Triboluminescence of Lanthanide Coordination Polymers with Face-to-Face Arranged Substituents


Abstract: Luminescence upon grinding solid materials (triboluminescence: TL) has long been a puzzling phenomenon in natural science, and has also attracted attention because of its broad application in optics. It has been generally considered that the TL spectra exhibit similar profiles as those of photoluminescence (PL), although they occur from distinct stimuli. Here we describe for the first time a large spectral difference of these two physical phenomena using lanthanideIII coordination polymers with efficient TL and PL properties. They are composed of emission centers (TbIII and EuIII ions), antenna (hexafluoroacetylacetonate: hfa), and bridging ligands (2,5-bis(diphenylphosphoryl)furan: dpf). The emission color upon grinding (yellow TL) is clearly different from that upon UV irradiation (reddish-orange PL) in TbIII/EuIII-mixed emission color upon grinding (yellow TL) is clearly different from that directly indicate the discrete excitation processes of PL and TL.

Because of their high spectral resolution arising from intracofigurational 4f-4f transitions,[7] Reddy and co-workers recently demonstrated bright red TL and PL of [Eu(DPPF)3(DDXPO)] (DPPF: 1-(4-(diphenylphosphino)phenyl)-4,4,5,5,5-pentafluoropentane-1,3-dione, DDXPO: 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene oxide).[8] They also reported slight decrease in TL intensity when dispersed in PMMA films, compared with the solid state.

In this study, we focused on the specific disordered arrangement of substituents in solid-state LnIII complexes. Sweeting and Rheingold reported that the disorder of phenyl rings and cations in [Eu(dbm)]+·[Et3NH]+ (dbm: dibenzoylmethanato) provided a sufficient source of localized polarity to induce TL activity.[9] Chen reported that the disorder of thieryl and trifluoromethyl (CF3) groups in EuIII complexes played an important role in creating randomly distributed sites of electron affinities at the faces of fractures.[6d] There have also been some reports on TL-active LnIII coordination polymers based on β-diketonato and aromatic bridging ligands.[10]

We consider that strong TL LnIII coordination polymers can be systematically constructed by introducing disordered arrangement of substituents between single polymer chains in the solid state. Novel LnIII coordination polymers composed of LnIII ions, hfa, and furan-based bridging ligands (2,5-bis(diphenylphosphoryl)furan: dpf) are introduced to provide the disordered face-to-face arrangement of CF3 substituents (Figure 1a). The polar character and small aromatic ring of the furyl-bridging ligand are expected to prevent the polymer chains from forming highly ordered alternate packing structures (Figure 1b). The reported coordination polymers with thiophene-based bridges, [Eu(hfa)3(dp)], (dp: 2,5-bis(diphenylphosphoryl)thiophene) and [Eu(hfa)3(dpdedt)], (dpdedt: 3,4-bis(diphenylphosphoryl)ethylenedioxythiophene), are also prepared for comparison of TL and PL properties.[11]

The relationships between coordination structures and TL activities are evaluated using single crystal X-ray analyses and TL observations. A large spectral difference between TL and PL is confirmed in TbIII/EuIII mixed polymers using a charge coupled detector (CCD) system (see supporting information Figure S1). The excitation processes in TL and PL are proposed on the basis of photo science.

[a] Y. Hirai
Graduate School of Chemical Sciences and Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido, 060-8628, Japan

[b] Dr. T. Nakanishi, Dr. Y. Kitagawa, Dr. K. Fushimi, Dr. T. Seki, Prof. Dr. H. Ito, Prof. Dr. Y. Hasegawa
Faculty of Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Sapporo, Hokkaido, 060-8628, Japan
E-mail: hasegaway@eng.hokudai.ac.jp

Supporting information for this article is given via a link at the end of the document.
The crystal structure of $[\text{Eu(hfa)}_3(\text{dpf})]_n$ is shown in Figure 2a. The Eu$^{III}$ ions are coordinated to eight oxygen atoms from three hfa ligands and two bridging ligands. The geometrical symmetry around Eu$^{III}$ ions was determined to be an 8-coordinated square-antiprismatic structure (point group: $D_{4d}$) without an inversion center (see supporting information for details). Multiple intermolecular CH/F and intramolecular CH/π interactions were identified within the distances of 3.0 Å for $[\text{Eu(hfa)}_3(\text{dpf})]_n$ (Figure 2b). On the other hand, intermolecular CH/π interactions, which usually contribute to tight packing structures, were not observed. Previously reported Ln$^{III}$ coordination polymers with tight-packing structures exhibit intermolecular CH/π interactions.$^{[12]}$ The relatively weak intermolecular interactions of $[\text{Eu(hfa)}_3(\text{dpf})]_n$ were attributed to the twisted structure of single polymer chains.

