Europium amphiphilic naphthalene based complex for the enhancement of linearly polarized luminescence in Langmuir-Blodgett films

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Europium amphiphilic naphthalene based complex for the enhancement of linearly polarized luminescence in Langmuir-Blodgett films †‡

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Linearly polarized luminescence (LPL) in films of europium ions was induced by using naphthoic acid adopted alkyl chain (NaphC15), which plays roles of both surfactant and photo-antenna. The synthesis of NaphC15 was newly developed, and of the Eu complex has composed in a 1:3 for Eu^{3+} ion and NaphC15 in the powder for comparison. The structual aspects of LB films with layered scheme were obtained with the measurements of synchrotron XRPD, X-ray photoelectron spectroscopy and waveguide polarized absorption spectra. Luminescence of europium in the film is strengthed more than that in powder complex. The luminescence efficiency calculated from observed luminescence lifetimes and quantum yields also supported their structure-enhanced luminescence. Finally, we revealed that the LPL was sensitized by the electronic dipole moment localized on the NaphC15 moieties aligned independently in Langmuir-Blodgett films.

Introduction

Polarized optical phenomena of europium (Eu) complexes have attracted continuous interest in the past few decades not only as a scientific curiosity[1], but also for applications such as security inks and display materials.[2] The luminescence assigned to the 4f-4f (abbreviated as ff) transitions localized on the Eu^{3+} ions is sensitized by photo-excitation of π-electronic skeletons of ligands through intramolecular energy transfer[3], since the ff transitions of the trivalent lanthanide ions are the Laporte forbidden. Methods and molecular designs to improve luminescence intensities have been extensively researched[4]. Recently, the number of papers on lanthanide complexes related to circularly and linearly polarized luminescence (abbreviated as CPL and LPL, respectively) increases, especially, CPL phenomena of Eu complexes were much reported with ligands. The principle to induce polarized phenomena of Eu complexes is still unknown, because it is generated after the energy transfer, and the electron cloud of the Eu^{3+} ion should be spherical with no polarization.

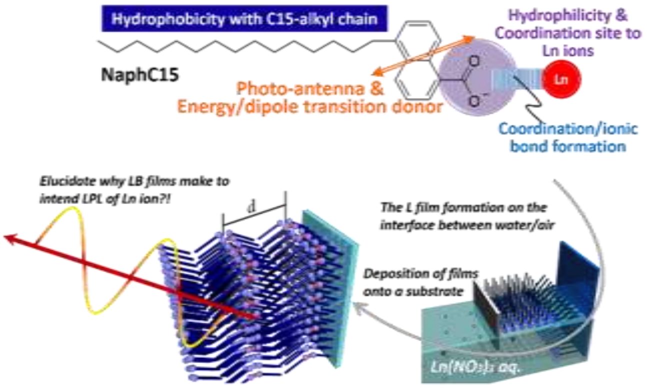

Fig. 1 Schematic representation of the design of naphthoic acid derivative (abbreviated as NaphC15) with alkyl chains (top), schematic images of this work. Ln, L and LB are lanthanide, Langmuir and Langmuir-Blodgett, respectively. The present LB films form a Y-type film on the hydrophobic substrate. *d* shows the interlayer distance of aligned Eu^{3+} ions in the Y-type films.

There are few papers on Eu complexes that generate LPL. For instance, Eu complexes exist in liquid crystals,[5] or polymer matrixes.[6-8] Heegar *et al.* reported a LPL polymer of Eu^{III} by using polymethacryl acid, and suggested the LPL of Eu^{III} would induced the direction of electronic dipole moment localized on the organic photo-antenna.[6] However, nobody knows the

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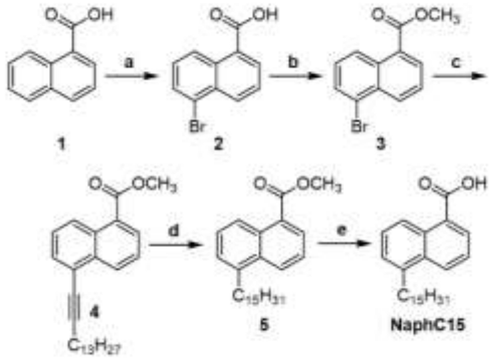
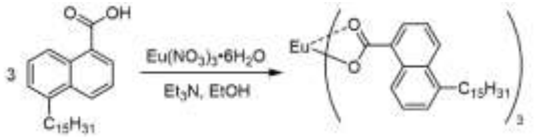
† *Dedicated to Professor Emeritus Dr. Isao Ono on the occasion of his 77th birthday.*

‡ *Electronic Supplementary Information (ESI) available: ^{1}H NMR, Attenuated total reflection FT-IR, electronic absorption, excitation and luminescence spectra with their decay profiles, synchrotron XRD patterns, XPS. For the syntheses, reaction scheme and ^{1}H-NMR spectra. See DOI: 10.1039/x0xx00000x*



Scheme 1 Synthesis of NaphC15. a) Br_2, CH_3COOH, Δ, 64%; b) CH_3OH, H_2SO_4, Δ, 73%; c) 1-pentadecyne, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, Δ, 40%; d) H2, Pd/C, EtOAc, rt, 33%; e) KOH, H_2O, THF, CH_3OH, rt, then HCl, 72%.



