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# Brilliant Triboluminescence of a Lanthanide Coordination Polymer with Low-Vibrational-Frequency and Non-Centrosymmetric Structural Networks

**Yasuchika Hasegawa,*[a] Ryo Hieda,[b] Kohei Miyata,[a] Tetsuya Nakagawa,[c] and Tsuyoshi Kawai*[b]**

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Characteristic triboluminescence from a lanthanide coordination polymer with a non-centrosymmetric structure is reported. The lanthanide coordination polymer is composed of luminescent $Eu^{III}$ ions and bidentate phosphane oxides, poly[3,3′-bis(diphenylphosphoryl)-2,2′-bipyridine][tris(hexafluoroacetylacetonate)]europium (poly-Eu-BIPYPO) crystals. The coordination geometry of poly-Eu-BIPYPO is categorized as an asymmetric eight-coordinate square antiprism (8-SAP). The space group of the crystal is also classified as the non-centrosymmetric *Cc*, which is suitable for piezoelectricity and triboluminescence. The photoluminescence quantum yield of poly-Eu-BIPYPO crystals excited at 380 nm is found to be 61 %. Triboluminescence of the lanthanide coordination polymer is observed upon breaking, even at ambient temperature and in daylight. The remarkable triboluminescence phenomenon and geometrical structure of lanthanide coordination polymer are demonstrated.

## Introduction

Coordination compounds serve as building components of various kinds of inorganic and metal–organic self-organized structures. A one-dimensional alternating sequence of metal ions and organic ligands, which forms the backbone of coordination polymers in their crystalline state, has attracted considerable attention in the area of inorganic chemistry, supramolecular chemistry, material chemistry, and polymer science.[1] Coordination polymers with various heavy metal ions, for example copper, zinc, nickel, cadmium, manganese, silver, and europium ions, have been recently reported.[2] In particular, emissive lanthanide coordination polymers and metal–organic frameworks have been studied extensively,[3] since lanthanide complexes exhibit clear and intense luminescence based on 4f orbitals[4] and are expected to be good candidates for use in electroluminescent (EL) devices, lasers, and biosensing applications.[5] The coordination number of lanthanide ions in solution is known to vary from 8 to 12 depending on the nature of the ligand molecules.[4] Specific geometrical and chemical structures with ligand molecules give rise to lanthanide coordination polymers with strong and characteristic luminescence properties.

We focus here on lanthanide coordination polymers with a remarkable luminescence property, triboluminescence. Triboluminescence is the emission of light originating from mechanical stress on bulk solid materials.[6] To date, a number of different types of materials that exhibit triboluminescence, such as organic crystals, polymers, and metal complexes, have been studied.[7,8] While there have been extensive discussions on the origin of triboluminescence, some studies have indicated a contribution of the piezoelectric effect upon breaking non-centrosymmetric bulk crystals.[9,10] Some lanthanide complexes have also been studied for their triboluminescence in the crystalline state. Strongly luminescent lanthanide coordination polymer crystals with non-centrosymmetric structure are expected to show efficient triboluminescence because of the generation of opposite electric charges on opposing faces of cracks perpendicular to their polar axis.[9] Here, we report a brilliant triboluminescence from lanthanide coordination polymer crystals with an ideal non-centrosymmetric structural network, namely poly[3,3′-bis(diphenylphosphoryl)-2,2′-bipyridine][tris(hexafluoroacetylacetonate)]europium (poly-Eu-BIPYPO) (Figure 1). The lanthanide coordination polymer with non-centrosymmetric structure is composed of luminescent $Eu^{III}$ complexes with hexafluoroacetylacetonate (hfa) and bidentate phosphane oxide ligands (BIPYPO). We previously reported that luminescent $Eu^{III}$ complexes with low-vibrational-frequency hfa and phosphane oxide ligands provide relatively high quantum yields of emission from the $^5D_0$ excited state of $Eu^{III}$ ions because of suppressed vi-

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[a] Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University,
Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan
Fax: +81-11-706-7114
E-mail: hasegaway@eng.hokudai.ac.jp
[b] Graduate School of Materials Science, Nara Institute of Science and Technology,
8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan
E-mail: tkawai@ms.naist.jp
[c] Center for Organic Photonics and Electronics Research, Kyushu University,
744 Motooka, Nishi, Fukuoka 819-0895, Japan

