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Temperature-dependent energy transfer in photo-sensitized luminescence of rare earth complexes

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Abstract

We have fabricated polymer thin films containing bis(triphenylphosphineoxide)-tris(hexafluoroacetylacetonato) terbium(III) [$Tb(HFA)_3(TPPO)_2$] as a thermo-sensor. The thermo-sensitivity of the thin film containing the Tb(III) complex was found to be 13.5%/°C. The emission intensity ratio normalized according to that at 0 °C observed for $Tb(HFA)_3(TPPO)_2$ in the thin film was not affected by pressure. The thermo-sensing thin film is expected to be useful in measuring surface-temperatures of bodies in wind-tunnel experiments.

Keywords: Thin film; Thermo analysis; Luminescence

1. Introduction

Lanthanide(III) complexes show characteristic luminescence with narrow emission bands, long emission lifetimes and high quantum yield [1]. Amao and co-workers reported a thermo-sensing dye based on europium(III) complex in 2003, having the thermo-sensitivity of 0.78%/°C [2]. In order to fabricate high sensitive thermo-sensors, we proposed a new idea to employ the temperature-dependent energy transfer process in Tb(III) complex, bis(triphenylphosphineoxide)-tris(hexafluoroacetylacetonato) terbium(III) [$Tb(HFA)_3(TPPO)_2$] (Fig. 1b) as a thermo-sensor [3]. The Tb(III) complex consists of hexafluoroacetylacetonato (HFA) ligands and triphenylphosphine oxide (TPPO) ligands. HFA ligands play a role of an accepter of the back energy, because the triplet state of HFA ligand (22,200 cm^{-1}) is much close to the emitting level of Tb(III) ion (20,500 cm^{-1}) [4]. In addition, TPPO ligands provide high emission efficiency to the Tb(III) complex [5].

Here, we have prepared the polymer thin films having thermo-sensing property (Fig. 1d). The thin films consist of polymethylmethacrylate (PMMA) containing the Tb(III) complex. We have observed that the thermo-sensing property of the Tb(III) thin film was found to be 13.5%/°C. This report demonstrates remarkable temperature-dependent luminescence of Tb(III) thin film based on the presence of the back-energy transfer having the energy barrier. The fabrication of polymer thin film containing the thermo-sensing Tb(III) complex is directly linked to the application for wind-tunnel experiment of air-craft [6].

2. Experiment

2.1. Materials

Terbium acetate tetrahydrate (99.9%), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HFA), triphenylphosphine oxide, methylmethacrylate polymer and acetone-d_6 (99.9%) were purchased from Wako Pure Chemical Industries Ltd. Isopentane, diethyl ether and ethanol were obtained from Nacalai

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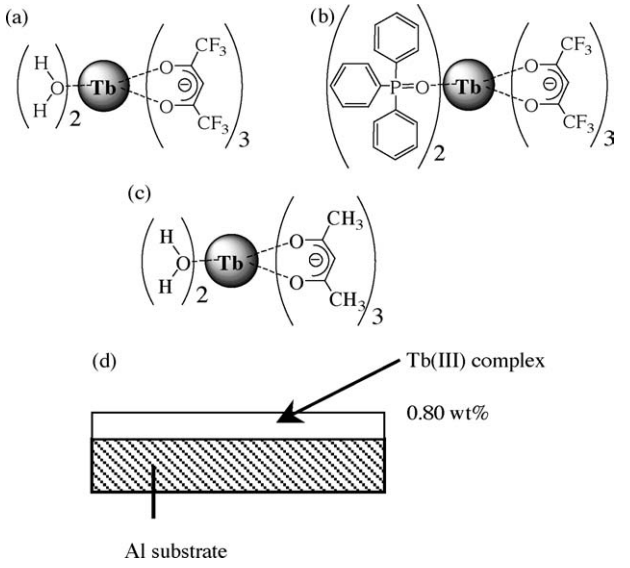

Fig. 1. Chemical structures of (a) $Tb(HFA)_3(H_2O)_2$, (b) $Tb(HFA)_3(TPPO)_2$ and (c) $Tb(acac)_3(H_2O)_2$. (d) Illustration of the polymer thin film containing Tb(III) complex.

