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Luminescence

Chameleon Luminophore for Sensing Temperatures: Control of Metal-to-Metal and Energy Back Transfer in Lanthanide Coordination Polymers**

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In the fields of fluid dynamics, aeronautical engineering, environment engineering, and energy technology, it is critical to accurately measure the physical parameters of a material surface.[1] Optoelectronic devices have generally been employed as temperature and pressure sensors.[2] However, their sensing area is limited to a single point on a surface. There is a need to measure entire surfaces and obtain multidimensional data for mapping surfaces. There are high expectations that materials for surface measurements, such as temperature and pressure-sensitive dyes, will overcome this intrinsic limitation of optoelectronic devices.

We seek to design temperature-sensitive dyes using luminescent lanthanide complexes. Lanthanide complexes exhibit characteristic luminescence with narrow emission bands (full width at half maximum, fwhm < 10 nm) and long emission lifetimes (> 1 μs),[3] which make them suitable for use in sensing devices. In 2003, Amao and co-workers reported the first temperature-sensitive dye that employed an Eu^{III} complex in a polymer film.[4] Khalil et al. demonstrated the high performance of an Eu^{III} complex for a temperature-sensitive paint (temperature sensitivity: 4.42 % °C^{-1}).[5] We have reported a Tb^{III} complex, $Tb(hfa)_3(H_2O)_2$ (hfa: hexafluoro acetylacetonato), that is suitable as a temperature-sensing probe since it exhibits effective energy back transfer (BEnT) from the emitting level of the Tb^{III} ion to the excited triplet state of the hfa ligand.[6] Since BEnT depends on the energy barrier of the process, the emission intensity varies with temperature.

To improve the thermosensing performance, it is necessary to develop a thermostable structure for high-temperature sensing and to implement a dual sensing unit for a high sensing ability. First, we focused on a lanthanide coordination polymer to produce a thermostable structure. Thermally stable coordination polymers and metal–organic frameworks have been widely studied.[7] Carlos and co-workers recently reported novel three-dimensional lanthanide-organic frameworks with 2,5-pyridinedicarboxylic acid.[8] Marchetti et al. developed thermostable Eu^{III} coordination polymers with 4-acyl-pyrazolone ligands.[9] Here, we consider that introducing Tb^{III} ion and hfa ligands to coordination polymer frameworks will produce a Tb^{III} coordination polymer that can be used as a temperature-sensing probe. The triplet state of hfa (22 000 cm^{-1}) is very close to the emitting level of the Tb^{III} ion (20 500 cm^{-1}), resulting in effective EnT1 and BEnT and thus high-performance thermosensing dyes (Figure 1 a). We also selected low-vibrational frequency phosphane oxide[10] as the linking part in the Tb^{III} coordination polymer because lanthanide complexes with high emission quantum yields composed of hfa and bidentate phosphane oxide ligands have been reported.[11]

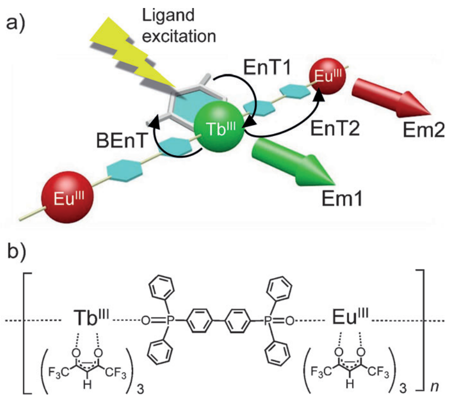

Figure 1. a) Energy transfer processes of the Eu^{III} and Tb^{III} coordination polymer (EnT: energy transfer, BEnT: energy back transfer, Em: emission). b) Chemical structure of $[Ln(hfa)_3(dpbp)]_n$ (Ln = Eu, Tb).

Second, we attempted to impart ratiometric temperature sensing by using luminescent Eu^{III} and Tb^{III} ions in the frameworks of the coordination polymer to realize a high thermosensing ability. Two independent emission bands are expected to enable more accurate thermal measurements than a previous single lanthanide complex.[12] Their emission

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intensities based on the energy transfer from Tb^{III} to Eu^{III}, EnT2 (Figure 1a) may also dependent on the temperature. Temperature-sensitive dyes with a thermostable structure and dual sensing units have not been previously reported.