Eu$^{III}$ coordination polymers linked with polar bridges tend to cancel out the dipole moment by giving a twist to single polymer chains. Coordination polymers with relatively small polar bridges balance the dipoles by intermolecular alternate arrangement. The twisted polymer backbones with disorderly-arranged CF$_3$ substituents in $[\text{Eu(hfa)}_3(\text{dpf})]_n$ might be due to the largest ground state dipole moment of dpf among the three bridging ligands ($D_\text{dip}: 5.80 > D_\text{dpedot}: 4.30 > D_\text{dpt}: 1.17$ D). The small furyl core also prevented the polymer chains from forming highly ordered packing structures, resulting in the absence of intermolecular CH/π interactions. Therefore, the novel furan-based bridging ligand with a large D value and a small aromatic core well contribute to the formation of a disordered face-to-face arrangement of CF$_3$ substituents in the crystal packing system, leading to a mechanically or a thermodynamically unstable structure.

The ability for generation of TL was ascertained by observing Eu$^{III}$-characteristic red emission upon grinding of solid Eu$^{III}$ coordination polymers (Figure 3a-c). The corresponding space fill models focused on crystal packing structures are also shown in Figure 3d-f. We observed slight red TL of $[\text{Eu(hfa)}_3(\text{dpt})]_n$ under dark, which exhibited a highly ordered arrangement to form a thermodynamically stable structure. The TL activity was clearly high in $[\text{Eu(hfa)}_3(\text{dpf})]_n$ and $[\text{Eu(hfa)}_3(\text{dpedot})]_n$, qualitatively, and their red TL can be observed even under daylight. TL intensities of $[\text{Eu(hfa)}_3(\text{dpf})]_n$ and $[\text{Eu(hfa)}_3(\text{dpedot})]_n$ were estimated to be approximately 50 times larger than those of $[\text{Eu(hfa)}_3(\text{dpt})]_n$. These observations indicate that the ability to generate TL strongly depends on the proportion of face-to-face CF$_3$ arrangement in crystal packing structures, since the TL is a fracture-induced phenomenon. Eliseeva and co-workers also demonstrated strong TL of an Eu$^{III}$ coordination polymer $[\text{Eu(hfa)}_3(\text{acetbz})]_n$ (hfa: hexafluoroacetylacetonate, acetbz: 1,4-diace toxybenzene) with similar arrangement of CF$_3$ groups between single polymer chains.$^{[10a]}$
transitions of 5D0 → 650 nm, corresponding to 4f-4f transitions of 5D4
ligands were responsible for the large band (Figure S5) generated by the stabilized energy level of hfa.

Φquantum yield (information) were carried out. The emission bands observed at 578, 591, 613, 650, and 698 nm were assigned to be 4f→4f transitions of Tb III ions (Figure 4, red line). Based on emission lifetime measurements and calculations, photophysical parameters were compared with those of previously reported coordination polymers (Table S2). The overall emission quantum yield excited by π→π* bands of hfa ligands (Φexc = 64%) and energy transfer efficiency (ηtrans = 88%) of [Eu(hfa)3(dpfl)]n were higher than those of previously reported solid-state EuIII coordination polymers.[11] The intrinsic emission quantum yield (Φr = 73%) was comparable to the previous compounds. The enhanced radiative rate constant (κr = 1.0 × 107 s−1) in [Eu(hfa)3(dpfl)]n was due to the polar character of bridging ligands and asymmetric coordination geometry without an inversion center around EuIII ions. The lower-lying absorption band (Figure S5) generated by the stabilized energy level of hfa ligands were responsible for the large Φabs and ηtrans values as reported for [Eu(hfa)3(dptl)]n.[11] [Tb(hfa)3(dpfl)]n also exhibited strong green PL with emission bands at 490, 540, 580, 620, and 650 nm, corresponding to 4f→4f transitions of 5D4 → 7FJ (J = 6, 5, 4, 3, 2) in TbIII ions (Figure 4, green line). The intrinsic emission quantum yield (Φe) and ηtrans values were found to be 88% and 45%, respectively. The relatively low ηtrans value was due to the energy back transfer (BET) from the emissive level of TbIII ions to the excited triplet state of hfa ligands.[13] Under the condition of grinding, [Eu(hfa)3(dpfl)]n, [Tb(hfa)3(dpfl)]n, and [Tb(hfa)3(dpfl)]n, exhibited strong red and green TL, respectively (see supporting information Figure S6 for TL and PL spectra of [Tb(hfa)3(dpfl)]n). When the same excitation process in TL and PL is assumed, the emission colors of TbIII/EuIII mixed coordination polymers should be the same under grinding and under UV irradiation. Thus, TbIII/EuIII mixed coordination polymers were prepared for understanding the relationships between TL and PL properties. We here considered that the dpf ligand is suitable for, since both [Tb(hfa)3(dpfl)]n and [Eu(hfa)3(dpfl)]n, exhibited strong TL and PL with isomorphic crystal structures (Table S3).

