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

Yuichi Hirai,[a] Takayuki Nakanishi,[b] Yuichi Kitagawa,[b] Koji Fushimi,[b] Tomohiro Seki,[b] Hajime Ito,[b] Yasuchika Hasegawa*[b]

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 lanthanide^{III} coordination polymers with efficient TL and PL properties. They are composed of emission centers (Tb^{III} and Eu^{III} 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 Tb^{III}/Eu^{III}-mixed coordination polymers $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 1). The results directly indicate the discrete excitation processes of PL and TL.

Luminescence upon grinding solid materials is called triboluminescence (TL). In the 17th century, it was first noted by Francis Bacon that: “It is well known that all sugar, whether candied or plain, if it be hard, will sparkle when broken or scraped in the dark.” TL materials, unlike well-known photoluminescence (PL) materials, have the advantage of emission without a light source. The fracture-induced luminescence properties of TL materials make them attractive for applications as structural damage sensors, pressure sensors, and advanced security marking techniques.[1]

TL phenomena have been widely found in inorganic and organic compounds,[2] and about half of all crystalline materials are predicted to show TL.[3] Wang demonstrated yellow-to-red TL of CaZnOS:Mn^{II} depending on the concentration of Mn^{II} ions.[4] Yamashita and co-workers reported blue TL of trifluoromethyl and pentafluoromethyl-substituted imide derivatives under daylight.[5] Coordination compounds including Cu^{I}, Pt^{II}, Mn^{II}, and lanthanide^{III} (Ln^{III}) ions have also been reported for their TL properties.[6] These TL-active compounds are known to show PL as well. TL and PL occur from distinct stimuli such as grinding and photo-irradiation; however, their spectra usually exhibit similar profiles. Relationships between TL and PL are still being discussed from a scientific point of view. In order to provide new insights into TL phenomena, we herein select Ln^{III} complexes with efficient TL and PL properties because of their high spectral resolution arising from intraconfigurational 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-pentafluoro-pentane-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 Ln^{III} complexes. Sweeting and Rheingold reported that the disorder of phenyl rings and cations in $[Eu(dbm)_4]^-$ $[Et_3NH]^+$ (dbm: dibenzoylmethanato) provided a sufficient source of localized polarity to induce TL activity.[9] Chen reported that the disorder of thienyl and trifluoromethyl (CF_3) groups in Eu^{III} 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 Ln^{III} coordination polymers based on β-diketonato and aromatic bridging ligands.[10]

We consider that strong TL Ln^{III} coordination polymers can be systematically constructed by introducing disordered arrangement of substituents between single polymer chains in the solid state. Novel Ln^{III} coordination polymers composed of Ln^{III} ions, hfa, and furan-based bridging ligands (2,5-bis(diphenylphosphoryl)furan: dpf) are introduced to provide the disordered face-to-face arrangement of CF_3 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, $[Eu(hfa)_3(dpt)]_n$ (dpt: 2,5-bis(diphenylphosphoryl)thiophene) and $[Eu(hfa)_3(dpedot)]_n$ (dpedot: 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 Tb^{III}/Eu^{III} 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.

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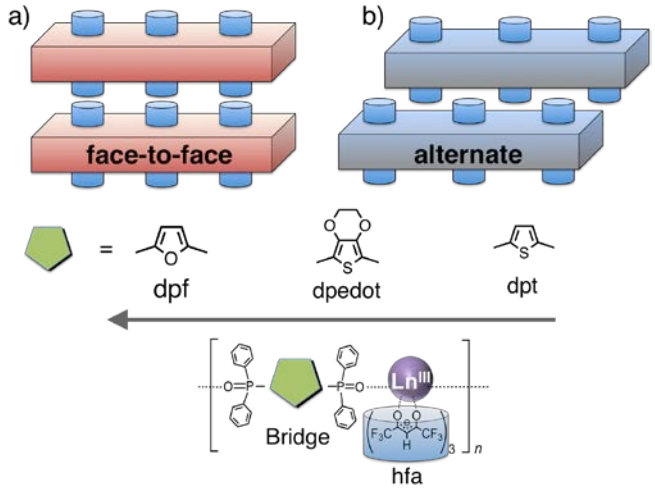

Figure 1. Schematic representation of Ln^{III} coordination polymers with a) face-to-face and b) alternate intermolecular packing structures.