Scheme 2 Syntheis of $Eu(NaphC15)_3$.

enough explanation from experimental evidences still now. One of the keys to enhance the LPL of molecular system is the film formation in polymer films or in self-assembly systems. Actually, the differences in molecular orientations of Eu complexes between powder and liquid crystals enhance their polarized photophenomena. There are only a few reports demonstrating polarized luminescence of Eu^{3+} ions in Langmuir-Blodgett (LB) films.[9] Furthermore, no studies were reported which experimentally elucidated the principle of LPL of Eu complexes as related to molecular aggregation or intramolecular energy transfer.

Here, we examine a new molecular aggregation system to induce bright LPL of Eu complexes in LB films made with an amphiphilic 1-naphthoic acid derivative (NaphC15; Fig. 1), and we elucidated possible explanation for LPL. Naphthalene and its derivatives have a high absorption coefficient[10] and fluorescence polarization of naphthalene derivatives was reported for an imaging procedure of biomaterials, since their transition dipole moment is high and their molecular rotation relaxation time on the protein is useful.[11] Additionally, the excitation state of naphthalene moiety acts as an efficient energy donor to Eu^{3+} ion.[12]

Results and discussion

Synthesis of surfactant ligand, NaphC15, and its Eu complex

NaphC15 was synthesized in five steps from commercial 1-naphthoic acid (**1**) (Scheme 1 and Fig. S1). Bromination of **1** gave 5-bromo-1-naphthoic acid (**2**).[13] The carboxyl group of **2** was converted into a methyl ester to afford **3**.[14] Sonogashira coupling reaction between **3** and 1-pentadecyne afforded alkynylated product **4**. Hydrogenation and subsequent hydroxylation of **5** gave desired NaphC15 as a white solid.

For the comparison of luminescence and structural properties between the film and powder, the Eu complex with NaphC15, abbreviated to $Eu(NaphC15)_3$, was also synthesized (Scheme 2 and Fig. S2). $Eu(NaphC15)_3$ was characterized as a 1:3 complex, which was reasonable because the same component ratios were reported in a Eu complex with 1-naphthoic acid[10e] The thermal analyses were also supported that $Eu(NaphC15)_3$ has one coordination water molecule and one crystalline water in the microcrystals (Fig. S3).

The formation condition and structure of LB films

LB films of NaphC15 was obtained by the deposition from the surface of neat water or aqueous solution. Especially, since the Ln complexes, $Ln(NaphC15)_3$, are not soluble in solution, the Eu/Gd-containing LB films of NaphC15 were deposited from the surface of europium nitrate-water to the quartz substrate. The isotherm curve of a liquid film of NaphC15 is shown in Fig. 2, and has the characteristic shape for monolayer formation. The 10-layered LB films of NaphC15 were deposited on a hydrophobic quartz substrate[15] from the interface of a 1.0×10^{-5} M aqueous solution of europium nitrate at surface pressures of 30, 35 and 40 mN/m (abbreviated as **LB30**, **LB35** and **LB40**, respectively).

An X-ray photoelectron spectroscopy (XPS) of **LB30**, and the existence of Eu^{3+} ions in the films was confirmed by Eu 3d XPS bands (Fig. 3). The nitrate ion of europium nitrate was replaced with the anionic 1-naphto ligand, indicated by the disappearance of the bands after complexation in the film. Similar behaviour of Eu 3d and N 1s bands also appeared in both **LB35** and **LB40** (Fig. S4), but intensities of the Eu 3d XPS band of **LB40** was relatively weak and broad more than those of **LB30** and **LB35**. It suggests that the complexation between NaphC18 and Eu in **LB40** will differ from those of other LB films.

LB30, **LB35** and **LB40** of the synchrotron X-ray diffraction (XRD) patterns observed by using an attachment for small angles

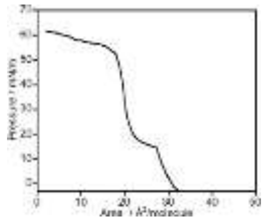


Fig. 2 Isothermal curve of NaphC15.

