

Photo-degradation Analysis of Luminescent Polymers with Lanthanide Complexes

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UV durability of luminescent Eu(III) complexes for future solar cell application is estimated using Fourier transform infrared spectroscopy (FT-IR). Sandwich-typed glass cells containing Eu(III) complexes powders under UV irradiation are used for the carbonyl index analysis (calculation of decomposition percentage of organic ligands) using FT-IR measurements. The durability of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ (hfa: hexafluoroacetylacetonate, TPPO: triphenylphosphine oxide) is five times larger than that of $\text{Eu}(\text{tta})_3(\text{phen})$ (tta: trifluoromethylthienylacetylacetonate, phen: phenanthroline). Photophysical performance of Eu(III) complexes under UV irradiation is also evaluated using emission lifetimes and external quantum efficiency measurements of the solar cell module using EVA films with Eu(III) complexes. Photo-degradation analysis of luminescent polymer thin films with Eu(III) complexes are demonstrated for the first time.

Keywords: Lanthanide, europium, complex, UV degradation, IR, Solar Cell

1. Introduction

Lanthanide complexes with characteristic emission caused by $4f$ orbital have been regarded as attractive luminescent materials for use in electroluminescent (EL) devices, laser, and luminescent bio-sensing applications [1-8]. At the present stage, a large number of scientific studies on luminescence lanthanide complexes have been reported [9-10]. Recently, photovoltaic application for enhancement of solar cell efficiency using strong red luminescent Eu(III) complexes have been focused. Wang and coworkers reported effective efficiency improvement of solar cell with EVA film composed of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (tta: trifluoromethylthienylacetylacetonate, TPPO: triphenylphosphine oxide, Fig 1a) [11]. Liu also observed similar improvement with PVA film composed of $\text{Eu}(\text{tta})_3(\text{Phen})$ (Phen: phenanthroline, Fig 1b) [12]. Nishiyama presented organogels designed for visible color tuning using $\text{Eu}(\text{hfa})_3(\text{Phen})$ (hfa: hexafluoroacetylacetonat) for optical devices (Fig 1c) [13].

Previous luminescent Eu(III) complexes, $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ and $\text{Eu}(\text{tta})_3(\text{Phen})$, are composed of Eu(III) ion and diketonate ligands with thienyl groups, tta ligands. The thienyl groups in tta ligand are decomposed under air because of their oxidation [14]. Mirochnik have also reported luminescence intensity degradation of $\text{Eu}(\text{phen})_2(\text{NO}_3)_3$ in low density polyethylene under UV irradiation [15]. Development of air-, thermal- and photo-stable structures of luminescent lanthanide complexes are required for future application in optical devices. We recently suggested about improvement of current efficiency and durability in the solar cell modulation using strong luminescent $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ without thienyl and phen ligands. In our previous studies, photo- and thermo- and moisture-stable luminescent PMMA copolymer beads composed of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ (emission quantum yield = 65 %, Figure 1d) have been described [16].

Decomposition of luminescent Eu(III) complexes leads to decrease of external quantum

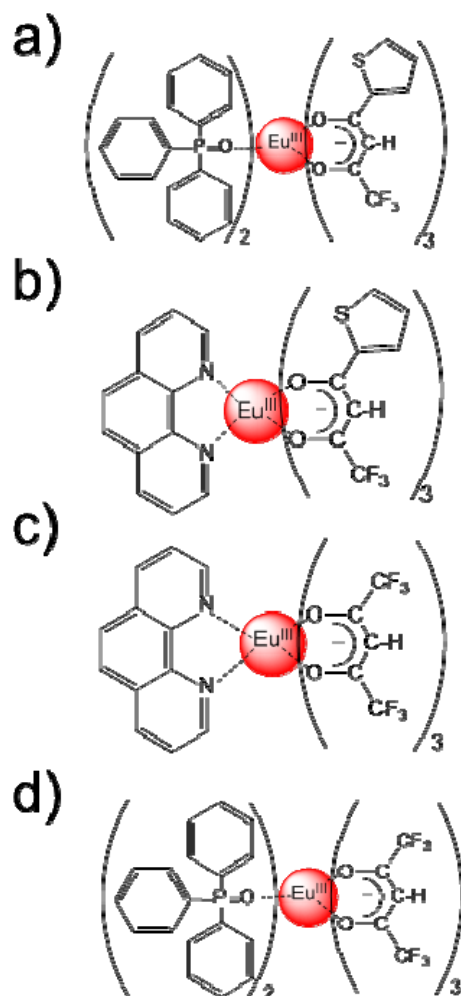


Figure 1. Chemical structure of a) $\text{Eu}(\text{tta})_3(\text{TPPO})_2$, b) $\text{Eu}(\text{tta})_3(\text{Phen})$, c) $\text{Eu}(\text{hfa})_3(\text{Phen})$, and d) $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$.

