

Bright Lanthanide^{III} Triboluminescence despite Low Photoluminescence, and Dual Triboluminescence and Mechano-Responsive Photoluminescence

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In pursuit of a new family of mechanically responsive luminescent materials, it is aimed to differentiate triboluminescence (TL) from photoluminescence (PL). A β -diketonate ligand with *tert*-butyl groups (2,2,6,6-tetramethylheptane-3,5-dionate: tmh) is selected to quench Eu^{III}-centered PL via ligand-to-metal charge transfer, whereas tmh provides efficient photosensitization of Tb^{III} ions. Bright TL is observed from the Eu^{III} and Tb^{III} homodinuclear complexes despite the fact that their PL quantum yields differed by a factor of >50. Nanomechanical tests reveal the ductility of the crystals, suggesting they are ideal for accumulating deformation energy before breakage. Furthermore, a TL/PL color difference is observed for a Tb^{III}/Eu^{III} heterodinuclear complex, and grinding results in mechanochromic luminescence (MCL); this is the first example of a dual TL- and MCL-active lanthanide^{III} coordination compound. The photophysical properties before, during, and after grinding are investigated and correlated with powder and single-crystal crystallographic data.

reactions in organic solvents. Mechano-chromic luminescence (MCL) describes the deformation of molecular conformations alongside changed optical properties in response to mechanical stimuli. Crystal-to-crystal/amorphous phase transitions produce shifts in the emission wavelength and/or changes in the emission intensities of organic and coordination compounds.^[3] Despite the first description of blue-glowing sugar having been described in 1605, and the broad versatility of these mechanically-triggered phenomena, triboluminescence (TL)—fracture-induced luminescence—is not yet understood in terms of a general molecular design, and the underlying photophysical processes remain unclear. TL is observed only in the moment in which force is applied and does not require a light source. Studying this instantaneous force-

to-photon conversion is of critical not only from the perspective of fundamental science but also for industrial applications, which include irradiation-free force/stress sensors, security marking techniques, and health care devices.^[4]

Bright TL has been reported for various lanthanide^{III} (Ln^{III}) complexes with dibenzoylmethide (dbm), thenoyl-trifluoroacetylacetonate (tta), and hexafluoroacetylacetonate (hfa) ligands,

Introduction

Solid-state chemical and physical phenomena triggered by mechanical stimuli have attracted increasing attention in the last decade. Mechano-responsive gels^[1] and solid-state coupling reactions^[2] have provided new organic chemistry and materials science research avenues based on modifying conventional chemical