The crystal structure of $[Eu(hfa)_3(dpf)]_n$ 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 $[Eu(hfa)_3(dpf)]_n$ (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 $[Eu(hfa)_3(dpf)]_n$ 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 $[Eu(hfa)_3(dpf)]_n$ might be due to the largest ground state dipole moment of dpf among the three bridging ligands (D_{dpf}: 5.80 > D_{dpedot}: 4.30 > D_{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.

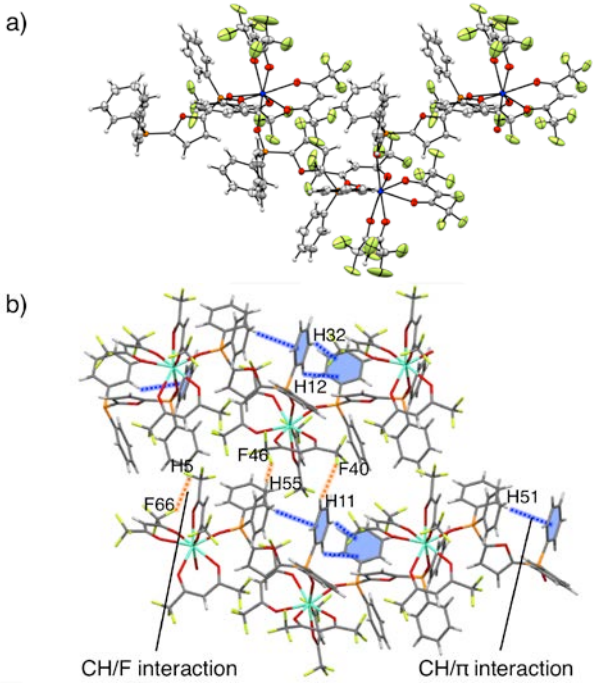

Figure 2. a) ORTEP drawing (showing 50% probability displacement ellipsoids) of single polymer chain and b) crystal packing structure focused on intra and intermolecular interactions of $[Eu(hfa)_3(dpf)]_n$.

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 $[Eu(hfa)_3(dpt)]_n$ under dark, which exhibited a highly ordered arrangement to form a thermodynamically stable structure. The TL activity was clearly high in $[Eu(hfa)_3(dpf)]_n$ and $[Eu(hfa)_3(dpedot)]_n$, qualitatively, and their red TL can be observed even under daylight. TL intensities of $[Eu(hfa)_3(dpf)]_n$ and $[Eu(hfa)_3(dpedot)]_n$ were estimated to be approximately 50 times larger than those of $[Eu(hfa)_3(dpt)]_n$. 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 $[Eu(hfa)_3(acetbz)]_n$ (hfa: hexafluoroacetylacetonate, acetbz: 1,4-diacetoxybenzene) with similar arrangement of CF_3 groups between single polymer chains.[10a]

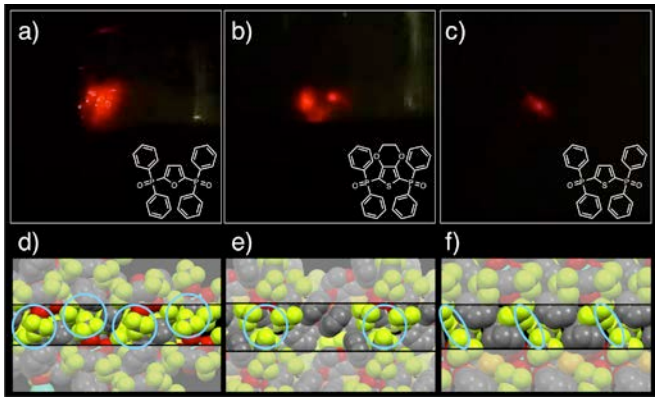

Figure 3. a-c) Pictures of TL and chemical structures of bridging ligands, and d-f) corresponding space filling models focused on intermolecular CF_3 arrangement in $[Eu(hfa)_3(dpf)]_n$, $[Eu(hfa)_3(dpedot)]_n$, and $[Eu(hfa)_3(dpt)]_n$.