efficiency of optical devices such as a solar cell application. Degradation of Eu(III) complexes under UV irradiation is caused by changing chemical structure of organic ligands. Time-dependent observation of the structural transformation under UV irradiation is expected to be useful for estimation of UV durability in optical device applications. Here, we have attempted to estimate the UV durability of Eu(III) complexes using Fourier transform infrared spectroscopy (FT-IR) for future solar cell application. FT-IR

analysis is widely used for structural identification and transformation of molecules, metal complexes, and polymer materials. Amin and Scott have described estimation of UV degradation of polyethylene [17]. Lamontagne and coworkers have suggested an estimation method for time-dependent degradation process of carbonyl group using FT-IR measurements, carbonyl index (calculation of decomposition percentage of organic molecules with carbonyl groups) in Bitumen Aging Test [18].

In this study, we report the carbonyl index analysis of Eu(III) complexes, $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (Figure 1a), $\text{Eu}(\text{tta})_3(\text{Phen})_2$ (Figure 1b), $\text{Eu}(\text{hfa})_3(\text{Phen})_2$ (Figure 1c) and $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ (Figure 1d) under UV irradiation for estimation of UV durability. Sandwich-typed glass cells containing Eu(III) complexes powders under UV irradiation are used for the carbonyl index analysis using FT-IR measurements. The emission properties of Eu(III) complexes were also estimated by the emission lifetimes. We also fabricated a solar cell modulation using EVA (ethylene vinyl acetate) film with Eu(III) complex for measurements of external quantum efficiency in solar cell. Photo-degradation analysis of luminescent polymer thin films with Eu(III) complexes using FT-IR measurements are demonstrated for the first time.

2. Experimental

2.1 Apparatus

FT-IR measurements were performed at room temperature by Perkin-Elmer system 2000 FT-IR spectrometer. ^1H NMR measurements were measured using JEOL AL-300 spectrometer (400MHz). Chemical shifts are reported in ppm and are referenced to an internal tetramethylsilane (TMS) standard for ^1H NMR spectroscopy. Decomposition point was measured by using Seiko instruments corporation TG-DTA 6200. External quantum efficiency of silicon solar cell module was obtained with SOMA OPTICS Solar cell evaluator S9241. UV irradiance were used by IWASAKI ELECTRIC EYE SUPER UV TESTER (63 °C, 1000W/m²).

2.2 Preparation of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$

Methanol (100 mL) containing $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ (4.28 g, 6 mmol) and triphenylphosphine oxide (TPPO) (2.78 g, 10 mmol) was refluxed under stirring for 12 hours. 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 toluene/cyclohexane gave white needle crystals ($\text{Eu}(\text{hfa})_3(\text{TPPO})_2$). Yield: 74%. ^1H NMR (400MHz, $\text{CD}_3\text{-COCD}_3$, TMS) : $\delta = 5.41$ (s, 3H : -CH), $\delta = 7.62\text{-}7.66$ (m, 12H : Ar), $\delta = 7.79\text{-}7.83$ (m, 6H : Ar), $\delta = 8.65$ (s, 12H : Ar) ppm. Selected IR (KBr): $\nu = 1125\text{ cm}^{-1}$ (P=O), $1150\text{-}1250\text{ cm}^{-1}$ (-CF), 1650 cm^{-1} (-C=O). Elemental analysis calculated (%) for $\text{C}_{51}\text{H}_{36}\text{EuF}_{18}\text{O}_8\text{P}_2$: C, 46.07, H, 2.50; found: C, 46.03, H, 2.51.