[Tb,Eu(hfa)3(dpfl)]n (Tb/Eu = 1) was selected to compare the TL and PL efficiencies of TbIII and EuIII ions under existence of same amount of emission centers. PL colors from TbIII/EuIII mixed hfa compounds are generally dominated by EuIII-centered emission.[14] For this reason, we also selected [Tb,Eu(hfa)3(dpfl)]n (Tb/Eu = 10) to tune TbIII- and EuIII-PL intensity to the same extent. The coordination polymers [Tb,Eu(hfa)3(dpfl)]n (Tb/Eu = 1, 10) were successfully prepared, and the obtained compounds exhibited strong TL and PL under UV irradiation and grinding. The TL and PL spectra were independently recorded using CCD system. The emission intensity of EuIII ions is larger than that of TbIII ions in the Tb/Eu = 1 compound under UV irradiation, resulting in reddish-orange PL. The PL colors of TbIII/EuIII mixed coordination polymers are dominated by EuIII-centered emission, since the TbIII-centered emission is affected by both the BET process and excitation energy transfer from TbIII to EuIII ions at room temperature.[14]

Interestingly, the observed TL colors were clearly different from those of PL. The Tb/Eu = 1 compound exhibited yellow TL and reddish-orange PL (Figure 5a), while the Tb/Eu = 10 compound exhibited green TL and greenish-yellow PL (Figure 5b). These spectral differences between TL and PL were the most remarkable among previously reported TL- and PL-active compounds. The TL colors of these coordination polymers might not be explained by the simple excitation mechanisms in PL. Since the TL colors correspond to the Tb/Eu mixture ratios, TL would be dominated by direct excitation of LnIII ions; though, the...
possibility of antenna ligand (hfa)-mediated emission cannot be ruled out. The hfa-centered blue TL and PL of [Gd(hfa)3(dpf)], were also observed in the range from 450 to 550 nm with identical spectral shapes (Figure S7), indicating the formation of excited states of hfa ligands under grinding. In the case of [Ln(hfa)3(dpdt)], (Ln = Tb, Eu), hfa-centered emission is quenched through efficient ligand-to-Ln(III) energy transfer, resulting in intense Ln(III)-centered emission.

The excitation process of TL in LnIII complexes has been basically discussed by ligand-excitation or direct LnIII-excitation. Sweeting and Rheingold reported that the charge separation upon cleavage excited the antenna ligands, followed by the formation of LnIII excited states via intramolecular energy transfer (ligand-excitation). Bourhill and co-workers also described LnIII excitation by electron bombardment (direct LnIII-excitation). TL phenomenon is based on an electric origin, which might be understood by comparison of electroluminescence (EL) spectra of the compounds (see supporting information, optical measurements).

In this study, we observed a large spectral difference between TL and PL. The contribution of TbIII-centered emission is larger than that of EuIII-centered emission in TL, in contrast to PL. According to the results, we consider the TL of LnIII coordination compounds to be responsible for both the ligand-excitation and direct LnIII-excitation (Figure 5c), unlike the selective excitation with a specific wavelength (e.g., λex = 380 nm) in PL. The photophysical parameters in Table 1 and Table S2 also indicate that the efficiency of direct LnIII-excitation is higher than that of ligand-excitation under the condition of mechanical grinding. Thus, the reddish-orange PL and yellow TL of [Tb,Eu(hfa)3(dpf)], (Tb/Eu = 1) can be explained by the higher Φff of TbIII ions (Φff,Tb = 88%) than that of EuIII ions (Φff,Eu = 73%). The greenish-yellow PL and green TL in the Tb/Eu = 10 polymer can also be explained by this difference. When considered in the same manner, the TbIII/EuIII mixed coordination polymers [Tb,Eu(hfa)3(X)], (Tb/Eu = 1, Φff,Tb < Φff,Eu) with yellow PL would exhibit orange or red TL. TbIII-to-EuIII energy transfer efficiencies are dependent on the TbIII/EuIII mixture ratios, coordination structures, and electronic structures of bridging ligands. We here assume that TbIII-to-EuIII energy transfer occurs in both TL and PL with same efficiency, and is not responsible for the drastic color change between TL and PL.