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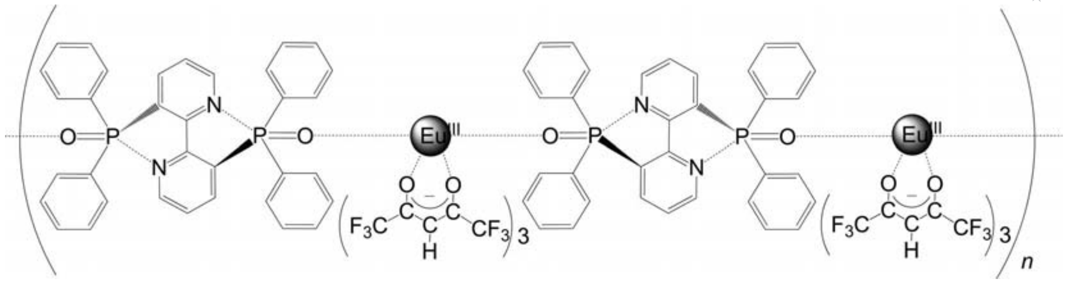

Figure 1. Chemical structure of poly-Eu-BIPYPO.

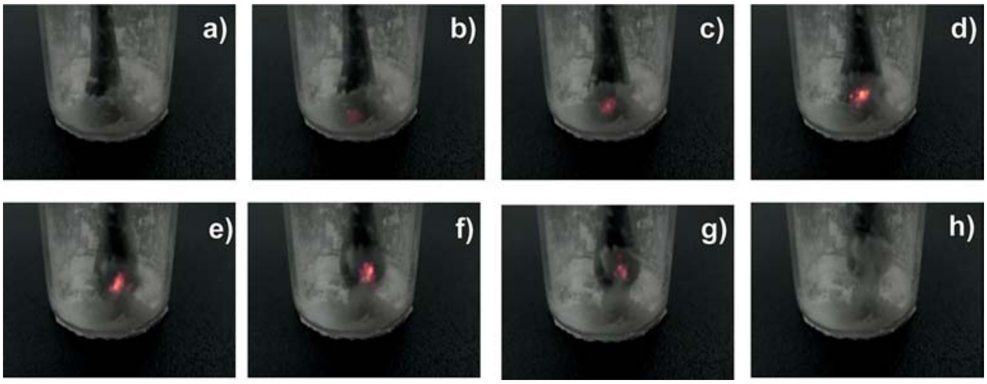

Figure 2. (a–h) Observed sequence-picture images of triboluminescence from poly-Eu-BIPYPO powder upon pushing with a black stick at ambient temperature and in daylight.

brational relaxation[11] and enhanced electric dipole transitions.[12] The present coordination polymer crystals exhibit effective triboluminescence because of their higher mechanical resistivity, in comparison with usual van der Waals crystals, as the previously reported triboluminescent lanthanide complexes.[8f,8k,8l,8n,8p,8r,8s,9] In this paper, we characterize the low-symmetry structure of poly-Eu-BIPYPO crystals, which are suitable for piezoelectricity, by single-crystal X-ray diffraction analysis. Triboluminescence and photophysical properties are characterized by the emission spectra, photoluminescence quantum yields, and diffuse-reflectance absorption spectra of the crystals. The photoluminescence quantum yield of the poly-Eu-BIPYPO crystals excited at 380 nm is as high as 61 %. This value is the highest value among those reported for the triboluminescent Eu$^{III}$ crystals. The novel lanthanide coordination polymer, with a specific coordination structure of low-vibrational-frequency and poly-Eu-BIPYPO coordination networks, exhibits intense triboluminescence upon breaking, which is clearly observed even at ambient temperature in daylight (Figure 2).

