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Luminescent Eu(III) coordination polymer cross-linked with Zn(II) complexes

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ABSTRACT

A structural design of new luminescent lanthanide coordination polymers composed of Eu^{3+} complex and Zn^{2+} complexes are introduced. The Eu^{3+} coordination polymer $[Eu(hfa)_3(dppy)_2ZnCl_2]_n$ (Eu–Zn) (hfa: hexafluoroacetylacetonato, dppy: 4-pyridyldiphenylphosphane oxide) were synthesized by the complexation of $Eu(hfa)_3(H_2O)_2$ with $ZnCl_2(dppy)_2$. The structure was characterized using XRD and TG-DTA. The photophysical properties were estimated using the emission spectra, the emission lifetimes, and the emission quantum yields. The emission quantum yields are larger then that of precursor Eu $(hfa)_3(H_2O)_2$. The emission quantum yield of Eu–Zn was found to be 59%. The preparations, structures and photophysical properties of Eu–Zn are demonstrated as a new luminescent Eu^{3+} coordination polymer for the first time.

1. Introduction

Luminescent lanthanide complexes are expected to be useful in photonic properties with *4f–4f* transitions. The *4f–4f* transitions of lanthanide complexes lead to narrow emission bands (FWHM < 10 nm) and long emission lifetime ($\tau > 1$ μs), resulting in formation of remarkable luminescent materials such as display devices and bio-imaging applications [1,2]. The strong and characteristic luminescence of lanthanide complexes including Eu^{3+}, Tb^{3+}, Sm^{3+}, Yb^{3+} and Pr^{3+} ions have been reported [3–5].

Recently, the lanthanide coordination polymers, which are composed of lanthanide ions and organic bridged ligands, have been reported as the new luminescent materials [6–8]. The lanthanide coordination polymers provide the characteristic chemical and physical properties such as thermostability [9], molecular-sensing [10] and strong luminescence [11], which can be synthesized using suitable selections of lanthanide ions and bridged organic ligands.

In the previous study, organic molecules were mainly used for bridge ligands of the lanthanide coordination polymer. We here have attempted to introduce the transition metal complex as bridge ligands for development of novel lanthanide coordination polymer.

In this study, Eu^{3+} coordination polymer cross-linked with Zn^{2+} complex (Eu–Zn) is reported for the first time (see Fig. 1c). The structures of Eu–Zn are characterized using XRD and TGA (thermogravimetric analysis). The photophysical properties are estimated using the emission spectra, the emission lifetimes, and the emission quantum yields. The preparations, structures and photophysical properties of Eu–Zn are demonstrated as a new luminescent coordination polymer.

2. Experimental

2.1. Materials

4-Bromopyridine hydrochloride (>98%), tetrakis(triphenylphosphine)palladium(0) (>97%), diphenylphosphine (>90%) and hexafluoroacetylacetone (>95%) was purchased from Tokyo Chemical Industry co., ltd. Europium(III) acetate n-hydrate (>99.9%) and zinc(II) chloride (>99.9%) were obtained from wako pure chemical industries, ltd. All other chemicals were reagent grade and were used without further purification.

2.2. Apparatus

^1H NMR spectra were recorded on a JEOL JNM-ECS400 (400 MHz). ^1H NMR chemical shifts were determined by

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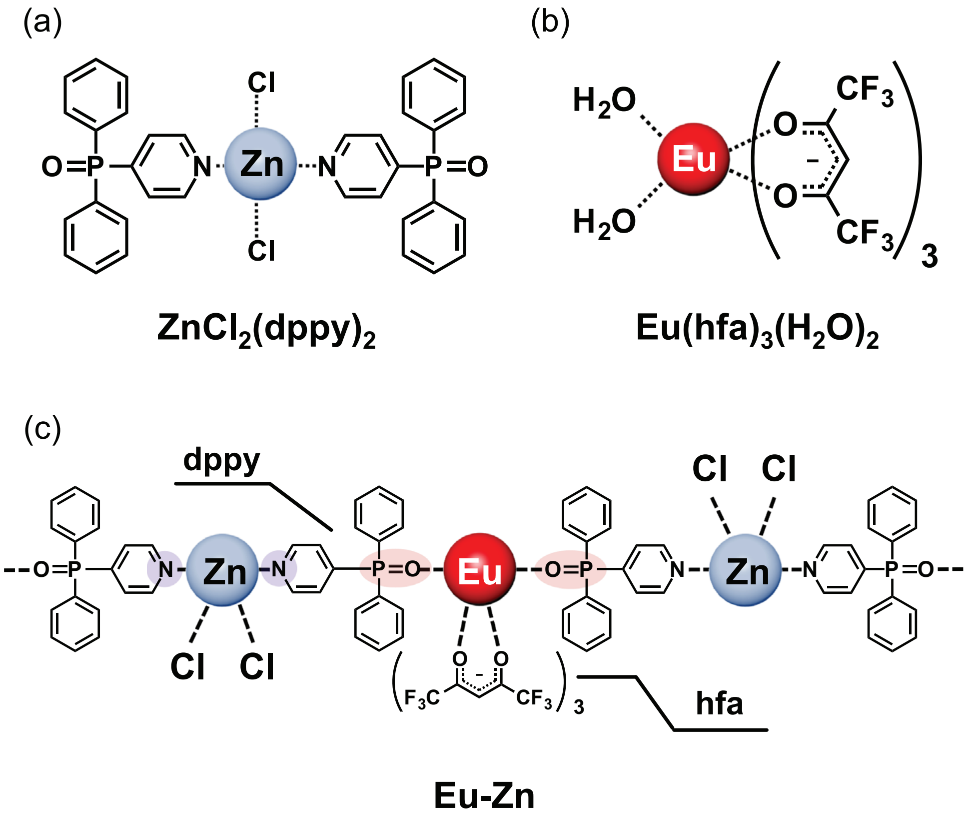

