Inorganic Chemistry



The Role of π -f Orbital Interactions in Eu(III) Complexes for an Effective Molecular Luminescent Thermometer

Yuichi Kitagawa,* Marina Kumagai, Takayuki Nakanishi, Koji Fushimi, and Yasuchika Hasegawa*

Cite This: https://dx.doi.org/10.1021/acs.inorgchem.9b03492



ACCESS I III Metrics & More III Article Recommendations III Supporting Information	ACCESS
--	--------

ABSTRACT: Luminescent Eu(III) complexes with a ligand-to-metal charge transfer (LMCT) state were demonstrated for the development of a molecular thermometer. The Eu(III) complex was composed of three anionic ligands (hfa: hexafluoroacetylacetonate) and a phosphine oxide derivative containing a chrysene framework (diphenylphosphorylchrysene (DPCO)). The chrysene framework induced a rigid coordination structure via intermolecular interactions, resulting in a high thermal stability (decomposition point: 280 °C). The Eu(III) complex also exhibited an extremely high molar absorption coefficient (490000 cm⁻¹ M⁻¹), high intrinsic emission quantum yields (73%), and temperature-dependent energy migration between ligands and Eu(III) ion. The characteristic energy migration system was explained by the presence of the LMCT state based on π -f orbital interactions.



■ INTRODUCTION

Thermosensitive paints are a next-generation analytical tool for measuring the surface temperatures of various substances. Luminescent molecular paints, in particular, have generated considerable attention because of their high detection sensitivity and rapid response time.^{1–7} Lanthanide complexes are promising materials for luminescent paints as their narrow emission bands arising from 4f–4f transitions (with a full-width at half-maximum (fwhm) < 10 nm) and long emission lifetimes (0.1 to 1 ms) allow for precise temperature imaging.^{8–13}

In 2004, Hasegawa and Yanagida^{14,15} described the temperature-sensing ability of a green luminescent Tb(III) complex arising from a back energy transfer (BEnT) from the excited state of Tb(III) $({}^{5}D_{4})$ to the excited triplet state of the ligands (T_1) . Following this, Tb(III) complexes experiencing BEnT were demonstrated to be useful for a highly responsive thermosensor. Lapaev¹⁶ reported a temperature-sensitive luminescent Tb(III) film based on the BEnT property for long-term temperature monitoring over 143–253 K. Koenig¹⁷ presented lipid vesicles with embedded amphiphilic Tb(III) complexes demonstrating strong temperature-dependent luminescence in the physiological range. Sun¹⁸ reported an effective thermometer utilizing nanoparticles composed of a Tb(III) complex with [(2-hydroxybenzoyl)-2-aminoethyl]amine for use in medicine. However, these luminescent Tb(III) complexes exhibited green luminescence, which has a low transparency in biological tissue; red-to-near-infrared persistent luminophores are more desirable for in vivo imaging due to their high transparencies in the same tissue. Thus, the construction of red or near-infrared luminescent lanthanide

complexes is a key factor for the development of effective thermometers in bioapplications. Thermometers based on deep-red luminescent $Sm(III)^{19}$ and near-infrared luminescent Yb(III) complex^{20,21} have good application potential because of high transparency in the same tissue. Herein, we focused on the red luminescent Eu(III) complex with relatively low nonradiative rate constants for the construction of highly emissive luminophores.

Both high optical brightness and excellent temperature sensitivity are essential for constructing an effective molecular thermometer. Recently, we successfully synthesized a brilliant Eu(III) complex using hfa (hexafluoroacetylacetonate) and 2-diphenylphosphoryltriphenylene ligands; this exhibited excellent light absorption ($\varepsilon = 180000 \text{ M}^{-1} \text{ cm}^{-1}$) and a high intrinsic emission quantum yield ($\Phi_{ff} = 76\%$).²² These characteristics were attributed to the rigid structure with intermolecular interactions between large polyaromatic hydrocarbon (triphenylene) units and hfa. Furthermore, Amao et al.²³ reported an Eu(III) complex with a low temperature sensitivity arising from a vibrational relaxation process.

Herein, we focused on ligand-to-metal (π -orbital to forbital) charge transfer states (LMCT) in the development of Eu(III) complexes with a high temperature sensitivity. In previous reports, a tetramethylheptanedionate (tmh) ligand

Received: November 30, 2019



was effective in inducing an Eu(III) emission quenching (LMCT) state^{24–30} ($E_{\rm HOMO} = -5.63$ eV, Figure S1), although the photosensitized energy transfer efficiency from the tmh ligands was quite low (<1%). We used Eu(hfa)₃ with phosphine oxide ligands with a chrysene framework^{31,32} (diphenylphosphorylchrysene (DPCO)) to construct a highly luminescent molecular thermometer using LMCT quenching (Figure 1a–b, Eu(hfa)₃(DPCO)₂). The highest occupied



Figure 1. (a) Molecular design concept and molecular structures of (b) $Eu(hfa)_3(DPCO)_2$ and (c) $Eu(hfa)_3(TPPO)_2$.

molecular orbital (HOMO) energy of the DPCO ligand $(E_{\rm HOMO} = -5.68 \text{ eV}$, Figure S1) was similar to that of the tmh ligand and could induce low-energy LMCT states for temperature-sensitive quenching. In the Eu(III) complex, hfa ligands also contributed to intramolecular CH–F interactions to construct a rigid coordination structure.²² The previously reported luminescent Eu(III) complex (Figure 1c, Eu(hfa)₃(TPPO)₂, TPPO: triphenylphosphine oxide)^{33,34} and Gd(hfa)₃(DPCO)₂ were also prepared for comparison of the photophysical data. In this study, we demonstrated a brilliant red-luminescent thermometer based on π –f interactions. Our findings could open up a new frontier in the field of lanthanide photophysics and molecular materials chemistry.