## Results and Discussion

### Characteristic Structure of the Lanthanide Coordination Polymer

The lanthanide coordination polymer crystal, poly-Eu-BIPYPO, was synthesized by the reaction of tris(hexafluoroacetylacetonato)europium dihydrate [Eu(hfa)$_3$(H$_2$O)$_2$] with 3,3′-bis(diphenylphosphoryl)-2,2′-bipyridine (BIPYPO) in methanol under reflux. Recrystallization from acetone/water gave colorless single crystals of poly-Eu-BIPYPO suitable for single-crystal X-ray diffraction analysis. The ORTEP view and crystal data are presented in Figure 3 and Table 1, respectively. The ORTEP view of poly-Eu-BIPYPO shows an eight-coordination structure with three hfa ligands and one bridging phosphane oxide ligand. The co-

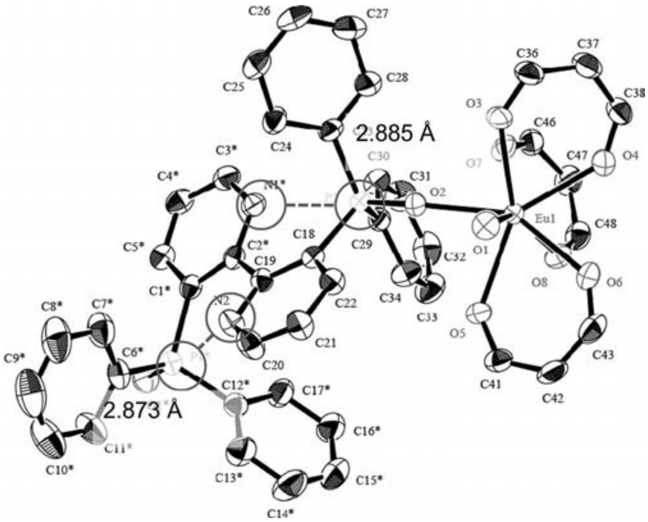

Figure 3. ORTEP view of poly-Eu-BIPYPO crystal.

Table 1. Crystal data of poly-Eu-BIPYPO.

| | Poly-Eu-BIPYPO |
|---|---|
| Chemical formula | $C_{49}H_{29}N_2O_8P_2F_{18}Eu$ |
| Formula weight | 1329.66 |
| Crystal color, habit | colorless, block |
| Crystal system | monoclinic |
| Lattice type | C-centered |
| Space group | *Cc* (#9) |
| $a$ /Å | 18.7253(4) |
| $b$ /Å | 17.9548(4) |
| $c$ /Å | 16.2296(3) |
| $\alpha$ /° | 90 |
| $\beta$ /° | 96.6903(7) |
| $\gamma$ /° | 90 |
| $V$ /Å$^3$ | 5419.4(2) |
| $Z$ | 4 |
| $D_{\text{calcd.}}$ /g cm$^{-3}$ | 1.630 |
| $T$ /°C | 193.1 |
| $m$ (Mo-$K_\alpha$) /cm$^{-1}$ | 13.279 |
| No. of measured reflections | 21537 |
| No. of unique reflections | 8927 |
| $R$ [$I > 2\sigma(\text{I})$][a] | 0.0194 |
| $R_w$ [$I > 2\sigma(\text{I})$][b] | 0.0515 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]\}^{1/2}$.

ordination geometry of poly-Eu-BIPYPO is categorized as eight-coordinate square antiprism (8-SAP). The 8-SAP structure without inversion center leads to a reduction in the geometrical symmetry.[13] The geometrical symmetry of lanthanide complexes is regarded as a significant factor that influences the transition probabilities. Lanthanide complexes with low-symmetry coordination structures exhibit enhancement of the probability of the electric dipole transition related to the emission quantum yield.[12a] The characteristic 8-SAP structure of this Eu$^{III}$ coordination polymer is expected to lead to increased emission quantum yields, because of the enhanced probability of the $^5D_0$–$^7F_2$ electric dipole transition. The distance between Eu ions is found to be 11.87 Å, which might be longer than the critical distance for nonradiative dipole–dipole energy transfer between Eu$^{III}$ ions.[11c]