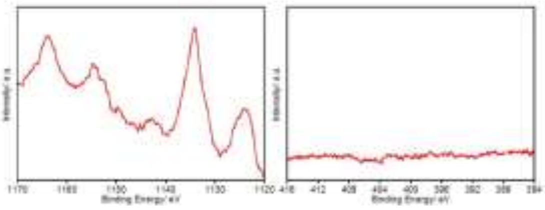


Fig. 3 X-ray photoelectron spectra of Eu 3d (left) and N 1s (right) band in **Eu30**. Binding energies were corrected by the Au 4f band (84.0 eV).

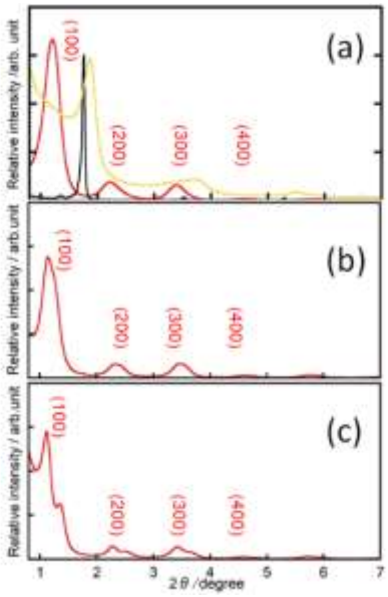


Fig. 4 Synchrotron XRD patterns of 10-layers in Eu-NaphC15 LB films (red lines) formed under surface pressures of (a) 30, (b) 35 and (c) 40 mN/m. The XRD patterns were recorded by using imaging plates.[18] Yellow and black lines in Fig. 2a are the powder diffraction patterns of Eu(NaphC15)$_3$ and its ligand NaphC15, respectively. Exposure time was 600 s, source light power was λ=1.000050 Å for powders and λ=0.999894 Å for films.

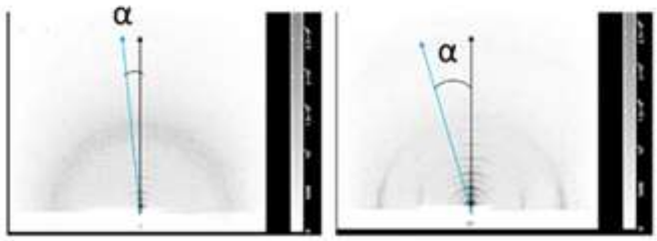


Fig. 5 X-ray diffractions recorded on imaging plates for **LB30** (left) and **LB35** (right).

sharply appeared (Fig. 4, and Fig. S5)[16] meaning the high ordering to an out-of-plane periodicity. Furthermore, their patterns in LB films completely differ from that in powder-state Eu(NaphC15)$_3$ which broadly appeared. It indicates that Eu(NaphC15)$_3$ LB films form a layered structure. The interlayer distance *d* in **LB30** was estimated to be ca. 49.8 Å (2θ = 1.15°) as a bilayer formation from Bragg's equation. This distance is shorter than the theoretical value of 52 Å, when the length of NaphC15 was used as 26 Å with a perpendicular alignment. It indicates the formation of the heling-born structure in the films as our initial assumption in Fig. 1.

The peak position in **LB30** was slightly shifted with an increase in the surface pressure, and appeared at high α angles according to the imaging plate-recording of all diffraction (Fig. 5). This suggests that layered species in the film aggregated randomly, when high surface pressure was applied during the film formation. In fact, each peak in **LB40** is split into two, indicating several molecular orientations existed. Thus, homogenization at a surface pressure of > 40 mN/m, must be applied in order to eliminate the polarized luminescence phenomenon. XRD patterns of LB films using Gd are similar to above results.

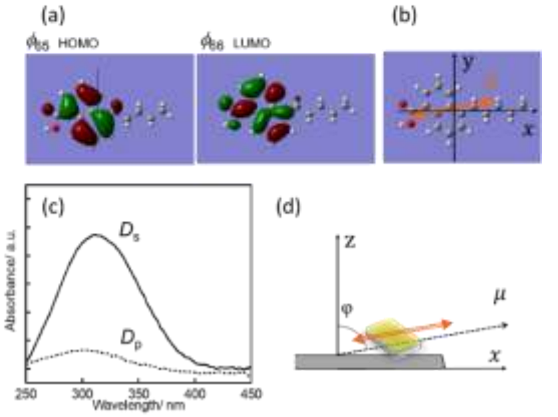


Fig. 6 (a) Selected MO's of 1-naphthoic acid calculated by TD-DFT (b) The transition dipole moment of the first singlet $\pi\pi^*$ transition. (c) Polarized optical waveguide absorption spectrum of Eu-NaphC15 LB films deposited at 30 mN/m. Dp and Ds show the primary and secondary polarized light, respectively. (d) Schematic representation of tilt angle ϕ for the determination by the polarized absorption spectrum by using equations[17] (see ESI and Fig. S9).