EXPERIMENTAL SECTION

General Methods. Electrospray ionization (ESI) mass spectrometry was performed using a JEOL JMS-T100 LP instrument. ¹H NMR spectra were recorded in CDCl₃ on a JEOL ECS-400 (400 MHz) spectrometer; CHCl₃ ($\delta_{\rm H}$ = 7.26 ppm) was used as the internal reference. Elemental analyses were performed using a Micro Corder JM10. Electronic absorption spectra were measured using a JASCO V-670 spectrophotometer. Diffuse-reflection spectra were recorded with a JASCO V-670 spectrophotometer equipped with an integratingsphere unit (JASCO ISN-723). Emission spectra, excitation spectra, and emission lifetimes ($\lambda_{ex} = 356$ nm) for Eu(hfa)₃(TPPO)₂ (emission spectrum in CHCl₃: 1.0×10^{-3} M, $\lambda_{ex} = 380$ nm; excitation spectrum in CHCl₃: 1.0×10^{-4} M, $\lambda_{em} = 613$ nm; emission spectrum in the solid state: $\lambda_{ex} = 365$ nm; excitation spectrum in the solid state: $\lambda_{em} = 613$ nm)^{33,34} and Eu(hfa)₃(DPCO)₂ (emission spectrum in CHCl_3 : 1.0 × 10⁻⁴ M, λ_{ex} = 380 nm; excitation spectrum in CHCl₃: 1.0×10^{-5} M, $\lambda_{em} = 610$ nm; emission spectrum in the solid state: λ_{ex} = 380 nm; excitation spectrum in the solid state: λ_{em} = 610 nm) were measured using a Horiba FluoroLog³ spectrofluorometer. Emission quantum yields were measured using a FP-6300 spectrofluorometer with an integration sphere (ILF-533). Emission spectra and emission lifetimes for $Gd(hfa)_3(TPPO)_2^{12}$ and Gd-(hfa)₃(DPCO)₂ were measured using a FP-6300 spectrofluorometer with a cryostat (Thermal Block Company SA-SB245T) and a temperature controller (Oxford Instruments ITC-502S). Thermogravimetric analyses (TGA) were performed using an EXSTAR 6000 TG/DTA 6300 instrument (Seiko Instruments Inc.).

Materials. Magnesium sulfate, anhydrous (>98.0% (titration)), *n*-butyllithium in hexane (for organic synthesis), and chloroform-d₁

(99.8%) were purchased from Kanto Chemical Co., Inc. Tetrahydrofuran (THF), super dehydrated, with a stabilizer (for organic synthesis), hydrogen peroxide (30%), potassium acetate, europium-(III) acetate *n*-hydrate (99.9%), gadolinium acetate tetrahydrate (99.9%), chrysene (95+%), and chloroform (spectroscopic grade) were purchased from Wako Pure Chemical Industries, Ltd. N-Bromosuccinimide (>98.0%), palladium(II) acetate (>98.0%), and chlorodiphenylphosphine (>97.0%) were purchased from Tokyo Chemical Industry Co., Ltd.

Preparation of Eu(hfa)₃(**TPPO**)₂. We prepared Eu(hfa)₃(**TPPO**)₂ according to a method previously reported.³³

Anal. calcd for $C_{51}H_{33}EuF_{18}O_8P_2\!\!:$ C, 46.07, H, 2.50. Found: C, 46.03, H, 2.51.

Preparation of 6-Bromochrysene. We prepared 6-bromochrysene according to a previous report.³⁵ A solution of chrysene (1.02 g, 4.45 mmol) and N-bromosuccinimide (796 mg, 4.47 mmol) were stirred for 20 h at 60 $^{\circ}$ C. The distilled water was added to a reactant solution, and the obtained powder was filtrated. The solid powder is washed with distilled water, methanol, and hexane.

Yield: 77% (1.05 g). ¹H NMR (400 MHz, $CDCl_3/TMS$) $\delta/ppm =$ 9.07 (s, 1H), 8.80 (d, 1H, *J* = 7.2 Hz), 8.71 (dd, 2H, *J* = 9.6 Hz, 10 Hz), 8.45 (d, 1H, *J* = 9.6 Hz), 8.02 (dd, 2H, *J* = 9.2 Hz, 6.0 Hz), 7.79–7.72 (m, 3H), 7.68–7.65 (m, 1H)

Preparation of 6-Diphenylphosphorylchrysene (DPCO). A solution of potassium acetate (481 mg, 4.90 mmol) and palladium acetate (8.8 mg, 3.91 \times 10^{-2} mmol) were added dropwise to a solution of 6-bromochrysene (1.22 g, 3.97 mmol) in dry DMA (14 mL).³⁶ Diphenylphosphine (0.7 mL, 4.03 mmol) was then added to the solution, which was subsequently stirred for 24 h at 60 °C. Then, 200 mL of water was added to the solution, and the powder obtained was filtrated. The product was extracted using CH₂Cl₂ and washed with distilled water before being dried over anhydrous MgSO4. Following evaporation, the powder was dissolved in CHCl₂ (30 mL), and the resulting solution was cooled before the addition of a 30% H_2O_2 aqueous solution (3 mL). The reaction mixture was stirred for 3 h. The product was extracted using CHCl₃ and washed with distilled water before being dried over anhydrous MgSO₄. The solvent was then evaporated to produce a white powder whose compounds were separated by silica gel chromatography (ethyl acetate: $CH_2Cl_2 = 1:4$). Recrystallization from CH₂Cl₂ produced transparent crystals of the title compound.