Tesque, Inc. Gadolinium acetate tetrahydrate (99%) were received from Mitsuwa Chemicals Co., Ltd.

2.2. Apparatus

Infrared spectra used to identify synthesized materials were obtained with a Perkin-Elmer FT-IR 2000 spectrometer. Elemental analyses were performed with a Perkin-Elmer 240C. ^{19}F NMR data were obtained with a JEOL EX-270 spectrometer. ^{19}F NMR chemical shifts were determined using hexafluorobenzene as an external standard ($\delta = -162.0$ (s, Ar–F) ppm).

2.3. Preparation of tris-(hexafluoroacetylacetonato) terbium(III) dehydrates [$Tb(HFA)_3(H_2O)_2$]

Terbium acetate tetrahydrate (5.0 g, 12.3 mmol) was dissolved in 20 mL of distilled water by stirring. 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7 g, 33.6 mmol) was added dropwise to the above solution. The mixture produced a precipitation of white green powder after stirring for 3 h. The reaction mixture was filtered. The resulting white green needle crystals were recrystallized in methanol/water (Fig. 1a). Yield: 70%. IR (KBr): 1650 (st, C=O), 1255–1141 (st, C–F) cm^{-1}. ^{19}F NMR (CD_3COCD_3) $\delta = -61.22$ (s, CF_3) ppm. Anal. calcd. for $C_{15}H_9F_{18}O_9Tb$: C, 21.60%; H, 1.09%. Found: C, 21.47%; H, 1.34%.

2.4. Preparation of tris(hexafluoroacetylacetonato) terbium(III) bis(triphenylphosphineoxide) [$Tb(HFA)_3(TPPO)_2$]

Methanol (50 mL) containing $Tb(HFA)_3(H_2O)_2$ (1.64 g, 2.04 mmol) and triphenylphosphine oxide (TPPO) (1.22 g, 4.38 mmol) was refluxed under stirring for 12 h. The reaction mixture was concentrated using a rotary evaporator. Reprecipitation by addition of excess hexane solution produced crude crystals, which were washed in toluene several times. Recrystallization from hot methanol gave green translucence crystals ([$Tb(HFA)_3(TPPO)_2$]). Yield: 56%. Anal. calcd. for $C_{51}H_{33}F_{18}O_8P_2Tb$: C, 45.83%; H, 2.49%. Found: C, 45.58%; H, 2.49%.

2.5. Preparation of tris-(acetylacetonato) terbium(III) dehydrates [$Tb(acac)_3(H_2O)_2$]

Terbium acetate tetrahydrate (5.0 g, 12.3 mmol) was dissolved in 20 mL of distilled water by stirring. 2,4-pentanedione (3.74 g, 37.4 mmol) was added dropwise to the above solution. This solution controlled pH 7 by inserting NH_3 aqueous solution. The mixture produced a precipitation of white powder after stirring for 3 h. The reaction mixture was filtered. The resulting white needle crystals were recrystallized in methanol/water (Fig. 1c). Yield: 50%. Anal. calcd. for $C_{15}H_{27}O_9Tb$: C, 35.31%; H, 5.33%. Found: C, 35.66%, H, 5.23%.

2.6. Preparation of polymer thin film containing Tb(III) complexes

Polymer matrices, methylmethacrylate polymer, were dissolved in acetone. The Tb(III) complex was then added to the solution. The Tb(III) thin film (Tb(III) complex: 0.80 wt%, PMMA: 99.2 wt%) was prepared on a aluminum substrate from the acetone solution via the spray-coat method. According to the preparation of polymer thin films containing $Tb(acac)_3(H_2O)_2$, we used methylene chloride as a solvent.