The distances between the nitrogen and the phosphorus atoms in BIPYPO (2.88 and 2.87 Å) are shorter than the sum of van der Waals radii (< 3.40 Å) and are similar to those reported for organic compounds with specific nitrogen–phosphorus interactions (2.89 Å).[14] The nitrogen–phosphorus interaction provides a stable liner-type structure for the lanthanide coordination polymer poly-Eu-BIPYPO. Two distinguishable structures of the BIPYPO ligand, assigned as BIPYPO A (*S*-form) and B (*R*-form), were observed in a poly-Eu-BIPYPO crystal, as illustrated in Figure 4a. These independent BIPYPO A and B forms generate a non-centrosymmetric and chiral structure in poly-Eu-BIPYPO. As illustrated in Figure 4b, an 1D polymer chain was observed in a columnar structure of the crystal. In this polymer chain structure, the Eu$^{III}$ ions are bridged by the BIPYPO A and B ligands alternatively. Because of the distorted structure of the polymer chain, the packing structure is non-centrosymmetric *Cc*, as shown in Table 1. This space group is suitable for piezoelectricity and triboluminescence.[6] The intense triboluminescence seems to originate from the non-centrosymmetric structure along with the polymer-like structure.

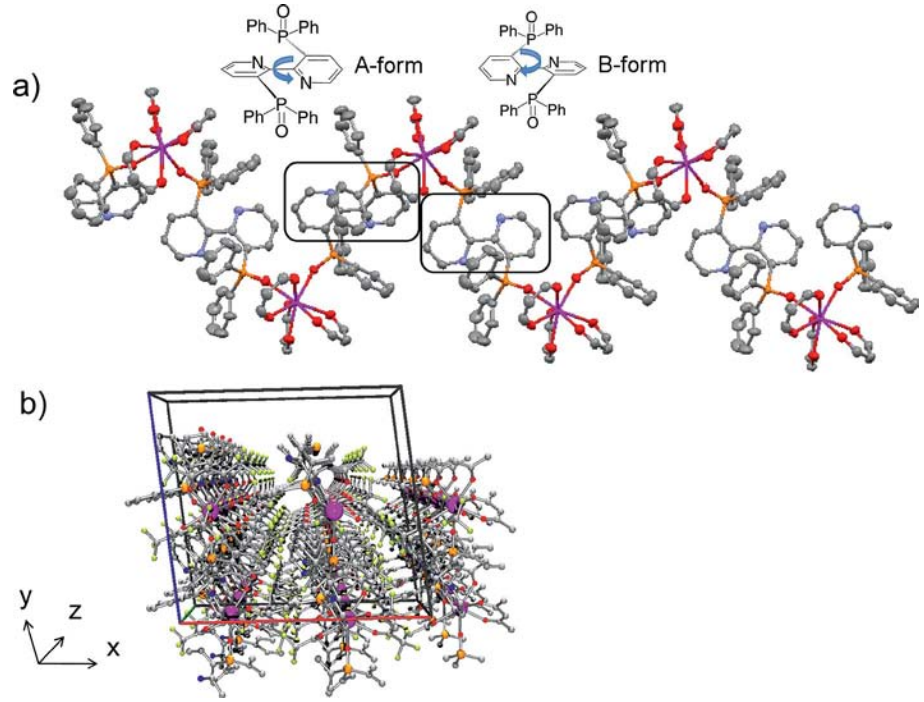

Figure 4. (a) A- and B-type structures of BIPYPO molecules in poly-Eu-BIPYPO crystals. (b) Packing structure of poly-Eu-BIPYPO crystals.