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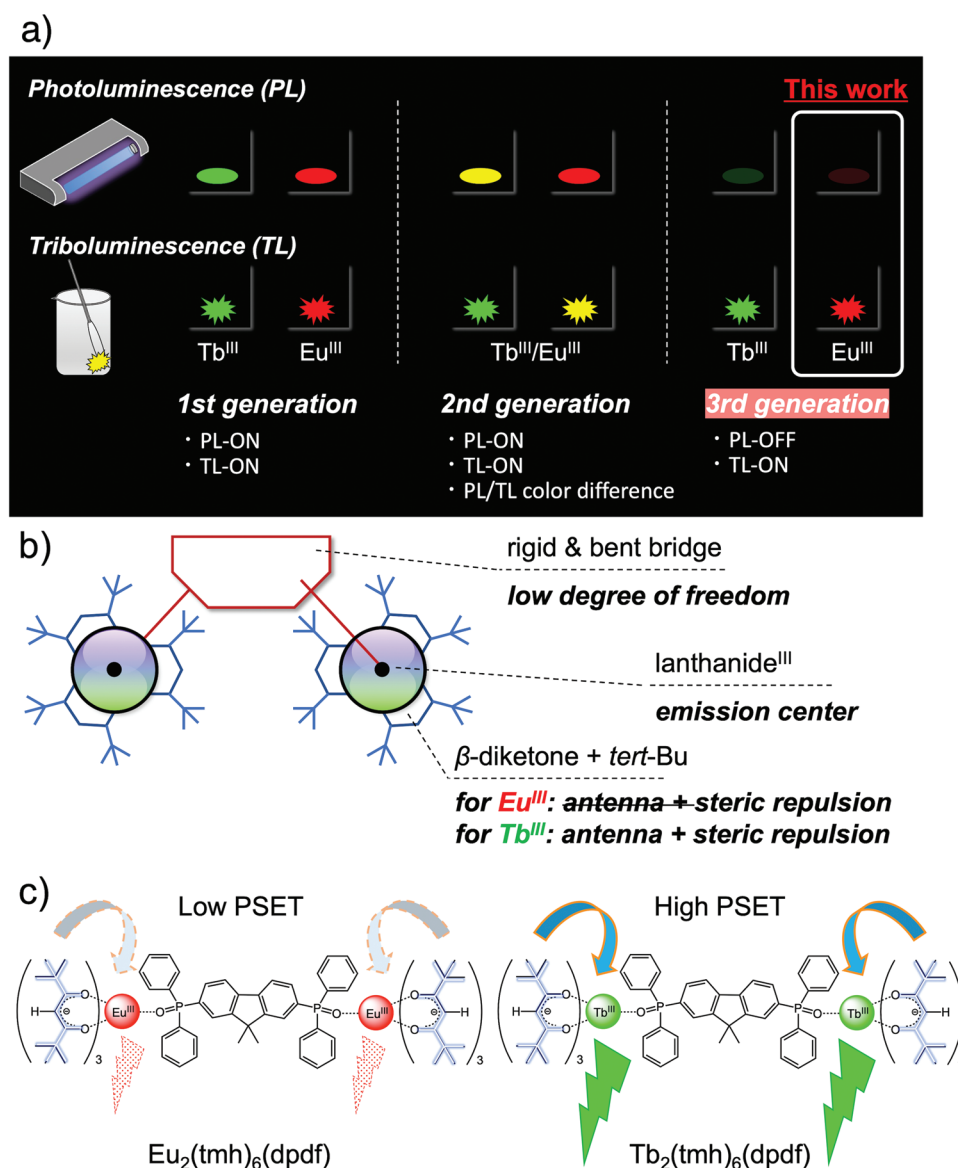


Figure 1. a) PL/TL properties of Ln^{III} complexes. b) Dinuclear Ln^{III} mechanophore design. c) Ln₂(tmh)₆(dpdpf) (Ln = Eu or Tb) structures.

and these complexes also exhibit photoluminescence (PL) upon UV irradiation.^[5] As the absorption coefficients of Ln^{III} ions are intrinsically small ($\epsilon_{\text{Ln}} < 1 \text{ cm}^{-1} \text{ M}^{-1}$)^[6] because the f–f transitions are parity-forbidden, the introduction of organic chromophores is essential to achieve efficient PL.^[7] Thus, ligand-to-metal photosensitized energy transfer (PSET) is a reasonable explanation for the brightness of Ln^{III} TL (Figure 1a, “1st generation”).^[8] Nevertheless, we previously reported that the Ln^{III} TL does not always have the same characteristics of the corresponding PL, and we observed distinct PL/TL color differences in Tb^{III}/Eu^{III} mixed coordination polymers (Figure 1a, “2nd generation”).^[9] Therefore, leveraging the intrinsic photophysical differences between PL and TL should lead to a theoretical breakthrough and the development of a new family of mechano-responsive luminescent materials.

The aim of this study was to distinguish TL and PL by designing a Ln^{III} complex with quenched PL but enhanced TL

(Figure 1a, “3rd generation”), which is an emerging option to clarify the PL/TL difference simply by the emission intensity. Based on our hypothesized “f–f priority rule,” which predicts that TL is more likely to be dominated by direct f–f transitions than ligand-mediated processes,^[10] we focused on three aspects: i) inefficient PSET, ii) low coordination geometry, and iii) high mechanical sensitivity (Figure 1b). To avoid efficient PSET, Eu^{III} ions were combined with 2,2,6,6-tetramethylheptane-3,5-dionate (tmh) ligands (Figure 1c). The ligand-to-metal charge transfer (LMCT) states of Eu^{III}-tmh systems are known to quench the Eu^{III}-centered emission, resulting in low PL quantum yields ($\approx 1\%$). Moreover, the low-symmetry seven-coordinate structures created by bulky tmh ligands are ideal for elevating the f–f transition probability.^[11] As Clegg et al. concluded based on their study of the TL of Ln(tmh)₃(DMAP) (Ln: Tb or Sm, DMAP: 4-dimethylaminopyridine),^[12] Ln^{III}.

