# Thermo-sensitive Luminescence Based on the Back Energy Transfer in Terbium(III) Complexes

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The emission intensities of Tb(hexafluoroacetylacetonato)$_3$($H_2O$)$_2$ [Tb(HFA)$_3$($H_2O$)$_2$] and Tb(HFA)$_3$(triphenylphosphine oxide)$_2$ [Tb(HFA)$_3$(TPPO)$_2$] in acetone-$d_6$ dramatically decreased with increasing temperature in contrast to no change observed for Tb($NO_3$)$_3$. The high thermal sensitivity is attributed to the back energy transfer from Tb(III) ion to triplet state of HFA having the energy barrier.

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In the study on fluid dynamics, aeronautical engineering, environment engineering, and energy technology, it is important to measure physical conditions of the surface of materials.[1] Opto-electronic devices have been generally employed as a temperature and pressure sensor.[2] However, their sensing area is an one-point on the surface. Surface measurement materials, for example, temperature and pressure-sensing dyes have been keenly desired to solve this intrinsic problem of opto-electronic device.

Our purpose is to design temperature-sensing dyes using luminescent lanthanide(III) (Ln(III)).[3] Ln(III) complexes show characteristic luminescence with narrow emission bands and long emission lifetimes, which allow them to be suited to sensing devices.[4] Here, we propose a new idea to employ the temperature-dependent energy transfer process in Ln(III) complexes for temperature-sensing. Our key point for creation of high-performance dyes for temperature-sensing is to apply the back-energy transfer from Ln(III) ion to triplet state of the ligands (Figure 1). The back-energy transfer will depend on temperature, when there is an energy barrier for the process, resulting in the temperature-dependence of the emission intensity of Ln(III). In order to realize dyes for temperature-sensing with the back energy transfer concept, the Tb(III) complexes including the hexafluoroacetylacetone (HFA), Tb(HFA)$_3$($H_2O$)$_2$ and Tb(HFA)$_3$(TPPO)$_2$ were selected (Figure 1), because the triplet state of the HFA (22200 cm$^{-1}$) is very close to the emitting level of Tb(III) ion (20500 cm$^{-1}$), probably resulting in the effective back energy transfer and then high-performance of the temperature-sensing dyes. Tb(III) complexes, tris(hexafluoroacetylacetonato)terbium(III) [Tb(HFA)$_3$($H_2O$)$_2$] and tris(hexafluoroacetylacetonato)-bis(triphenylphosphineoxide)terbium(III) [Tb(HFA)$_3$(TPPO)$_2$], were prepared according to the procedure described in a literature.[5] The emission spectra were measured by a SPEX-Fluorolog $\tau$-3 (Jobin Yvon Inc.) with a thromo-stat and -sensor. The emission quantum yield was measured by a HITACHI F-4500 spectrophotometer with an integrating sphere.[5] Decay profiles monitored at 547 nm were recorded with a photomultiplier coupled to a Tektronix TDS3052 oscilloscope upon excitation with the third harmonic of a Nd:YAG laser (355 nm).

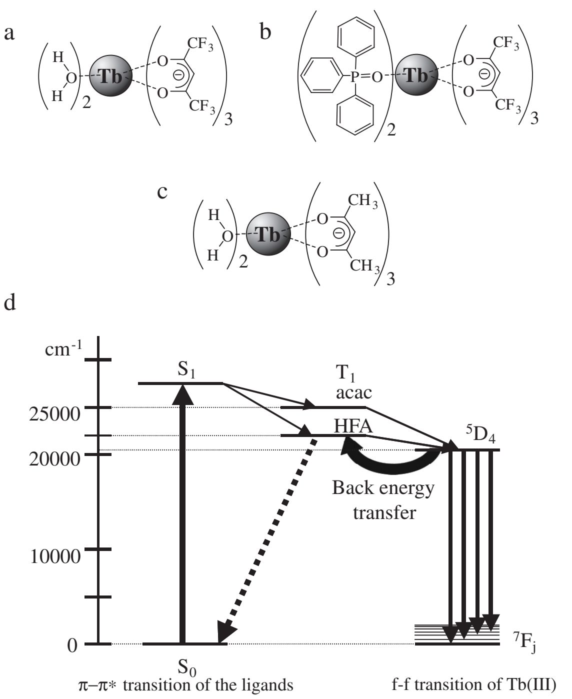

**Figure 1.** Chemical structures of a) Tb(HFA)$_3$($H_2O$)$_2$, b) Tb(HFA)$_3$(TPPO)$_2$, and c) Tb(acac)$_3$($H_2O$)$_2$. d) Energy diagram of Tb(III) complexes and back energy transfer processes.

