer (BEnT) mechanism, we estimated the back energy transfer rate constants (k_{BEnT}) by kinetic analysis. The temperature dependence of k_{BEnT} was expected to follow an Arrhenius-type equation with an activation energy ΔE_a,[31] which is defined by,

$$\mathrm{Ln}\left(\frac{1}{\tau_{obs}}-\frac{1}{\tau_{300K}}\right)=\mathrm{Ln}k_{BEnT}=\mathrm{Ln}A-\frac{\Delta E_a}{R}\times T^{-1} \quad (1)$$

in which τ_{obs}, τ_{300K}, A, ΔE_a, R, and T are the observed emission lifetime, emission lifetime at 300 K, frequency factor, activation energy, gas constant, and temperature, respectively. The ΔE_a of $[Eu(hfa)_3(tppa)_n]_m$ is estimated to be 5,400 cm^{-1} (Figure 5b, see supporting information at around glass-transition temperature, Figure S3), which is higher than that of thermosensitive Tb^{III} complexes ($[Tb(hfa)_3(tppo)_2]$: 3,200 cm^{-1}). The higher ΔE_a value for $[Eu(hfa)_3(tppa)_n]_m$ promotes effective emission quantum yield at room temperature and drastic changes of temperature-sensing property at higher temperature (> 100°C). We consider that the energy transfer from $^5D_0$ excited state of Eu^{III} to the T_1 state on LLCT is effective for thermosensitive paint (Figure 5c).

Conclusion

Lanthanide coordination polymer with glass transition ability, lanthanide coordination-glass, opens-up a new frontier field of molecular material science. In this study, luminescent Eu^{III} coordination polymer with amorphous transformation and thermo-sensitive property in higher temperature range was successfully prepared. The glass transition and thermo-sensing ability were achieved by introduction of triphenylamine unit of tridentate linker ligand in $[Eu(hfa)_3(tppa)_n]_m$. The characteristic tight-packed amorphous network structure of Eu^{III} coordination polymer also promoted effective emission quantum yield (Φ_{4f-4f} = 69 %), high glass transition and decomposition temperatures (T_g = 142°C, d.p.= 270°C).

Temperature-sensitive paints (TSPs) are promising molecules to accurately measure the physical parameters of a material surfaces.[32] The combination of PSPs and TSPs would also be useful for detection of surface condition on the various materials.[33, 34]

Supporting Information Summary

Experimental procedure, structural characterizations, estimations and calculations of photophysical properties of $[Eu(hfa)_3(tppa)_n]_m$, and Emission spectra of $[Eu(hfa)_3(tppa)_n]_m$ coordination polymer at 300 K and 450 K are available in supporting information.

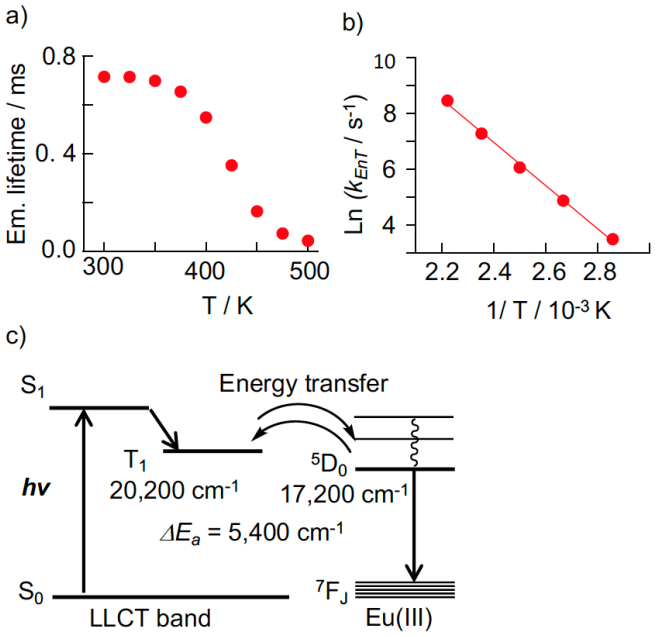

Figure 5. a) Temperature-dependent emission lifetimes of $[Eu(hfa)_3(tppa)_n]_m$ in solid. b) Arrhenius plot for energy-transfer rate of $[Eu(hfa)_3(tppa)_n]_m$ c) Illustration of 4f–4f emission ($^5F_0$-^7F_J) and energy transfer processes of $[Eu(hfa)_3(tppa)_n]_m$. The energy level of the excited triplet state of $[Eu(hfa)_3(tppa)_n]_m$ was estimated through TD-DFT calculation (B3LYP level with the basis set 6-31G(d)).

Acknowledgements

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Keywords: luminescence• lanthanide• europium• coordination polymer • amorphous

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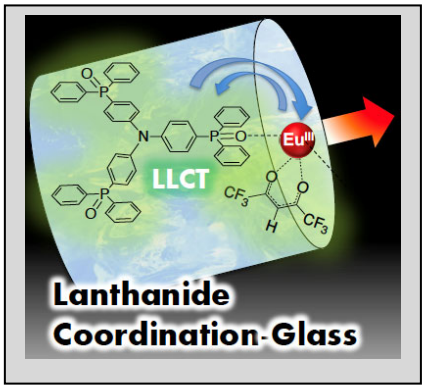

Luminescent Eu^{III} coordination polymer with amorphous transformation and thermo-sensing abilities under higher temperature. The intrinsic emission quantum yield was estimated to be 69% at room temperature. The Eu^{III} coordination-glass shows effective decrease in the emission lifetime upon increasing the temperature from 320 to 400 K. Thermo-sensitive lanthanide luminophore with stable glass formation in higher temperature is useful for surface temperature detection.