Mechanistic Investigation of Inducing Triboluminescence in Lanthanide(III) β–Diketonate Complexes

Ho-Yin Wong, Wai-Sum Lo, Wesley Ting Kwok Chan, and Ga-Lai Law*

Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hung Hom, Hong Kong

ABSTRACT: In this work, we synthesized a series of lanthanide(III) β-diketonate complexes to investigate the induction of triboluminescence. Triboluminescence (TL) spectra, solid-state emission spectra, and luminescence lifetimes of the complexes were obtained to prove consistent emitting species for steady-state and triboluminescence measurements. Detailed analyses of the crystal lattice packing were conducted in an attempt to correlate crystal symmetry, gas discharge, and structural arrangements with "triboexcitation", and it is found that either noncentrosymmetric or centrosymmetic compounds can be TL-active. Furthermore, an intensely TL compound, $Eu(dbm)_4TMP$, was achieved, and its light emission can be seen under daylight upon mechanical stress.
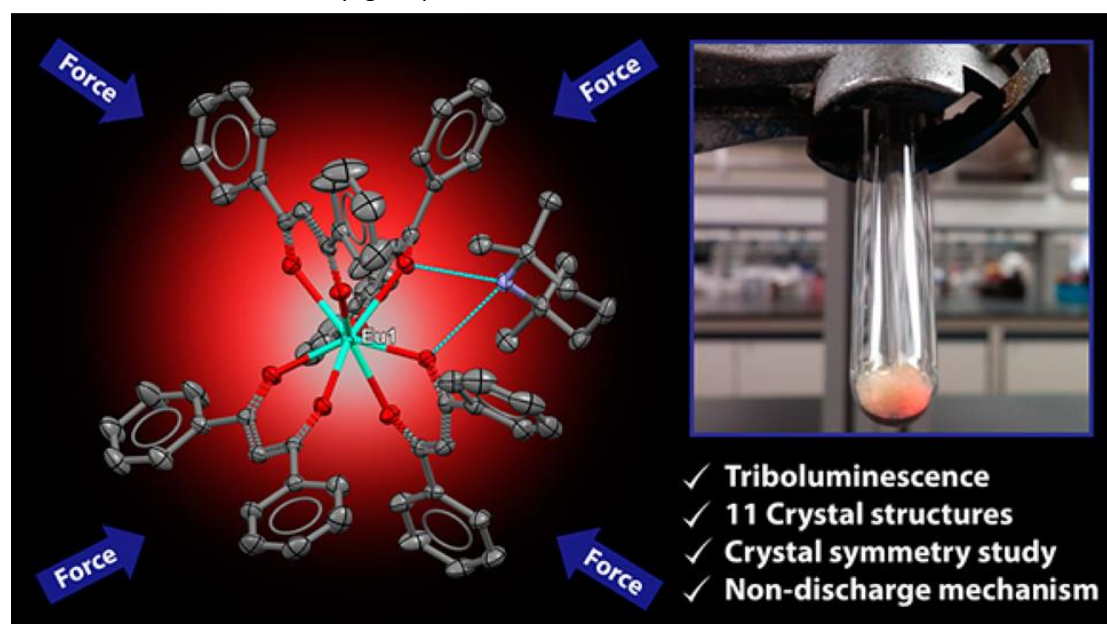
INTRODUCTION

Triboluminescence (TL) is a form of light emission caused by mechanical force applied to crystalline solids.[1] Although commonly observed, for example, blue emission resulting from the fracture of sugar crystals,[2] this phenomenon has been investigated less well than other forms of luminescence have been because of the hardware limitations, including spectro- photometers and X-ray diffractometers decades ago.[3] It was demonstrated that TL compounds have great potential in stress sensing applications.[4] However, little is known about the mechanism of TL because of the complication during crystal fracture that might lead to heat generation, charge separation, static electrification, radical formation, etc.[5] The currently accepted explanation for "triboexcitation" generally arises from the electric field resulting from charge separation caused by the fracture of noncentrosymmetric materials.[6] The surrounding nitrogen gas molecules are then ionized, and discharge ensued, giving rise to the second positive band of N_2 with the $C^3\Pi_u \rightarrow B^3\Pi_g$ transition, which may excite emissive compounds and lead to photoluminescence (PL). Pioneering groups like those of Chandra and Zink attempted to construct a structure– activity relationship and thus correlated noncentrosymmetric crystals with TL,[7] but numerous exceptions can be found.[8] In light of this problem, it is necessary to document more examples of either TL-active or -inactive crystals to correlate any relationship.

In this work, crystal structures, PL, and TL of a series of lanthanide(III) β-diketonate complexes were studied. We decided to utilize lanthanide complexes as the basis of our study not only because of their well-known triboluminescence properties[9] but also because of their large antenna-generated shifts[10] to eliminate the complications of self-absorption and interference between the UV–violet emissions of nitrogen gas and organic chromophores. Although quite a number of TL- active lanthanide compounds have been reported,[11] we hope to achieve a systematic study of TL-active compounds and crystal structures by using neutral and ionic Eu^{III} complexes and obtain a compound with intense TL. Our ionic complexes are formed by a tetrakis(β-diketonate) and an ammonium counterion, while neutral complexes are tris(β-diketonates) complemented with a neutral ligand, either 1,10-phenanthroline or 2,2′- bipyridine (Figure 1).
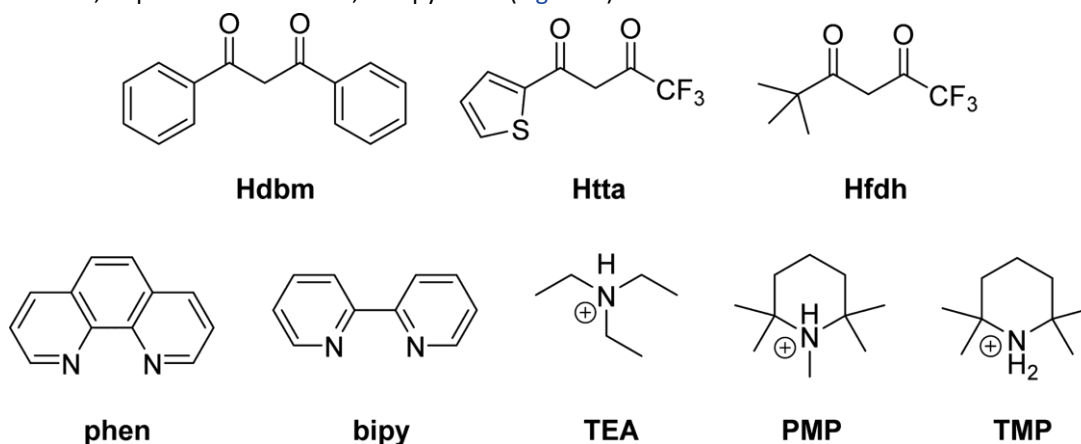

Figure 1. Compounds studied herein.

