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Author(s)	Hasegawa, Yasuchika; Sawanobori, Takuya; Kitagawa, Yuichi; Shoji, Sunao; Fushimi, Koji; Nakasaka, Yuta; Masuda, Takao; Hisaki, Ichiro
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An Europium(III) Luminescent with Pressure-sensing Units: Effective Back Energy Transfer in Coordination Polymers with Hexadentate Porous Stable Networks

Yasuchika Hasegawa,^{* [a], [b]} Takuya, Sawanobori,^[b] Yuichi Kitagawa,^{[a], [b]} Sunao, Shoji,^[b] Koji Fushimi,^[b] Yuta Nakasaka,^[b] Takao Masuda,^[b] Ichiro Hisaki^[c]

Abstract: A luminescent Eu^{III} coordination polymer with O₂-sensing units under air, Eu^{III}-hcpt (hcpt: 2,3,6,7,10,11-hexakis(4-carboxyphenyl)triphenylene), is reported. The hexadentate carboxylic acids in hcpt ligands play an important role in the formation of tight-packed three-dimensional networks in Eu^{III}-hcpt, producing hyper thermo-stable ability (decomposition temperature = 420 °C). The three-dimensional porous network promotes bright luminescence (4f-4f emission quantum yield = 70%). The emission lifetime of Eu^{III}-hcpt under vacuum (0.86 ms) was twice as large as that under O₂ (0.48 ms, 1 atom:101.3 kPa). The Arrhenius analysis of the emission decay profile indicates that the back energy transfer (BEnT) from the emitting level of the Eu^{III} ion to the excited T₁ state of the hcpt ligand should be activated at room temperature. The gradual decrease of emission lifetime is caused by the BEnT process in Eu^{III}-hcpt. In this study, an advanced pressure-sensitive luminescent is demonstrated.

In the fields of aerodynamic science and engineering, pressure-sensitive paints (PSPs) are promising molecules to accurately measure the physical parameters of a material surfaces.^[1] The luminescent PSPs provide multi-dimensional pressure data for the mapping of surfaces, whereas optoelectronic sensors analyze only single points on a surface.^[2] There are high expectations that the luminescent PSPs for surface measurements will overcome this intrinsic limitation of optoelectronic devices. Recent high-speed aircraft and automobiles have been designed using luminescent PSP techniques in wind-tunnel experiments.^[3]

The pressure-sensing ability of luminescent PSPs is based on the excited quenching process of phosphorescent materials in an oxygenated environment. The electronic configuration of oxygen molecules (O₂) is normally a spin-active triplet state, which promotes effective luminescence quenching of the excited triplet state (T₁) of phosphorescent materials.^[4] Luminescent metal complexes exhibit effective metal-to-ligand charge transfer (MLCT) phosphorescence at room temperature. Various types of phosphorescent metal complexes with O₂-sensing properties have been reported to date.^[5] Teets described a phosphorescent

Ir^{III} complex with fluorescent BODIPY for ratiometric O₂-sensor.^[5a] Yersin presented brightly luminescent and O₂-sensitive Pt^{II} cyclometalated with carborane.^[5e] Photosensitized luminescence of lanthanide complexes is also attractive for PSPs.^[6] Amao presented the first PSP using luminescent Eu^{III} complex based on the O₂-quenching in the T₁ state of the photosensitized ligand.^[6a] We have reported oxygen-sensitive near-infrared luminescent phosphorescent composed of porous Yb^{III} coordination porous networks for PSPs.^[6b] The O₂-sensitive metal complex is expected to be useful for PSP applications in aerodynamics.

Recently, time-resolved analysis using the emission decay profile of phosphorescent materials has been a focus for fluid dynamics, aeronautical and environmental engineering.^[7] The emission lifetime-based PSP systems have shown significant potential for unsteady flow diagnostics of aircrafts, high-speed vehicles and turbomachinery.^[8] Environment-visualized analysis using time-resolved phosphorescence (> μs) can also remove some short-lifetime luminescent noises on the luminescent surfaces such as organic light-emitting devices (OLEDs) and biomedical applications.^[9] However, general transition-metal complexes lead to a significant decrease of their phosphorescence lifetimes in the presence of small amounts of O₂, which results in the formation of non-emission compounds in air. According to the luminescent lanthanide complexes, their 4f-4f emission lifetimes are independent of O₂-quenching in the T₁ state of the photosensitizer.^[6b] Novel time-resolved analysis of phosphorescence under a highly concentration of O₂ environments is thus required.