## Triboluminescence and Photoluminescence of the Lanthanide Coordination Polymer

Triboluminescence and photoluminescence spectra of poly-Eu-BIPYPO crystals were measured at room temperature. The triboluminescence spectrum is shown in Figure 5a. The intense red emission observed upon rubbing the white-yellow powder crystals indicated emission bands at 579, 592, 615, 650 and 700 nm (Figure 5a). These bands are characteristic of 4f–4f transitions, $^5D_0$–$^7F_J$ ($J$ = 0, 1, 2, 3, 4, respectively), of Eu$^{III}$ ions. The energy gap between the first and second lines in the $^5D_0$–$^7F_2$ band of the triboluminescence was estimated to be 101 cm$^{-1}$, as shown in the inset of Figure 5a. These spectral features of the triboluminescence are almost the same as those observed in a photoluminescence spectrum of the crystal under excitation with UV light at 380 nm (excitation of π–π* transition of hfa ligands). The spectral profile of the emission and the specific energy gap are directly related to Stark splitting based on the geometry of the coordination structure.[12] Interestingly, these photoluminescence and triboluminescence spectra were considerably different from the emission spectrum of Eu-BIPYPO in a methanol solution (Figure 5b). Hence, the geometrical symmetry of the complex in the solution phase seems to be different, to some extent, from that of the crystals with the coordination polymer structure. The emission spectrum of Eu-BIPYPO in a [D$_6$]acetone solution is much more similar to that of Eu(hfa)$_3$(BIPHEPO) in [D$_6$]acetone solution. Single-crystal X-ray diffraction analysis of Eu(hfa)$_3$(BIPHEPO) has already been reported.[12b] The emission spectral shape of Eu(hfa)$_3$(BIPHEPO) in [D$_6$]acetone solution is the same as that in the solid state. We consider that the solution structure of Eu-BIPYPO is much more similar to the geometrical structure from the single-crystal X-ray analysis of Eu(hfa)$_3$(BIPHEPO). Single units of [Eu(hfa)$_2$(BIPYPO)]$^-$ are also observed in solution by using ESI-MS. In the solution phase, the Eu$^{III}$ ions are expected to exist in "monomer" complexes that should have a bidentate BIPYPO ligand such as a bidentate BIPHEPO ligand.[15] The monomeric Eu-BIPYPO complex seems to exhibit ring-opening polymerization upon crystal growth, which forms the coordination polymer structure.

The photoluminescence quantum yield of the poly-Eu-BIPYPO crystal excited at 380 nm was as high as 61 %. This value is the highest value among those reported for triboluminescent Eu$^{III}$ crystals measured by high-resolution optical systems with monochromator and photomultiplier. The lifetimes of Eu-BIPYPO in the solid state and in [D$_6$]acetone were found to be 0.82 and 1.16 ms, respectively. The intrinsic emission quantum yield of Eu-BIPYPO in [D$_6$]acetone excited at 465 nm (absorption band of Eu$^{III}$) was estimated to be 71 %. From these results, the high photoluminescence quantum yield might be due to: (1) a suppressed vibrational relaxation promoted by the low-vibrational-frequency hfa and phosphane oxide ligands,[16] (2) an enhanced radiative transition probability as a result of the asymmetric 8-SAP coordination structure,[17] and/or (3) an efficient photosensitized energy transfer from the hfa ligands to the Eu$^{III}$ ions.

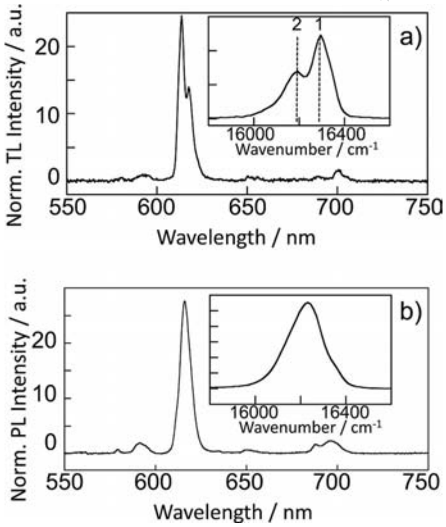

Figure 5. (a) Triboluminescence spectrum of poly-Eu-BIPYPO crystals and (b) photoluminescence spectrum of poly-Eu-BIPYPO in methanol excited at 380 nm (2.7 × 10$^{-5}$ M).