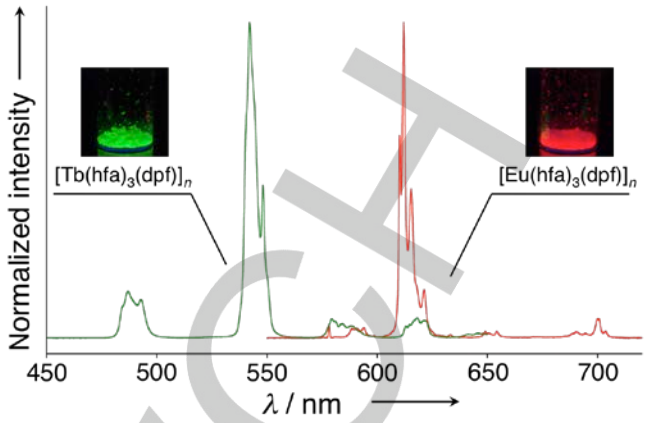

Figure 4. Emission spectra of $[Tb(hfa)_3(dpf)]_n$ (green line) and $[Eu(hfa)_3(dpf)]_n$ (red line) in solid state (λ_{ex} = 380 nm).

$[Eu(hfa)_3(dpf)]_n$ also exhibited strong PL under UV irradiation in solid state (λ_{ex} = 380 nm). In order to evaluate the PL performance of $[Eu(hfa)_3(dpf)]_n$, PL measurements and calculations of photophysical parameters (eq. 2-4 in supporting information) were carried out. The emission bands observed at 578, 591, 613, 650, and 698 nm were assigned to be 4f-4f transitions of $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) in Eu^{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 (Φ_{tot} = 64%) and energy transfer efficiency (η_{sens} = 88%) of $[Eu(hfa)_3(dpf)]_n$ were higher than those of previously reported solid-state Eu^{III} coordination polymers.[11] The intrinsic emission quantum yield (Φ_{ff} = 73%) was comparable to the previous compounds. The enhanced radiative rate constant (k_r = 1.0 × 10^3 s^{-1}) in $[Eu(hfa)_3(dpf)]_n$ was due to the polar character of bridging ligands and asymmetric coordination geometry without an inversion center around Eu^{III} ions. The lower-lying absorption band (Figure S5) generated by the stabilized energy level of hfa ligands were responsible for the large Φ_{tot} and η_{sens} values as reported for $[Eu(hfa)_3(dpt)]_n$.[11] $[Tb(hfa)_3(dpf)]_n$ also exhibited strong green PL with emission bands at 490, 540, 580, 620, and 650 nm, corresponding to 4f-4f transitions of $^5D_4 \rightarrow {}^7F_J$ (J = 6, 5, 4, 3, 2) in Tb^{III} ions (Figure 4, green line). The intrinsic emission quantum yield (Φ_{ff}) and η_{sens} values were found to be 88% and 45%, respectively. The relatively low η_{sens} value was due to the energy back transfer (BET) from the emissive level of Tb^{III} ions to the excited triplet state of hfa ligands.[13]

Under the condition of grinding, $[Eu(hfa)_3(dpf)]_n$ and $[Tb(hfa)_3(dpf)]_n$ exhibited strong red and green TL, respectively (see supporting information Figure S6 for TL and PL spectra of $[Tb(hfa)_3(dpf)]_n$). When the same excitation process in TL and PL is assumed, the emission colors of Tb^{III}/Eu^{III} mixed coordination polymers should be the same under grinding and under UV irradiation. Thus, Tb^{III}/Eu^{III} 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 $[Tb(hfa)_3(dpf)]_n$ and $[Eu(hfa)_3(dpf)]_n$ exhibited strong TL and PL with isomorphic crystal structures (Table S3).

$[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 1) was selected to compare the TL and PL efficiencies of Tb^{III} and Eu^{III} ions under existence of same amount of emission centers. PL colors from Tb^{III}/Eu^{III} mixed hfa compounds are generally dominated by Eu^{III}-centered emission.[14] For this reason, we also selected $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 10) to tune Tb^{III}- and Eu^{III}-PL intensity to the same extent. The coordination polymers $[Tb,Eu(hfa)_3(dpf)]_n$ (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 Eu^{III} ions is larger than that of Tb^{III} ions in the Tb/Eu = 1 compound under UV irradiation, resulting in reddish-orange PL. The PL colors of Tb^{III}/Eu^{III} mixed coordination polymers are dominated by Eu^{III}-centered emission, since the Tb^{III}-centered emission is affected by both the BET process and excitation energy transfer from Tb^{III} to Eu^{III} 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 Ln^{III} ions; though, the

possibility of antenna ligand (hfa)-mediated emission cannot be ruled out. The hfa-centered blue TL and PL of $[Gd(hfa)_3(dpf)]_n$ 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 $[Ln(hfa)_3(dpf)]_n$ (Ln = Tb, Eu), hfa-centered emission is quenched through efficient ligand-to-Ln(III) energy transfer, resulting in intense Ln(III)-centered emission.