tmh systems are potentially mechano-responsive; this is probably because of the face-to-face *tert*-butyl groups arrangement in the crystal packing system. A rigid and bent organic linker (2,7-bis(diphenylphosphoryl)-9,9-dimethylfluorene: dpdf)^[13] was adopted to generate intermolecular steric repulsion. Based on a report of a dinuclear Ln^{III} complex with a biphenylene bridging ligand containing a twisted C–C bond between phenyl groups,^[14] we deduced that a bent non-rotatable linker should reduce the degrees of freedom of the discrete dinuclear unit and promote the formation of a mechanically strained packing structure.

1. Results and Discussion

The dinuclear complex $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ was prepared using the method shown in Scheme S1 (Supporting Information). $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$ which has a high PSET efficiency was also

synthesized for comparison. Block crystals of both the Eu^{III} and Tb^{III} complexes were obtained, and single crystal X-ray analyses revealed an identical structure consisting of two Ln^{III} ions, six tmh ligands, and one bridging ligand (Figure S1a, left, Supporting Information). The crystal structure belongs to the non-centrosymmetric space group $Fdd2$, which can generate a piezoelectric current on the cleavage upon fracturing. The dinuclear surface is surrounded by the bulky *tert*-butyl groups. The π -aromatic system of the bridging ligand barely contributes to specific intermolecular contacts, such as edge-to-face C–H $\cdots\pi$ and face-to-face $\pi\cdots\pi$ interactions (Figure S1a, right, Supporting Information). Hirshfeld surface (HS) analysis^[15]—which generates quantitative crystal packing descriptions—indicated that 87% of the entire surface is dominated by H \cdots H contacts (Figure S1b, Supporting Information). The high ρ indicator^[16] ($\rho = \% \text{C}\cdots\text{H} / \% \text{C}\cdots\text{C} = 96$), curvedness plots without flat surface patches, and featureless shape-index plots^[15,17] also suggest