In the present study, we report a novel thermosensing dye that consists of a lanthanide coordination polymer; $[Ln(hfa)_3(dpbp)]_n$ and $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ (dpbp: 4,4′-bis(diphenylphosphoryl) biphenyl, Ln = Eu, Tb), as shown in Figure 1b. Its thermal stability and luminescence properties are characterized by thermogravimetric analysis (TGA) and by emission quantum yield and emission lifetime measurements. This coordination polymer has a high emission quantum yield ($\Phi = 40\,\%$ for $[Tb(hfa)_3(dpbp)]_n$ at room temperature) and a temperature sensitivity over a wide temperature range of 200–500 K. The thermosensing dye composed of Tb^{III} and Eu^{III} coordination polymers is expected to open up new fields in the molecular chemistry of temperature-sensing materials.

$[Ln(hfa)_3(dpbp)]_n$ and $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ (Ln = Eu, Tb) were synthesized by complexing phosphane oxide ligands (dpbp) and $Ln(hfa)_3(H_2O)_2$ in methanol for 2 h (see the Supporting Information). The structure of $[Eu(hfa)_3(dpbp)]_n$ was determined by X-ray single-crystal analyses in Table S1 and Figure S1 in the Supporting Information. Phosphane oxide ligands acted as a bidentate bridge between lanthanide ions in one-dimensional polymeric chains. The coordination sites of $[Eu(hfa)_3(dpbp)]_n$ comprised three hfa ligands and two phosphane oxide units. This coordination structure was categorized as an eight-coordinated square antiprism.[13] The powder XRD spectra of $[Eu(hfa)_3(dpbp)]_n$, $[Tb(hfa)_3(dpbp)]_n$, and $[Tb_{0.99}\ Eu_{0.01}(hfa)_3(dpbp)]_n$ are shown in Figure S2. The XRD patterns of $[Tb(hfa)_3(dpbp)]_n$ and $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ are the same as that of $[Eu(hfa)_3(dpbp)]_n$, because of their ionic radii (Eu^{III}: 0.95 Å, Tb^{III}: 0.92 Å). These results indicate that the coordination structures of $[Tb(hfa)_3(dpbp)]_n$ and $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ are similar to that of $[Eu(hfa)_3(dpbp)]_n$.

To evaluate the thermal stability of lanthanide coordination polymers, we conducted TGA in an argon atmosphere at a heating rate of $1\,°C\,min^{-1}$ (Figure S3). The thermograms reveal that $[Eu(hfa)_3(dpbp)]_n$ and $[Tb(hfa)_3(dpbp)]_n$ have decomposition points of 308 and 317 °C, respectively (Table 1). In contrast, the Tb^{III} complex, $Tb(hfa)_3(H_2O)_2$, was found to have a decomposition point of 177 °C. The high thermal stability of $[Eu(hfa)_3(dpbp)]_n$ and $[Tb(hfa)_3(dpbp)]_n$ may be due to their tight-binding structures in coordination polymer units.[13]

Figure 2 shows temperature-dependent emission spectra of $Tb(NO_3)_3$, $[Tb(hfa)_3(dpbp)]_n$, and $[Eu(hfa)_3(dpbp)]_n$ in the solid state. The emission intensities of $[Tb(hfa)_3(dpbp)]_n$ decrease dramatically with increasing temperature. In contrast, the emission intensities of $Tb(NO_3)_3$ and $[Eu(hfa)_3(dpbp)]_n$ remain constant with temperature. The energy gaps between the emitting level of the lanthanide ion and the excited triplet state of the hfa ligand in $[Tb(hfa)_3(dpbp)]_n$ and $[Eu(hfa)_3(dpbp)]_n$ are 1700 and 4900 cm^{-1}, respectively.[6,14] The BEnT from the lanthanide ion to the ligands is enhanced when the energy gap is less than 1850 cm^{-1}.[15] Therefore, the combination of Tb^{III} ions with hfa ligands is expected to enhance BEnT, resulting in a high-temperature sensitivity.

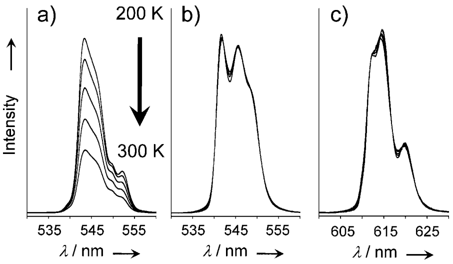

Figure 2. Temperature-dependent emission spectra of a) $[Tb(hfa)_3(dpbp)]_n$, b) $Tb(NO_3)_3$, and c) $[Eu(hfa)_3(dpbp)]_n$ in the solid state in the temperature range of 200–300 K ($\lambda_{ex} = 380$ nm).