We herein select an Eu^{III} coordination compound attached with triphenylene units for the back energy transfer (BEnT) process. The BEnT process with activation energy of the luminescence could be a key point for construction of a novel time-resolved O₂-analysis.^[10] In our previous study, an Eu^{III} complex with triphenylene phosphine-oxide, [Eu(hfa)₃(dppto)₂] (hfa: hexafluoroacetyl-acetonate, dppto: 2-diphenylphosphoryl-triphenylene), had a long T₁ lifetime on a low-lying energy level (20,490 cm⁻¹).^[11] The low-lying energy level of the photosensitization ligand is much close to that of the emitting level of the Eu^{III} ion (⁵D₀: 17,200 cm⁻¹), which promotes BEnT with activation energy from the excited Eu^{III} complex. Multi-dentate coordination sites should also be attached in the photosensitization triphenylene unit for the formation of a thermo-stable structure.^[6b] The multidentate coordination sites are expected to construct the thermo-stable tight packing networks and an O₂-active porous structure in the Eu^{III} coordination polymer.

On the basis of the two criteria for an advanced pressure-sensitive luminescent, a novel Eu^{III} coordination polymer with multidentate triphenylene-based bridges, Eu^{III}-hcpt (hcpt: 2,3,6,7,10,11-hexakis(4-carboxyphenyl)triphenylene) with the photosensitized energy transfer (EnT), back energy transfer

[a] Prof. Dr. Y. Hasegawa, Dr. Y. Kitagawa
Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan

E-mail: hasegaway@eng.hokudai.ac.jp
[b] Prof. Dr. Y. Hasegawa, T. Sawanobori, Dr. Y. Kitagawa, Dr. S. Shoji, Dr. K. Fushimi,
Faculty of Engineering, Hokkaido University
Kita-13, Nishi-8, Sapporo, Hokkaido, 060-8628, Japan

[c] Prof. Dr. I. Hisaki
Graduate School of Engineering Science, Osaka University
1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

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(BEnT) and O_2 -quenching (O_2 -Q) processes is here designed (Figs. 1a and b). The hcpt possesses benzene-spacers for the construction of a porous structure of a three-dimension networks.^[12] The Eu^{III} coordination polymer with hcpt networks successfully exhibited O_2 -dependent emission lifetimes linked with the BEnT process (decrease of non-radiative rate constant, k_{nr}). The photophysical parameters of previously reported Eu^{III} complexes, with or without triphenylene units, $[Eu(hfa)_3(dppto)_2]$ or $[Eu(hfa)_3(tppo)_2]$ (tppo: triphenylphosphine oxide), were also estimated as standard references (Figs. 1c and d). In this study, an advanced pressure-sensitive luminophore for aerodynamics applications is demonstrated.