2.3 Preparation of $\text{Eu}(\text{tta})_2(\text{TPPO})_2$

4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (tta, 0.67 g, 3.0 mmol), triphenylphosphine oxide (TPPO, 0.56 g, 2.0 mmol) and 2,2'-iminodiethanol (0.32 g, 3.0 mmol) were dissolved in 40 ml of isopropanol. To this solution, a solution obtained by dissolving europium chloride (III) hexahydrate (0.37 g, 1 mmol) in 20 ml of a mixed solvent of water/isopropanol (1/4) was added dropwise at room temperature taking 2 hours, and stirring was further continued at room temperature for 1 hour. The precipitate formed was filtered by suction, and washed with water and isopropanol. The resulting light yellow powder was dried under vacuum at 50°C . Yield: 72%. ^1H NMR (400 MHz, $\text{CD}_3\text{-COCD}_3$, TMS) : $\delta = 5.9$ (s, 3H : -CH), $\delta = 6.31\text{-}6.35$ (m, 12H : Ar), $\delta = 6.97\text{-}6.99$ (m, 12H : Ar), $\delta = 7.65\text{-}7.83$ (m, 24H : Ar). Selected IR (KBr): $\nu = 1121\text{ cm}^{-1}$ (P=O), $1150\text{-}1300\text{ cm}^{-1}$ (-CF), 1610 cm^{-1} (-C=O). Elemental analysis calculated (%) for $\text{C}_{60}\text{H}_{45}\text{EuF}_9\text{O}_8\text{P}_2\text{S}_3$: C, 52.52, H, 3.09; found: C, 51.82, H, 3.01.

2.4 Preparation of $\text{Eu}(\text{hfa})_3(\text{Phen})_2$

$\text{Eu}(\text{hfa})_3(\text{Phen})_2$ were obtained by the reaction of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ with phen ligand in methanol under reflux using the same method as previous reported [13,19]. ^1H NMR (400 MHz, CDCl_3 , δ ,

ppm): $\delta = 8.11\text{-}8.42$ (m, 2H : phen), $\delta = 9.24\text{-}9.39$ (m, 4H : phen), $\delta = 11.24\text{-}11.46$ (m, 2H : phen), $\delta = 5.30$ (s, 3H : -CH).

2.5 Preparation of $\text{Eu}(\text{tta})_3(\text{Phen})_2$

$\text{Eu}(\text{tta})_3(\text{Phen})_2$ were obtained by the reaction of $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ with phen ligand in methanol under reflux using the same method as previous reported [20-21]. ^1H NMR (400 MHz, CDCl_3 , δ , ppm): $\delta = 8.43\text{-}8.54$ (m, 2H : phen), $\delta = 9.47\text{-}9.58$ (m, 2H : phen), $\delta = 10.00\text{-}10.45$ (m, 4H : phen), $\delta = 5.30$ (s, 3H : -CH), $\delta = 3.08$ (s, 3H : Ar), $\delta = 6.17$ (d, 3H : Ar), $\delta = 6.49$ (t, 3H : Ar), $\delta = 6.94$ (d, 3H : Ar). Elemental analysis calculated (%) for $\text{C}_{36}\text{H}_{20}\text{EuF}_9\text{N}_2\text{O}_6\text{S}_3$: C, 34.02, H, 1.16, N, 2.94; found: C, 43.21, H, 2.16, N, 2.96.

2.6 Preparation of laminated glass cells with $\text{Eu}(\text{III})$ complexes for carbonyl index analysis.

Prepared powders of $\text{Eu}(\text{III})$ complexes were sandwiched by a glass plate (low iron glass: thickness = 3mm). The sandwiched glass cells are irradiated UV light (Methalhalide lamp: $1000\text{W}/\text{m}^2$). After irradiation, the sandwiched glass cells were evaluated by FT-IR measurements.

2.7 Preparation of solar sealing EVA film containing $\text{Eu}(\text{III})$ complexes

In the first step, obtained EVA resin (VA = 26%), t-butyl peroxy-2-ethylhexyl monocarbonate (0.5 part of by weight based on 100 parts by weight of the ethylene-vinyl acetate copolymer), triarylisocyanate (0.5 part), silancoupling agent (0.5 part), $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (0.3 part). All chemicals were impregnated or dispersed with EVA resin, before kneading process. All materials were fed to a roll mill, and kneaded at temperature 75°C , was formed by calendaring process and cooled to prepare a solar sealing film (thickness 0.5 mm).

