

# Luminescence of Lanthanide–Dimethyl Sulfoxide Compound Solutions

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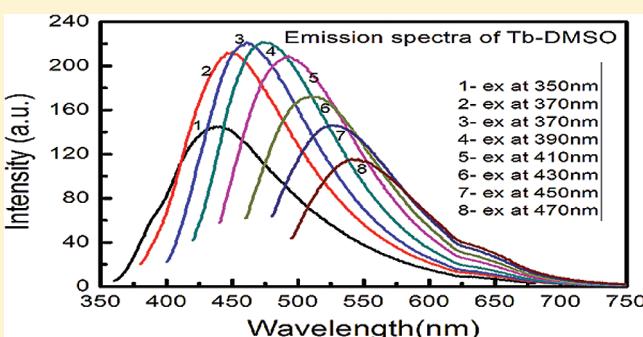
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**ABSTRACT:** Dimethyl sulfoxide (DMSO) has the ability to penetrate living tissues without causing significant damage. Of foremost importance to our understanding of the possible functions of DMSO in biological systems is its ability to replace some of the water molecules associated with the cellular constituents or to affect the structure of the omnipresent water. Luminescence probes have been widely used for biological studies such as labeling, imaging, and detection. Luminescence probes formed in DMSO may find new applications. Here luminescence compounds formed by refluxing lanthanide nitrates of Ce, La, Tb, Yb, Nd, Gd, and Eu in DMSO are reported and their luminescence properties investigated. On the basis of their luminescence spectral properties, the compounds can be classified into four classes. For compounds I with Yb, Ce, and La, the excitation and emission spectra are very broad and their excitation or emission peaks are shifted to longer wavelengths when the monitored emission or excitation wavelength is longer. For compounds II with Gd and Nd, both the excitation and emission spectra are very broad but their emission wavelengths change little at different excitation wavelengths. For Tb–DMSO as compound III, both the typical emissions from the f–f transitions of  $Tb^{3+}$  and a broad emission at 445 nm are observed. At low reaction temperatures, the f–f emissions are dominant, while at high reaction temperatures such as 180 °C, the broad emission at 445 nm is dominant. For compound IV, Eu–DMSO, the dominant emissions are from the f–f transitions of  $Eu^{3+}$  and only a weak broad emission is observed, which is likely from the d–f transition of  $Eu^{2+}$  rather than from metal-to-ligand charge transfer states.



## 1. INTRODUCTION

Luminescence materials have many applications, including solid-state lighting, sensing, biological imaging, and labeling for explosive and radiation detection for homeland security.<sup>1</sup> Lanthanide compounds play a very important role in these areas. Most trivalent lanthanide ions except  $Ce^{3+}$  exhibit sharp emissions derived from the electronic transitions with the 4f shell (f–f transitions).<sup>2</sup> Since the f electrons are greatly shielded, their excitation and emission spectra consist of sharp lines. Because the f–f transitions are not allowed, the absorption coefficients are small, their emission efficiencies are low, and their luminescence lifetimes are quite long.<sup>3</sup> One strategy to improve their luminescence is to functionalize the lanthanide ions with suitable ligands that can absorb light and subsequently transfer the absorbed energy to the lanthanide ions for luminescence.<sup>4</sup> In this way, luminescence can be greatly enhanced, leading to many studies and applications in solid-state lighting,<sup>5,6</sup> optical memory,<sup>7</sup> and biological detection.<sup>8</sup>

Lanthanide–dimethyl sulfoxide (DMSO) compounds may find new and interesting applications due to the unique properties. However, little attention has been paid to luminescent

lanthanide–DMSO compounds.<sup>9,10</sup> DMSO is a clear, colorless to yellow liquid with a characteristic bitter odor and taste. DMSO is soluble in water, ethanol, acetone, diethyl ether, benzene, and chloroform and is a good solvent for unsaturated, nitrogen-containing, and aromatic compounds.<sup>11–13</sup> DMSO has been used widely as a cryoprotective agent for protection of live cells and tissues against freezing damage as well as a cryopreservative in allogous bone marrow and organ transplants.<sup>13</sup> DMSO itself is also a drug which was approved by the FDA in 1970 for the treatment of musculoskeletal disorders in dogs and horses and in 1978 in humans for the therapy of interstitial cystitis, which is a painful disabling urinary bladder inflammation.<sup>14</sup> DMSO has many other clinical properties. It has been used successfully as an adjuvant, for its analgesic properties, in the treatment of pulmonary adenocarcinoma, rheumatologic and dermatologic diseases, and chronic prostatitis, and as a topical analgesic.<sup>11–13</sup> In addition, DMSO has been considered as an alternative treatment