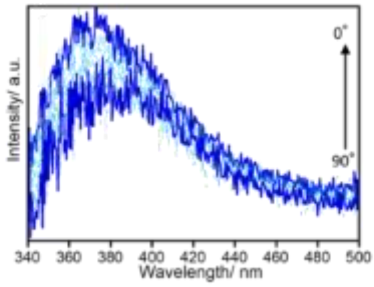


Fig. 7 Linearly polarized fluorescence spectra (λ_{ex} = 310 nm) localized on naphthalene moiety by using the 10 layer-LB film of NaphC15 deposited at 20 mN/m. The angles mean the rotation angles of the polarizer in front of the detector.

The temperature dependence on the synchrotron XRPD for NaphC15 and Eu(NaphC15)$_3$ in powder states was also observed and have no changed (Fig. S5(d)), which resulting to the stable orientation without shrinking even at 80 K.

Polarized electronic absorption and luminescence spectra localized on NaphC15 in the LB films

Nature of electronic structure of ligand moiety in the lanthanide complexes and the LB films supports to understand the enhancement of ff transitions through excitation energy transfer from the ligand. NaphC15 in chloroform shows the absorption band at 317 and 327 (sh) nm which correspond to the 308 and 325 (sh) nm bands of naphthalene itself (Fig. S6). It means that the electronic bands of naphthalene skeleton after the derivation of alkyl chain are shifted to a longer-wavelength side.

Linearly polarized absorption spectra localized on the ligand in the mainly contributing MO's for its first $\pi\pi^*$ electronic transition. The tilt angles of the naphthalene skeletons in the film were determined by using polarized absorption spectra attached with the optical wave guide method (see ESI for the calculation).[17] A bilayer of **LB30** deposited on a waveguide quartz plate show the band at 315 nm assigned to the first $^1\pi\pi^*$ transition. This band was calculated at 324.7 nm with an oscillator strength, f =0.1413, which contributed the HOMO-LUMO transition of 49% from the excited wavefunctions, Ψ_1 =0.69$\varphi_{65,66}$ +... . The transition dipole moment μ was also calculated and is shown in Fig. 6b.

The optical density D_s is much higher than that of D_p at the first $^1\pi\pi^*$ transition position. The peak top in D_s is shifted more to the red than that of D_p. These anisotropic results indicate that the naphthoic acid moieties are aligned in the films. The tilt angles φ of the naphthoic acid moieties in the films were estimated[17] as 77° and 67° for **LB30** and **LB35**, respectively (Fig. S10). The film obtained at 40 mN/m showed no intensity differences between its D_p and D_s due to the random molecular assembling. Thus, the surface pressure can be tuned to refine the production of LPL devices by LB techniques. It supports to the discussion obtained from the synchrotron XRD. The surface pressure at 40 mN/m is too much strong for their film formation and will affect to collapse the monolayer at the water surface.

The linearly polarized fluorescence (the $^1\pi\pi^*$ transition) of NaphC15 were observed in the LB film (Fig. 7). The fluorescence intensities decreased with increasing the angles of polarizer direction of the a LB film in association with the band shifting from 390 to 375 nm. This indicates that the π–electronic system of NaphC15 will act as an energy donor with the refined transition dipole moment for the ff luminescence after the complexation with Eu^{3+} ion.

The ff-luminescence spectra of Eu complexes with NaphC15 and their polarized phenomena in LB films

Luminescence and its excitation spectra of $Eu(NaphC15)_3$ in the solid state were shown in Fig. 8. The luminescence bands of Eu^{3+} ion in the complex appear at 579, 593, 612.5, 649 and 698.3 nm assigned to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions, respectively. The excitation spectrum monitored at 612.5 nm has a broad band around 340 nm and a sharp one at 393.1 nm. The former band corresponds to the ππ* electronic absorption band localized on the naphthalene skeleton, and latter one is the ff absorption band of Eu^{3+} ion. The corresponding bands appear at mostly same position in **LB30**, **LB35** and **LB40** as shown in Fig. S7. Thus, the ligand acts as an energy donor to enhance ff emission of Eu through the coordination bond in LB films. Incidentally, there is no information of all spectra in solution of $Eu(NaphC15)_3$ due to its quite low solubility into solvents.