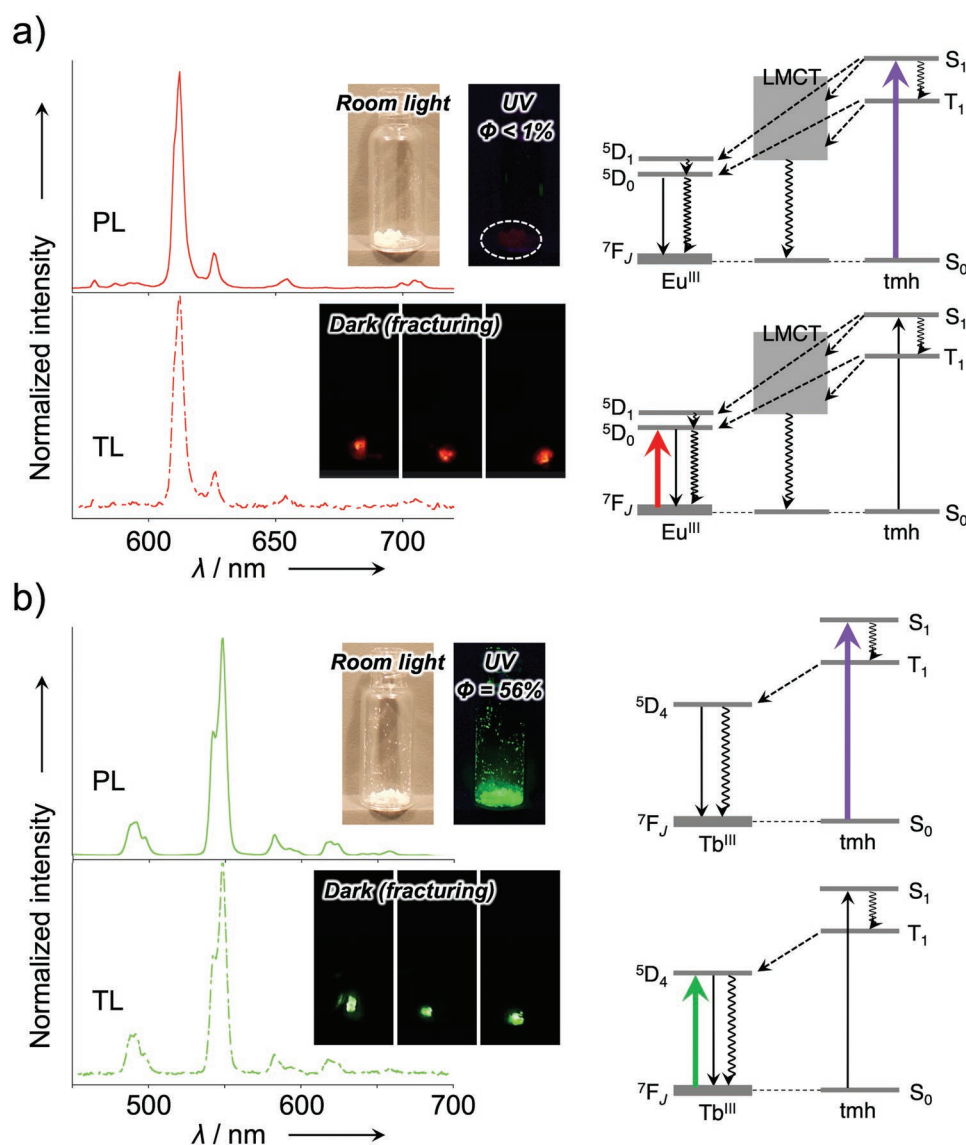


Figure 2. PL and TL spectra and corresponding energy-transfer diagrams of a) $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ and b) $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$ (colored arrows: dominant excitation processes). The insets are photographs acquired under white light or UV illumination, or during fracturing.

that face-to-face stacking does not occur (see Figure S1c, Supporting Information).

$\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ and $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$ showed weak red ($\Phi_{\text{total}} < 1\%$) and intense green ($\Phi_{\text{total}} = 56\%$) PL upon UV irradiation owing to the quenching via LMCT states for Eu^{III} ions and the enhancement via PSET for Tb^{III} ions, respectively (Figure 2, solid lines). Despite the significant difference in PL quantum yields (>50-fold), bright TL, recognizable by the naked eye under room light, was observed for both compounds (Figure 2, dashed lines). The TL intensities of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ and $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$ were similar (1061 and 1820 photon counts, respectively). The TL spectral profiles are identical to the PL spectral profiles, which implies that TL and PL occur from the same excited states ($^5\text{D}_0$ and $^5\text{D}_4$ for the Eu^{III} and Tb^{III} ions, respectively), without distortion of the coordination geometry around the Ln^{III} ions. As the crystallinity and crystal grain size of the samples are not quantified, we did not estimate the “light yield” of the TL, which is typically measured using a drop-tower method with a reference sample.^[18]

The faint PL and intense TL of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ are counterintuitive to the conventional idea that efficient PSET plays a key role in bright Ln^{III} TL. Thus, the TL of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ instead correlates with the bombardment of electrons^[19] that are effectively generated across cracks in the crystal belonging

to a non-centrosymmetric space group. This results in the direct population of the Eu^{III} $^5\text{D}_0$ excited state, followed by efficient $^5\text{D}_0 \rightarrow ^7\text{F}_j$ transitions ($J = 0-4$, $\Phi_{\text{eff}} = 75\%$) owing to the low-symmetry seven-coordinate geometry. This mechanism is consistent with the aforementioned “f-f priority rule,” and PSET does not play an important role in the formation of the Ln^{III} excited states (Figure 2, right). As TL requires the crystal deformation and the excited species are generated across growing cracks,^[20] intermolecular face-to-face *tert*-butyl groups arrangement should enhance the mechano-responsiveness on the molecular scale by suppressing the formation of robust hydrogen-bonded networks. Mononuclear $\text{Ln}(\text{tmh})_3(\text{DMP})$ ^[12] has a similar packing arrangement. Moreover, we reported the high TL activity of Ln^{III} -hfa coordination polymers in which fluorine atoms face each other.^[9]

Nanoindentation tests were also performed to provide the mechanical fingerprint of the crystals (Figure 3a). Although the appearance of the crystals differed, smooth load–displacement (p – h) curves were obtained across the series without the “pop-ins” that usually appear as a result of rapid crack initiation and propagation.^[21] Here, such behaviors were not identified, implying that the applied deformation energy was absorbed by the crystal before fracture. The reduced Young’s modulus (E_r) and hardness (H) of the crystals were estimated using