▍ EXPERIMENTAL SECTION

General Considerations.

All chemicals used for synthesis were obtained from Sigma-Aldrich and used without further purification. The elemental analysis was performed using an Elementar Vario MicroCube elemental analyzer. The HR-ESI mass spectra were recorded with an Orbitrap Fusion Lumos Tribrid mass spectrometer.

Synthesis of Tris(β-diketonate) Complexes.

The general procedure is demonstrated for Eu(dbm)₃phen. Solvents used for recrystallization are stated for each compounds

Eu(dbm)₃phen.

To the mixture of dibenzoylmethane (0.67 g, 3 mmol) and 1,10-phenanthroline (0.18 g, 1 mmol) in 5 mL of ethanol at 80 °C was added 1 M sodium hydroxide (3 mL), followed by the dropwise addition of 1 mL of an aqueous solution of europium chloride hexahydrate (0.37 g, 1 mmol). Precipitate was formed immediately, and the mixture was heated for 12 h. The solid was suction-filtered and washed with water several times. Single crystals were obtained by recrystallization with acetonitrile. Yield: 64%. Elemental analysis (%) calcd for $C_{57}H_{41}EuN_2O_6$: C, 68.33; H, 4.12; N, 2.80. Found: C, 68.53; H, 4.13; N, 2.81. HRMS (m/z) calcd for $C_{42}H_{30}EuN_2O_4$ [M − dbm]⁺: 779.1418, found 779.1401.

Gd(dbm)₃phen.

Recrystallization with acetonitrile. Yield: 66%. Elemental analysis (%) calcd for $C_{57}H_{41}N_2O_6Gd$: C, 67.97; H, 4.10; N, 2.78. Found: C, 68.10; H, 3.93; N, 2.71.

Eu(dbm)₃bipy.

Recrystallization with acetonitrile. Yield: 70%. Elemental analysis (%) calcd for $C_{55}H_{41}EuN_2O_6$: C, 67.55; H, 4.23; N, 2.86. Found: C, 67.68; H, 4.07; N, 2.75. HRMS (m/z) calcd for $C_{40}H_{30}EuN_2O_4$ [M − dbm]⁺: 755.1418, found 755.1403.

Gd(dbm)₃bipy.

Recrystallization with acetonitrile. Yield: 64%. Elemental analysis (%) calcd for $C_{55}H_{41}N_2O_6Gd$: C, 67.19; H, 4.20; N, 2.85. Found: C, 67.39; H, 4.14; N, 2.79.

Eu(tta)₃phen.

Recrystallization with acetone. Yield: 53%. Elemental analysis (%) calcd for $C_{36}H_{20}EuF_9N_2O_6S_3$: C, 43.43; H, 2.02; N, 2.81. Found: C, 42.88; H, 2.13; N, 2.70. HRMS (m/z) calcd for $C_{28}H_{16}EuF_6N_2O_4S_2$ [M − tta]⁺: 774.9668, found 774.9650.

Gd(tta)₃phen.

Recrystallization with acetone. Yield: 52%. Elemental analysis (%) calcd for $C_{36}H_{20}F_9N_2O_6S_3Gd$: C, 43.20; H, 2.01; N, 2.80. Found: C, 43.78; H, 2.06; N, 2.67. HRMS (m/z) calcd for $C_{28}H_{16}F_6N_2O_4S_2Gd$ [M − tta]⁺: 776.9697, found 776.9702.

Eu(tta)₃bipy.

Recrystallization with acetonitrile. Yield: 42%. Elemental analysis (%) calcd for $C_{34}H_{20}EuF_9N_2O_6S_3$: C, 42.03; H, 2.07; N, 2.88. Found: C, 42.05; H, 2.11; N, 2.77. HRMS (m/z) calcdfor $C_{26}H_{16}EuF_6N_2O_4S_2$ [M − tta]⁺: 750.9668, found 750.9653.

Gd(tta)₃bipy.

Recrystallization with acetonitrile. Yield: 40%. Elemental analysis (%) calcd for $C_{34}H_{20}F_9N_2O_6S_3Gd$: C, 41.80; H, 2.06; N, 2.87. Found: C, 41.83; H, 2.04; N, 2.81. HRMS (m/z) calcdfor $C_{26}H_{16}F_6N_2O_4S_2Gd$ [M − tta]⁺: 755.9697, found 755.9700.

Eu(fdh)₃phen.

Recrystallization with acetonitrile. Yield: 27%. Elemental analysis (%) calcd for $C_{36}H_{38}EuF_9N_2O_6$: C, 47.12; H, 4.17; N, 3.05. Found: C, 47.19; H, 4.02; N, 3.01. HRMS (m/z) calcdfor $C_{28}H_{28}EuF_6N_2O_4$ [M − fdh]⁺: 723.1166, found 723.1153.

Sm(fdh)₃phen.

Recrystallization with acetonitrile. Yield: 31%. Elemental analysis (%) calcd for $C_{36}H_{38}F_9N_2O_6Sm$: C, 47.20; H, 4.18; N, 3.06. Found: C, 47.18; H, 4.15; N, 2.98. HRMS (m/z) calcdfor $C_{28}H_{28}F_6N_2O_4Sm$ [M − fdh]⁺: 722.1151, found 722.1138.

Tb(fdh)₃phen.

Recrystallization with acetonitrile. Yield: 28%. Elemental analysis (%) calcd for $C_{36}H_{38}F_9N_2O_6Tb$: C, 46.76; H, 4.14; N, 3.03. Found: C, 45.58; H, 3.98; N, 2.92. HRMS (m/z) calcdfor $C_{28}H_{28}F_6N_2O_4Tb$ [M − fdh]⁺: 729.1207, found 729.1287.

Gd(fdh)₃phen.

Recrystallization with acetonitrile. Yield: 30%. Elemental analysis (%) calcd for $C_{36}H_{38}F_9N_2O_6Gd$: C, 46.85; H, 4.15; N, 3.04. Found: C, 46.89; H, 4.10; N, 2.89. HRMS (m/z) calcdfor $C_{28}H_{28}F_6N_2O_4Gd$ [M − fdh]⁺: 728.1194, found 728.1202.

Eu(fdh)₃bipy.