Yield: 40% (733 mg). ¹H NMR (400 MHz, CDCl₃/TMS) δ /ppm = 8.83 (d, 1H, *J* = 8.0 Hz), 8.73 (dd, 2H, *J* = 6.0 Hz, 3.2 Hz), 8.63 (d, 1H, *J* = 17 Hz), 8.11 (d, 1H, *J* = 9.2 Hz), 8.05 (d, 1H, *J* = 8.0 Hz), 8.98 (d, 1H, *J* = 8.0 Hz), 7.79 (dd, 4H, *J* = 6.8 Hz, 5.2 Hz), 7.71 (t, 1H, *J* = 8.0 Hz, 7.6 Hz), 7.65–7.50 (m, 9H); ESI-MS: *m*/*z* calcd for C₃₀H₂₁OP, [M + H]⁺ = 429.14; found, 429.14. Elemental analysis calcd (%) for [DPCO + 0.5 CH₂Cl₂]: C 77.79, H 4.71; found C 77.66, H 4.53.

Preparation of Gd(hfa)₃(**DPCO**)₂. Dichloromethane (12 mL) containing Gd(hfa)₃(H₂O)₂ (181 mg, 0.300 mmol) and DPCO (257 mg, 0.599 mmol) was stirred for 12 h. The reaction mixture was concentrated using a rotary evaporator. Recrystallization from CH₂Cl₂/hexane solution gave transparent crystals.

Yield: 68% (334 mg). ESI-MS: m/z calcd for $C_{70}H_{44}GdF_{12}O_6P_2$, $[M - hfa]^+ = 1428.17$; found 1428.08. Elemental analysis calcd (%) for $C_{75}H_{45}GdF_{18}O_8P_2$: C 55.08, H 2.77; found C 55.21, H 2.61. IR (ATR) = 1653 (st, C=O), 1251 (st, C=F), 1143 (st, P=O) cm⁻¹.

Preparation of Eu(hfa)₃(**DPCO**)₂. Dichloromethane (15 mL) containing Eu(hfa)₃(H₂O)₂ (531 mg, 0.656 mmol) and DPCO (180 mg, 0.419 mmol) was stirred for 12 h. The reaction mixture was concentrated using a rotary evaporator. Recrystallization from CH₂Cl₂/hexane solution gave transparent crystals.

Yield: 36% (251 mg). ESI-MS: m/z calcd for $C_{70}H_{44}EuF_{12}O_6P_2$, $[M - hfa]^+ = 1421.15$; found 1421.16. Elemental analysis calcd (%) for $C_{76}H_{47}EuF_{18}O_8P_2Cl_2$ [M + CH₂Cl₂]: C 53.23, H 2.76; found C 53.52, H 2.52. IR (ATR) = 1653 (st, C=O), 1251 (st, C=F), 1133 (st, P=O) cm⁻¹.

Single-Crystal X-ray Structure Determination. X-ray crystal structure and crystallographic data for DPCO, Eu(hfa)₃(DPCO)₂,

(a)

Figure 2. ORTEP drawings (ellipsoids set at 50% probability) of (a) DPCO, (b) $Eu(hfa)_3(DPCO)_2$, and coordination polyhedron of $Eu(hfa)_3(DPCO)_2$.

and Gd(hfa)₃(DPCO)₂ are shown in Figure 2, Figure S2, and Table 1, respectively. Measurements were made by using a Rigaku RAXIS RAPID (for DPCO and a Eu(hfa)₃(DPCO)₂) imaging-plate area detector with graphite-monochromated Mo–K α radiation or a Rigaku VariMax RAPID imaging-plate diffractometer with confocal mirror-monochromated Mo–K α radiation (for Gd(hfa)₃(DPCO)₂). The calculations were performed using a crystal-structure crystallographic software package (for DPCO and Eu(hfa)₃(DPCO)₂) or Olex (for Gd(hfa)₃(DPCO)₂). The CIF data were confirmed by the check CIF/PLATON service. CCDC 1965674 (for DPCO), CCDC 1969066 (for Eu(hfa)₃(DPCO)₂), and CCDC 1966176 (for Gd(hfa)₃(DPCO)₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Calculation of Luminescence Quantum Yield.³⁷ The emission quantum yield excited by 4f–4f transition (Φ_{ff}) and the radiative (k_r) and nonradiative (k_{nr}) rate constants were estimated using the following equations:

$$\tau_{\rm rad} = \frac{1}{k_{\rm r}} \tag{1}$$

$$\tau_{\rm obs} = \frac{1}{k_{\rm r} + k_{\rm nr}} \tag{2}$$

$$\Phi_{ff} = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm nr}} = \frac{\tau_{\rm obs}}{\tau_{\rm rad}}$$
(3)

$$k_{\rm nr} = \frac{1}{\tau_{\rm obs}} - \frac{1}{\tau_{\rm rad}} \tag{5}$$

where *n* is the refractive index of the medium, $A_{\rm MD,0}$ is the spontaneous luminescence probability for the ${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$ transition *in vacuo* (14.65 s⁻¹), and $I_{\rm tot}/I_{\rm MD}$ is the ratio of the total area of the Eu(III) luminescence spectrum to the area of the ${}^{5}\mathrm{D}_{0} \rightarrow {}^{7}\mathrm{F}_{1}$ transition band.