2.7. Optical measurements

The emission spectra were measured by SPEX-Fluorolog τ-3 with thermo-stat and -sensor. The emission quantum yield was measured by 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). The thermo-sensing property of polymer thin film was measured by calibrated experimental setup, shown in Fig. 2 as diagrammic illustration.

3. Results and discussion

3.1. Thermo-sensing properties of polymer thin film

We reported that $Tb(HFA)_3(TPPO)_2$ was the best dye in the view point of good thermo-sensing properties and high-luminous efficiency. The thermo-sensing property of $Tb(HFA)_3(TPPO)_2$ was found to be 2.0%/°C. We suggested the combination of Tb(III) ion with HFA should lead to an

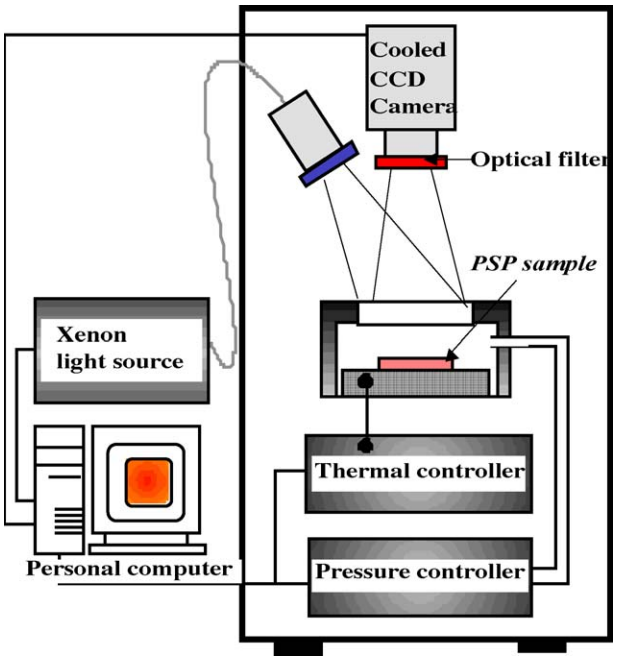

Fig. 2. The diagrammic illustration of calibrated experimental setup.

optimum condition for enhancement of the back energy transfer, then resulting in the high thermo-sensitivity.

In order to demonstrate thermo-sensor containing the high-performance thermo-sensing dye, we have prepared polymer thin films containing $Tb(HFA)_3(TPPO)_2$. Temperature-dependency of the polymer thin films doped with Tb(III) complexes are shown in Fig. 3. The thermo-sensing properties were found to be 1.35%/°C. Amao and co-workers reported the temperature-sensing polymer-films including Eu(TTA)Phen (0.78%/°C). In contrast, no temperature-dependency of the emission intensity of $Tb(NO_3)_3$ and $Tb(acac)_3(H_2O)_2$ in the films were observed. These temperature dependencies of the emission intensities of the complexes in the polymer films were similar

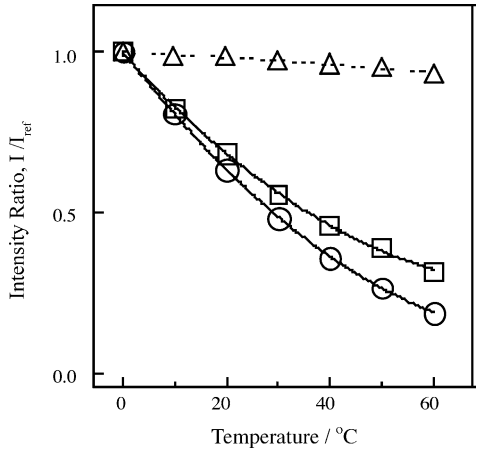

Fig. 3. Temperature dependencies of the emission of the polymer thin films with $Tb(HFA)_3(H_2O)_2$ (□), $Tb(HFA)_3(TPPO)_2$ (○) and $Tb(acac)_3(H_2O)_2$ (△).