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for cancer.<sup>15</sup> DMSO readily crosses the blood–brain barrier<sup>16</sup> and has anti-inflammatory and reactive oxygen species scavenger actions.<sup>11–13</sup> DMSO has been used for the local treatment of extravasation in chemotherapy,<sup>17</sup> and it can reduce the ulcer size from Adria extravasation and cure necrosis.<sup>18,19</sup> It has been reported that DMSO increases the radio-iodination yield for radiopharmaceuticals.<sup>20</sup> It can be used as an adjunct to tissue expansion for breast reconstruction.<sup>21</sup> In the central nervous system, it has been used in the treatment of traumatic brain edema and schizophrenia and has been suggested for the treatment of Alzheimer's disease.<sup>22</sup> Of foremost importance to our understanding of the possible functions of DMSO in biological systems is its ability to replace some of the water molecules associated with the cellular constituents or to affect the structure of the omnipresent water. It has been reported that DMSO can penetrate the body's membranes of lower animals and man at various concentrations. The process is reversible, and the integrity of most membranes is not affected except at extremely high concentrations of 90–100% employed.<sup>23</sup> This property has been exploited as an indicator or probe to study changes in the barrier properties of human skin in certain disease states such as atopic dermatitis<sup>24</sup> or damage due to exposure of skin to ultraviolet radiation.<sup>25</sup> In addition, DMSO has the ability to enhance the transport of other drugs through the membranes and therefore is a successful drug carrier for disease targeting.<sup>13</sup> DMSO is mutagenic for *Salmonella typhimurium* TA1573 and TA2637 and *Escherichia coli* WP2uvrA in the Ames mutagenicity assay with a preincubation modification.<sup>26</sup> This property and its unique membrane penetration make DMSO potentially applicable for bacteria decontamination. It is well-known that luminescence has been widely applied in biological investigations. DMSO-based luminescent materials may find interesting applications in biological and biomedical investigations due to its above unique properties. Here we report the formation and luminescence of lanthanide–DMSO (Ln–DMSO) compounds formed in high-temperature reactions. It should be pointed out that lanthanide–DMSO compounds have been extensively studied and reported in the literature.<sup>27–33</sup> However, most Ln–DMSO compounds reported in the literature were prepared by simply dissolving lanthanide salts in DMSO at room temperature or very low temperatures.<sup>28–31</sup> Also, Ln–DMSO crystals were grown by slow evaporation of a solution of an authenticated sample of the lanthanide salt–DMSO solution in acetonitrile or methanol at very low or room temperature.<sup>27,32,33</sup> In this study, we prepared the Ln–DMSO compounds by heating them at high temperatures in DMSO. This reaction method is significantly different from that of previous reports and results in products with different luminescence properties.

## 2. EXPERIMENTAL DETAILS

The synthesis of metal–DMSO compounds is relatively simple. Cerium(III) nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ; 99.9%), terbium(III) nitrate pentahydrate ( $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; 99.9%), ytterbium(III) nitrate pentahydrate ( $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; 99.9%), neodymium(III) chloride hexahydrate ( $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ; 99.9%), gadolinium(III) nitrate hexahydrate ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ; 99.9%), lanthanum(III) nitrate hydrate ( $\text{La}(\text{NO}_3)_3 \cdot \text{XH}_2\text{O}$ ; 99.9%), and europium(III) nitrate pentahydrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; 99.9%) were all purchased from Sigma-Aldrich. All of the reagents were used as received, without further purification. A 0.1 mM concentration of each of the above lanthanide compounds was

respectively dissolved in 20 mL of DMSO and heated with vigorous stirring at around 180 °C overnight under the protection of nitrogen.