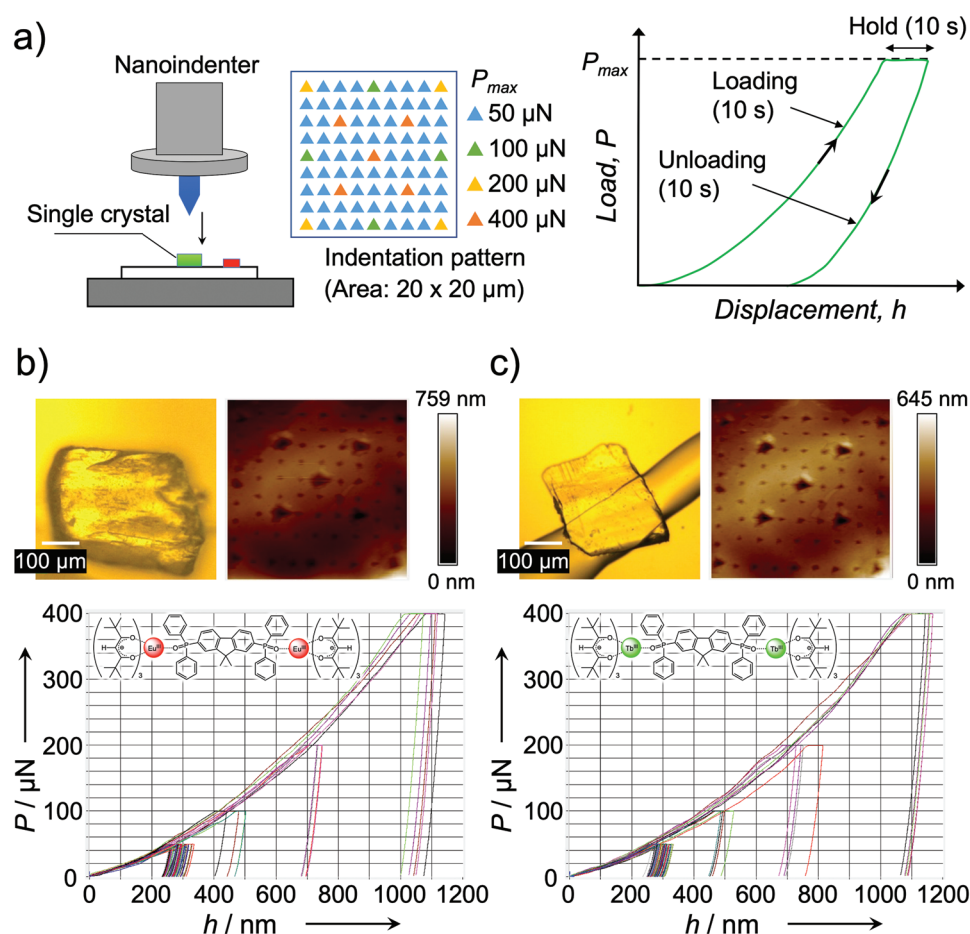


Figure 3. a) Nanomechanical testing schematic. Optical micrographs of pristine crystals (top left), in situ surface probe microscopy images after indentations (top right, $20 \times 20 \mu\text{m}$), and load–displacement curves of b) $\text{Eu}_2(\text{tmh})_6(\text{dpdpf})$ and c) $\text{Tb}_2(\text{tmh})_6(\text{dpdpf})$.

the Oliver-Pharr method^[22] to be 5.8 ± 0.44 GPa and 0.28 ± 0.024 GPa, respectively, for $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$, and 5.3 ± 0.29 GPa and 0.27 ± 0.018 GPa, respectively, for $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$. Thus, the target crystals can be categorized as “ductile” materials, even in comparison with organic compounds,^[23] which are generally described as “soft” materials.