RESULTS AND DISCUSSION

pubs.acs.org/IC

Structural Analysis. Single crystals of DPCO and $Ln(hfa)_3(DPCO)_2$ (Ln = Eu, Gd) (Figure 2 and Figure S2) were obtained by recrystallization from CH₂Cl₂ and CH₂Cl₂/ hexane, respectively. The crystallographic data are summarized in Table 1. The chrysene framework in the DPCO ligand was slightly distorted from its typically flat structure (Figure 2a). The coordination site of $Eu(hfa)_3(DPCO)_2$ comprises three hfa ligands and two phosphine oxide ligands incorporating large aromatic systems. The two phosphine oxide ligands of $Eu(hfa)_3(DPCO)_2$ are located on the same side due to dipole-dipole interactions between the DPCO ligands. Intermolecular CH-F interactions (3.0 Å) between hfa and polyaromatic compounds in phosphine oxide ligands were observed for Eu(hfa)₃(DPCO)₂ (Figure 2b). The steric structure of Gd(hfa)₃(DPCO)₂ (Figure S2) is almost identical to that of $Eu(hfa)_3(DPCO)_2$. The coordination geometry around the Eu(III) ion is related to the radiative rate constant and emission quantum efficiency.³⁸ The continuous shape measure factor S was calculated to estimate the degree of distortion of the coordination structure in the first coordination sphere based on crystal structure data.³⁹ The S value is given by following equation:

$$S = \min \frac{\sum_{k}^{N} |Q_{k} - P_{k}|^{2}}{\sum_{k}^{N} |Q_{k} - Q_{0}|^{2}} \times 100$$
(6)

Table 1. Crystal Data of DPCO, Eu(hfa)₃(DPCO)₂, and Gd(hfa)₃(DPCO)₂

	DPCO	$Eu(hfa)_3(DPCO)_2$	$Gd(hfa)_3(DPCO)_2$
chemical formula	C ₃₀ H ₂₁ OP	$C_{75}H_{45}EuF_{18}O_8P_2$	$C_{75}H_{45}GdF_{18}O_8P_2$
formula weight	428.44	1630.02	1635.30
crystal system	monoclinic	triclinic	monoclinic
space group	P2 ₁ /c	PĪ	$P2_1/n$
a/Å	18.0383(6)	16.3014(5)	19.0468 (3)
b/Å	8.2865(3)	19.0565(5)	16.3054 (2)
c/Å	15.7280(5)	22.7253(6)	22.7852 (3)
$lpha/{ m deg}$	90	106.189(8)	90
$\beta/{ m deg}$	98.812(3)	90	106.1634
γ/deg	90	90	90
volume/Å	2323.18(14)	6779.6(4)	6796.59(17)
Ζ	4	4	4
density/g cm ⁻³	1.225	1.597	1.598
temperature/°C	20	-150	-150
μ (Mo Ka)/cm ⁻¹	1.38	10.80	11.30
max $2\theta/\deg$	57.808	54.970	58.772
reflections	24122	99794	144871
independent refl.	5474	30473	17310
R	0.0370	0.0494	0.0283
wR ₂	0.1087	0.1210	0.0728

(4)

Inorganic Chemistry

where Q_k denotes the vertices of the actual structure, Q_0 is the center of mass of the actual structure, N is the number of vertices, and P_k denotes the vertices of an ideal structure. From the calculation, Eu(hfa)₃(DPCO)₂ was categorized as a SAP (square-antiprism, D_{4d}) structure (S = 0.358) with asymmetric coordination geometry and is expected to show highly efficient luminescence.³⁸ The average bond length between the coordinated atoms and the Eu(III) ion is estimated to be 2.39 Å, which is almost same as that of the Eu(hfa)₃(DPCO)₂ is shown in Figure 3. The decomposition temperature of Eu(hfa)₃(DPCO)₂ was found to be 281 °C. The high thermostability suggested that the chrysene frameworks form



Figure 3. Thermogravimetric profile of $Eu(hfa)_3(DPCO)_2$.

rigid coordination structures with CH–F and dipole–dipole intermolecular interactions.

Photophysical Properties. The electronic absorption spectrum of DPCO in CHCl₃ was measured to estimate its light-harvesting ability. The absorption coefficient maximum (DPCO: $\varepsilon_{max} = 220000 \text{ M}^{-1} \text{ cm}^{-1}$) (Figure 4a) was ten times larger than that of typical effective photosensitizing ligands such as hfa. The electronic absorption spectra of Eu(hfa)₃(TPPO)₂ and Eu(hfa)₃(DPCO)₂ are shown in Figure 4b. The molecular absorption coefficient of Eu(hfa)₃(DPCO)₂ was much larger than that of Eu(hfa)₃(TPPO)₂. The shoulder band of Eu(hfa)₃(DPCO)₂ is observed at around 365 nm



Figure 4. Electronic absorption spectra of DPCO (a, black solid line), $Eu(hfa)_3(TPPO)_2$ (b, black broken line), and $Eu(hfa)_3(DPCO)_2$ (b, black solid line) in CHCl₃.

(arrow in Figure 4b, $\varepsilon = 6500 \text{ cm}^{-1} \text{ M}^{-1}$). The maximum absorption coefficient at around 280 nm was extremely high (490000 cm⁻¹ M⁻¹) and comparable to that for macrocyclic porphyrinic compounds.⁴⁰

The emission spectra of $Eu(hfa)_3(TPPO)_2$ and $Eu(hfa)_3(DPCO)_2$ in CHCl₃ are shown in Figure 5a. The emission spectra are almost identical, with peaks at 579, 593, 613, 654, and 699 nm assigned to ${}^{5}D_0 \rightarrow {}^{7}F_0$, ${}^{5}D_0 \rightarrow {}^{7}F_1$, ${}^{5}D_0$



Figure 5. Emission (solid line) and excitation spectra (broken line) of $Eu(hfa)_3(TPPO)_2$ (black line) and $Eu(hfa)_3(DPCO)_2$ (red line) in CHCl₃ (a) and in the solid state (b). The spectra were normalized by the intensity maxima.