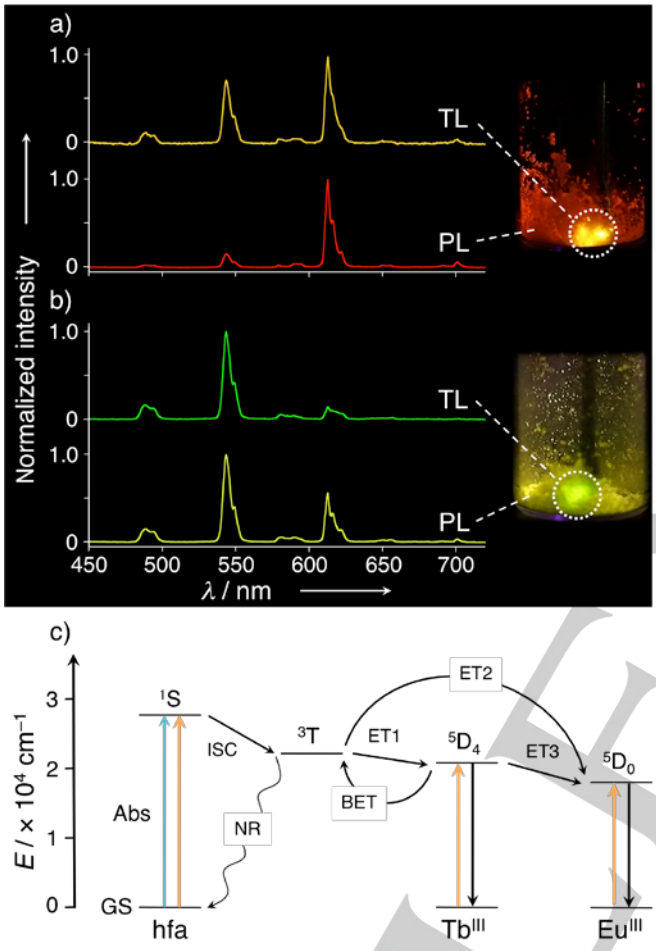

Figure 5. Normalized TL and PL spectra and pictures of a) $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 1) and b) $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 10). c) A simplified diagram of excitation processes of TL (orange line) and PL (blue line) in Tb^{III}/Eu^{III} mixed coordination polymers (Abs: absorption, ET: energy transfer, GS, ground state, ^{1}S: singlet excited state, ^{3}T: triplet excited state, ISC: intersystem crossing, NR: non-radiative relaxation).

The excitation process of TL in Ln^{III} complexes has been basically discussed by ligand-excitation or direct Ln^{III}-excitation. Sweeting and Rheingold reported that the charge separation upon cleavage excited the antenna ligands, followed by the formation of Ln^{III} excited states via intramolecular energy transfer (ligand-excitation).[9] Bourhill and co-workers also described Ln^{III} excitation by electron bombardment (direct Ln^{III}-excitation).[15] 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 Tb^{III}-centered emission is larger than that of Eu^{III}-centered emission in TL, in contrast to PL. According to the results, we consider the TL of Ln^{III} coordination compounds to be responsible for both the ligand-excitation and direct Ln^{III}-excitation (Figure 5c), unlike the selective excitation with a specific wavelength (e.g., λ_{ex} = 380 nm) in PL. The photophysical parameters in Table 1 and Table S2 also indicate that the efficiency of direct Ln^{III}-excitation is higher than that of ligand-excitation under the condition of mechanical grinding. Thus, the reddish-orange PL and yellow TL of $[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 1) can be explained by the higher Φ_{ff} of Tb^{III} ions ($\Phi_{ff,Tb}$ = 88%) than that of Eu^{III} ions ($\Phi_{ff,Eu}$ = 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 Tb^{III}/Eu^{III} mixed coordination polymers $[Tb,Eu(hfa)_3(X)]_n$ (Tb/Eu = 1, $\Phi_{ff,Tb} < \Phi_{ff,Eu}$) with yellow PL would exhibit orange or red TL. Tb^{III}-to-Eu^{III} energy transfer efficiencies are dependent on the Tb^{III}/Eu^{III} mixture ratios, coordination structures, and electronic structures of bridging ligands.[14c] We here assume that Tb^{III}-to-Eu^{III} energy transfer occurs in both TL and PL with same efficiency, and is not responsible for the drastic color change between TL and PL.