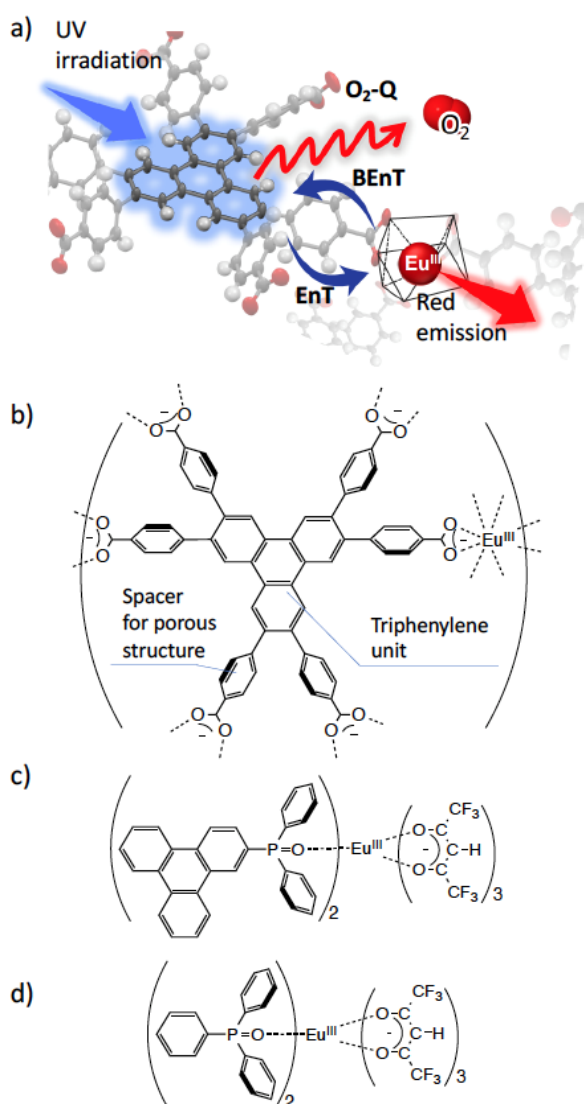


Figure 1. a) Schematic representation of Eu^{III} coordination polymers with photosensitized energy transfer (EnT), back energy transfer (BEnT), and O_2 quenching process (O_2 -Q). Figure Images based on the X-ray single crystal data (CCDC1424089). Chemical structures of b) Eu^{III} -hcpt c) $[Eu(hfa)_3(dppto)_2]$, and d) $[Eu(hfa)_3(tppo)_2]$.

The precursor hexakis(4-methoxycarbonylphenyl)triphenylene (hmcpt) was prepared by the boron-coupling reaction of 2,3,6,7,10,11-hexabromo-triphenylene with 4-methoxycarbonylphenyl boronic acid, a Pd catalyst, and Na_2CO_3 in toluene/dioxane for 46 hrs, according to our previous reported paper.^[12] The hexadentate triphenylene unit hcpt-H (hexakis(4-carboxylphenyl)triphenylene) was synthesized by the hydrolysis reaction of hmcpt with KOH in THF/water (CCDC1424089).^[12] The Eu^{III} coordination polymer Eu^{III} -hcpt was obtained by the reaction of $Eu(NO_3)_3 \cdot 6H_2O$ with hcpt-H and triethylamine in NN-dimethylacetamide (DMA) at 130 °C for 72 hrs.

The crystalline structure of Eu^{III} -hcpt was characterized using IR and XRD measurements (XRD data: Fig. 2a, IR data: Supporting Information Fig. S1). The IR stretching signal of carbonyl groups in Eu^{III} -hcpt (1536 cm^{-1}) was smaller than that in the hcpt-H ligand (1693 cm^{-1}). The signal shift is due to the formation of carboxylate groups with Eu^{III} ions. The XRD pattern of $Eu(hcpt)_n$ (Figs. 2a-ii) is highly different from that of hcpt-H (Figs. 2a-i). The average crystal grain size from the XRD signal at 8.7° was calculated to be 23 nm. The XRD patterns of the prepared Eu^{III} -hcpt (Fig. 2a-ii) agrees well with that of Eu^{III} -hcpt after heat treatment at 200 °C and 300 °C (Figs. 2a-iii and iv). The decomposition temperature using thermal gravimetric analysis was estimated to be 420 °C (see Supporting Information Fig. S2).