The temperature dependence of the BEnT rate is expected to follow an Arrhenius-type equation with an energy barrier E_a. To analyze the BEnT mechanism in detail, we estimated the energy back-transfer rates (k_{back}) using kinetic analysis. k_{back} is assumed to obey the following Arrhenius-type Equation (1),

$$\ln k_{back} = \ln\left(\frac{1}{\tau_{obs}} - \frac{1}{\tau_{77K}}\right) = \ln A - \frac{E_a}{RT} \qquad (1)$$

where τ_{obs} is the emission lifetime, τ_{77K} is the emission lifetime at 77 K, A is the frequency factor, E_a is the activation energy, R is the gas constant, and T is the temperature. This assumption is supported by the findings of Blasse and Grabmaier.[16] To estimate E_a using Equation (1), we measured the temperature dependences of the emission lifetimes of $Tb(hfa)_3(H_2O)_2$ and $[Tb(hfa)_3(dpbp)]_n$. Figure S4 shows the temperature dependences of the emission lifetimes and the

Table 1: The emission and thermal properties at 300 K in the solid state.

	Decomposition point [°C][a]	Φ [%][b]	τ_{obs} [ms][b,c]	E_a [$kJ\,mol^{-1}$][d]	$\Delta G^{\ddagger}$ [$kJ\,mol^{-1}$]	Temperature sensitivity [$\%\,°C^{-1}$][e]
$Tb(NO_3)_3$	–	–	0.86	–	–	< 0.03
$Tb(hfa)_3(H_2O)_2$	177	27[f]	0.37	33	57	0.70
$[Tb(hfa)_3(dpbp)]_n$	317	40[f]	0.35	24	58	0.64
$[Eu(hfa)_3(dpbp)]_n$	308[h]	72[g,h]	0.85[g]	–	–	< 0.05

[a] TGA thermograms are shown in Figure S3. [b] At room temperature. [c] Emission lifetimes (τ_{obs}) were measured by excitation at 355 nm (Nd:YAG 3ω). [d] From the slope of the Arrehenius plot (Figure S4). [e] In the temperature range of 200–300 K. [f] Excited at 380 nm. [g] Excited at 465 nm. [h] From Ref. [13].

Arrhenius plots for k_{back} and Table 1 lists the calculated activation energy E_a and the activation Gibbs function $\Delta G^{\neq}$ values. We found that $[Tb(hfa)_3(dpbp)]_n$ has similar E_a and $\Delta G^{\neq}$ values to $Tb(hfa)_3(H_2O)_2$. These results indicate that phosphane oxide ligands may not affect the BEnT rate.

Table 1 also summarizes the emission and thermosensing properties of lanthanide coordination polymers in the solid state. $Tb(hfa)_3(H_2O)_2$ and $[Tb(hfa)_3(dpbp)]_n$ are estimated to have emission quantum yields Φ of 27 and 40% at room temperature, respectively. The quantum yields of $[Tb(hfa)_3(dpbp)]_n$ are approximately 1.5 times larger than that of $Tb(hfa)_3(H_2O)_2$. The phosphane oxide ligands are expected to enhance the emission of the Tb^{III} coordination polymer since they should suppress vibrational relaxation. $[Tb(hfa)_3(dpbp)]_n$ shows as a thermo-sensing dye the highest performance.

To investigate the ratiometric temperature-sensing properties of coordination polymers, $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ containing Tb^{III} and Eu^{III} ions has been synthesized. Figure 3a shows temperature-dependent emission spectra of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ in the solid state in the temperature range of 200–450 K and Figure 3b shows photographs that indicate the colors of the samples. The characteristic emission bands at 543 and 613 nm are attributed to the f–f transitions of Tb^{III} ($^5D_4$–$^7F_5$) and Eu^{III} ($^5D_0$–$^7F_2$), respectively. Their emission intensities at 543 nm decrease dramatically with increasing temperature. In contrast, the emission intensities at 613 nm increase slightly. $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ exhibits brilliant green, yellow, orange, and red photoluminescence under UV irradiation (365 nm) at 250, 300, 350, and 400 K, respectively. We achieved color tuning of the coordination polymers in response to temperature changes.