2.8 Preparation of silicon solar module using $\text{Eu}(\text{tta})_3(\text{TPPO})_2$.

A glass plate (low iron glass: thickness; 3 mm), each of the resultant solar cell sealing film, solar cell, solar cell sealing film without $\text{Eu}(\text{III})$ complex and a polyvinyl fluoride film (ISOVOLTA ICOSOLAR 2442: thickness; 0.35 mm) were

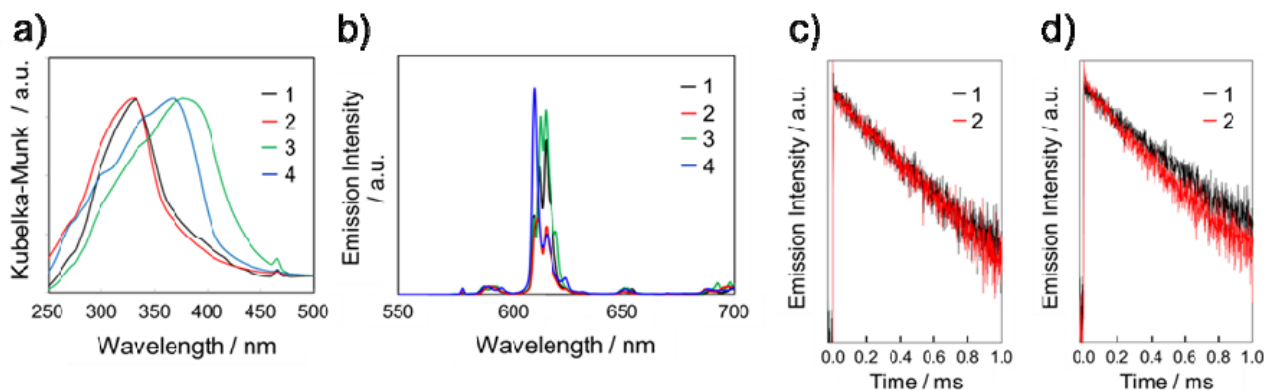


Figure 2. a) Absorption spectra of 1) $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$, 2) $\text{Eu}(\text{hfa})_3\text{Phen}$, 3) $\text{Eu}(\text{tta})_3(\text{TPPO})_2$, and 4) $\text{Eu}(\text{hfa})_3(\text{Phen})$ in solid-state at room temperature. b) Emission spectra of 1) $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$, 2) $\text{Eu}(\text{hfa})_3\text{Phen}$, 3) $\text{Eu}(\text{tta})_3(\text{TPPO})_2$, and 4) $\text{Eu}(\text{hfa})_3(\text{Phen})$ in solid-state at room temperature. Excited at 465 nm. The emission spectra were normalized with respect to the magnetic dipole transition ($^3\text{D}_0\text{-}^7\text{F}_1$). c) Emission decay profiles of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ under UV irradiation (1: 0 h 2: 24 h). d) Emission decay profiles of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation (1: 0 h 2: 24 h).

laminated in this order. The laminate was temporary bonded under application of pressure by using a vacuum laminator at 90 °C, and heated to gel fraction of 90%. The resultant laminated was used as module for measurement of photovoltaic efficiency.

3. Results and discussion

3.1 Photophysical properties of Eu(III) complexes under UV irradiation

$\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ was synthesized by the ligand exchange reaction of TPPO with $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ and in methanol, according to our previous report [22]. On the other hand, $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ was prepared by the complexation of TPPO, tta ligands and europium chloride in mixed solvent of water/isopropanol under room temperature. $\text{Eu}(\text{hfa})_3(\text{Phen})$ and $\text{Eu}(\text{tta})_3(\text{Phen})$ were synthesized by ligand exchange reaction of $\text{Eu}(\text{hfa})_3(\text{H}_2\text{O})_2$ or $\text{Eu}(\text{tta})_3(\text{H}_2\text{O})_2$ with Phen ligand in methanol. Their chemical structures were identified by using NMR measurements, IR spectroscopies and elemental analyses.

The absorption spectra in solid state are shown in Figure 2a. The absorption bands of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ and $\text{Eu}(\text{hfa})_3\text{Phen}$ was observed at

320 nm, which are assigned to the $\pi\text{-}\pi^*$ transition of the hfa ligands. On the other hand, the $\pi\text{-}\pi^*$ transition bands of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ and $\text{Eu}(\text{tta})_3(\text{Phen})$ were observed at 375nm. The red-shift of the absorption band of Eu(III) complexes with tta ligands is due to smaller energy gap between π (HOMO) and π^* (LUMO) orbitals of diketonate ligand molecule with thienyl group. Extra red-shift of $\text{Eu}(\text{tta})_3(\text{Phen})$ might be caused by specific $\pi\text{-}\pi$ stack interaction between tta and phen molecules.