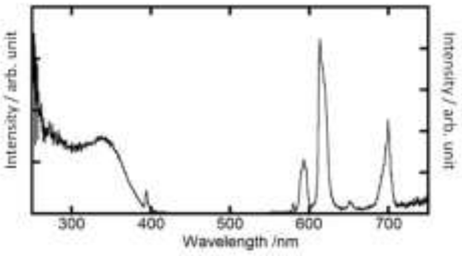


Fig. 8 Luminescence and excitation spectra of Eu(NaphC15)3 in the powder state. λ_{ex}=310 nm and λ_{mon}=612 nm

The fluorescence and phosphorescence band at 385 and 510 nm, respectively, localized on NaphC15 in the Gd-NaphC15 LB film was able to be observed, but was not done in solid state as a Gd complex. It means that the film formation is also suitable to keep the stable excited triplet state of the ligand moiety. The phosphorescence band position and its broad shape are effective to be an energy donor to Eu, and to induce the ff emission of Eu (Fig. S10).

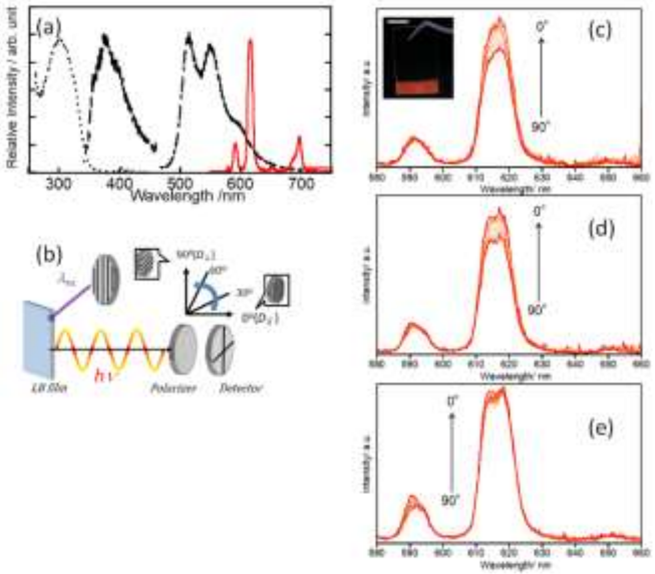


Fig. 9 Luminescence spectra of ff emission (red line) of Eu^{3+} ions in **LB30** (a: λ_{ex} = 310 nm). The excitation spectrum monitored at 615 nm are shown in dotted line. Fluorescence (dashed line) and phosphorescence (dotted-dash line; at 77 K) localized on π-electronic systems of the NaphC15 LB film with Gd ion. (b) Setup for the linearly polarized luminescence (LPL) spectral measurement. LPL of the Eu-NaphC15 LB film deposited at various surface pressures (c: 30; d: 35; and e: 40 mN/m).[8] Inset in Fig. 3c is a photograph of luminescence of LB30 under UV light (scale bar: 20 mm).

Table 1 Photophysical data of the luminescence lifetimes τ_{ff}^* (ms; Fig. S8), quantum yields φ_{obs}^{**}, radiative rate constant k_R (s^{-1}), non-radiative rate constant k_{NR} (s^{-1}), net quantum yield φ_{Ln} and energy transfer efficiencies η_{EnT} of the Eu-NaphC15 LB films and the powder $Eu(NaphC15)_3$.

	τ_{ff1}	τ_{ff2}	τ_{ff3}	φ_{obs}	k_R	k_{NR} x10^3	φ_{Ln}	η_{EnT}
Powder	0.07 62%	0.03 38%	-	0.1 %	450	15.8	2.7%	33 %
LB30	0.26 48%	0.08 39%	0.56 13%	5.8 %	490	2.5	16%	49 %
LB35	0.79 38%	0.29 37%	0.09 25%	5.0 %	410	1.2	25%	19 %
LB40	0.29 49%	0.65 29%	0.07 22%	6.2 %	440	1.7	20%	30 %

* λ_{ex} = 340 nm, λ_{mon}= 615 nm, **λ_{ex} = 310 nm, λ_{mon} = 550 – 720 nm

The LPL of the Eu-containing LB film with NaphC15 was successfully observed as shown in Fig. 9. The intensities were normalized at each electric dipole transition, $^5D_0 \rightarrow {}^7F_1$. The luminescence intensity of the $^5D_0 \rightarrow {}^7F_2$ transition assigned to the magnetic dipole transition in **LB30** or **LB35** drastically changed with different angles of the polarizer placed in front of the detector. While **LB40** shows no LPL behaviour nor did the complex in solution as well as in powder of Eu(NaphC15)$_3$. It indicates that the structure as an assembly of **LB40** is more random than those in **LB30** and **LB35**. This is supported by the XRD as described above. The similarities of **LB30** and **LB35** in such LPL and above photophysical properties are enhanced with the periodically stacking of molecular layers more than that in **LB40**.