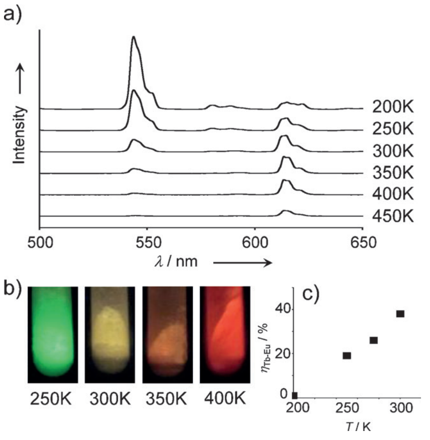

Figure 3. a) Temperature-dependent emission spectra of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ in the solid state in the temperature range of 200–450 K ($\lambda_{ex}=380$ nm). b) Color pictures of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ under UV (365 nm) irradiation, which show brilliant green, yellow, orange, and red emission. c) Temperature-dependence of the energy transfer efficiency ($\eta_{Tb\text{-}Eu}$).

$[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ has a higher temperature sensitivity (0.83 % °C^{-1}) than $[Tb(hfa)_3(dpbp)]_n$ (0.64 % °C^{-1}). This result indicates that energy is transferred to both the excited triplet state of the hfa ligands (BEnT) and to the Eu^{III} ion from the emitting level of the Tb^{III} ion. The energy transfer efficiency from the Tb^{III} ion to Eu^{III} ion ($\eta_{Tb\text{-}Eu}$) is calculated using Equation (2),[17]

$$\eta_{Tb-Eu} = 1 - \left(\frac{\tau_{obs}}{\tau_{Tb}}\right) \tag{2}$$

where τ_{obs} and τ_{Tb} are the emission lifetimes of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ and $[Tb(hfa)_3(dpbp)]_n$, respectively. The relation between $\eta_{Tb\text{-}Eu}$ and the temperature (200–300 K) are shown in Figure 3c. The values of $\eta_{Tb\text{-}Eu}$ at 200, 250, 275, and 300 K are estimated to be 1, 19, 26, and 38 %, respectively. $\eta_{Tb\text{-}Eu}$ increases with increasing temperature. The energy transfer occurs to both the excited triplet state of hfa ligands and to the Eu^{III} ion.

Finally, we demonstrated that the luminescence reversibly undergo repeated thermo-cycles. The reversible changes of emission intensity ratio of Eu^{III} and Tb^{III} (I_{Eu}/I_{Tb}) of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ are observed by the alternative thermo-cycles in the range of 300 and 400 K (Figure S5). The changes in the emission intensity ratio are stably repeated between the I_{Eu}/I_{Tb} values of 1.0 (300 K, yellow emission) and 8.7 (400 K, red emission). $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ also exhibits red emission under UV irradiation, even at 500 K (Figure 4). We thus successfully synthesized an effective luminophore with a wide temperature sensing range of 200 to 500 K.

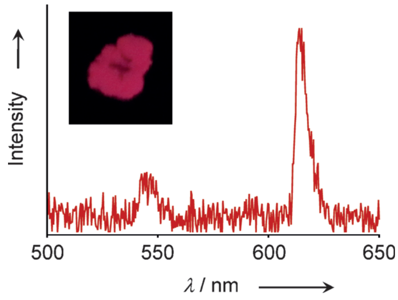

Figure 4. Emission spectra of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ in the solid state at 500 K ($\lambda_{ex}=380$ nm, $I_{Eu}/I_{Tb}=10$). Inset: Emission of $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ under UV (365 nm) irradiation at 500 K.

In summary, a novel thermosensing dye composed of a lanthanide coordination polymer was successfully synthesized. This coordination polymer is thermally stable and exhibits a high emission quantum yield ($\Phi=40\%$ for $[Tb(hfa)_3(dpbp)]_n$ at room temperature) and a temperature sensitivity over a wide temperature range of 200–500 K. The results obtained in this study will provide insights for designing lanthanide coordination polymers for developing temperature-sensing devices based on their luminescence. In future, the chameleon luminophore $[Tb_{0.99}Eu_{0.01}(hfa)_3(dpbp)]_n$ are expected to be promising candidates for temperature-sensitive dyes, which are used for temperature distribution measurements of material surfaces such as an aerospace plane in wind tunnel experiments. Such lanthanide coordination polymers with thermosensing properties have the potential to open up new fields in supramolecular chemistry, polymer science, and molecular engineering.

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Keywords: dyes · lanthanides · luminescence · metal–organic frameworks · phosphane ligands

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