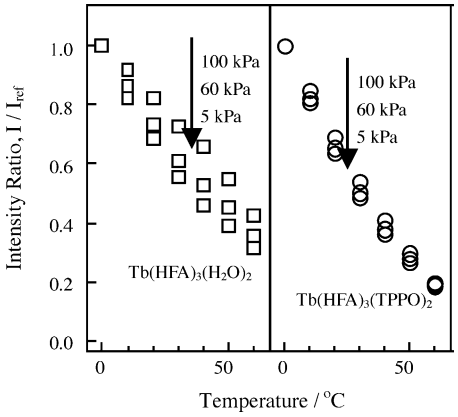

Fig. 4. The emission intensity ratio normalized according to that at 0 °C observed for $Tb(HFA)_3(TPPO)_2$ in the thin film (100 kPa → 5 kPa).

to those in the corresponding liquid media. However, the thermo-sensitivity of $Tb(HFA)_3(TPPO)_2$ in polymer films (1.35%/°C) was lower than that in organic liquid media (2.0%/°C). This might be due to the difference in the rates of the back energy transfer of $Tb(HFA)_3(TPPO)_2$ in polymer films and organic liquid media.

3.2. Pressure dependencies of thermo-sensing properties of thin films

We examined pressure-dependence of the emission of the thin films in the same experimental chamber. The emission intensity ratio in Fig. 4 was normalized by the emission intensity at 0 °C of Tb(III) complexes in the thin film. The normalized emission intensity ratio of $Tb(HFA)_3(TPPO)_2$ was not changed by increasing pressure (Fig. 4a), although that of $Tb(HFA)_3(H_2O)_2$ was affected by pressure (Fig. 4b). Generally, pressure dependence of the emission is concerned with the percentage of dioxygen in the systems [2]. Actually, the absolute emission intensity of theTb(III) complexes depended on the pressure. The triplet-state of the excited ligands is quenched by dioxygen. However, the non-dependence of the emission intensity ratio normalized according to that at 0 °C of $Tb(HFA)_3(TPPO)_2$ in the thin film on the pressure shows that the film can be employed as a temperature-sensor by which the pressure can be measured separately using the emission.

4. Conclusion

We have successfully fabricated the thermo-sensing polymer thin film containing Tb(III) complex. Temperature-dependency of the luminescence of the polymer thin film including $Tb(HFA)_3(TPPO)_2$ was observed. In contrast, the emission intensity ratio normalized according to that at 0 °C of $Tb(HFA)_3(TPPO)_2$ in the thin film was not affected by pressure.

In the wind-tunnel experiments, thermo-sensing property of dyes should be independent of pressure, so that tempera-

tures can be determined without correcting according to the effect of pressures. Our results indicate that polymer thin film including $Tb(HFA)_3(TPPO)_2$ can give us an accurate thermo-information without adjustment according to pressures.

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References

[1] G. Blasse, B.C. Grabmaier, Review on luminescence behaviors, in: Luminescent Materials, Springer–Verlag, New York, 1994.
[2] M. Mitsuishi, S. Kikuchi, T. Miyashita, Y. Amao, J. Mater. Chem. 13 (2003) 2875.
[3] S. Katagiri, Y. Hasegawa, Y. Wada, S. Yanagida, Chem. Lett. 33 (2004) 1438.
[4] S. Sato, M. Wada, Bull. Chem. Soc. Jpn. 43 (1970) 1955.
[5] Y. Hasegawa, M. Yamamuro, Y. Wada, N. Kanehisa, Y. Kai, S. Yanagida, J. Phys. Chem. A 107 (2003) 1697.
[6] K. Asai, Proceedings of MOSAIC (Molecular Sensors for Aero-Thermodynamic Research), Tokyo, Japan, November 10–11, 2003.