A diffuse-reflectance absorption spectrum of poly-Eu-BIPYPO crystals is shown in Figure 6a. The absorption band at 330 nm is attributed to a π–π* transition of the hfa ligands, which was observed in methanol at around 300 nm. The small band at 465 nm is assigned to the $^5D_2$–$^7F_0$ transition in the Eu$^{III}$ ion. We also found a specific absorption band of the poly-Eu-BIPYPO crystals at 390 nm, which could be assigned to the interligand charge transfer (ILCT) via charge redistribution of the hfa ligands.[15] In methanol solution, the characteristic absorption band at around 390 nm of the Eu$^{III}$ complex composed of Eu(hfa)$_3$ and BIPYPO is not observed (Figure 6b). Recently, Bünzli et al. have reported the effective photosensitized luminescence of a lanthanide complex through the ILCT band.[16] We consider that the relatively large emission quantum yield of the poly-Eu-BIPYPO crystals under excitation with UV light

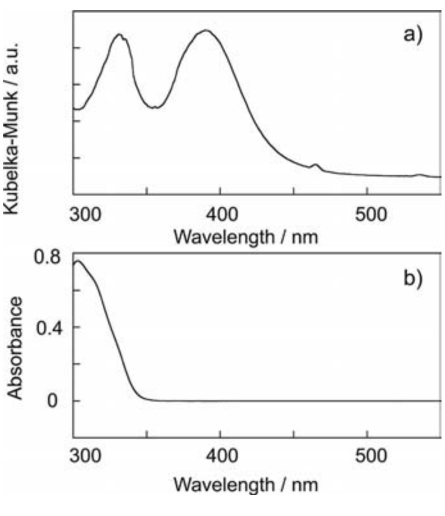

Figure 6. (a) Diffuse-reflectance absorption spectrum of poly-Eu-BIPYPO crystals and (b) absorption spectrum poly-Eu-BIPYPO in methanol (2.7 × 10$^{-5}$ M).

might be due not only to the suppressed vibrational relaxation and the enhancement of the radiative transition probability, but also to the effective photosensitized luminescence through the ILCT band.

## Conclusions

In summary, brilliant triboluminescence of a novel lanthanide coordination polymer with non-centrosymmetric structural networks, poly-Eu-BIPYPO, was successfully observed upon breaking even at ambient temperature and in daylight. The coordination structure and space group of lanthanide coordination polymer crystals are categorized as eight-coordinate square antiprism (8-SAP) and non-centrosymmetric *Cc*, respectively. The characteristic structure is suitable for enhancement of emission quantum yield and for the piezoelectric effect observed upon breaking the non-centrosymmetric bulk crystals. The low-vibrational-frequency structure of poly-Eu-BIPYPO also leads to suppression of radiationless transition through vibrational relaxation, resulting in effective triboluminescence. The overall triboluminescence efficiency of is the product of the efficiency of excited-state formation and the efficiency of radiative relaxation from this excited-state.[18] Recently, Eliseeva and co-workers have reported on triboluminescent Eu$^{III}$ coordination with low-vibrational-frequency hexafluoroacetylacetonato (hfa) ligands.[19] We herein propose a molecular-level strategy and an ideal model for effective triboluminescent materials. Luminescent coordination polymers composed of strongly luminescent Eu$^{III}$ units are expected to provide a remarkable basis for novel photofunctional materials.

## Experimental Section

**Apparatus:** $^1$H NMR spectra were obtained with a JEOL AL-300 spectrometer. Infrared spectra were recorded with a JASCO FT/IR-4200 spectrometer. Elemental analyses were carried out with a Perkin–Elmer 2400 II instrument. Electrospray ionization mass spectrometry (ESI-MS) was performed with a JEOL JMS-700 mass spectrometer.

**Materials:** Europium(III) acetate tetrahydrate (99.9%) and [D$_6$]acetone (99.9%) were obtained from Wako Pure Chemical Industries, Ltd. 1,1,1,5,5,5-hexafluoropentane-2,4-dione (hfa) was purchased from Aldrich Chemical Co., Inc. All other organic compounds were reagent grade and used as received.