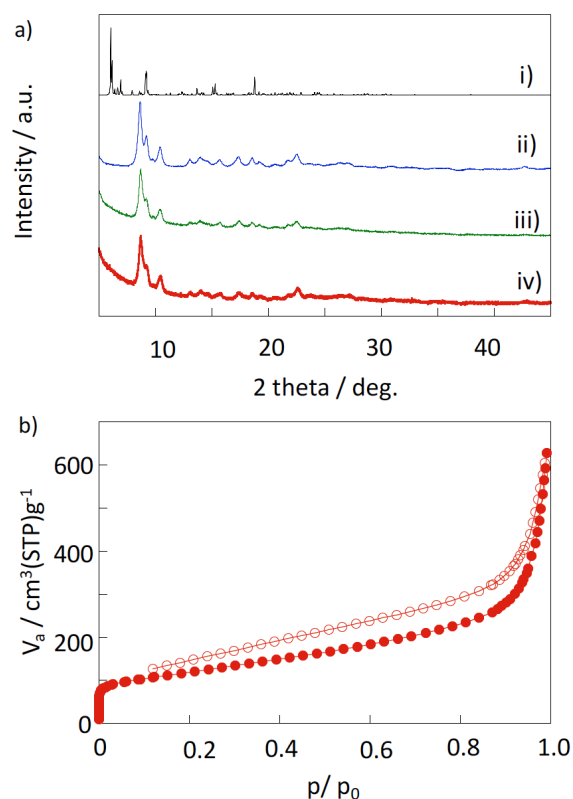


Figure 2. a) XRD profiles of i) hcpt from cif file (CCDC1424089), ii) prepared Eu^{III} -hcpt, iii) Eu^{III} -hcpt after heat treatment at 200 °C, and iv) Eu^{III} -hcpt after heat-treatment at 300 °C. b) Nitrogen adsorption isotherm of Eu^{III} -hcpt measured after heat-treatment at 200 °C for 6 hrs.

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The decomposition temperature of $\text{Eu}^{\text{III}}\text{-hcpt}$ is much higher than those of previous Eu^{III} coordination polymers with bidentate and tridentate phosphine oxides (< 360 °C). The hexadentate carboxylic acids play an important role in the formation of tight-packed three-dimensional networks in $\text{Eu}^{\text{III}}\text{-hcpt}$, producing hyper thermo-stable ability.

The gas adsorption capacity of $\text{Eu}^{\text{III}}\text{-hcpt}$ was estimated by measuring its nitrogen adsorption isotherm measurements, as shown in Fig. 2b. The difference between the adsorption and desorption rate constants for this material produced hysteresis in the isotherm. The effective increase in the plot at $p/p_0 \approx 0$ was attributed to the adsorption of gas in the nanopores. Using the ideal gas law, the amount nitrogen adsorption amount at a pressure (P) of 101.25 kPa and a temperature (T) of 273.15 K (that is, STP conditions) was calculated using the ideal gas constant (R) of $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ and a volume (V) of 64.69 cm^3 ($p/p_0=1.0$). The amount of nitrogen adsorption was evaluated to be $8.4 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$, which is similar to that of previously reported porous Yb^{III} coordination polymer with octadentate pyrene units ($8.0 \times 10^{-2} \text{ cm}^3 \text{ g}^{-1}$).^[6b] The specific surface area of $\text{Eu}^{\text{III}}\text{-hcpt}$ was estimated using Brunauer-Emmet-Teller (BET) calculation as $407 \text{ m}^2 \text{ g}^{-1}$ (Fig. S3). Overall, these results indicate that $\text{Eu}^{\text{III}}\text{-hcpt}$ has a three-dimensional network structure and nano-sized porous cavities suitable for O_2 adsorption.

The $\text{Eu}^{\text{III}}\text{-hcpt}$ exhibited strong luminescence under UV irradiation in the solid state ($\lambda_{\text{ex}} = 340 \text{ nm}$, Fig. 3 red line and inset picture). The emission bands observed at 578, 590, 614, 652, and 700 nm were assigned to be $4f\text{-}4f$ transitions of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 0, 1, 2, 3, \text{ and } 4$) in Eu^{III} ions. The broad excitation bands at around 380 nm were contributed to the $\pi\text{-}\pi^*$ transition of the hcpt ligand, indicating effective photosensitized energy transfer from hcpt to Eu^{III} ions in the Eu^{III} coordination polymer. The sharp excitation bands at 393, 463 and 534 nm were assigned to the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_1$ transitions of Eu^{III} ions, respectively.

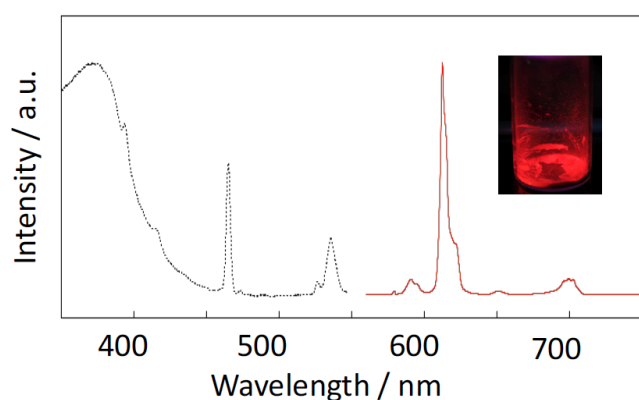


Figure 3. Excitation (black dot line) and emission spectra (red line) of $\text{Eu}^{\text{III}}\text{-hcpt}$ in solid state under air at 300K. Excitation wavelength for emission spectrum: 340 nm. Emission wavelength for excitation spectrum: 610 nm. Inset figure is image of red luminescence of $\text{Eu}^{\text{III}}\text{-hcpt}$ under air.