 \rightarrow ⁷F₂, ⁵D₀ \rightarrow ⁷F₃, and ⁵D₀ \rightarrow ⁷F₄ transitions, respectively. The excitation spectrum shoulder band (Figure 5a, red broken line) were consistent with the absorption spectrum shoulder band of DPCO (Figure 4b, inset), indicating the existence of the energy transfer from the chrysene framework to Eu(III) ion. The solid-state emission spectrum (Figure 5b, red solid line) of $Eu(hfa)_3(DPCO)_2$ was also similar to that of Eu- $(hfa)_3(TPPO)_2$ (Figure 5b, black solid line). The photophysical properties of the Eu(III) complexes are summarized in Table 2. $Eu(hfa)_3(DPCO)_2$ demonstrated a high intrinsic emission quantum yield (Φ_{ff}) of 73%, arising from a large radiative rate constant $(1.0 \times 10^3 \text{ s}^{-1})$ and small nonradiative rate constant $(3.8 \times 10^2 \text{ s}^{-1})$. The latter indicated ineffective electronic coupling of the Eu(III) ion to large vibrational frequencies (C-H: >3000 cm⁻¹) in the large aromatic moieties by the phosphine oxide spacer. The luminescence efficiency due to ligand excitation (Φ_{tot}) and the energytransfer efficiency (η_{sens}) of Eu(hfa)₃(DPCO)₂ were estimated to be 22% and 30%, respectively. The lower luminescent quantum efficiencies compared to Eu(hfa)₃(TPPO)₂ ($\Phi_{tot} =$ 51%) are caused by the presence of moderate energy quenching states at room temperature. In contrast, the brightness of Eu(hfa)₃(DPCO)₂ excited by UV-LED (I_{365 nm} $= \varepsilon_{365} \times \Phi_{tot} = 1.4 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) was much higher than those of Eu(hfa)₃(TPPO)₂ ($I_{365 \text{ nm}} = 3.1 \times 10^1 \text{ M}^{-1} \text{ cm}^{-1}$). Moreover, the emission quantum yield excited by the ligand of the previously reported temperature-sensitive Eu(III) complex based on the LMCT band 24,25 is considerably low (<1%) and electronic absorption is not strong ($\varepsilon_{365 \text{ nm}}$ < 100 M⁻¹ cm⁻¹). The brightness of $Eu(hfa)_3(DPCO)_2$ is 2000 times higher than that of previously reported Eu(III) complexes with the LMCT quenching system.

Inorganic Chemistry			pubs.acs.org/	pubs.acs.org/IC					
Table 2. Photophysical Properties of Eu(III) Compounds in Solid State									
	$\varepsilon_{\rm max}^{~~a}/{\rm cm}^{-1}~{\rm M}^{-1}$	$ au_{ m obs}$	$k_{\rm r}^{\ b}/{\rm s}^{-1}$	$k_{\rm nr}^{\ b}/{\rm s}^{-1}$	$\Phi_{\!f\!f}^{b}$	$\Phi_{ m tot}{}^c$	η_{sens}		

	max /	ODS	r,	hr , s	JJ	tot	/ sens
Eu(hfa) ₃ (DPCO) ₂	490000	0.65	1.0×10^{3}	3.8×10^{2}	73	22	30
$Eu(hfa)_3(TPPO)_2^{26}$	25000	0.80	8.1×10^{2}	4.4×10^{2}	65	51	78
^{<i>a</i>} Measured in CHCl ₃ . (Eu(hfa) ₃ (TPPO) ₂). ³⁴	^b The Φ_{f-p} k_{r} , and k_{nr} we	re calculated	using equations. ^{22,37}	$^{c}\lambda_{\mathrm{ex}} = 380 \mathrm{nm}$	(Eu(hfa) ₃ (D	$(\text{PCO})_2$). λ_{ex}	= 355 nm

Under high-temperature conditions of around 500 K, Eu(hfa)₃(DPCO)₂ still exhibited bright emissions due to its high thermostability (Figure 6a, left). In contrast, there was a large decrease in the emission intensity of Eu(hfa)₃(TPPO)₂ upon its decomposition at 500 K (Figure 6b, right, and Figure



Figure 6. (a) Emission photograph of $Eu(hfa)_3(DPCO)_2$ and $Eu(hfa)_3(TPPO)_2$ at 500 K. (b) Temperature-dependent emission lifetime of $Eu(hfa)_3(DPCO)_2$.

S3). Temperature-dependent emission lifetimes were evaluated for the highly thermostable $Eu(hfa)_3(DPCO)_2$ complex to determine its thermosensitive properties. The Eu(III) complexes showed a decrease in the emission lifetime, which went from 300 to 500 K (Figure 6b). Although the temperature sensitivity (-0.62% K⁻¹) is almost identical to those of previously reported Eu(III) complexes with LMCT quenching sites,^{24,25} the present thermometer is effective in not only the physiologically relevant temperature range (300–350 K)⁴ but also at high temperatures (-500 K), which makes it applicable for temperature-sensitive paints in aerospace fields.⁴¹

This lifetime change was due to BEnT from excited states of the Eu(III) ion to quenching states. To analyze the BEnT mechanism, the BEnT rate constants ($k_{\rm BET}$) were estimated by kinetic analysis. The temperature dependence of $k_{\rm BET}$ was expected to follow an Arrhenius-type equation with an activation energy E_a , defined as follows:^{12,13,42,43}

$$\ln \left(\frac{1}{\tau_{\rm obs}} - \frac{1}{\tau_{\rm 100K}} \right) = \ln k_{\rm BET} = \ln A - \frac{E_{\rm a}}{R} \times T^{-1}$$

From the Arrhenius plot, the activation energy E_a and the frequency factor A of Eu(hfa)₃(DPCO)₂ were estimated to be 3120 cm⁻¹ and $1.1 \times 10^7 \text{ s}^{-1}$, respectively.

To clarify the origin of the thermosensitive properties, the T_1 state was evaluated using phosphorescence measurements for Gd(hfa)₃(TPPO)₂ and Gd(hfa)₃(DPCO)₂ at 100 K (Figure 7).¹² The T_1 energies of Gd(hfa)₃(TPPO)₂ and Gd(hfa)₃(DPCO)₂ were estimated to be 21700 cm⁻¹ and 19300 cm⁻¹, respectively, and the emission lifetimes of



Figure 7. Phosphorescence spectra of $Eu(hfa)_3(TPPO)_2$ (black solid line) and $Eu(hfa)_3(DPCO)_2$ (red solid line) in solid states. The spectra were normalized by the intensity maxima.