The changes of the emission of the three Tb(III) complexes in acetone-$d_6$ depending on temperatures are shown in Figure 2. The emission intensities of Tb(HFA)$_3$($H_2O$)$_2$ in acetone-$d_6$ (ex. at 363 nm; ligand excitation) dramatically decreased with increasing temperature in clear contrast with small decrease observed for Tb(acac)$_3$($H_2O$)$_2$. On the other hand, the emission intensity of Tb($NO_3$)$_3$ observed under direct excitation at 370 nm was slightly changed.

The emission intensities of the Tb(III) complexes are plotted

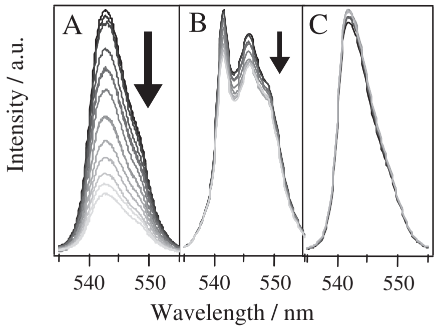

**Figure 2.** Temperature-dependence of the emission spectra of A) Tb(HFA)$_3$($H_2O$)$_2$ (ex. at 363 nm), B) Tb(acac)$_3$($H_2O$)$_2$ (ex. at 345 nm), and C) Tb($NO_3$)$_3$ (ex. at 370 nm) in acetone-$d_6$ in the temperature range of 10–50 °C.

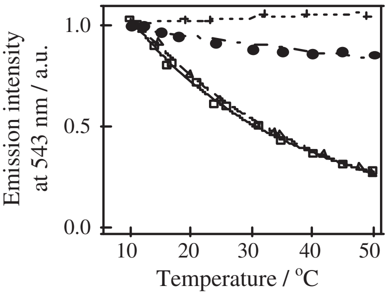

**Figure 3.** Temperature-dependence of the emission intensities of $Tb(NO_3)_3$ (+), $Tb(acac)_3(H_2O)_2$ (●), $Tb(HFA)_3(H_2O)_2$ (□), and $Tb(HFA)_3(TPPO)_2$ (△).

against the temperatures in Figure 3. The decrease of the emission intensity of $Tb(acac)_3(H_2O)_2$ was much smaller than those of $Tb(HFA)_3(H_2O)_2$ and $Tb(HFA)_3(TPPO)_2$. In order to estimate the energy gaps between the emitting level of Tb(III) and the triplet levels of the ligands, we measured the phosphorescence spectra using $Gd(HFA)_3(H_2O)_2$ and $Gd(acac)_3(H_2O)_2$. The energy gaps in $Tb(HFA)_3(H_2O)_2$ and $Tb(acac)_3(H_2O)_2$ were found to be 1700 and 4300 $cm^{-1}$ respectively. When the energy gap is less than 1850 $cm^{-1}$, the back energy transfer from Tb(III) ion to the ligands is enhanced.[6] Therefore, the combination of Tb(III) ion with HFA should lead to an optimum condition for enhancement of the back energy transfer, then resulting in the high temperature-sensitivity. In contrast, the emission intensities of $Tb(NO_3)_3$ were slightly increased with increasing temperature (0.12%/°C), being much smaller than the change of the emission intensities of Tb complexes with HFA.