The luminescence intensity of $\text{Eu}^{\text{III}}\text{-hcpt}$ under vacuum is much larger than that in air. Emission lifetime measurements were conducted under vacuum, argon (Ar), air, Ar-O_2 (1:1 v/v), and O_2 environments to quantitatively estimate the O_2 -quenching efficiency. Their emission lifetimes were gradually decreased with an increase in O_2 concentration (Figs. 4a and b, relative emission spectra: supporting information Fig. S8). The emission lifetime of $\text{Eu}^{\text{III}}\text{-hcpt}$ under vacuum (τ_{Eu} 0.86 ms) was twice as large as that under O_2 ($\tau_{\text{Eu}} = 0.48 \text{ ms}$, 1 atom:101.3 kPa). The Stern-Volmer plot was dependent on the O_2 concentration and showed a pseudo-linear correlation ($\tau_{0\%}/\tau_{100\%} = 1.81$, see Supporting Information Fig. S4). The gradual lifetime-response in high O_2 concentration for aerodynamics was successfully observed.

The photophysical parameters and time-decay profiles of $\text{Eu}^{\text{III}}\text{-hcpt}$ are summarized in Table 1. The gradual decrease of the emission lifetime of $\text{Eu}^{\text{III}}\text{-hcpt}$ is caused by the increase of the non-radiative rate constant k_{nr} . On the other hand, radiative rate constant k_r of $\text{Eu}^{\text{III}}\text{-hcpt}$ under vacuum is similar to those under Ar, air, Ar-O_2 (1:1), and O_2 conditions. In the tight-packed $\text{Eu}^{\text{III}}\text{-hcpt}$ system, the coordination geometry related to k_r could be independent of the surrounding environment. The emission quantum yield $\Phi_{4f\text{-}4f}$ of $\text{Eu}^{\text{III}}\text{-hcpt}$ under vacuum was calculated to be 70%, which is similar to those of bright luminescent $[\text{Eu}(\text{hfa})_3(\text{dppto})_2]$ and $[\text{Eu}(\text{hfa})_3(\text{tppo})_2]$.^[11] The large $\Phi_{4f\text{-}4f}$ of $\text{Eu}^{\text{III}}\text{-hcpt}$ is also due to the small non-radiative rate constant for the tight-packing structure in this solid. The emission lifetimes of $[\text{Eu}(\text{hfa})_3(\text{dppto})_2]$ and $[\text{Eu}(\text{hfa})_3(\text{tppo})_2]$ under vacuum are similar with those measured in air. These results indicate that the nanoporous structure of $\text{Eu}^{\text{III}}\text{-hcpt}$ plays a role in the O_2 -sensing properties.

The gradual decrease of the emission lifetime in O_2 could be directly linked to the BEnT in $\text{Eu}^{\text{III}}\text{-hcpt}$. The ligand-phosphorescence of the Gd^{III} coordination polymer with hcpt ligands was therefore measured to analyze the BEnT process.

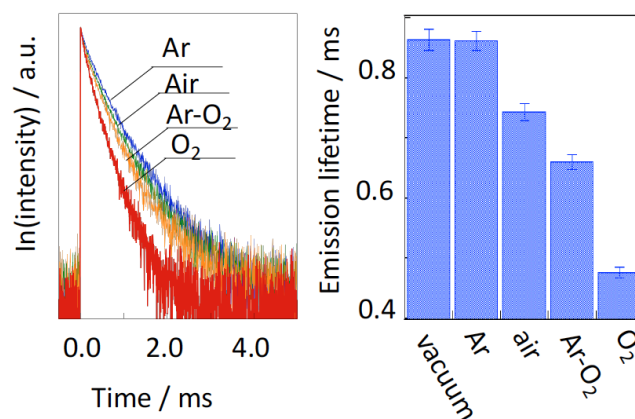


Figure 4. a) Emission decay profiles and b) histograms of the emission lifetime of $\text{Eu}^{\text{III}}\text{-hcpt}$ in solid state under vacuum, Ar, air, Ar-O_2 (1:1) and O_2 atmosphere. Excitation source: Nd: YAG (wavelength: 355 nm (3ω), plus width 10 ns).