The steady-state emission spectra of the $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$, $\text{Eu}(\text{hfa})_3\text{Phen}$, $\text{Eu}(\text{tta})_3\text{Phen}$, and $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ in solid state are shown in Figure 2b. Emission bands for the Eu(III) complexes are observed at 578, 592, 613, 650, and 698 nm and are attributed to the $4f\text{-}4f$ transitions of $^5\text{D}_0\text{-}^7\text{F}_J$ with $J = 0, 1, 2, 3,$ and 4 , respectively. The time-resolved emission profile of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ and $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation (0 h, 4 h, 12 h and 24 h) reveals single-exponential decay with lifetimes of millisecond timescale as shown Fig. 2c and 2d, respectively. The lifetime of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ after UV irradiation for 0 h, 4 h, 12 h and 24 h were found to be 0.93 ms, 0.96 ms, 0.97 ms, and 0.97 ms, respectively. The drastical

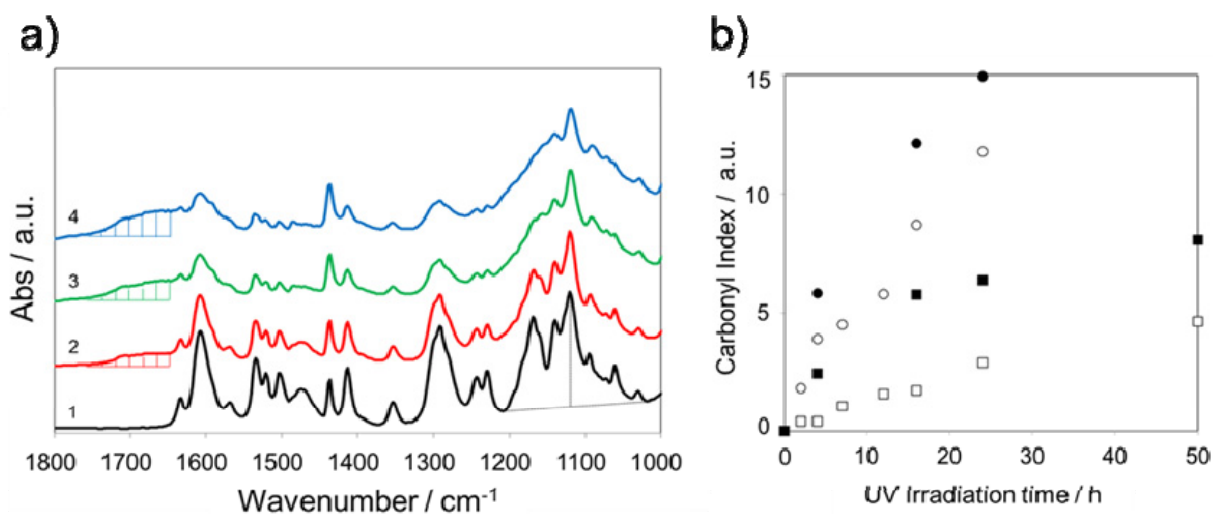


Figure 3. a) FT-IR spectra of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation (1: 0 h, 2: 4 h, 3: 12 h and 4: 24h). b) Time-dependence of carbonyl index of $\text{Eu}(\text{tta})_3\text{Phen}$ (black circles), $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (white circles), $\text{Eu}(\text{hfa})_3\text{phen}$ (black squares) and $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ (white squares). The carbonyl index is calculated from the integral calculus of absorbance at around 1680-1750 cm^{-1} normalized absorption band of C-F stretch vibration ($\nu = 1130 \text{ cm}^{-1}$).