Recrystallization with acetonitrile. Yield: 26%. Elemental analysis (%) calcd for $C_{34}H_{38}EuF_9N_2O_6$: C, 45.70; H, 4.29; N, 3.13. Found: C, 45.76; H, 4.40; N, 3.09. HRMS (m/z) calcd for $C_{26}H_{28}EuF_6N_2O_4$ [M − fdh]⁺: 699.1166, found 699.1153.

Gd(fdh)₃bipy.

Recrystallization with acetonitrile. Yield: 31%. Elemental analysis (%) calcd for $C_{34}H_{38}F_9N_2O_6Gd$: C, 45.43; H, 4.26; N, 3.12. Found: C, 45.44; H, 4.16; N, 2.97. HRMS (m/z) calcd for $C_{26}H_{28}F_6N_2O_4Gd$ [M − fdh]⁺: 704.1194, found 704.1198.

Synthesis of Tetrakis(β-diketonate) Complexes.

The procedures for the [Eu(dbm)₄]⁻ and [Eu(tta)₄]⁻ series are different.

Eu(dbm)₄TEA.

The mixture of dibenzoylmethane (0.90 g, 4 mmol) and triethylammine (0.40 g, 4 mmol) in 30 mL of ethanol was heated at 80 °C for 20 min, followed by slow dropwise addition of europium(III) nitrate hydrate (1 mmol). The mixture was cooled slowly at room temperature overnight. Crystals can be formed by placing the mixture undisturbed overnight. A single crystal can be obtained by recrystallization with ethanol. Yield: 60%. Elemental analysis (%) calcd for $C_{66}H_{60}EuNO_8H_2O$: C, 68.03; H, 5.36; N, 1.20. Found: C, 67.56; H, 5.06; N, 1.55. HRMS (m/z) calcd for $C_{60}H_{44}EuO_8$ [M − TEA]⁻: 1045.2249, found 1045.2309.

Eu(dbm)₄PMP.

Recrystallization with ethanol. Yield: 44%. Ele- mental analysis (%) calcd for $C_{70}H_{66}EuNO_8$: C, 69.99; H, 5.54; N, 1.17. Found: C, 69.44; H, 5.61; N, 1.10. HRMS (m/z) calcd for $C_{60}H_{44}EuO_8$ [M − PMP]⁻: 1045.2249, found 1045.2309.

Eu(dbm)₄TMP.

Recrystallization with ethanol. Yield: 34%. Ele- mental analysis (%) calcd for $C_{69}H_{64}EuNO_8$: C, 69.81; H, 5.43; N, 1.18. Found: C, 69.93; H, 5.65; N, 1.12. HRMS (m/z) calcd for $C_{60}H_{44}EuO_8$ [M − TMP]⁻: 1045.2249, found 1045.2268.

Eu(tta)₄PMP.

To 5 mL ethanol solution of 2-thenoyltrifluoroace- tone (0.44 g, 2 mmol) and 1,2,2,6,6-pentamethylpiperidine (0.31 g, 2 mmol) was added a 2.5 mL aqueous solution of europium(III) nitrate hydrate (0.5 mmol), and 20 mL of water was added to solidify the sticky precipitate. The solid was suction-filtered, washed with water, and recrystallized with ethanol. Yield: 23%. Elemental analysis (%) calcd for $C_{41}H_{36}EuF_{12}NO_8S_4H_2O$: C, 41.66; H, 3.23; N, 1.16. Found:C, 41.67; H, 3.30; N, 1.12. HRMS (*m/z*) calcd for $C_{32}H_{16}EuF_{12}O_8S_4[M - PMP]^-$: 1036.8749, found 1036.8796.

Eu(tta)₄TMP.

Recrystallization with ethanol. Yield: 18%. Elementalanalysis (%) $C_{41}H_{36}EuF_{12}NO_8S_4H_2O$: C, 41.14; H, 3.20; N, 1.17. Found: C, 40.65; H, 3.26; H, 1.10. HRMS (*m/z*) calcd for $C_{32}H_{16}EuF_{12}O_8S_4$ [M − TMP]⁻: 1036.8749, found 1036.8781.

Crystallographic Data.

A suitable crystal was picked and mounted using the "oil-drop mounting" technique,[12] and its data were collected using either the Bruker Smart Apex II or Bruker D8- Venture single-crystal diffractometer. Multiscan absorption correction was then applied to the data using the Bruker SAINT/SADABS software.[13,14] The SHELX program suite[15] was used to calculate the initial structural solution through either the direct method or thePatterson method, which would then be refined by full matrix least squares on F2.

Photoluminescence Measurement.

Steady-state room-temper- ature solid-state photoluminescence measurements were performed with an Edinburgh Instrument FLSP920 spectrophotometer equipped with a Xe900 continuous xenon lamp, a *μ*920 microsecond flashlamp, and a single-photon counting photomultiplier tube. Spectra were corrected with the bundled F900 software. The solid sample was prepared by crushing the crystal with a pestle and mortar. The powderwas clipped between two quartz plates, held by a sample holder from Edinburgh Instrument. The lifetimes were fitted as monoexponential decays with OriginPro 8.

Triboluminescence Measurement.

A home-built drop tower was employed to obtain the TL lifetime using the literature setup.[16] In general, a 1.25 in. PVC pipe was inserted perpendicularly into a sealedbox. Plexiglass was attached under the PVC pipe, and the solid sampleswere placed on top of the plate (10 mg for each measurement). A 130g steel ball with a diameter of 1.25 in. was released from the top of thepipe to crush the samples. The light emission was captured by a photodiode (Thorlabs SM05PD2A) bound under the Plexiglass plate and connected to a photodiode amplifier (Thorlabs PDA200C) that transmitted the signal to an oscilloscope (Tektronix TPS2012B). Five drops of each sample were performed. The lifetimes were fitted as monoexponential decays with OriginPro 8. The oscilloscope was cross-calibrated with a literature setup

by using Eu(dbm)$_4$TEA as the standard. By 17 trials, the measured lifetime was 546 ± 22 μs while the literature value is 545 ± 7 μs,[16] which showed good agreement with the result. Depending on the complexes, the time domain was set in a different frame. Their corresponding setting is displayed in Table S17, and the measured TL lifetime is listed in Table S18.

The TL spectra were recorded using a compact CCD spectrometer (Thorlabs CCS100). A glass rod is used to crush the crystal sample (5mg) held in a thin vial positioned perpendicularly on top of the fiber-in port in a completely dark room. The spectra were processed with Thorlabs OSA software. The integration time was set to 3 s, during which the crystal sample was crushed continuously with a glass rod. Because of the limitation of the compact spectrometer, more noise appeared in the spectrum of Eu(dbm)3bipy. The spectra of weak TL compounds [Eu(dbm)4TMP and Eu(dbm)4PMP] could not be acquired. The measured spectra are displayed in Figure S39.