Table 1. Summary of emission lifetimes, calculated intrinsic emission quantum yields, radiative and non-radiative rate constants of Eu^{III} coordination compounds in various condition at 300 K.

sample	condition	$\tau_{Eu}^{[a]}$ / ms	$\Phi_{4f-4f}^{[b]}$ / %	$k_r^{[b]}$ / s ⁻¹	$k_{nr}^{[b]}$ / s ⁻¹
Eu ^{III} -hcpt	vacuum	0.86±0.02	70	8.1×10 ²	3.5×10 ²
	Ar	0.86±0.01	69	8.0×10 ²	3.6×10 ²
	air	0.74±0.01	56	7.7×10 ²	6.0×10 ²
	Ar-O ₂	0.66±0.01	52	7.9×10 ²	7.3×10 ²
	O ₂	0.48±0.01	37	7.8×10 ²	1.3×10 ³
[Eu(hfa) ₃ (dppto) ₂]	vacuum	0.71±0.06	73	1.0×10 ³	3.8×10 ²
	air	0.69±0.06	71	1.0×10 ³	4.2×10 ²
[Eu(hfa) ₃ (tppo) ₂]	vacuum	0.71±0.05	76	1.1×10 ³	3.3×10 ²
	air	0.70±0.05	76	1.1×10 ³	3.4×10 ²

[a] The excitation wavelength: 355 nm (3 ω for Nd: YAG). The τ_{Eu} were determined by fitting analyses of emission decay profiles. [b] Calculated using equations 1-5 in supporting information.

The Gd^{III} complex without the 4f-4f transition in the visible region is well-known as a typical compound for estimation of the T₁ level of the organic ligand. The T₁ level of Gd^{III}-hcpt estimated using phosphorescence spectra with vibrational Gaussian fitting curves was calculated to be 19,000 cm⁻¹ (Fig. 5). The T₁ level is much close to that of the ⁵D₀ emitting level of the Eu^{III} ion (17,200 cm⁻¹). The energy gap between excited T₁ and ⁵D₀ levels is smaller than the acceptable gap for BEnT in reported previously (< 1,850 cm⁻¹).^[13] The phosphorescence time decay profile of Gd^{III}-hcpt showed two emissive components with long decay profiles (120 ms and 2000 ms: see Supporting Information Fig. S5). The long decay phosphorescence promotes an effective quenching process for O₂-sensing properties (O₂-Q process). The activation energy from the Eu^{III} ion to T₁ state was also calculated by Arrhenius analysis (Supporting Information Fig. S6). The calculated activation energy E_a at around room temperature was 3.6×10³ cm⁻¹. This calculated parameter is similar to that of thermo-sensitive [Tb(hfa)₃(tppo)₂] at room temperature (E_a = 3.0×10³ cm⁻¹).^[10] The Arrhenius analysis indicates that the BEnT from Eu^{III} to the T₁ state should be activated at room temperature. We consider that the gradual decrease of emission lifetime is caused by the BEnT process in Eu^{III}-hcpt.

Figure 5b shows a schematic diagram with a summary of the EnT, BEnT and O₂-Q processes. The Arrhenius plot of the emission quantum yields of Eu^{III}-hcpt in solid under vacuum is shown in Figure S6. The emission spectral shape of lanthanide complex is generally affected by coordination geometry. The crystal phase transition of Eu^{III}-hcpt under 400 °C was not observed. The spectral shape of lanthanide complex was not also depended on the temperature. From these results, the temperature-dependend luminescence intensity is related to the non-radiative rate constant, the emission quantum yield and the emission lifetime. On the other hand, the oxygen-dependend

emission lifetime of Eu^{III} complex with triphenylene phosphine-oxide (dppto) was not observed, although triplet level of dppto (20490 cm⁻¹) is much similar to that of hcpt ligands (19000cm⁻¹). The reference compounds [Eu(hfa)₃(dppto)₂] in CH₂Cl₂ (1 mM) showed small oxygen-quenching of the emission (see supporting information Fig. S9). The activation energy for back energy transfer of [Eu(hfa)₃(dppto)₂] in CH₂Cl₂ should be larger than that of Eu-hcpt in solid. The specific LC band of Eu^{III}-hcpt was not observed. From these photophysical aspects, effective oxygen process of Eu-hcpt might be produced by not only small E_a, but also the porous structure.