Further grinding with a pestle and mortar reduced the TL intensity and crystallinity, and TL was not observed in the end (hereafter, the “ground form”). Note that fracturing was realized using a spatula, and the ground form with a pestle. Diffraction patterns obtained from synchrotron radiation wide-angle X-ray scattering measurements confirmed that the grinding process only lowers the crystallinity of the sample and does not induce a transition to another crystalline phase (Figure S4, Supporting Information). Interestingly, the PL properties of the ground and pristine forms were different (Figure S5, Supporting Information). In particular, the relative intensities of the UV-vis excitation bands ($^5\text{D}_2 \leftarrow ^7\text{F}_0$ at 464 nm) were inverted for $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$. As the PL intensity ratio for the magnetic ($^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 592 nm) and electric dipole transitions ($^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 612 nm) did not change, the non-radiative process, including the state transitions, must have been suppressed in the ground form. We suggest that this was because of deformation of the intermolecular packing structure, which can alter the ligand-metal spacing and corresponding LMCT band energy levels.^[24] Indeed, a comparison between the diffuse reflectance spectra of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ and $\text{Gd}_2(\text{tmh})_6(\text{dpdf})$ demonstrated that the characteristic low-lying band of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ disappeared after grinding (Figure S6, Supporting Information).

Taking advantage of the sensitivity of the PL to mechanical grinding, the $\text{Eu}^{\text{III}}/\text{Tb}^{\text{III}}$ heterodinuclear complex $\text{EuTb}(\text{tmh})_6(\text{dpdf})$ was also prepared as a TL- and MCL-active Ln^{III} mechanophore. MCL has not often been reported for Ln^{III} complexes because the dominant emission bands of homo- Ln^{III} complexes are inert to the external environment (although their Stark-splittings may change). Moreover, the responses of mixed- Ln^{III} complexes to temperature and pressure condition variation,^[14,25] but not mechanical stimuli, have been examined. Grinding changed $\text{EuTb}(\text{tmh})_6(\text{dpdf})$ PL from yellow to orange-yellow (Figure 4a,b, dashed and solid blue lines, respectively) because the relative contribution of the Eu^{III} -centered emission was lower for the pristine sample. The corresponding Commission Internationale de l'Éclairage (CIE) 1931 chromaticity coordinates were $\approx(0.46, 0.51)$ and $(0.48, 0.48)$ for pristine and ground forms, respectively. To the best of our knowledge, the only mechano-optically coupled Ln^{III} PL is the sonication-induced mechanochemical transformation of Ln^{III} -supramolecules accompanied by a white-to-blue or yellow-to-red PL color change owing to competing organic fluorescence.^[26] Nevertheless, there are no reports of MCL based on ratiometric Ln^{III} emission (red ($\lambda_{\text{em,Eu}} = 612$ nm)/green ($\lambda_{\text{em,Tb}} = 549$ nm)) realized simply by grinding. Similar to $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ and $\text{Tb}_2(\text{tmh})_6(\text{dpdf})$, bright yellow TL was also confirmed upon fracturing the $\text{EuTb}(\text{tmh})_6(\text{dpdf})$ crystals (Figure 4b, black line). As a slight change in TL color, assigned to dynamic axial-to-equatorial molecular conformation change, was reported for a phenothiazine derivative,^[27] we conducted a continuous TL/PL measurements (Figure S7 and Table S2, Supporting Information). The emission color did not change