RESULTS AND DISCUSSION

Synthesis of Complexes and Crystal Structures.

Thecomplexes were obtained by reacting ligands with europium(III) salt in a 4:1 ratio in the presence of a base (aqueous NaOH for neutral complexes and amine for ionic complexes). Upon slow evaporation of solvent, five centrosymmetric and six noncentrosymmetric crystals were obtained. Detailed crystallo-graphic data are shown in the Supporting Information. A summary is given in Table 1. Some crystal structures were reported in the literature, such as those of Eu(dbm)$_3$phen,[17] Eu(tta)$_3$phen,[18] Eu(tta)$_3$bipy,[8c] and Eu(dbm)$_4$TEA.[19] Only Eu(dbm)$_3$phen shows a space group different from that from the literature.

Table 1. Summary of TL and Crystal Structure Properties of Eu^{III} Complexes

| compound	TL activity	space group	crystal symmetry
Neutral Complexes			
Eu(dbm)$_3$phen	inactive	$P2_1/c$	centrosymmetric
Eu(dbm)$_3$bipy	active	$P\bar{1}$	centrosymmetric
Eu(tta)$_3$phen	active	$Pca2_1$	noncentrosymmetric
Eu(tta)$_3$bipy	active	$P2_1/n$	centrosymmetric
Eu(fdh)$_3$phen	inactive	$P4_12_12$	noncentrosymmetric
Eu(fdh)$_3$bipy	active[a]	$P\bar{1}$	centrosymmetric
Ionic Complexes			
Eu(dbm)$_4$TEA	active	Cc	noncentrosymmetric
Eu(dbm)$_4$PMP	inactive	$P\bar{1}$	centrosymmetric
Eu(dbm)$_4$TMP	active	$Pca2_1$	noncentrosymmetric
Eu(tta)$_4$PMP	active	$P\bar{4}2_1c$	noncentrosymmetric
Eu(tta)$_4$TMP	active	$P\bar{4}2_1c$	noncentrosymmetric

[a] TL-inactive after recrystallization.
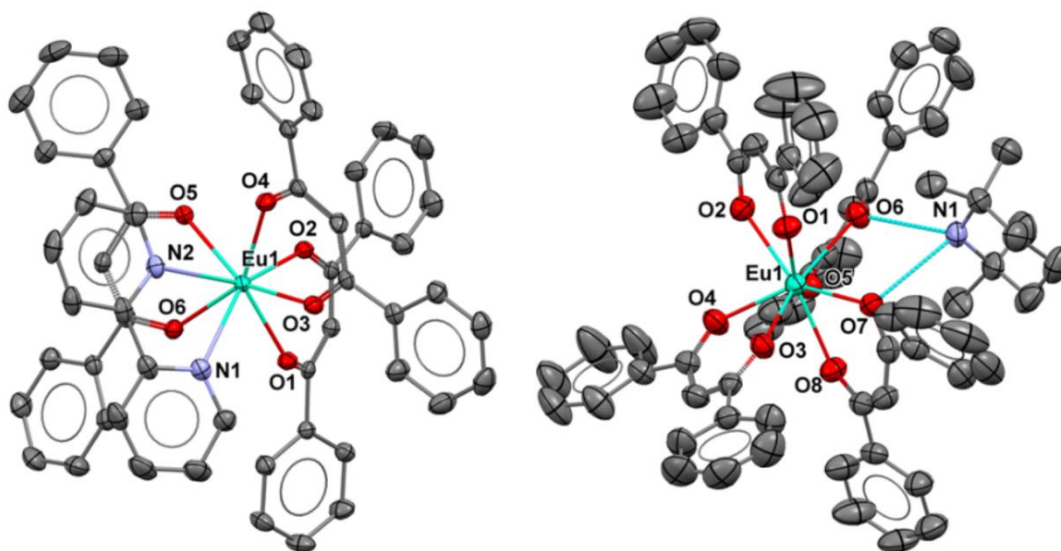
Figure 2. Crystal structures of Eu(dbm)$_3$bipy (left) and Eu-(dbm)$_4$TMP (right). The ellipsoid is drawn at the 50% probability level. Hydrogen atoms have been omitted for the sake of clarity.

The complexes are eight-coordinate and surrounded by four ligands, as displayed in Figure 2 for Eu(dbm)$_3$bipy and Eu(dbm)$_4$TMP. Their coordination geometries can be described as a distorted square antiprism. The Eu−O and Eu−N bond lengths are in good agreement with literature values (from 2.236 to 2.556 Å and from 2.493 to 2.811 Å, respectively) obtained from the Cambridge Crystallographic Database.[20] The average O−Eu−O and N−Eu−N bond angles within the chelate rings are also within the ranges from 62.067° to 77.321° and from 58.054° to 67.503°, respectively.[17] The shortest Eu−Eu distances are long enough to prevent metal− metal interactions. In Eu(tta)$_4$PMP and Eu(tta)$_4$TMP, the trifluoromethyl moiety of tta was found to have hindered H-bond formation between the cation and the complex. The fluorine atoms rotate into the cavity and block the cation's entry (Figure 3), leaving a space for a water molecule to exploit and coordinate to the Eu^{III} center.
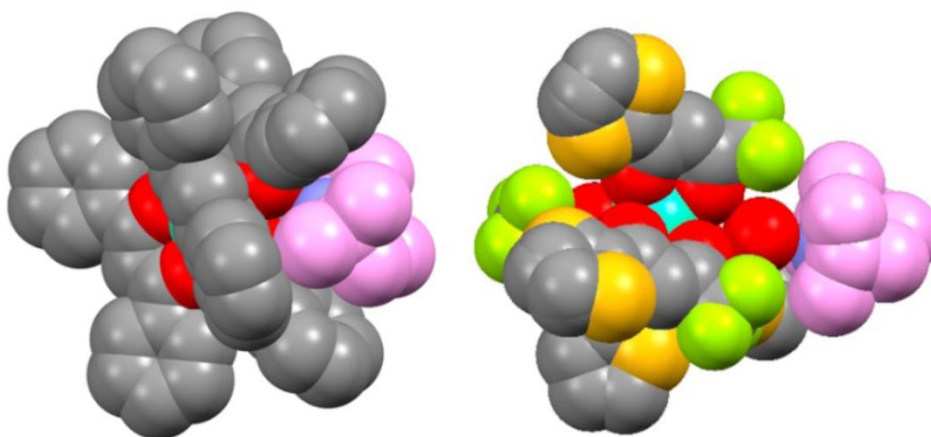

Figure 3. Perspective view of packing of Eu(dbm)$_4$TMP (left) and Eu(tta)$_4$TMP (right). The carbon atoms in the cation are coloredpurple.