Fig. 1. Chemical structure of (a) [$ZnCl_2(dppy)_2$] and (b) [$Eu(hfa)_3(H_2O)_2$]. (c) Chemical schematic of [$Eu(hfa)_3(dppy)_2ZnCl_2$]$_n$ (Eu–Zn).

tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed using a J-SCIENCE MICRO CORDER JM10. ESI-MS and FAB-MS were performed using a JEOL JMS-T100LP and a JEOL JMS-700TZ. Thermogravimetric analyses were performed using a MAC TG-DTA 2000 under an argon atmosphere at a heating rate of 1 °C min^{-1}.

2.3. *Preparation of 4-pyridyldiphenylphosphine oxide (dppy) $C_{17}H_{14}NOP$*

4-Bromopyridine hydrochloride (1.96 g, 10 mmol) and Ttetrakis (triphenylphosphine)palladium(0) (1.16 g, 10 mmol%) were added into a 40 ml of toluene under argon. Triethylamine (2.8 ml, 20 mmol) and diphenylphosphine (1.8 ml, 10 mmol) were added into the toluene solution. The reaction mixture was heated to 80 °C for 18 h. After the reaction, the product was extracted with dichloromethane (30 ml × 3), and then washed with brine for three times. The dichloromethane solution was dried using anhydrous $MgSO_4$ and concentrated to dryness. The obtained brown oil added into 20 ml of dichloromethane, and cooled under 0 °C and then hydrogen peroxide aqueous solution (30%) was add to the solution. The reaction mixture was stirred for 3 h. After the reaction, the product was extracted with dichloromethane (30 ml × 3), and then washed with brine for three times. The dichloromethane solution was dried using anhydrous $MgSO_4$ and concentrated to dryness. The crude materials were separated using a silica-gel chromatography (hexane/acetone 1:4), and dppy was obtained as a white solid (1.24 g, 43%).

^1H NMR (400 MHz, $CDCl_3$/TMS): δ8.74–8.79 (t, 2H, py), 7.48–7.71 (m, 12H, Ar) ppm. ESI-MS: Calcd. for [dppy+H]$^+$: 280.09 Found, 280.09. Elemental analysis: Calcd. for $C_{17}H_{14}NOP$: C, 73.11; H, 5.05; N, 5.02, Found: C, 73.03; H, 5.07; N, 4.95.

2.4. *Preparation of Zn^{2+} complex $ZnCl_2(dppy)_2$ (see Fig. 1a)*

Zinc(II) chloride (0.28 g, 2.00 mmol) and 4-pyridyl diphenyl phosphine oxide (0.84 g, 3.00 mmol) was dissolved in ethanol (40 ml). The solution was heated at 80 °C and refluxed while stirring for 24 h. The solvent was evaporated to afford a white powder of the titled compound. (0.42 g, 30%)

^1H NMR (400 MHz, $CDCl_3$/TMS): δ=8.84–8.89 (t, 4H, py), 7.71-7.77 (d, 4H, py), 7.62–7.70 (m, 12 H, Ar), 7.50–7.57(m, 8 H, Ar)ppm. ESI-MS: Calcd. for [$ZnCl(dppy)_2$]$^+$: 692.03 Found, 692.03. Elemental analysis: Calcd. for $C_{34}H_{28}Cl_2N_2O_2P_2Zn$: C, 58.77; H, 4.06; N, 4.03, Found: C, 59.27; H, 4.31; N, 3.73.

2.5. *Preparation of precursor Eu^{3+} complex $Eu(hfa)_3(H_2O)_2$ (see Fig. 1b) [12]*

$Eu(hfa)_3(H_2O)_2$ was prepared according to the literature references.

Elemental analysis: Calcd. for $C_{15}H_2O_8F_{18}Eu$: C, 22.48; H, 0.88, Found: C, 22.12; H, 1.01.

2.6. *Preparation of Eu–Zn programing polymer [$Eu(hfa)_3(dppy)_2ZnCl_2$]$_n$ (see Fig. 1c)*

Zn^{2+} complex $ZnCl_2(dppy)_2$ (1 equiv.) and [$Eu(hfa)_3(H_2O)_2$] (1 equiv.) were dissolved in methanol. The solution was refluxed while stirring for 5 h, and the reaction mixture was concentrated to dryness.

FAB-MS: Calcd. for [$Eu(hfa)_3(dppy)ZnCl_2$]$^+$: 1258.9 Found, 1259.9.

2.7. *Optical measurements*

Emission spectra were measured with a HORIBA Fluorolog-3 spectrofluorometer and corrected for the response of the detector