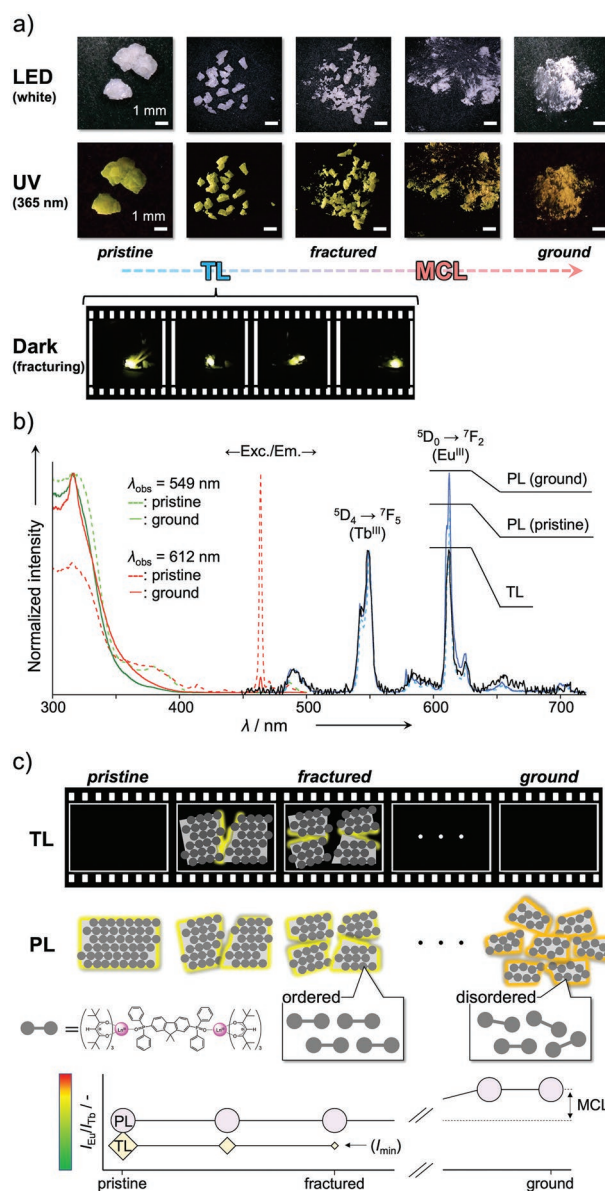


Figure 4. a) Micrographs of $\text{EuTb}(\text{tmh})_6(\text{dpdf})$ before and after fracturing and grinding. b) PL excitation/emission spectra ($\lambda_{\text{exc}} = 360$ nm; $\lambda_{\text{obs}} = 549/612$ nm for excitation; dotted/solid lines: pristine/ground forms) and TL spectra. c) Schematic showing molecular packing and TL/PL properties. The size of each symbol on the graph indicates the emission intensity; I_{min} = minimum intensity for detection.

over time for either TL ($I_{\text{Eu}}/I_{\text{Tb}} = 1.00 \pm 0.06$ for 10 successive TL spectra) or PL ($I_{\text{Eu}}/I_{\text{Tb}} = 1.48$ (pristine) or 1.47 (fractured)). Alongside the ductile nanomechanical properties of the crystals, MCL was observed when the applied force exceeded a certain limit and/or the particle size was sufficiently decreased to deactivate TL (Figure 4c). It is important to emphasize that the magnetic and electric dipole transition ratios ($I_{\text{electric}}/I_{\text{magnetic}}$) of $\text{Eu}_2(\text{tmh})_6(\text{dpdf})$ were identical for PL (pristine/ground) and TL. Therefore, the same excited states were populated and the local geometry around the Eu^{III} ions was not deformed by fracturing or grinding. In contrast, the different Eu^{III} -to- Tb^{III}

intensity ratios ($I_{\text{Eu}}/I_{\text{Tb}}$) for $\text{EuTb}(\text{tmh})_6(\text{dpdf})$ indicate distinct TL and PL excitation probabilities and energy-transfer efficiencies.

3. Conclusion

We presented a new molecular strategy for Ln^{III} -based mechanophores. By introducing bulky β -diketonate and rigid fluorene-based bridging ligands, we produced bright TL even though the ligand-excited PL quantum yield was negligible ($< 1\%$). This suggested the existence of direct mechanically stimulated Ln^{III} excitation mechanisms in TL, while photo-irradiation of the ligands is essential to efficiently sensitize Ln^{III} ions in PL. Furthermore, nanomechanical testing indicated that the ductility that allows crystals to restore the deformation energy could be critical for TL activity from a mechanical point of view. Moreover, a $\text{Eu}^{\text{III}}/\text{Tb}^{\text{III}}$ heterodinuclear complex showed not only PL/TL color difference but also MCL, which implies that Ln^{III} coordination materials with two or more metal ions—such as dimers, clusters, and polymers—also potentially exhibit MCL. As typical MCL materials are organic or d -block transition metal complexes with broad emission bands, sharp f -centered emissions expand the application scope of MCL-active compounds and should promote solid-state photophysics research. The presented strategy for Ln^{III} mechanophores will advance the development of next-generation mechano-responsive luminescent materials, and further nanomechanical studies will provide deeper insights into the relationships between the structure and mechanical and photophysical properties of such materials.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

europium, nanoindentation, photoluminescence, terbium, triboluminescence

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