We believe this is influential in the reduced TL of these compounds because of luminescence quenching by thevibrational overtones of the O–H oscillators, which isenhanced upon mechanical stimulation.[21] On the other hand,in the [Eu(dbm)$_4$]$^-$ series, H-bonds could be observed between the cation and the complexes as the benzoyl groups in dbm could rotate and avoid close contact with the cations (Figure 3 and Table 2), and the TL was not quenched. Hence, the crystal packing of Eu(dbm)$_4$TEA and that of Eu(dbm)$_4$TMP are similar; i.e., the countercation (amine) sits between the Eu(dbm) – anion, repeating infinitely along one direction (Figures S31–S33).

Table 2. H-Bond Parameters for Ionic Complexes

compound	interactions	D (Å)^a	d (Å)^b	angle (deg)^c
Eu(dbm)$_4$TEA	N(1)–H(1N)···O(1)=C(1)	2.883	2.143	152.14
Eu(dbm)$_4$TMP	N(1)–H(11)···O(6)=C(33)	2.820	2.100	142.57
	N(1)–H(12)···O(7)	2.885	2.031	158.28
Eu(tta)$_4$PMP	N(1)–H(1)···O(9)–H(9A2)	2.814	1.817	173.38
	O(9)–H(9W1)···O(6)=C(19)	2.844	2.041	166.34
	O(9)–H(9W2)···O(8)=C(27)	2.988	2.353	133.15
Eu(tta)$_4$TMP^d	N(1)–H(1B)···O(9)	2.808	1.903	173.09
	O(9)···O(8)=C(31)	2.943	–	–
	O(9)···O(6)=C(23)	2.838	–	–

^{a}Measured distance between the donor and acceptor.

^{b}Measured distance between the hydrogen and acceptor.

^{c}Measured N–H···O or O–H···O angle. Some distances and angles are unavailable as the positions of protons could not be accurately determined.

^{d} The H atoms in the water molecule cannot be calculated accurately.

Photoluminescence Properties.

Using Eu(dbm)$_4$TMP as an example, a broad, high-energy, ligand-centered band in the excitation spectra (Supporting Information) confirms ligand-to-metal energy transfer the antenna effect from dbm.[22] The direct excitation peak corresponding to the $^5D_2 \leftarrow {}^7F_0$ transition could also be observed at 465 nm.[23] Under 375nm excitation, the peaks corresponding to the $^5D_0 \rightarrow {}^7F_J$ transitions of Eu^{III} are found at 580 nm ($J = 0$), 591 nm ($J = 1$),613 nm ($J = 2$), 652 nm ($J = 3$), and 704 nm ($J = 4$) (Figure 4).
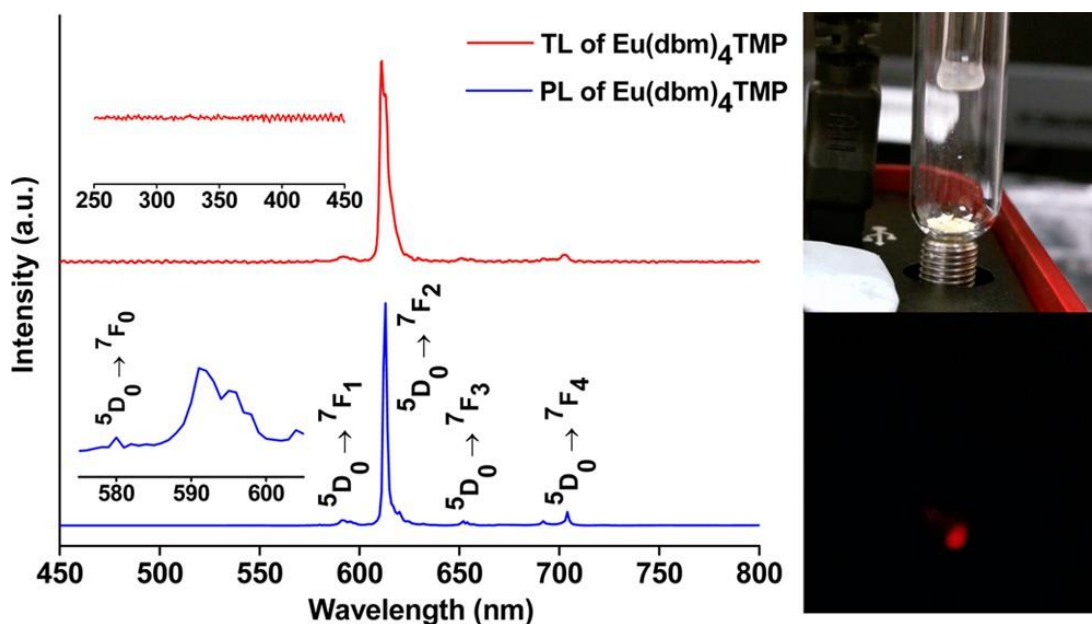
Figure 4. Triboluminescence (TL) and solid-state photoluminescence (PL) (λex = 375 nm) spectra of Eu(dbm)4TMP (left) at room temperature. The images on the right show the CCD spectrometer capturing light emission induced by fracture of the crystals.

The asymmetric ratio, comparing the intensities of the J = 2 and J = 1 transition, is 16.14; the large value is attributed to the low symmetry of the EuIII center,[24] and this is in agreement with the crystal structure (C2 point group). A monoexponential solid-state luminescence lifetime of 494 ± 3 µs was measured for the $5D_0 \rightarrow 7F_2$ transition of Eu(dbm)4TMP. The photophysical data are similar for the other complexes (see the Supporting Information). The phosphorescence of Gd(dbm)3phen, Gd(dbm)3bipy, Gd(dbm)3·2H2O, Gd(tta)3phen, Gd(tta)3bipy, Gd(tta)3·2H2O, Gd(fdh)3phen, Gd(fdh)3bipy, and Gd(fdh)3·2H2O were measured at 77 K in 2-methyltetrahydrofuran (Figure S37 and Table S16), and the literature values of dbm, tta, phen, and bipy triplet states were also obtained[25] to construct the energy level diagram of the triplet states of ligands and lanthanide ions, which is illustrated in Figure 5. The $3\pi\pi^*$ 0-phonon was assigned to be the first peak of the emission spectra, and the lifetime was recorded to confirm the fluorescence and phosphorescence of ligands. The T1 triplet energy levels were calculated to be 20534, 20450, 22883, 22321, and 23420 cm−1, which are above the least emissive $5D_0$ state of the EuIII ion to ensure sensitization. In contrast, the least emissive $5D_4$ state of the TbIII ion (20500 cm−1) lies higher than the T1 state of dbm and tta, causing ineffective sensitization, but it is lower than those of fdh, phen, and bipy, allowing Tb(fdh)3phen and Tb(fdh)3bipy emission at room temperature (Figure S35). Interestingly, the triplet levels of GdIII tris(β-diketonate) complexes are localized on their corresponding β-diketonate ligands except Gd(fdh)3phen where the triplet of phen was observed instead of fdh because the triplet of phen lies lower than fdh.

