

Luminescence from lanthanide(III)-mixed coordination polymers upon mechanical-grinding and photo-irradiation

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Luminescence upon grinding solid materials (triboluminescence: TL) has long been a puzzling phenomenon. TL materials, unlike photoluminescence (PL) materials, have the advantage of emission without a light source. TL has been observed in inorganic, organic, and coordination compounds.^[1] These TL-active compounds usually show PL with similar profiles, although they occur from distinct stimuli.^[2] In order to provide new insights into TL, we here select lanthanide(III) (Ln(III)) coordination compounds due to their high spectral resolution arising from 4f-4f transitions.^[3] In this study, Ln(III) coordination polymers composed of Ln(III) ions, hexafluoroacetylacetonato (hfa), and furan-based bridging ligands (2,5-bis(diphenylphosphoryl)furan: dpf) are designed to induce high ligand-to-Ln(III) energy transfer efficiency for strong PL and mechanically unstable structure for strong TL. The reported Ln(III) coordination polymers with thiophene-based bridges (3,4-bis(diphenylphosphoryl)ethylenedioxythiophene: dpedot and 2,5-bis(diphenylphosphoryl)thiophene: dpt) are also prepared for comparison of TL and PL properties.⁴

The bridging ligands (dpf, dpedot, and dpt) were synthesized using α -substitution reaction of hetero(aromatic) compounds starting from 2,5-dibromofuran, 3,4-ethylenedioxythiophene, and 2,5-dibromothiophene, respectively. The corresponding Ln(III) coordination polymers [Ln(hfa)₃(X)]_n (X = dpf: **1**, dpedot: **2**, dpt: **3**) were prepared by refluxing Ln(hfa)₃(H₂O)₂ and bridging ligands in methanol.

The ability for generation of TL was ascertained by observing Eu(III)-characteristic red emission upon grinding solid Eu(III) coordination polymers. We observed quite weak TL for **3**, which exhibited an intermolecular alternate arrangement of CF₃ groups to form a mechanically stable structure. The TL activity was clearly high in **1** and **2** with face-to-face CF₃ arrangement between single polymer chains. These observations indicate that the TL-activity strongly depends on the arrangement of bulky CF₃ groups in crystal packing structures.

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 UV irradiation. We thus prepared [Tb,Eu(hfa)₃(dpf)]_n (Tb/Eu = 1, 10), and the obtained compounds exhibited strong TL and PL.

PL colors are dominated by Eu(III)-centered emission under UV irradiation, since the Tb(III)-centered emission is quenched by both energy back transfer from Tb(III) ions to hfa ligands and excitation energy transfer from Tb(III) to Eu(III) ions at room temperature. On

the contrary to PL, the observed TL colors were dominated by Tb(III)-centered emission (Table 1). The large TL/PL spectral differences were independently recorded using CCD system. We here considered the TL of Ln(III) coordination compounds to be responsible for both the ligand-excitation and direct Ln(III)-excitation, unlike photo-excitation with specific wavelength in PL.

Table 1. TL and PL ($\lambda_{\text{ex}} = 365 \text{ nm}$) colors of Tb(III)/Eu(III) mixed coordination polymers $[\text{Ln}(\text{hfa})_3(\text{dpf})]_n$ in solid state.

Sample	PL color	TL color
$[\text{Tb}(\text{hfa})_3(\text{dpf})]_n$	Green	Green
$[\text{Tb},\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ (Tb/Eu = 1)	Reddish-orange	Yellow
$[\text{Tb},\text{Eu}(\text{hfa})_3(\text{dpf})]_n$ (Tb/Eu = 10)	Greenish-yellow	Green
$[\text{Eu}(\text{hfa})_3(\text{dpf})]_n$	Red	Red

In conclusion, strong TL/PL Ln(III) coordination polymers were prepared by introducing a furan-based bridging ligand. The relationships between crystal structures and TL activity were systematically demonstrated using Eu(III) coordination polymers with face-to-face/alternate arrangements of CF_3 substituents between single polymer chains. The intermolecular arrangement of bulky substituents plays an important role in providing efficient TL property. The potential differences between TL and PL were clearly demonstrated by the TL and PL spectra of Tb(III)/Eu(III) mixed coordination polymers. Based on the results, the existence of discrete excitation mechanisms for TL and PL were suggested.

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