The excitation and emission spectra were measured on a Shimadzu RF-5301PC fluorometer. Luminescence lifetimes were collected using the frequency-doubled output of a synchronously pumped picosecond dye laser operating at 610 nm. The doubled output was focused onto the samples and emission collected at a right angle to the input. The emission was spectrally filtered and the lifetime measured using time-correlated single photon counting. The instrument resolution was determined to be about 50 ps fwhm using a standard scattering material. All measurements were conducted at room temperature.

X-ray luminescence was measured in a light-proof X-ray cabinet equipped with an optic fiber connection to an outside detector. Irradiation was performed using a Faxitron RX-650 cabinet X-ray system (Faxitron X-ray Corp., Lincolnshire, IL) using 60 kV, a 12 ft source–object distance, and a 5 mm optic fiber–object distance at 135°. The X-ray is produced from a tungsten target, and the energy is 110 keV.

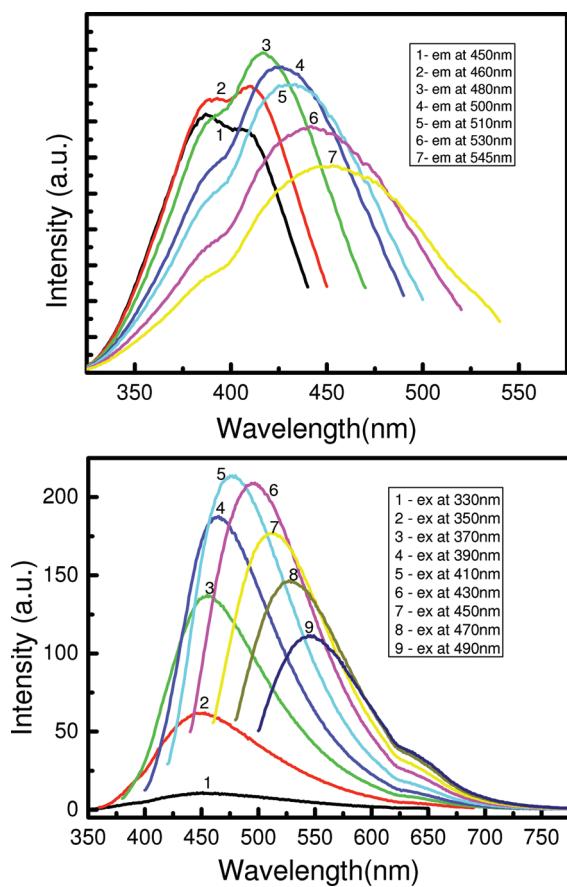
The quantum yield was determined by comparing the luminescence with that of rhodamine B in ethanol (quantum yield near 69% at 580 nm). The optical densities of Ln–DMSO solutions and the standard were adjusted to be within 0.05 AU of each other at the excitation wavelength of 350 nm. The quantum yield was calculated according to the formula

$$\eta_{\text{Ln-DMSO}} = \eta_S \left( \frac{I_{\text{Ln-DMSO}}}{I_S} \right) \left( \frac{\text{OD}_S}{\text{OD}_{\text{Ln-DMSO}}} \right) \quad (1)$$

where  $\eta_{\text{Ln-DMSO}}$  and  $\eta_S$  are the quantum yields of Ln–DMSO compounds and the standard sample,  $I_{\text{Ln-DMSO}}$  and  $I_S$  are the integrated areas of the luminescence peaks of Ln–DMSO compounds and the standard sample, and  $\text{OD}_{\text{Ln-DMSO}}$  and  $\text{OD}_S$  are the optical densities of Ln–DMSO compounds and the standard sample at the excitation wavelength (350 nm).