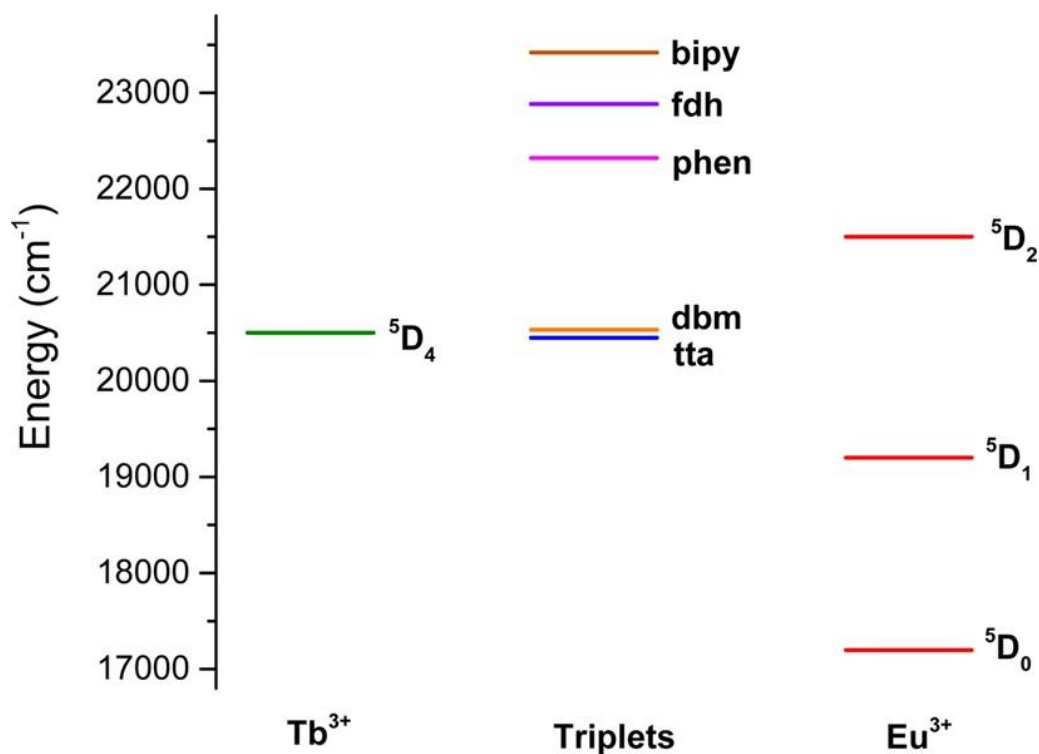Figure 5. Energy level diagram of the excited state of Eu^{3+} and Tb^{3+}ion and the triplet of ligands.

Triboluminescence Property and Mechanistic Investigation.

Among 11 compounds in Table 1, eight of them are TL-active. The emission of our TL-active compounds could be observed by the naked eye, but not all could be measured by our compact CCD spectrometer when the crystal was crushed with a glass rod due to the limitation of the instrument. Spectral features of the measured TL spectra were very similar to those of the corresponding PL spectra with the $^5D_0{\rightarrow}^7F_2$ transitions dominating the emission spectra, and the lifetimes of TL and PL were found to be similar (Tables S15 and S18), indicating that the TL- and PL-emitting species are identical. In addition, the unique discharge emission profile6 was not observed in our TL spectra (inset of Figure 4), and this raises the fundamental question for our investigation of the role of nitrogen gas in inducing triboluminescence.

The gas discharge mechanism postulates that nitrogen gas plays the role of an excited energy donor, whereas in certain triboluminescent materials that are not photoluminescent, it acts as the emitter.[4-6] While the excitation energy comes from the electric *fi*eld generated during fracture of the non-centrosymmetric crystal, we suspected whether the compound itself could be excited in lieu of nitrogen gas; hence, we performed our TL experiments under vacuum (see the video in the Supporting Information). All of the TL-active crystals exhibited TL under vacuum, proving that the TL of our Eu^{III} *β*-diketonate complexes was not excited via the nitrogen discharge mechanism, but in fact by a nondischarge mechanism, even in the presence of an ambient atmosphere as no obvious change in TL intensity was observed.

Furthermore, the ambiguous relationship between TL and crystal symmetry was reviewed. In the past few decades, TL researchers have been attempting to elucidate a correlation between crystal symmetry and TL activity; the scope of compounds, however, was too large to establish a fair ground for debate. However, as we narrow the scope to EuIII β- diketonate complexes, our results presented in Table 1 could not propose a straightforward correlation either. The enigmatic excitation process may actually involve multiple nonexclusive subprocesses that are dependent on the environment.

The notion that noncentrosymmetric crystals would trigger TL is reinforced by the series of [Eu(dbm)$_4$]$^-$. Because centrosymmetric Eu(dbm)$_4$PMP is TL-inactive, the intense TL of the noncentrosymmetric Eu(dbm)$_4$TEA and Eu(dbm)$_4$TMP (their TL can be observed in daylight) indicates the importance of piezoelectricity for triggering TL, and for the [Eu(tta)$_4$]$^-$ series, the TL is weakened by the presence of a water molecule, as mentioned above. However, an example of a TL-inactive noncentrosymmetric compound is Eu(fdh)3phen, and the results were complicated by its SmIII and TbIII analogues (Table S1 and Figures S22–S24). Although they all have the same space group ($P4_12_12$), Eu(fdh)$_3$phen and Sm(fdh)$_3$phendo not exhibit TL while Tb(fdh)$_3$phen is TL-active. The TL- inactive nature of Sm(fdh)$_3$phen can be attributed to its intrinsically low quantum efficiency, especially compared to that of Eu(fdh)$_3$phen where there are more excited states,[10b] but the difference in TL activity between Eu(fdh)$_3$phen and Tb-(fdh)$_3$phen is obscure, given that they are photoluminescent (Figure S35). According to Zink, a polar space group results in TL because piezoelectricity is triggered under compression, torsion, and hydrostatic strain, while crystals with nonpolar space groups can trigger piezoelectric charge only under torsionstrain.[7] You's group also demonstrated that a polar space groupis required for TL.[26] However, our results present the contrary, that the crystal space group is not a major factor governing TL,resonating Cotton's previous report[27] that Na$_3$[Eu- (oxidicetate)$_3$]·8H$_2$O with a polar space group (Cc) is TL- inactive.