Gd(hfa)₃(DPCO)₂ were found to be 1.2 s. The relatively large energy gap between the T₁ and ⁵D₀ levels ($\Delta E = 2,100$ cm⁻¹)⁴⁴ and the long lifetime of T₁ suggested that the T₁ is not a quenching state for Eu(III) emission. Thus, the temperature sensitivity was likely due to the existence of an additional quenching state. To conduct further analysis of the BEnT process in Eu(hfa)₃(DPCO)₂, the diffuse reflection spectra of Eu(hfa)₃(DPCO)₂ and Gd(hfa)₃(DPCO)₂ were recorded (Figure 8).^{24–30,45} Absorption bands of both complexes were observed at around 350 nm and assigned to $\pi - \pi^*$ transitions of the DPCO moieties. Absorption bands were also observed



Figure 8. Diffuse reflection spectra of $Gd(hfa)_3(DPCO)_2$ (black broken line) and $Eu(hfa)_3(DPCO)_2$ (black solid line). The spectra were normalized by the intensity maxima.

at around 430 nm for the $Eu(hfa)_3(DPCO)_2$ complex and assumed to be due to LMCT from DPCO ligands to the Eu(III) ion. To understand LMCT states of the Eu(III)complexes, DFT calculations [Eu(III): SDD, other atoms: B3LYP/6-31G(d)] were performed on $Eu(hfa)_3(DPCO)_2$ and $Eu(hfa)_3(TPPO)_2$ on the basis of the X-ray crystal structure.³³ The calculated LUMO level of $Eu(hfa)_3(DPCO)_2$ (-1.84 eV) is lower than that of $Eu(hfa)_3(TPPO)_2$ (-1.77 eV). These results indicated that the formation of the LMCT band in the low energy level was originated from the modulation of Eu(III)LUMO and HOMO levels of the ligand. To the best of our knowledge, this is the first example of brilliant temperaturesensitive Eu(III) emission arising from the LMCT band. The results are ascribed to both the strong light absorption and

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are particularly grateful for experimental assistance by H. Ito, T. Seki, and S. Nakatsuji of Hokkaido University. This work was supported by Grant-in-Aids (17K14467, 19H04556, 18H04497, and 18H02041). This work was also supported by the Institute for Chemical Reaction Design and Discovery (ICReDD), established by the World Premier International Research Initiative (WPI) of MEXT, Japan. This study was supported in part by Grants-in-Aids via a regional R&D Proposal-Based Program from the Northern Advancement Center for Science & Technology of Hokkaido, Japan.

REFERENCES

(1) Wang, X.; Wolfbeis, O. S.; Meier, R. J. Luminescent Probes and Sensors for Temperature. *Chem. Soc. Rev.* **2013**, *42*, 7834–7869.

(2) Cui, Y.; Zhu, F.; Chen, B.; Qian, G. Metal-Organic Frameworks for Luminescence Thermometry. *Chem. Commun.* **2015**, *51*, 7420–7431.

(3) Rocha, J.; Brites, C. D.; Carlos, L. D. Lanthanide Organic Framework Luminescent Thermometers. *Chem. - Eur. J.* 2016, 22, 14782–14795.

(4) Zhou, H.; Sharma, M.; Berezin, O.; Zuckerman, D.; Berezin, M. Y. Nanothermometry: from Microscopy to Thermal Treatments. *ChemPhysChem* **2016**, *17*, 27–36.

(5) Lustig, W. P.; Mukherjee, S.; Rudd, N. D.; Desai, A. V.; Li, J.; Ghosh, S. K. Metal-Organic Frameworks: Functional Luminescent and Photonic Materials for Sensing Applications. *Chem. Soc. Rev.* **2017**, *46*, 3242–3285.

(6) Cheng, Y.; Gao, Y.; Lin, H.; Huang, F.; Wang, Y. Strategy Design for Ratiometric Luminescence Thermometry: Circumventing the Limitation of Thermally Coupled Levels. *J. Mater. Chem. C* **2018**, *6*, 7462–7478.

(7) Hasegawa, Y.; Kitagawa, Y. Thermo-sensitive Luminescence of Lanthanide Complexes, Clusters, Coordination Polymers and Metal-Organic Frameworks with Organic Photosensitizers. *J. Mater. Chem. C* **2019**, *7*, 7494–7511.

(8) Bünzli, J.-C. G. On the Design of Highly Luminescent Lanthanide Complexes. *Coord. Chem. Rev.* 2015, 293–294, 19–47.

(9) Binnemans, K. Interpretation of Europium(III) Spectra. Coord. Chem. Rev. 2015, 295, 1–45.

(10) Gschneidner, K. A.; Bünzli, J.-C. G.; Pecharsky, V. K. Handbook on the Physics and Chemistry of Rare Earths; Elsevier: New York, 2007; Vol. 36.

(11) Moore, E. G.; Samuel, A. P. S.; Raymond, K. N. From Antenna to Assay: Lessons Learned in Lanthanide Luminescence. *Acc. Chem. Res.* **2009**, *42*, 542–552.

(12) Yamamoto, M.; Kitagawa, Y.; Nakanishi, T.; Fushimi, K.; Hasegawa, Y. Ligand-Assisted Back Energy Transfer in Luminescent Tb^{III} Complexes for Thermosensing Properties. *Chem. - Eur. J.* **2018**, 24, 17719–17726.

(13) Miyata, K.; Konno, Y.; Nakanishi, T.; Kobayashi, A.; Kato, M.; Fushimi, K.; Hasegawa, Y. Chameleon Luminophore for Sensing Temperatures: Control of Metal-to-Metal and Energy Back Transfer in Lanthanide Coordination Polymers. *Angew. Chem., Int. Ed.* **2013**, *52*, 6413–6416.