It is worthwhile to note that the luminescence quantum yield φ_{obs} at the ff emission in **LB30** is 5.8% which is much greater than that in the powder of 0.1% (Table 1). The luminescence decay profiles for Eu(NaphC15)$_3$, **LB30**, **LB35** and **LB40** are shown in Fig. S8 The luminescence lifetimes of the Eu-NaphC15 LB films are also higher than that in the powder. The radiative rate constants k_R and efficiencies of energy transfer η_{EnT} were calculated. These values in the LB films correspond to those in the powder of Eu(NaphC15)$_3$, while non-radiative rate constants k_{NR} in the LB films are drastically decreased more than that in the powder. The FT-IR, elemental and thermal analyses show the existence of coordinating water in the complex Eu(NaphC15)$_3$ in the powder. It means that the differences of intermolecular interaction between the powder and films affect to the luminescence ability of Eu with the enhancement of coordinating water molecules resulting in the low k_{NR} value in the films.

That is, the film formation of NaphC15 by the LB method containing Eu^{3+} ions is suitable to obtain LPL of ff emissions according to the assembled independently existing NaphC15 in the film, and to enhance the excitation energy transfer from NaphC15 to Eu without any water interactions

Experimental

Syntheses of and characterization of NaphC15[14,15] and the Eu complex

5-bromo-1-naphtoic acid(1)

1-Naphthoic acid (9.65 g 56.0 mmol; TCI Co. Ltd.) and acetic acid (40 mL; TCI) were placed in a three-necked flask. This mixture was heated at 110 °C and stirred during the addition of bromine (3.20 mL 61 mmol); TCI), then it was refluxed for 2 hours. A yellow solid was precipitated during heating, and then stirred at room temperature overnight. The mixture was poured into ice water. The solid was filtered, washed with water, and crystallized from acetic acid (250 mL; Kanto Chemical Co. Ltd.) to afford 9.05 g (64 %) of bromo acid as a white solid. ^1H NMR (CD_3OD): δ 7.44 (dd, 1H), 7.65 (dd, 1H), 7.86 (dd, 1H), 8.23 (d, 1H), 8.47 (d, 1H) and 8.90 (d, 1H).

Methyl 5-bromo-1-naphthoate(2)

To a suspension of 5-bromo-1-naphthoic acid (9.05 g, 36 mmol) in anhydrous methanol (360 mL) was added concentrated H_2SO_4 (9 mL), and the resulting mixture was refluxed for 6 hours. The mixture was cooled and concentrated *in vacuo* to one-third the volume. The organic phase was washed with water, dried ($MgSO_4$), and concentrated in vacuo. Silica gel column chromatography using hexane/EtOAc (2:1) afforded 7.07 g (73%) of methyl 5-bromo-1-naphthylcarboxylate. ^1H NMR ($CDCl_3$): δ 4.01 (s, 3H), 7.43 (dd, 1H), 7.62 (dd, 1H), 7.83 (dd, 1H), 8.20 (dd, 1H), 8.49 (d, 1H), 8.87 (d, 1H).

Methyl 5-(pentadec-1-yn-1-yl)-1-naphthoate(3)

Methyl 5-bromo-1-naphthoate (1.00 g, 3.81 mmol), 1-pentadecyne (0.79 g, 3.81 mmol), bis(triphenylphosphane)palladium(II) dichloride (133 mg, 0.19 mmol), copper(I) iodide (33 mg, 0.19 mmol), and triphenylphosphane (99 mg, 0.38 mmol) were placed in a two-necked flask. After three successive vacuum/argon cycles, THF (20 mL) and triethylamine (20 mL) were introduced, both by syringe. The reaction mixture was stirred at 66 °C. The crude product was concentrated onto silica. Purification by HPLC yielded the product as a white solid (409.9 mg, 40%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.84 (d, 1 H), 8.60 (d, 1 H), 8.19 (d, 1 H), 7.66 (d, 1 H), 7.49–7.57 (m, 2 H), 4.01 (s, 3 H), 2.56 (t, 2 H), 1.71 (quint, 2 H), 1.53 (quint, 2 H), 1.39–1.25 (m, 18 H), 0.88 (t, 3H) .