On the other hand, TL-active centrosymmetric crystals of Eu(dbm)$_3$bipy, Eu(tta)$_3$bipy, and Eu(fdh)$_3$bipy were obtained. While Chen et al. proposed the TL of Eu(tta)$_3$bipy is due to disorder of the -CF$_3$ group in tta, which facilitates chargeseparation during fracture,[8c] we believe the same does not applyto explain the TL activity of our Eu(fdh)$_3$bipy, as after recrystallization, the TL activity of Eu(fdh)$_3$bipy was lost; the presence of impurity within the crystal lattice should be attributed instead. Moreover, no disorder was found in the crystal structure of Eu(dbm)$_3$bipy, but TL could still be observed after recrystallization several times, suggesting impurities should not be responsible for TL in this case. This situation is similar to the case for [MnBr$_2$(DPEPO)], an intensely triboluminescent compound with a centrosymmetric $P\bar{1}$space group without disorder.[8d] Therefore, by means of elimination, we believe that processes other than surface piezoelectrification during fracture are important for achieving TL. Although centrosymmetric crystals were found to be TL, noncentrosymmetric crystals showed more intense TL. It is proposed that the piezoelectricity of Eu(dbm)$_4$TMP within the crystal triggered by pressure would lead to the high TL intensity.

CONCLUSION

A new intensely triboluminescent compound, Eu(dbm)₄TMP, was prepared, and this result reinforces the notion that noncentrosymmetric crystals would largely result in "triboexcitation" by generating an electric field upon fracture. Our TL experiments performed in vacuum added a new perspective to the discussion of the TL mechanism to prove that while nitrogen gas once had a role to play as either the excited energydonor (due to discharge) or the emitter (such as TL in sugar), its role in the excitation process of Ln^{III} β-diketonate complexesis greatly reduced, if not irrelevant. Likewise, examples of TL-active compounds with nonpolar space groups further suggest that a nondischarge mechanism circumventing piezoelectrifica-tion governs the excitation of TL. Future work will elucidate more of the piezoelectric nature of these compounds to develop more highly triboluminescent compounds and materials.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ga-lai.law@polyu.edu.hk.

ORCID

Ga-Lai Law: 0000-0002-2192-6887

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

dbm, dibenzoylmethane; tta, 2-thenoyltrifluoroacetone; fdh, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione; TL, tribolumines- cence; PL, photoluminescence

REFERENCES

(1) Walton, A. J. Triboluminescence. *Adv. Phys.* 1977, *26*, 887−948.

(2) Zink, J. I.; Hardy, G. E.; Sutton, J. E. Triboluminescence of Sugar. *J. Phys. Chem.* 1976, *80*, 248−249.

(3) Jha, P.; Chandra, B. P. Survey of the Literature on Mechanoluminescence from 1605 to 2013. *Luminescence* 2014, *29*, 977−993.

(4) Sage, I.; Bourhill, G. Triboluminescence Materials for StructuralDamage Monitoring. *J. Mater. Chem.* 2001, *11*, 231−245.

(5) Zink, J. I. Triboluminescence. *Acc. Chem. Res.* 1978, *11*, 289−295.

(6) Zink, J. I. Squeezing Light out of Crystals: Triboluminescence. *Naturwissenschaften* 1981, *68*, 507−512.

(7) Hardy, G. E.; Kaska, W. C.; Chandra, B. P.; Zink, J. I. Triboluminescence-Structural Relationships in Polymorphs of Hex- aphenylcarbodiphosphorane and Anthranilic Acid, Molecular Crystals,and Salts. *J. Am. Chem. Soc.* 1981, *103*, 1074−1079.

(8) (a) Chandra, B. P.; Tiwari, S.; Ramrakhiani, M.; Ansari, M. H. Mechanoluminescence in Centrosymmetric Crystals. *Cryst. Res. Technol.* 1991, *26*, 767−781.
(b) Rheingold, A.; King, W. Crystal Structures of Three Brilliantly Triboluminescent Centrosymmetric Lanthanide Complexes: Piperidinium Tetrakis(benzoylacetonato)- europate, Hexakis(antipyrine)terbium Triiodide, And Hexaaquadi- chloroterbium Chloride. *Inorg. Chem.* 1989, *28*, 1715−1719.
(c) Chen,X.-F.; Zhu, X.-H.; Xu, Y.-H.; Shanmuga Sundara Raj, S.; Öztürk, S.; Fun, H.-K.; Ma, J.; You, X.-Z. Triboluminescence and Crystal Structures of Non-ionic Europium Complexes. *J. Mater. Chem.* 1999,*9*, 2919−2922.
(d) Chen, J.; Zhang, Q.; Zheng, F.-K.; Liu, Z.-F.; Wang, S.-H.; Wu, A.-Q; Guo, G.-C. Intense Photo- and Tribo-Luminescence of Three Tetrahedral Manganese(II) Dihalides with ChelatingBidentate Phosphine Oxide Ligand. *Dalton Trans.* 2015, *44*, 3289-3294.

(9) Binnemans, K. Rare-Earth *β*-diketonates. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Bünzli, J. C. G., Pecharsky, V. K., Eds.; Elsevier Science B. V.: Amsterdam, 2005; Vol. *35*, Chapter 225, pp 107−269.

(10) (a) Moore, E. G.; Samuel, A. P. S.; Raymond, K. N. From Antenna to Assay: Lessons Learned in Lanthanide Luminescence. *Acc.Chem. Res.* 2009, *42*, 542−552.
(b) Chan, C.-F.; Li, H.; Seto, C.; Tam,H.-L.; Law, G.-L.; Wong, K.-L. Synthesis, Characterization, Photo- physical Properties of Lanthanide Complexes with Flexible Tripodal Carboxylate Ligands. *Polyhedron* 2013, *52*, 939−944.
(c) Tanner, P. A. *Chem. Soc. Rev.* 2013, *42*, 5090−5101.