Table 1. Summary of TL and PL properties of furan-bridged polymers $[Ln(hfa)_3(dpf)]_n$ (Ln = Eu, Tb, Tb/Eu).

Sample	Φ_{tot}[a] / %	Φ_{ff}[b] / %	η_{sens} / %	τ_{obs}[c] / ms	PL color	TL color
$[Eu(hfa)_3(dpf)]_n$	64	73	88	0.72	Red	Red
$[Tb(hfa)_3(dpf)]_n$	40	88[d]	45	0.60	Green	Green
$[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 1)	-	-	-	0.32 (τ_{Tb})	Reddish-orange	Yellow
$[Tb,Eu(hfa)_3(dpf)]_n$ (Tb/Eu = 10)	-	-	-	0.36 (τ_{Tb})	Greenish-yellow	Green

[a] λ_{ex} = 380 nm. [b] Equations 2-4 in supporting information. [c] λ_{ex} = 355 nm. τ_{Tb} was determined by fitting analyses of emission decay profiles (Figure S8). [d] Φ_{ff} for Tb^{III} complex was estimated by $\Phi_{ff,Tb}$ = ($\tau_{obs,RT}$ / $\tau_{obs,100\ K}$) × 100, assuming that the τ_{obs} at 100 K is a lifetime without non-radiative process.

In conclusion, highly TL-active and strong PL Ln^{III} 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 Eu^{III} coordination polymers $[Eu(hfa)_3(dpf)]_n$, $[Eu(hfa)_3(dpedot)]_n$, and $[Eu(hfa)_3(dpt)]_n$ 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 Tb^{III}/Eu^{III} 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 Tb^{III} and Eu^{III} 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.

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

[1] a) D. O. Olawale, T. Dickens, W. G. Sullivan, O. I. Okoli, J. O. Sobanjo, B. Wang, *J. Lumin.* **2011**, *131*, 1407-1418; b) X. D. Wang, H. L. Zhang, R. M. Yu, L. Dong, D. F. Peng, A. H. Zhang, Y. Zhang, H. Liu, C. F. Pan, Z. L. Wang, *Adv. Mater.* **2015**, *27*, 2324-2331; c) D. O. Olawale, K. Kliewer, A. Okoye, T. J. Dickens, M. J. Uddin, O. I. Okoli, *J. Lumin.* **2014**, *147*, 235-241; d) R. S. Fontenot, W. A. Hollerman, K. N. Bhat, M. D. Aggarwal, B. G. Penn, *Polym. J.* **2014**, *46*, 111-116.

[2] a) G. P. Williams, T. J. Turner, *Solid State Commun.* **1979**, *29*, 201-203; b) J. I. Zink, *Inorg. Chem.* **1975**, *14*, 555-558; c) J. I. Zink, G. E. Hardy, J. E. Sutton, *J. Phys. Chem.* **1976**, *80*, 248-249; d) G. E. Hardy, J. C. Baldwin, J. I. Zink, W. C. Kaska, P.-H. Liu, L. Dubois, *J. Am. Chem. Soc.* **1977**, *99*, 3552-3558; e) K. F. Wang, L. R. Ma, X. F. Xu, S. Z. Wen, J. B. Luo, *Sci. Rep.* **2016**, *6*, 1-9.

[3] A. J. Walton, *Adv. Phys.* **1977**, *26*, 887-948.

[4] J.-C. Zhang, L.-Z. Zhao, Y.-Z. Long, H.-D. Zhang, B. Sun, W.-P. Han, X. Yan, X. Wang, *Chem. Mater.* **2015**, *27*, 7481-7489.

[5] a) H. Nakayama, J.-i. Nishida, N. Takada, H. Sato, Y. Yamashita, *Chem. Mater.* **2012**, *24*, 671-676; b) J.-i. Nishida, H. Ohura, Y. Kita, H. Hasegawa, T. Kawase, N. Takada, H. Sato, Y. Sei, Y. Yamashita, *J. Org. Chem.* **2016**, *81*, 433-441.