## 3. RESULTS AND DISCUSSION

In our experiments, we observed that all DMSO solutions have luminescence when lanthanide salts, such as lanthanide nitrates, lanthanide chlorides, or lanthanide acetates, are heated to boiling in DMSO. Lanthanide–DMSO compounds are likely formed in the heating process. We could not reveal the compositions and the crystal structures of these compounds because their solubility in DMSO is very high and no solid samples could be precipitated from the solutions. Here we focus on the study of the luminescence properties of these compounds. On the basis of their luminescence spectral properties, the compounds can be classified into four classes. For the compounds with Yb, Ce, and La (referred to as lanthanide–DMSO compounds I), the excitation and emission spectra are very broad and their emission peaks are shifted to longer wavelengths with longer excitation wavelength. For the compounds with Gd and Nd (referred to as lanthanide–DMSO compounds II), both the excitation and emission are very broad but their emission wavelengths change very little at different excitation wavelengths. For Tb–DMSO as compound III, both the typical emissions from the f–f transitions of  $\text{Tb}^{3+}$  and a broad emission at 445 nm are observed. At low reaction temperatures, the f–f emissions are dominant, while at high temperatures such as 180 °C, the broad emission at 445 nm is dominant. For compound IV, Eu–DMSO, the dominant emissions are from the f–f transitions of  $\text{Eu}^{3+}$  and only a weak broad



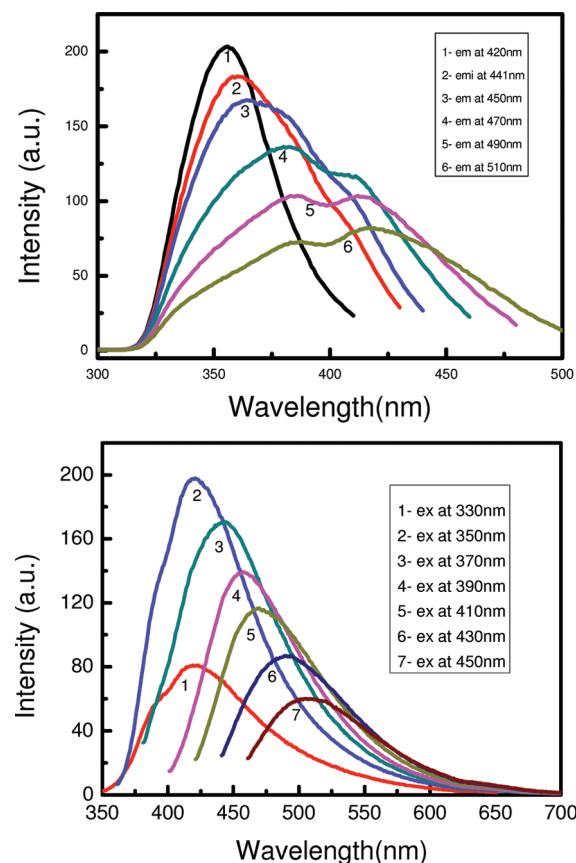
**Figure 1.** Excitation (top) and emission (bottom) spectra of Yb–DMSO solution.

emission is observed, which is likely from the d–f transition of Eu<sup>2+</sup> rather than from the metal-to-ligand charge transfer states.

**3.1. Luminescence of Lanthanide–DMSO Compounds I.** Yb–DMSO, Ce–DMSO, and La–DMSO belong to compounds I, and their excitation and emission spectra are shown in Figures 1–3, respectively. All their excitation and emission spectra look similar. In their excitation spectra, there are two peaks. At shorter emission wavelengths, the short wavelength side peak is stronger and the long wavelength peak increases in intensity gradually as the monitored emission wavelength becomes longer. Overall, the excitation maximum shifts to longer wavelengths when longer emission wavelengths are monitored. The emission bands are very broad and are consistent with 2–3 emission peaks. As the excitation wavelength becomes redder, the emission maxima shift to longer wavelengths and the emission intensity increases, reaches a peak, and then decreases. The details are described below.

Figure 1 displays the excitation and emission spectra of Yb–DMSO compound solutions. The excitation spectrum has two peaks at 385 and 480 nm. The emission spectrum displays a shoulder at 640 nm, and the dominant peak is at around 480 nm. As the excitation wavelength increases, the emission intensity first increases, approaches a maximum when the excitation wavelength is at 380 nm, and then decreases gradually.