In conclusion, we successfully synthesized a luminescent Eu^{III} coordination polymer with hexadentate triphenylene porous units. The Eu-hcpt is a metal-coordination polymer, which is prepared by the chemical equilibrium in methanol solution. The synthetic process and three-dimensional coordination bonds in Eu-hcpt provide insoluble and tight-packing white powder, which is much different from normal organic polymer linked with covalent bonds. The crystalline and porous structural data of Eu-hcpt were shown in Fig. 2 (a: XRD, b: Nitrogen adsorption isotherm data) and Fig. S3 (BET data). The O₂-pressure sensing properties of Eu^{III}-hcpt were also examined at highly temperature (127 °C, See Supporting Information Fig. S7). The thermo-stable structure of Eu^{III}-hcpt (decomposition temperature ≈ 420 °C) promotes effective O₂-pressure sensing at high temperature, although previous PSPs (pressure sensitive paints) perform under 70 °C. The O₂-pressure sensing ability of Eu^{III}-hcpt is based on the a novel photophysical mechanism with the BEnT process.

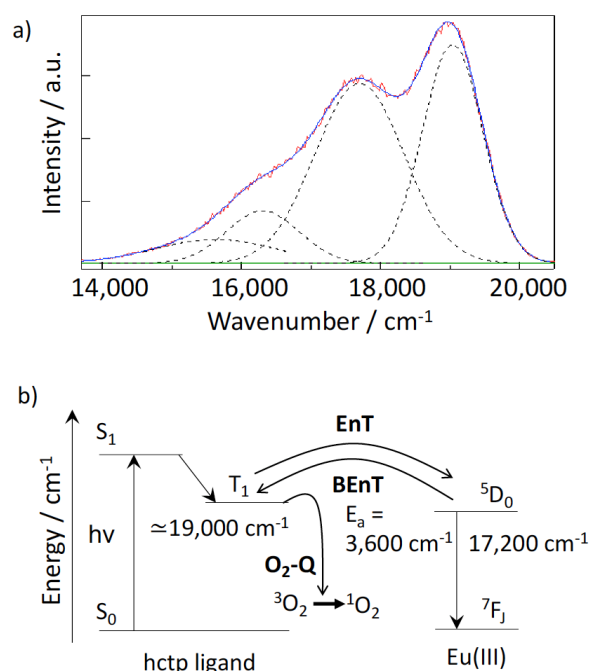


Figure 5. a) Phosphorescence spectra with vibrational Gaussian fitting curves of Gd^{III}-hcpt in solid state at 77 K. Red line: phosphorescence spectrum, Blue and black dot lines: Gaussian fitting functions. Green line: difference between phosphorescence spectrum and Gaussian functions. b) The schematic diagram of the back energy transfer (BEnT) from ⁵D₀ emitting level of Eu^{III} to T₁ state of hcpt ligand in Eu^{III}-hcpt.

The advanced PSPs in the high temperature region are expected to be useful for not only for the body design of future aircraft and spaceship, but also for research on submarine volcanoes under the sea.^[1c] This molecular design of an O₂-pressure sensor for aerodynamics analysis in this study is significantly different from the low level of O₂-detection using previously reported metal complexes in liquid media. We have also reported color-changeable Temperature Sensitive paint (TSP) using Eu^{III}/Tb^{III} coordination polymers known as chameleon luminophores.^[14,15] The combination of PSPs and TSPs would also be useful for architecture designs and bio-medical applications.^[16,17] Advanced PSPs are thus expected to open-up a frontier field between photophysical science, molecular chemistry and fluid engineering.

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Keywords: coordination polymer • energy transfer • europium • luminescence • oxygen sensor

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Entry for the Table of Contents

Layout 1:

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Oxygen-sensitive Eu^{III} coordination polymers with strong luminescence properties under air was successfully fabricated by introducing hexadentate tight and porous three-dimensional networks. The O_2 -sensing property is based on the back energy transfer with activation energy. The O_2 -sensitive coordination polymers have potential application in aerodynamic experiments.



Yasuchika Hasegawa,* Takuya Sawanobori, Yuichi Kitagawa, Koji Fushimi, Yuta Nakasaka, Takao Masuda, Ichiro Hisaki

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