(14) Katagiri, S.; Hasegawa, Y.; Wada, Y.; Yanagida, S. Thermosensitive Luminescence Based on the Back Energy Transfer in Terbium(III) Complexes. *Chem. Lett.* **2004**, *33*, 1438–1439.

(15) Katagiri, S.; Tsukahara, Y.; Hasegawa, Y.; Wada, Y. Energy-Transfer Mechanism in Photoluminescent Terbium(III) Complexes Causing Their Temperature-Dependence. *Bull. Chem. Soc. Jpn.* **200**7, *80*, 1492–1503.

(16) Lapaev, D. V.; Nikiforov, V. G.; Lobkov, V. S.; Knyazev, A. A.; Galyametdinov, Y. G. A Photostable Vitrified Film Based on a

improved quantum efficiency. The quantum efficiency (22%) was dramatically improved by the change in the ligand electronic structure, compared with those of the previously reported complexes (<1%). This improvement indicates that the LMCT quenching system based on the phosphine oxide system can be applied for the construction of an effective molecular thermometer through LMCT quenching.

CONCLUSION

Herein, we synthesized brilliant Eu(III) complexes demonstrating a temperature sensitivity originating from LMCT. Phosphine oxide ligands with chrysene frameworks were used to build rigid coordination structures via intermolecular interactions, resulting in a high thermostability and internal emission quantum yield. These phosphine oxide ligands containing large aromatic compounds were revealed to participate in LMCT for effective energy quenching. This finding, which is based on the photophysics of π -f orbital interactions, provides new insights into lanthanide photophysics and materials chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03492.

DFT calculations, X-ray crystal structure of Gd- $(hfa)_3(DPCO)_2$, photographs of $Eu(hfa)_3(TPPO)_2$ powder, and cyclic voltammogram measurements (PDF)

Accession Codes

CCDC 1965674, 1966176, and 1969066 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/ data_request/cif, or by emailing data_request@ccdc.cam.ac. uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Authors

Yuichi Kitagawa – Faculty of Engineering and Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan;
orcid.org/0000-0003-1487-2531; Phone: +81 11 706 7114; Email: y-kitagawa@eng.hokudai.ac.jp

Yasuchika Hasegawa – Faculty of Engineering and Institute for Chemical Reaction Design and Discovery (WPI-ICReDD), Hokkaido University, Sapporo, Hokkaido 060-8628, Japan;
orcid.org/0000-0002-6622-8011; Email: hasegaway@ eng.hokudai.ac.jp

Authors

Marina Kumagai – Graduate School of Chemical Sciences and Engineering, Sapporo, Hokkaido 060-8628, Japan

Takayuki Nakanishi – National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan; ^(b) orcid.org/0000-0003-3412-2842

Koji Fushimi – Faculty of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.9b03492

Terbium(iii) β -Diketonate Complex as a Sensing Element for Reusable Luminescent Thermometers. J. Mater. Chem. C 2018, 6, 9475–9481.

(17) Bhuyan, M.; Koenig, B. Temperature Responsive Phosphorescent Small Unilamellar Vesicles. *Chem. Commun.* **2012**, *48*, 7489– 7491.

(18) Sun, L.; Yu, J.; Peng, H.; Zhang, J. Z.; Shi, L.-Y.; Wolfbeis, O. S. Temperature-sensitive Luminescent Nanoparticles and Films Based on a Terbium (III) Complex Probe. J. Phys. Chem. C 2010, 114, 12642–12648.

(19) Anderson, B. R.; Gunawidjaja, R.; Eilers, H. Soluble Sm-based Ternary Complexes for Non-contact Molecular Thermometry. J. Lumin. 2018, 204, 341–348.

(20) Tang, M.; Huang, Y.; Wang, Y.; Fu, L. An Ytterbium Complex with Unique Luminescence Properties: Detecting the Temperature Based on a Luminescence Spectrum Without the Interference of Oxygen. *Dalton Trans.* **2015**, *44*, 7449–7457.

(21) Ning, Y.; Liu, Y.-W.; Meng, Y.-S.; Zhang, J.-L. Design of Nearinfrared Luminescent Lanthanide Complexes Sensitive to Environmental Stimulus Through Rationally Tuning the Secondary Coordination Sphere. *Inorg. Chem.* **2018**, *57*, 1332–1341.

(22) Kitagawa, Y.; Suzue, F.; Nakanishi, T.; Fushimi, K.; Hasegawa, Y. A Highly Luminescent Eu(iii) Complex Based on an Electronically Isolated Aromatic Ring System with Ultralong Lifetime. *Dalton Trans* **2018**, 47, 7327–7332.

(23) Mitsuishi, M.; Kikuchi, S.; Miyashita, T.; Amao, Y. Characterization of an Ultrathin Polymer Optode and Its Application to Temperature Sensors Based on Luminescent Europium Complexes. *J. Mater. Chem.* **2003**, *13*, 2875–2879.

(24) Yanagisawa, K.; Kitagawa, Y.; Nakanishi, T.; Akama, T.; Kobayashi, M.; Seki, T.; Fushimi, K.; Ito, H.; Taketsugu, T.; Hasegawa, Y. Enhanced Luminescence of Asymmetrical Seven-Coordinate Eu^{III} Complexes Including LMCT Perturbation. *Eur. J. Inorg. Chem.* **201**7, 2017, 3843–3848.

(25) Yanagisawa, K.; Kitagawa, Y.; Nakanishi, T.; Seki, T.; Fushimi, K.; Ito, H.; Hasegawa, Y. A Luminescent Dinuclear Eu^{III}/Tb^{III} Complex with LMCT Band as a Single-Molecular Thermosensor. *Chem. - Eur. J.* **2018**, *24*, 1956–1961.