Figure 2 displays the excitation and emission spectra of Ce–DMSO compound solutions. The excitation spectrum has two peaks at 355 and 418 nm. When the monitored emission wavelength increases, the short-wavelength peak decreases but the long-wavelength peak increases in intensity. The emission



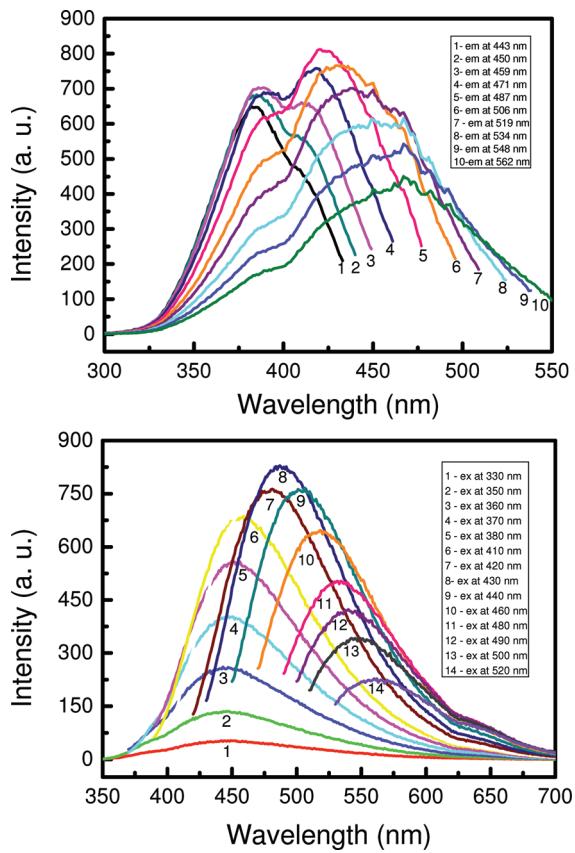
**Figure 2.** Excitation (top) and emission (bottom) spectra of Ce–DMSO solution.

spectrum contains two shoulders at 370 and 640 nm, and the dominant peak is at around 440 nm.

Figure 3 shows the excitation and emission spectra of La–DMSO compound solutions. The excitation spectrum has two peaks at 380 and 475 nm. Similar to the other compounds, as the monitored emission wavelength increases, the short-wavelength peak decreases but the long-wavelength peak increases in intensity. The emission spectrum contains a shoulder at 640 nm, and the dominant peak is at around 500 nm. The emission intensity is the highest when the excitation wavelength is at 430 nm.

**3.2. Luminescence of Lanthanide–DMSO Compounds II.** These lanthanide–DMSO compounds have broad excitation and emission bands, but their excitation and emission wavelengths do not shift significantly with the monitored emission or excitation wavelength. Gd–DMSO and Nd–DMSO compounds fall into this group. Figure 4 shows the excitation and emission spectra of Gd–DMSO solutions. The excitation spectrum has a shoulder at 390 nm and a broad peak at 438 nm. As observed in Figure 4 (top), the excitation spectra are almost identical in shape and position at the monitored wavelengths of 490, 500, and 520 nm. The emission from Gd–DMSO is also very broad. The main emission peak is at 490 nm with a small shoulder at 645 nm. As the excitation wavelength increases from 320 to 400 nm, the emission intensity increases but the emission wavelength and shape are almost the same or change very little.

The excitation and emission spectra of Nd–DMSO solutions are shown in Figure 5. The excitation spectrum has two peaks at 280 and 370 nm. When the monitored emission is at 330 nm,