The rate of the back energy transfer should depend on temperature, following an Arhenus type equation having an energy barrier $E$. We carried out the measurements of the emission of $Tb(HFA)_3(H_2O)_2$ and $Tb(acac)_3(H_2O)_2$ by excitation at 487 nm (ion direct excitation) at different temperatures (Figure 4). Decrease of the emission intensities of $Tb(HFA)_3(H_2O)_2$ with increasing temperature was observed as observed for the excitation at 363 nm ($\pi$–$\pi^*$ of the ligand). Additionally, the decrease in the emission intensity of $Tb(acac)_3(H_2O)_2$ depending on temperature was as small as was observed for the ligands exciatition at 345 nm. These facts indicate that the temperature dependence of the emission should be attributed not to the f–f transition but to the back energy transfer from Tb(III) to the ligand, when it is taken into account that $Tb(NO_3)_3$ does not show the temperature dependence. In order to prove the back energy transfer mechanism, we carried out the emission lifetime measurements at 77 K. The emission lifetimes of $Tb(HFA)_3(H_2O)_2$, $Tb(acac)_3(H_2O)_2$ and $Tb(NO_3)_3$ at 77 K were found to be 0.6, 0.8, and 0.8 ms, respectively. The dramatical increase of the emission lifetime was observed for $Tb(HFA)_3(H_2O)_2$ at 77 K compared to that observed at room temperature, in spite of similar values of $Tb(acac)_3(H_2O)_2$ and $Tb(NO_3)_3$ to those observed at room temperature (Table 1). Furthermore, the emission lifetime of $Tb(HFA)_3(H_2O)_2$ was similar to those of $Tb(acac)_3(H_2O)_2$ and $Tb(NO_3)_3$ at 77 K. The results supported that the back energy transfer process has the barrier $E$ with temperature-dependency. We have concluded that the high temperature-sensitivity is derived from the back energy transfer from the ion to the triplet of the ligand.

**Table 1.** The emission and thermo-sensing properties of Tb(III) complexes (at room temperature)

| Complex | Emission Quantum Yield[a] | Lifetime / ms | Temperature-sensing Property / %/°C |
|---|---|---|---|
| $Tb(HFA)_3(H_2O)_2$ | 0.017 | 0.0046 | 1.81 |
| $Tb(HFA)_3(TPPO)_2$ | 0.30 | 0.083 | 1.90 |
| $Tb(acac)_3(H_2O)_2$ | 0.59 | 0.63 | 0.45 |
| $Tb(NO_3)_3$ | — | 1.0 | −0.12 |

[a] Ex. at 355 nm. The emission quantum yields of $Tb(HFA)_3(H_2O)_2$, $Tb(HFA)_3(TPPO)_2$ were measured by excitation at 363 nm, the emission quantum yields of $Tb(acac)_3(H_2O)_2$ were measured by excitation at 346 nm.

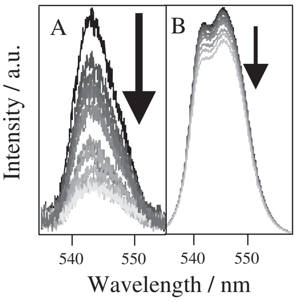

**Figure 4.** Temperature-dependence of the emission spectra of A) $Tb(HFA)_3(H_2O)_2$ (ex. at 487 nm) and B) $Tb(acac)_3(H_2O)_2$ (ex. at 487 nm) in acetone-$d_6$ in the temperature range of 10–50 °C.

The emission quantum yields and lifetimes of $Tb(HFA)_3(TPPO)_2$ in acetone-$d_6$ were found to be 0.30 and 83 μs, respectively (Table 1). The emission intensity of $Tb(HFA)_3(TPPO)_2$ was much stronger than that of $Tb(HFA)_3(H_2O)_2$ ($\Phi = 0.017$, $\tau = 4.6$ μs). TPPO ligands should contribute to the enahanced emission of Tb(III) complexes. $Tb(HFA)_3(TPPO)_2$ is the best dye in the view point of high temperature-sensitivity. The temperature-sensing property of $Tb(HFA)_3(TPPO)_2$ was determined to be 2.0%/°C. Amao and co-workers reported the temperature-sensing polymer-films including $Eu(TTA)_3$phen (0.78%/°C). We are now trying to fabricate the temperature-sensing films using $Tb(HFA)_3(TPPO)_2$. Understanding of the detail kinetics would lead to a new strategy for designing the high-performance dye as a new-type temperature-sensor.

## References and Notes

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