(11) a) Clegg, W.; Sage, I.; Oswald, I.; Brough, P.; Bourhill, G. Two Isostructural Triboluminescent Lanthanide Complexes. *Acta Crystal-logr. Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* 2000, *56*, 1323− 1325.
(b) Clegg, W.; Bourhill, G.; Sage, I. Hexakis(antipyrine- O)Terbium(III) Triiodide at 160 K: Confirmation of a Centrosym- metric Structure for a Brilliantly Triboluminescent Complex. *Acta Crystallogr., Sect. E: Struct. Rep. Online* 2002, *58*, m159−m161.
(c) Li,X.-L.; Zheng, Y.; Zuo, J.-L.; Song, Y.; You, X.-Z. Synthesis, Crystal Structures and Triboluminescence of a Pair of Eu(III)-based Enantiomers. *Polyhedron* 2007, *26*, 5257−5262.
(d) Eliseeva, S. V.; Pleshkov, D. N.; Lyssenko, K. A.; Lepnev, L. S.; Bünzli, J.-C. G.; Kuzmina, N. P. Highly Luminescent and Triboluminescent Coordi- nation Polymers Assembled from Lanthanide *β*-Diketonates and Aromatic Bidentate O-Donor Ligands. *Inorg. Chem.* 2010, *49*, 9300−9311.
(e) Hasegawa, Y.; Hieda, R.; Miyata, K.; Nakagawa, T.; Kawai, T. Brilliant Triboluminescence of a Lanthanide Coordination Polymer with Low-Vibrational-Frequency and Non-Centrosymmetric Structural Networks. *Eur. J. Inorg. Chem.* 2011, *2011*, 4978−4984.
(f) Biju, S.;Gopakumar, N.; Bünzli, J.-C. G.; Scopelliti, R.; Kim, H. K.; Reddy, M. L. P. Brilliant Photoluminescence and Triboluminescence from Ternary Complexes of Dy[III] and Tb[III] with 3-Phenyl-4-propanoyl-5- isoxazolonate and a Bidentate Phosphine Oxide Coligand. *Inorg. Chem.* 2013, *52*, 8750−8758.
(g) Mikhalyova, E. A.; Yakovenko, A. V.; Zeller, M.; Kiskin, M. A.; Kolomzarov, Y. V.; Eremenko, I. L.; Addison, A. W.;Pavlishchuk, V. V. Manifestation of *π*−*π* Stacking Interactions in Luminescence Properties and Energy Transfer in Aromatically-DerivedTb, Eu and Gd Tris(pyrazolyl)borate Complexes. *Inorg. Chem.* 2015,*54*, 3125−3133.

(12) *SAINT*; Bruker AXS Inc.: Madison, WI, 2007.

(13) *SAINT*; Bruker AXS Inc.: Madison, WI, 2012.

(14) *SADABS*; Bruker AXS Inc.: Madison, WI, 2001.

(15) Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, *64*, 112−122.

(16) Fontenot, R. S.; Hollerman, W. A.; Aggarwal, M. D.; Bhat, K. N.; Goedeke, S. M. A Versatile Low-cost Laboratory Apparatus for Testing Triboluminescent Materials. *Measurement* 2012, *45*, 431−436.

(17) Ahmed, M. O.; Liao, J.-L.; Chen, X.; Chen, S.-A.; Kaldis, J. H. Anhydrous Tris(dibenzoylmethanido)(o-phenanthroline)europium- (III), [Eu(DBM)₃(Phen)]. *Acta Crystallogr., Sect. E: Struct. Rep. Online* 2003, *59*, m29−m32.

(18) Takada, N.; Hieda, S.; Sugiyama, J.; Katoh, R.; Minami, N. Mechanoluminescence from Piezoelectric Crystals of an Europium Complex. *Synth. Met.* 2000, *111−112*, 587−590.

(19) (a) Sweeting, L. M.; Rheingold, A. L. Crystal Disorder and Triboluminescence. *J. Am. Chem. Soc.* 1987, *109*, 2652−2658.
(b) Cotton, F. A.; Daniels, L. M.; Huang, P. Refutation of an Alleged Example of a Disordered but Centrosymmetric Triboluminescent Crystal. *Inorg. Chem. Commun.* 2001, *4*, 319−321.

(20) Groom, C. R.; Allen, F. H. The Cambridge Structural Databasein Retrospect and Prospect. *Angew. Chem., Int. Ed.* 2014, *53*, 662−671.

(21) (a) Hardy, G. E.; Baldwin, J. C.; Zink, J. I.; Kaska, W. C.; Liu, P.- H.; Dubois, L. Triboluminescence of Aromatic Compounds. *J. Am. Chem. Soc.* 1977, *99*, 3552−3558.
(b) Bünzli, J.-C. G.; Piguet, C. Taking Advantage of Luminescent Lanthanide Ions. *Chem. Soc. Rev.*2005, *34*, 1048−1077.

(22) Bünzli, J.-C. G.; Moret, E.; Foiret, V.; Schenk, K. J.; Wang, M.;Jin, L. Structural and Photophysical Properties of Europium(III) Mixed Complexes with *β*- Diketonates and O- Phenanthroline. *J. Alloys Compd.* 1994, *207−208*, 107−111.

(23) Carnall, W. T.; Fields, P. R.; Rajnak, K. Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. IV. Eu^{3+}. *J. Chem. Phys.* 1968,*49*, 4450−4455.

(24) (a) Binnemans, K. Interpretation of Europium(III) Spectra. *Coord. Chem. Rev.* 2015, *295*, 1−45.
(b) Yip, Y. W.; Wen, H.; Wong, W. T.; Tanner, P. A.; Wong, K. L. Increased Antenna Effect of the Lanthanide Complexes by Control of a Number of Terdentate N- Donor Pyridine Ligands. *Inorg. Chem.* 2012, *51*, 7013−7015.

(25) (a) Sager, W. F.; Filipescu, N.; Serafin, F. A. Substituent Effectson Intramolecular Energy Transfer. I. Absorption and Phosphor- escence Spectra of Rare Earth *β*-Diketone Chelates. *J. Phys. Chem.* 1965, *69*, 1092−1100.
(b) Gropper, H.; Dörr, F. Die Orientierung der optischen Übergangsmomente in Phenanthren und seinen Azader-ivaten. *Ber. Bunsen-Ges. Phys. Chem.* 1963, *67*, 46−54. (c) Gondo, Y.; Kanda, Y. The Phosphorescence Spectra of 2, 2′- and 4, 4′-Bipyridyls.*Bull. Chem. Soc. Jpn.* 1965, *38*, 1187−1190.

(26) Li, D.-P.; Li, C.-H.; Wang, J.; Kang, L.-C.; Wu, T.; Li, Y.-Z.; You, X.-Z. Synthesis and Physical Properties of Two Chiral Terpyridyl Europium(III) Complexes with Distinct Crystal Polarity. *Eur. J. Inorg.Chem.* 2009, *2009*, 4844−4849.

(27) Cotton, F. A.; Huang, P. Further Observations on the Non- Rigorous Relationship between Triboluminescence and CrystalCentricity. *Inorg. Chim. Acta* 2003, *346*, 223−226.