[6] a) F. Marchetti, C. Di Nicola, R. Pettinari, I. Timokhin, C. Pettinari, *J. Chem. Educ.* **2012**, *89*, 652-655; b) C.-W. Hsu, K. T. Ly, W.-K. Lee, C.-C. Wu, L.-C. Wu, J.-J. Lee, T.-C. Lin, S.-H. Liu, P.-T. Chou, G.-H. Lee, Y. Chi, *ACS Appl. Mater. Inter.* **2016**, *8*, 33888-33898; c) J. Chen, Q. Zhang, F.-K. Zheng, Z.-F. Liu, S.-H. Wang, A. Q. Wu, G.-C. Guo, *Dalton Trans.* **2015**, *44*, 3289-3294; d) X.-F. Chen, X.-H. Zhu, Y.-H. Xu, S. Shanmuga Sundara Raj, S. Ozturk, H.-K. Fun, J. Ma, X.-Z. You, *J. Mater. Chem.* **1999**, *9*, 2919-2922; e) J. P. Duignan, I. D. H. Oswald, I. C. Sage, L. M. Sweeting, K. Tanaka, T. Ishihara, K. Hirao, G. Bourhill, *J. Lumin.* **2002**, *97*, 115-126.

[7] a) S. V. Eliseeva, J.-C. G. Bünzli, *Chem. Soc. Rev.* **2010**, *39*, 189-227; b) J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048-1077; c) K. Binnemans, *Chem. Rev.* **2009**, *109*, 4283-4374; d) S. J. Butler, D. Parker, *Chem. Soc. Rev.* **2013**, *42*, 1652-1666; e) S. Petoud, G. Muller, E. G. Moore, J. Xu, J. Sokolnicki, J. P. Riehl, U. N. Le, S. M. Cohen, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 77-83; f) S. Petoud, S. M. Cohen, J.-C. G. Bünzli, K. N. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324-13325.

[8] T.M. George, M.J. Sajan, N. Gopakumar, M.L.P. Reddy, *J. Photochem. Photobiol. A: Chem.* **2016**, *317*, 88-99.

[9] L. M. Sweeting, A. L. Rheingold, *J. Am. Chem. Soc.* **1987**, *109*, 2652-2658.

[10] a) S. V. Eliseeva, D. N. Pleshkov, K. A. Lyssenko, L. S. Lepnev, J.-C. G. Bünzli, N. P. Kuzmina, *Inorg. Chem.* **2010**, *49*, 9300-9311; b) Y. Hasegawa, R. Hieda, K. Miyata, T. Nakagawa, T. Kawai, *Eur. J. Inorg. Chem.* **2011**, 4978-4984.

[11] Y. Hirai, T. Nakanishi, Y. Kitagawa, K. Fushimi, T. Seki, H. Ito, Y. Hasegawa, *Angew. Chem. Int. Ed.* **2016**, *55*, 12059-12062.

[12] K. Miyata, T. Ohba, A. Kobayashi, M. Kato, T. Nakanishi, K. Fushimi, Y. Hasegawa, *ChemPlusChem* **2012**, *77*, 277-280.

[13] S. Katagiri, Y. Hasegawa, Y. Wada, S. Yanagida, *Chem. Lett.* **2004**, *33*, 1438-1439

[14] a) K. Miyata, Y. Konno, T. Nakanishi, A. Kobayashi, M. Kato, K. Fushimi, Y. Hasegawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 6413-6416; b) Y. Hirai, T. Nakanishi, K. Miyata, K. Fushimi, Y. Hasegawa, *Mater. Lett.* **2014**, *130*, 91-93; c) M. Hatanaka, Y. Hirai, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Morokuma, *Chem. Sci.* **2017**, *8*, 423-429.

[15] I. Sage, G. Bourhill, *J. Mater. Chem.* **2001**, *11*, 231-245.

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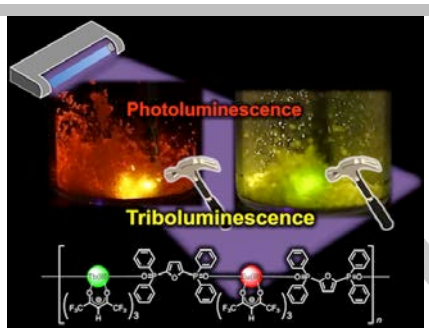
Layout 1:

COMMUNICATION

Lanthanide coordination polymers with strong tribo- and photo-luminescence 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.



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

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