Methyl 5-pentadecyl-1-naphthoate(4)

To a solution of Methyl 5-(pentadec-1-yn-1-yl)-1-naphthoate (409.2 mg, 1.04 mmol) in ethyl acetate (60 ml) was added 10% palladium on activated carbon (42 mg, 10 wt%). The mixture was well stirred under an atmospheric pressure of hydrogen for 2 days. The catalyst was removed by filtration. Purification by HPLC yielded the product as a white solid (137 mg, 33%).

5-pentadecyl-1-naphthoic acid(Naph-C$_{15}$)(5)

66.9 mg of ester and 2.8 mL of THF: methanol = 1 : 1 were placed in round-bottomed flask mounted over magnetic stirrer. 0.56mL 6 *N* KOH aqueous was added and the contents were stirred for 72 hours. The aqueous was acidified to *pH* = 2 with hydrochloric acid. The carboxylic acid precipitated on standing, was washed with water and filtered off, and dried under vacuum.

Eu(NaphC$_{15}$)$_3$

$Eu(NO_3)_3 \cdot 6H_2O$ (45.4mg, 102 μM) in ethanol (7 mL) was slowly added to a solution of Naph-C$_{15}$ (38 mg, 99.3 μM) with triethylamine (0.07 mL). After stirring 24h, the white precipitate was filtered and washed with ethanol (50.1 mg, 94.4 %). Eu(NaphC15)$_3$ was characterized as a 1:3 complex with a water molecule. Anal. Calcd for $C_{78}H_{113}O_7Eu$ as Eu(NaphC15)$_3$·H_2O: C 71.3%, H 8.7%; Found: C 71.9%, H 8.6%; yield >94%. The existence of a coordinating- and a crystal-water molecule were also found around 220 and 74 °C, respectively, as endothermic peaks in the thermal gravimetric analyses (Fig. S3).

Deposition of LB films

A Milli-Q water purification system (Millipore Co.) was used to purify water for the subphase. Non-fluorescent quartz substrates were pre-coated with Octadecyl-trichlorsilan, 95% (ACROS ORGANICS Co.) to prepare the surface hydrophobicity.

A mixed chloroform solution of a 1:7 molar ratios of NaphC15 and stearic acid (abbreviated to SA) were used to form the monolayers on the water/air interface.

Owing to the Ln containing deposition of the films, above solution of NaphC15 was spread on the water subphase containing $Ln(NO_3)_3\cdot 6H_2O$ (1.0×10^{-5} M; Ln = Eu or Gd) in a Langmuir trough (Filgen, Inc.) at 293 K. The monolayers were transferred on the hydrophobic quartz substrate[16] as a Y-type model (10 layers) at a surface pressure of 30, 35 or 40 mN/m by the vertical depositing method with a transfer rate of 10 mm/min. At the same condition, the single monolayer was deposited on a 0.2 mm-thickness quartz plate for the ATR absorption spectral measurement.

Apparatus

^{1}H-NMR spectra were recorded on a JEOL JMN-500II spectrometer in $CDCl_3$ with tetramethylsilane. ATR FT-IR spectra were measured using a Nicolet iS5 spectrometer (Thermo Scientific). XPS measurements were performed on a KRATOS AXIS ULTRA DLD (Shimadzu) equipped with a monochromatic Al-Kα X-ray source (1253.6 eV); the binding energies were calibrated at the Au 4*f* level (84.0 eV).

Synchrotron XRPD patterns were recorded on a large Debye-Scherrer camera installed at SPring-8 BL02B2 (JASRI/SPring-8) using an imaging plate as a detector.[18a] Powder samples were prepared in capillaries with a 0.3 mm radius and observed an automatically recording system. [18b]

Fast atom bombardment mass spectrometry (FAB-MS) was performed using the MStation JMS-700A (JEOL). Thermal analysis and differential scanning calorimetry were performed with DTA50 and DSC60 (Shimadzu), respectively.

Electronic absorption spectra in the solid state and in solution were obtained using the diffused reflection method with conversion of the *y*-axis by UV-3100 and UV-3600S (Shimadzu), respectively. Polarized electronic absorption spectra using optical waveguide system was used a modified SIS5100 attached with a Glan-Taylor polarizer prism (System Instruments Co.)

Luminescence and excitation spectra were recorded on a Fluorolog 3-22 (Horiba Jobin Yvon). Absolute luminescence quantum yields and luminescence lifetimes were determined using an absolute luminescence quantum yield C9920-02 spectrometer (Hamamatsu Photonics K. K.) and a Quantaurus-Tau C11367-12 spectrometer (Hamamatsu Photonics K. K.), respectively, with pulsed excitation light sources.