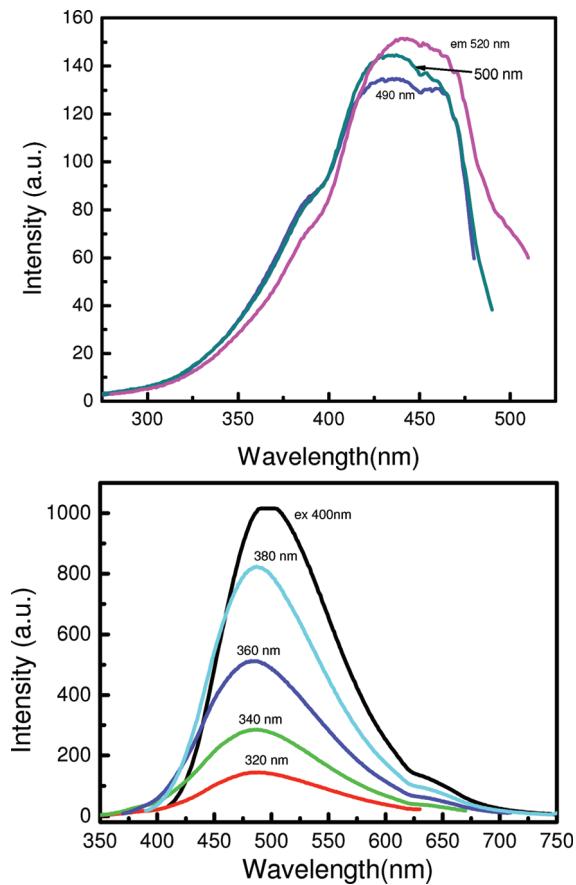


**Figure 3.** Excitation (top) and emission (bottom) spectra of La—DMSO solution.

the 280 nm peak is dominant, but the 370 nm peak is dominant when the monitored emission is at 440 nm. Similarly, there are two emission peaks observed, one at 330 nm and the other at 440 nm. When the solution sample is excited at 280 nm, the 330 nm emission is dominant and the 440 nm emission is very weak. When the solution samples are excited at wavelengths from 350 to 400 nm, only the 440 nm emission is observed. The emission peak position and shape are almost the same at different excitation wavelengths.

**3.3. Luminescence of Tb—DMSO Solutions (Compound III).** Figure 6 shows the excitation and emission spectra of Tb—DMSO compound solutions prepared at 180 °C and reacted overnight. The excitation spectrum has two peaks at 370 and 450 nm. When the monitored emission wavelength becomes longer, the short-wavelength peak decreases but the long-wavelength peak increases in intensity. The emission of Tb—DMSO solutions is very broad, covering the UV through the visible range. Clearly, there are two shoulders at 360 and 640 nm, and the dominant peak is at around 480 nm. When the excitation wavelength becomes longer, the emission intensity first increases, approaches a maximum when the excitation wavelength is at 380 nm, and then decreases gradually. Overall, the emission peak shifts to longer wavelengths at longer wavelengths of excitation.

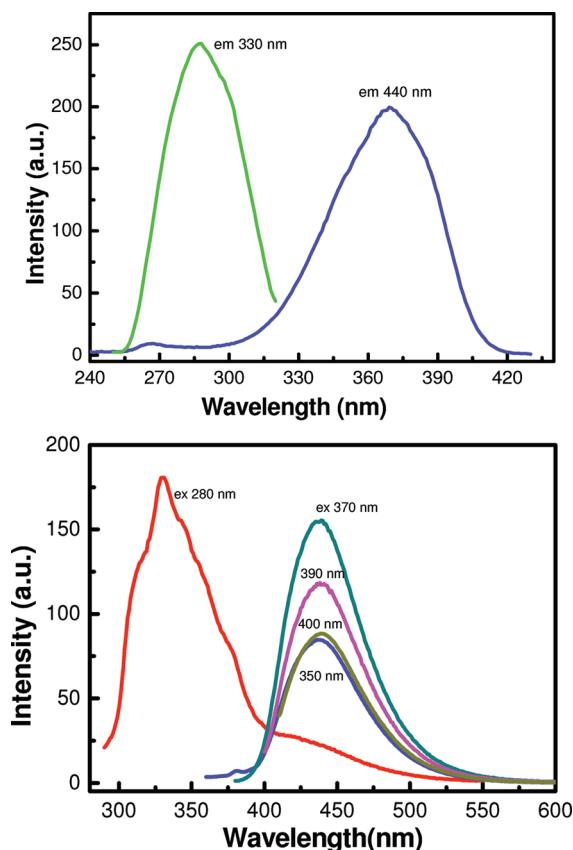
It is noted that in the literature only the typical f–f emissions were observed in Tb—DMSO compounds.<sup>28,29,31</sup> However, Tb—DMSO compounds were synthesized by dissolving  $\text{Tb}(\text{NO}_3)_3$  in DMSO at room temperature or low temperatures.<sup>28,29,31</sup> If we simply dissolve  $\text{Tb}(\text{NO}_3)_3$  in DMSO at room or low temperatures lower than 100 °C, we see exactly the same emission