(26) Miranda, Y. C.; Pereira, L. L. A. L.; Barbosa, J. H. P.; Brito, H. F.; Felinto, M. C. F. C.; Malta, O. L.; Faustino, W. M.; Teotonio, E. E. S. The Role of the Ligand-to-Metal Charge-Transfer State in the Dipivaloylmethanate-Lanthanide Intramolecular Energy Transfer Process. *Eur. J. Inorg. Chem.* **2015**, 2015 (18), 3019–3027.

(27) An, Y.; Schramm, G. E.; Berry, M. T. Ligand-to-Metal Charge-Transfer Quenching of the $Eu^{3+}({}^{5}D_{1})$ State in Europium-Doped Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)gadolinium (III). *J. Lumin.* **2002**, 97, 7–12.

(28) Berry, M. T.; May, P. S.; Xu, H. Temperature Dependence of the $Eu^{3+5}D_0$ Lifetime in Europium Tris(2,2,6,6-Tetramethyl-3,5-Heptanedionato). J. Phys. Chem. 1996, 100, 9216–9222.

(29) Schwendemann, T. C.; May, P. S.; Berry, M. T.; Hou, Y.; Meyers, C. Y. Effect of Ligand Deuteration on the Decay of $Eu^{3+}({}^{5}D_{0})$ in Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)europium(III). *J. Phys. Chem. A* **1998**, *102*, 8690–8694.

(30) Faustino, W. M.; Malta, O. L.; Teotonio, E. E. S.; Brito, H. F.; Simas, A. M.; de Sa, G. F. Photoluminescence of Europium(III) Dithiocarbamate Complexes: Electronic Structure, Charge Transfer and Energy Transfer. J. Phys. Chem. A **2006**, 110, 2510–2516.

(31) Jones, R. N. The Ultraviolet Absorption Spectra of Aromatic Hydrocarbons. *Chem. Rev.* **1943**, 32, 1–46.

(32) Morgan, D. M.; Warshawsky, D.; Atkinson, T. The Relationship between Carcinogenic Activities of Polycyclic Aromatic Hydrocarbons and Their Singlet, Triplet, and Singlet-Triplet Splitting Energies and Phosphorescence Lifetimes. *Photochem. Photobiol.* **1977**, 25, 31–38.

(33) Hasegawa, Y.; Yamamuro, M.; Wada, Y.; Kanehisa, N.; Kai, Y.; Yanagida, S. Luminescent Polymer Containing the Eu(III) Complex Having Fast Radiation Rate and High Emission Quantum Efficiency. *J. Phys. Chem. A* **2003**, *107*, 1697–1702. (34) Nakajima, A.; Nakanishi, T.; Kitagawa, Y.; Seki, T.; Ito, H.; Fushimi, K.; Hasegawa, Y. Hyper-Stable Organo-Eu^{III} Luminophore under High Temperature for Photo-industrial Application. *Sci. Rep.* **2016**, *6*, 24458.

(35) George, S. R. D.; Frith, T. D. H.; Thomas, D. S.; Harper, J. B. Putting Corannulene in Its Place. Reactivity Studies Comparing Corannulene with Other Aromatic Hydrocarbons. *Org. Biomol. Chem.* **2015**, *13*, 9035–9041.

(36) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. Water Soluble Phosphines VII. Palladium-Catalyzed P-C Cross Coupling Reactions between Primary or Secondary Phosphines and Functional Aryliodides — a Novel Synthetic Route to Water Soluble Phosphines. J. Organomet. Chem. **1996**, 522, 69–76.

(37) Werts, M. H. V.; Jukes, R. T. F.; Verhoeven, J. W. The Emission Spectrum and the Radiative Lifetime of Eu³⁺ in Luminescent Lanthanide Complexes. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1542–1548.

(38) Miyata, K.; Nakagawa, T.; Kawakami, R.; Kita, Y.; Sugimoto, K.; Nakashima, T.; Harada, T.; Kawai, T.; Hasegawa, Y. Remarkable Luminescence Properties of Lanthanide Complexes with Asymmetric Dodecahedron Structures. *Chem. - Eur. J.* **2011**, *17*, 521–528.

(39) Casanova, D.; Llunell, M.; Alemany, P.; Alvarez, S. The Rich Stereochemistry of Eight-Vertex Polyhedra: A Continuous Shape Measures Study. *Chem. - Eur. J.* 2005, *11*, 1479–1494.

(40) Rimington, C. Spectral-Absorption Coefficients of Some Porphyrins in the Soret-Band Region. *Biochem. J.* **1960**, 75, 620–623. (41) Liu, T. *Pressure- and Temperature-Sensitive Paints*; Springer:

Berlin, 2005.

(42) Buterbaugh, J. S.; Toscano, J. P.; Weaver, W. L.; Gord, J. R.; Hadad, C. M.; Gustafson, T. L.; Platz, M. S. Fluorescence Lifetime Measurements and Spectral Analysis of Adamantyldiazirine. *J. Am. Chem. Soc.* **1997**, *119*, 3580–3591.

(43) Olofsson, J.; Önfelt, B.; Lincoln, P. Three-state Light Switch of $[Ru(phen)_2 dppz]^{2+}$: Distinct Excited-State Species with Two, One, or No Hydrogen Bonds from Solvent. *J. Phys. Chem. A* **2004**, *108*, 4391–4398.

(44) Latva, M.; Takalo, H.; Mukkala, V.-M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kankare, J. Correlation between the Lowest Triplet State Energy Level of the Ligand and Lanthanide Luminescence Quantum Yields. *J. Lumin.* **1997**, *75*, 149–169.

(45) Napier, G. D. R.; Neilson, J. D.; Shepherd, T. M. Charge-Transfer Excited State in Tris(acetylacetonato) europium(III). *Chem. Phys. Lett.* **1975**, *31*, 328–330.