Figure 5. Normalized TL and PL spectra and pictures of a) [Tb,Eu(hfa)3(dpf)], (Tb/Eu = 1) and b) [Tb,Eu(hfa)3(dpf)], (Tb/Eu = 10). c) A simplified diagram of excitation processes of TL (orange line) and PL (blue line) in TbIII/EuIII mixed coordination polymers (Abs: absorption, ET: energy transfer, GS, ground state, 1S: singlet excited state, 3T: triplet excited state, ISC: intersystem crossing, NR: non-radiative relaxation).

Table 1. Summary of TL and PL properties of furan-bridged polymers [Ln(hfa)3(dpdt)], (Ln = Eu, Tb, Tb/Eu).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Φff,Eu</th>
<th>Φff,Tb</th>
<th>ηNR</th>
<th>τobs,RT</th>
<th>τobs,100 K</th>
<th>PL color</th>
<th>TL color</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Eu(hfa)3(dpdt)]</td>
<td>64</td>
<td>40</td>
<td>88</td>
<td>0.72</td>
<td>0.60</td>
<td>Green</td>
<td>Green</td>
</tr>
<tr>
<td>[Tb(hfa)3(dpdt)], (Tb/Eu = 1)</td>
<td>40</td>
<td>89</td>
<td>45</td>
<td>0.32</td>
<td>(τTb)</td>
<td>Reddish-orange</td>
<td>Yellow</td>
</tr>
<tr>
<td>[Tb,Eu(hfa)3(dpdt)], (Tb/Eu = 1)</td>
<td>40</td>
<td>88</td>
<td>45</td>
<td>0.36</td>
<td>(τEu)</td>
<td>Greenish-yellow</td>
<td>Green</td>
</tr>
</tbody>
</table>

[a] Λex = 380 nm. [b] Equations 2-4 in supporting information. [c] ηNR was determined by fitting analyses of emission decay profiles (Figure S8). [d] Φff for TbIII complex was estimated by Φff,Tb = (Iobs,RT / Iobs,100 K) × 100, assuming that the τobs at 100 K is a lifetime without non-radiative process.

In conclusion, highly TL-active and strong PL LnIII coordination polymers were successfully prepared by introducing a furan-based polar bridging ligand. The relationships between crystal structures and TL activity were systematically studied using EuIII coordination polymers [Eu(hfa)3(dpdt)], [Eu(hfa)3(dpdedot)], and [Eu(hfa)3(dpdt)], with face-to-face/alternate intermolecular packing structures. The face-to-face arrangement of bulky substituents of the ligands plays an important role in providing strong TL activity. The potential differences between TL and PL were clearly demonstrated by the TL and PL spectra of TbIII/EuIII mixed coordination polymers for the first time. Based on our observations, we suggested the existence of discrete excitation mechanisms for TL and PL phenomena.
The strategy for constructing strong TL-active compounds would be a key to reveal the ambiguous relationships between luminescence and mechanical stress. These compounds with TbIII and EuIII ions in particular are also expected to be useful as optical sensors in the field of fluid dynamics and aeronautical engineering, being sensitive to impact, pressure, and temperature to visualize damage and fluid flow on material's surfaces. In addition, compounds with varied emission colors depending on mechanical stress and photo-irradiation are highly attractive as advanced security materials for future identification cards. The results of this work should lead to an understanding of triboluminescence, which has long been a puzzling phenomenon in the field of natural science. We are now trying to carry out more precise and quantitative experiments to get more insight into the mechanisms of triboluminescence.

Acknowledgements

We appreciate RIGAKU Co., Application Laboratories and Frontier Chemistry Center Akira Suzuki "Laboratories for Future Creation” Project. This work was partly supported by Grants-in-Aid for Scientific Research on Innovative Areas of "New Polymeric Materials Based on Element-Blocks (no. 2401)" (no. 24102012) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. We also thank the Frontier Chemistry Center Akira Suzuki ‘Laboratories for Future Creation’ Project for their support.

Keywords: europium • terbium • coordination polymer • triboluminescence • photoluminescence


COMMUNICATION

Entry for the Table of Contents

Layout 1:

COMMUNICATION

Lanthanide coordination polymers with strong tribo- and photoluminescence properties were successfully fabricated by introducing face-to-face arrangement of substituents between single polymer chains. These compounds exhibited large spectral differences upon grinding and UV irradiation.

Yuichi Hirai, Takayuki Nakanishi, Yuichi Kitagawa, Koji Fushimi, Tomohiro Seki, Hajime Ito, Yasuchika Hasegawa*

Page No. – Page No.

Triboluminescence of Lanthanide Coordination Polymers with Face-to-Face Arranged Substituents