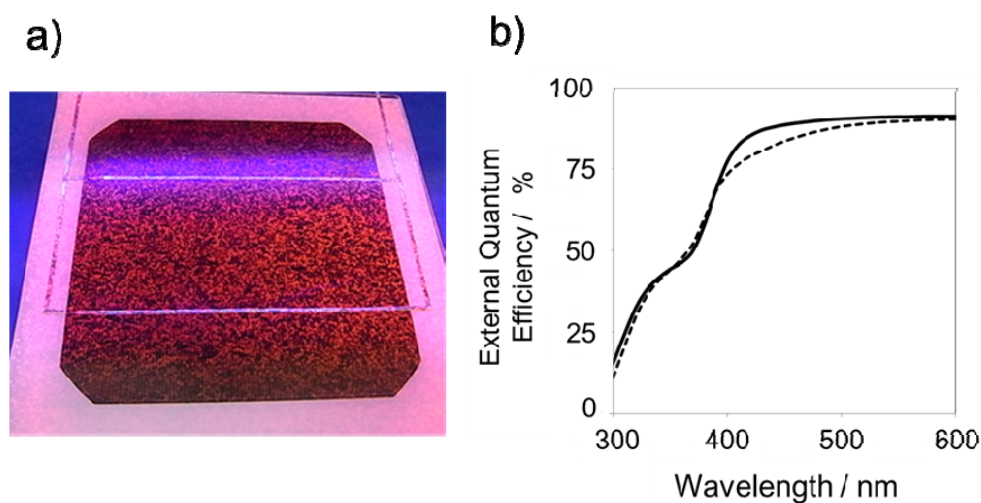


Figure 4. a) Image of photovoltaic module using EVA film composed of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation. b) External quantum efficiency of photovoltaic module using EVA film composed of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation (bold line: 0 h, dot line: 12 h).

change of the emission lifetime of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ under UV irradiation were not observed. On the other hand, we found effective decrease of the emission lifetimes of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (0 h: 0.77 ms, 4 h: 0.77 ms, 12 h: 0.71 ms and 24 h: 0.68 ms). The

decrease of the emission lifetime should be caused by degradation of molecular structure under UV irradiation.

3.2. Degradation analysis under UV irradiation

In order to estimate the degradation process of Eu(III) complexes under UV irradiation, we carried out carbonyl index analysis using FT-IR measurements. The FT-IR spectra for carbonyl index analysis are shown in Figure 3a. Absorption bands of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ at around 1130, 1150-1300 and 1615 cm^{-1} are assigned to P=O, C-F and C=O stretch vibrations, respectively (Figure 3a (1)). We observed increase of broad absorption band at around $1650\text{--}1750\text{ cm}^{-1}$ and decrease of C=O stretch bands at 1615 cm^{-1} under UV irradiation (Figure 3a (2)-(4)). The spectral change comes from decomposition of C=O groups in diketonate ligands.

The carbonyl index is calculated from the integral calculus of absorbance at around $1680\text{--}1750\text{ cm}^{-1}$ normalized absorption band of C-F stretch vibration ($\nu = 1130\text{ cm}^{-1}$). Time dependence of carbonyl index of Eu(III) complexes under UV irradiation are shown in Figure 2b. After 24 h of UV irradiation at $63\text{ }^\circ\text{C}$, we observed drastic increase of the carbonyl index of $\text{Eu}(\text{tta})_3\text{Phen}$ (black circle: carbonyl index = 15) and $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ (white circles: carbonyl index = 12). Carbonyl index of $\text{Eu}(\text{hfa})_3\text{Phen}$ under UV irradiation for 24 h was found to be 15 (black square). In contrast, carbonyl index of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ under UV irradiation for 24 h was estimated to be 3 (white square). The durability of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ is five times larger than that of $\text{Eu}(\text{tta})_3(\text{phen})$.

We here fabricated EVA films containing $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ for solar cell modulation to analyze the degradation under UV irradiation. The solar modulation attached with EVA film containing $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ shows homogeneous red emission excited at UV irradiation. After UV irradiation for 12 h, the red emission are changed to sparse yellowish emission, which is caused by degradation of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ under UV irradiation. External quantum efficiency (EQE) of the solar cell module using EVA films composed of $\text{Eu}(\text{tta})_3(\text{TPPO})_2$ before and after UV irradiation are shown Figure 4b. Decrease of EQE at around 420 nm is the result of loss of light absorption because of the degraded complex. This result indicate that $\text{Eu}(\text{tta})_3(\text{TPPO})_2$

is not suitable in application for optical materials such as solar cells and display devices. We consider that photo-stable Eu(III) complex composed of hfa and TPPO ligand is the most stable for industrial optical devices such as a solar cell application.

4. Conclusions

Photo-degradation of luminescent polymers with lanthanide complexes was successfully estimated by carbonyl index analysis under UV irradiation. The carbonyl index analysis using FT-IR measurements is a quantitative tool for evaluation of UV durability of optical materials with luminescent Eu(III) complexes. In this study, we observed that the durability of $\text{Eu}(\text{hfa})_3(\text{TPPO})_2$ was five times larger than that of Eu(III) complex with thienyl group. The structural decomposition of Eu(III) complexes affects performance of optical devices such as solar cells, directly. Detailed degradation analysis of Eu(III) complexes using FT-IR measurements is expected to be useful for evaluation in the field of industrial applications such as solar cells, display, and illuminations.

Acknowledgements

This work was partly supported by Grants-in-Aid for Scientific Research on Innovative Areas of "New Polymeric Materials Based on Element-Blocks (No. 2401)" (24102012) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

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