Time-dependent (TD) DFT calculation

The singlet ground state of NaphC15 was optimized using DFT with three-parameterized Becke-Lee-Yang-Parr (Restricted B3LYP) hybrid exchange-correlation functional, combined with the 6-31G(d,p) basis set for the non-metal atoms. The optimization was performed using a single crystal X-ray structure of 1-naphthoic acid[19] as a starting geometry. UV-vis spectrum was studied using the TD-DFT method on the basis of optimized ground states with the same functional and basis set.

Estimation of photophysical constants

The total emission quantum yield of EuIII sensitized by the ligand (ϕ_{obs}) was determined by the triplet yield of the ligand (ϕ_{ISC}), the efficiency of energy transfer (η_{EnT}) and the efficiency of the metal centred luminescence (ϕ_{Ln}), as follows.[20]

$$\phi_{obs} = \phi_{\mathrm{ISC}} \times \eta_{\mathrm{EnT}} \times \phi_{\mathrm{Ln}} \qquad (1)$$

Because of the nπ* character of the ligand and the high spin-orbit coupling constants of the lanthanide ion, it can be assumed that ϕ_{ISC} was approximately 1.[21, 22] The value of ϕ_{Ln} can be calculated from the observed emission lifetime (τ_{ff}) and the radiative rate constant (k_{R}) of the lanthanide ion, as shown below.

$$\eta_{\mathrm{Ln}} = k_{\mathrm{R}} \times \tau_{\mathrm{ff}} \qquad (2)$$

The k_{R} value of the emissive excited state, $^5D_0$, is the sum of the spontaneous emission probabilities, $A_{(0,J)}$, to the lower ^7F_J levels in Eu^{III}, and can in turn be calculated from the following equation.

$$k_{\mathrm{R}} = \sum_J A(0,J) = A(0,1) \times \frac{I_{\mathrm{Total}}}{I(0,1)} \times n^3 \qquad (3)$$

Here, $I_{\mathrm{Total}}/I_{(0,1)}$ is the ratio of the total integrated intensity of the corrected Eu^{III} emission spectrum to the intensity of the $^5D_0 \rightarrow {}^7F_1$ band. In this case, we obtained values of 9.0, 10, 8.3, and 8.9 for $I_{\mathrm{Total}}/I_{(0,1)}$ in powder, LB30, LB35, and LB40, respectively. The spontaneous emission probability of the magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition, $A_{(0,1)}$, is virtually independent of the ligand field or the environment of the ions (14.65 s^{-1} *in vacuo*) [23] .

Conclusions

The valuable ligand, NaphC15, was synthesized to induce the LPL of the ff transition on Eu^{3+} ions in LB films. The luminescence of the Eu^{3+} ions incorporated into the films was induced through the excited triplet state of coordinating NaphC15, and was more intense than that in the powder. The conformation and transition dipole moment of the naphthalene skeleton both play a role in inducing LPL of the Eu^{3+} ion through energy transfer. Additionally, our previous report[8, 9b] was not enough luminescence intensity for more evaluation. For instance, the luminescence quantum yield of ff emission was less than 1% of the Eu^{3+} ion in the film. Here, the ligand design was successful to obtain the film and strong luminescence through energy transfer from the ligand to Eu^{3+}. The LB film technique is a historical methodology,[24] but this work suggests new possibilities for optical device or bioactive membrane materials.

Conflicts of interest

There are no conflicts to declare.

Author Contributions

M. Hasegawa, M. Yamanaka, A. Ishii and K. Goto conceived and designed the study. K. Yoshihara performed the syntheses, LB film formation, and most spectral and structural observations. S. Ogata, S. Mizushima, S. Kanno, J. Tsuchiyagaito, K. Kondo, T. Kondo, D. Iwasawa, H. Komiya and A. Saso, S. Kawaguchi contributed to optimizing the experiments at SPring-8. H. Takahashi precisely modified the optical waveguide spectrometer for the LB films and evaluated the spectra.

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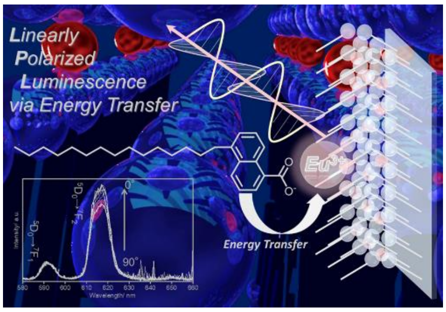
Table of Contents

The complexation in LB films induces the linearly polarized luminescence of europium by the excitation energy transfer of amphiphilic 1-naphthoic acid.



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