**2,2′-Bipyridine-3,3′-diol:** 2,2′-Bipyridine-3,3′-diol was prepared by the same method as previously reported.[20] NiCl$_2$ (3.9 g, 30 mmol), zinc powder (5.9 g, 90 mmol), and Ph$_3$P (32 g, 120 mmol) were dissolved in anhydrous DMF (150 mL), and the mixture was heated to 50 °C. After 1 h, 2-bromopyridine-3-ol (5.2 g, 90 mmol) in anhydrous DMF (100 mL) was added, and the mixture was kept for another 20 h at 50 °C. The warm mixture was poured into aqueous NaOH (10 N, 100 mL) and vigorously stirred for 30 min. The precipitated Ph$_3$P was filtered and poured into aqueous NaOH (10 N, 50 mL) again. The reaction product was precipitated by the addition of conc. HCl to the combined NaOH solution (pH = 4), and the mixture was stirred for 30 min. The solid was immediately filtered, washed with distilled water, and dried in a desiccator. The residue was purified by column chromatography on silica gel to afford the 2,2′-bipyridine-3,3′-diol (0.70 g, 25%) as a yellow solid. $R_f$ = 0.7 (chloroform). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.06 (d, 2 H), 7.43 (d, 2 H), 7.30 (dd, 2 H) ppm. EI-MS: *m*/*z* = 188.0586 [M]$^+$.

**2,2′-Bipyridine-3,3′-diyl Bis(trifluoromethanesulfonate):** 2,2′-bipyridine-3,3′-diol (0.57 g, 3.0 mmol) was dissolved in anhydrous dichloromethane (25 mL) under nitrogen at room temperature followed by the addition of pyridine (1.6 mL, 18 mmol). Trifluoromethanesulfonic anhydride (1.5 mL, 9.0 mmol) was then added dropwise. The color of the solution changed from yellow to red, and white fume evolved. The reaction mixture was allowed to stir at room temperature for 17 h. Water was added into the solution, and then the reaction mixture was extracted with dichloromethane. The combined organic phase was washed with water and brine, and dried with MgSO$_4$. The residue was purified by column chromatography on silica gel to afford the 2,2′-bipyridine-3,3′-diyl bis(trifluoromethanesulfonate) (1.3 g, 94%) as a white solid. $R_f$ = 0.4 (hexane/ethyl acetate = 3:1). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.79 (d, 2 H), 7.82 (d, 2 H), 7.58 (dd, 2 H) ppm. EI-MS: *m*/*z* = 451.9570 [M]$^+$. FTIR (ATR): $\tilde{\nu}$ = 1587 (pyridine C=C, C=N), 1424 (pyridine C=C, C=N), 1270–1170 (br., S=O), 1260–1070 (br., C–F) cm$^{-1}$.

**3,3′-Bis(diphenylphosphoryl)-2,2′-bipyridine (BIPYPO):** Diphenylphosphane (1.8 mL, 10 mmol) was added to a stirred solution of 2,2′-bipyridine-3,3′-diyl bis(trifluoromethanesulfonate) (1.5 g, 3.4 mmol), triethylamine (1.2 mL), and palladium acetate (0.31 g, 1.4 mmol) in dry DMF (20 mL), to instantly give a red coloration. The solution was heated at 90 °C under nitrogen for 24 h. Water was added into the solution, and then the reaction mixture was extracted with dichloromethane. The combined organic phase was washed with water and brine, and dried with MgSO$_4$. The residue was dissolved in dichloromethane. The solution was cooled to 0 °C, and hydrogen peroxide (30%, 7.0 mL) was then added. The mixture was stirred for 12 h. The reaction mixture was extracted with dichloromethane. The combined organic phase was washed with water and brine, and dried with MgSO$_4$. The residue was purified by column chromatography on silica gel to afford the 3,3′-bis(diphenylphosphoryl)-2,2′-bipyridine (0.71 g, 38%) as a yellow solid. $R_f$ = 0.1 (THF). $^1$H NMR (300 MHz, CDCl$_3$, 25 °C): $\delta$ = 8.26 (t, 2 H), 7.75–7.68 (m, 10 H), 7.46–7.37 (m, 12 H), 7.11 (dd, 2 H) ppm. EI-MS: *m*/*z* = 556.1470 [M]$^+$. FTIR (ATR): $\tilde{\nu}$ = 1647, 1580–1540 (pyridine, C=C, C=N), 1460–1360 (pyridine, C=C, C=N), 1210–1160 (br., P=O), 1140–1000 cm$^{-1}$.

**Tris(hexafluoroacetylacetonato)europium Dihydrate [Eu(hfa)$_3$(H$_2$O)$_2$]:** Europium acetate monohydrate (5.0 g, 13 mmol) was dissolved in distilled water (20 mL) in a 100 mL flask. A solution of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (7.0 g, 34 mmol) was added dropwise to the solution. The reaction mixture produced a precipitation of white yellow powder after stirring for 3 h at room temperature. The reaction mixture was filtered, and the resulting powder was recrystallized from methanol/water to afford colorless needle crystals of the title compound. Yield: 9.6 g (95%). IR (KBr): $\tilde{\nu}$ = 1650 (st, C=O), 1145–1258 (st, C–F) cm$^{-1}$. $C_{15}H_7EuF_{18}O_8$ (809.91): calcd. C 22.48, H 0.88; found C 22.12, H 1.01.

**Poly-Eu-BIPYPO Crystals:** [Eu(hfa)$_3$(H$_2$O)$_2$] (0.49 g, 0.60 mmol) and BIPYPO (0.28 g, 0.50 mmol) were dissolved in methanol (100 mL). The solution was heated at reflux and stirred for 12 h, and then concentrated. The residue was washed with chloroform and diethyl ether several times to afford poly-Eu-BIPYPO (0.43 g, 62%) as a white solid. Recrystallization from acetone/water gave a colorless crystal of the title compound. $^1$H NMR (300 MHz,

$CDCl_3$, 25 °C): $\delta$ = 8.77 (br., 4 H), 8.37 (br., 2 H), 8.13 (dd, 2 H), 7.80 (br., 6 H), 7.50 (br., 4 H), 6.76 (br., 4 H), 5.79 (br., 4 H) ppm. ESI-MS: *m*/*z* = 1123.0358 [M – (hfa)]$^+$. FTIR (ATR): $\tilde{\nu}$ = 1680–1630 (s, C=O), 1580–1430 (pyridine, C=C, C=N), 1210–1180 (P=O), 1170–1040 (br., C–F) $cm^{-1}$. $C_{49}H_{29}EuF_{18}N_2O_8P_2$ (1329.65): calcd. C 44.26, H 2.20, N 2.11; found C 44.13, H 1.85, N 2.11.

**Optical Measurements:** Triboluminescence was observed from poly-Eu-BIPYPO powder upon pushing with a black stick in the dark. Triboluminescence and photoluminescence spectra of poly-Eu-BIPYPO crystals were measured at room temperature with a HAMAMATSU Photonics multichannel Analyzer PMA-11 corrected for the response of the detector system. Absorption and diffuse-reflectance absorption spectra were recorded by using a JASCO spectrophotometer V-600 with an integrating sphere unit ISV-723. The photoluminescence quantum yield of poly-Eu-BIPYPO crystals excited at 380 nm was estimated by using a JASCO FP-6500DS spectrofluorometer equipped with a JASCO ILF-533 integrating sphere unit ($\phi$ = 100 mm). Quantum yield, $\Phi$, was estimated by using the following equation.

$$\Phi = \frac{N_{emission}}{N_{absorption}} = \frac{\int \frac{\lambda}{hc} I_{em}(\lambda) d\lambda}{\int \frac{\lambda}{hc} \left\{ I_{ex}(\lambda_{ref}) - I_{ex}(\lambda_{sam}) \right\} d\lambda}$$

The corrected profiles of light absorption from the above-mentioned equation [$I_{ex}(\lambda_{ref})$: without sample (white $BaSO_4$ powder) and $I_{ex}(\lambda_{sam})$: with sample (crystal powder of poly-Eu-BIPYPO)] were determined from the excitation spectra of the system (450–480 nm), whereas the corrected intensity profile of the emission, $I_{em}(\lambda)$, was determined from the emission spectra (550–750 nm).

**Crystallography:** All measurements were made with a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-$K_\alpha$ radiation. The data were collected at a temperature range of 193.1 ± 1 °C to a maximum $2\theta$ value of 48.8°. Corrections for decay and Lorentz polarization effects were made with empirical absorption correction, solved by direct methods and expanded by using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. All calculations were performed by using the crystal structure crystallographic software package SHELXS-97.[21]

CCDC-833471 contains 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.

**Supporting Information** (see footnote on the first page of this article): Movie illustrating the triboluminescence of the lanthanide complex.

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