**Figure 4.** Excitation (top) and emission (bottom) spectra of Gd—DMSO solution.

spectrum for Tb—DMSO as reported previously in the literature.<sup>28,29,31</sup> However, when the  $\text{Tb}(\text{NO}_3)_3$ —DMSO solutions were heated to higher temperatures than 150 °C, we observed that the typical f–f emissions of  $\text{Tb}^{3+}$  decrease in intensity and a broad emission at 445 nm appears and increases as shown in Figure 7. The broad emission is likely from the metal-to-ligand charge transfer (MLCT) state of the Tb—DMSO compounds. The intensity ratio of the MLCT emission to the f–f emission is related to not only the reaction temperature but also the concentration of Tb in DMSO, which will be described in a forthcoming publication. Our observations indicate that Tb—DMSO compounds have two kinds of emissions—the broad MLCT emission at around 445 nm and the typical f–f emissions from  $\text{Tb}^{3+}$  ions.

**3.4. Photoluminescence and X-ray Luminescence of Eu—DMSO Solutions.** Eu—DMSO is the only lanthanide—DMSO compound formed at high temperature that shows the typical luminescence from f–f transitions of the lanthanide ion and is also the only compound from which X-ray luminescence is observed. The excitation spectrum of Eu—DMSO is shown in Figure 8 (top). The absorption peaks are from the f–f transitions of  $\text{Eu}^{3+}$  ions, and their assignments are labeled in the spectrum. The emission spectra excited at 350, 360, 370, 380, 390, and 400 nm are shown in Figure 8 (bottom). The emissions from the f–f transitions of  $\text{Eu}^{3+}$  are dominant, and in addition, a very weak broad emission is observed at 450 nm as shown in the inset of Figure 7b. The emission peaks between 575 and 725 nm are attributed to the  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  transitions, which have been assigned in the spectra on the basis of the emission spectra of  $\text{Eu}^{3+}$ .



**Figure 5.** Excitation (top) and emission (bottom) spectra of Nd–DMSO solution.

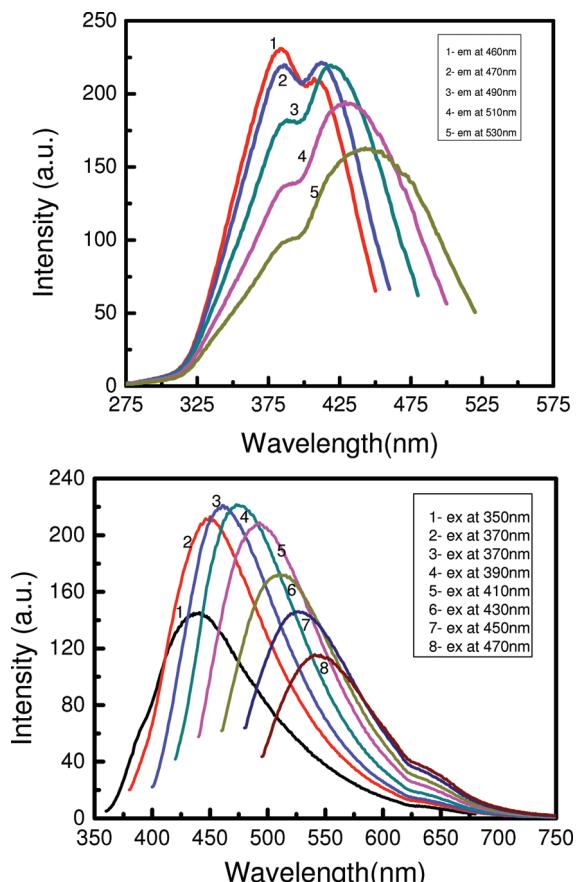
reported in the literature.<sup>34,35</sup> The two weak emission peaks at 536 and 555 nm are from the  $^5D_1 \rightarrow ^7F_1$  and  $^5D_1 \rightarrow ^7F_2$  transitions of Eu<sup>3+</sup>.<sup>36</sup> The emission shape and positions are the same at different excitation wavelengths.

The excitation and emission spectra of the broad emission from Eu–DMSO solution are shown in Figure 9. The emission position is almost identical at different excitation wavelengths. The excitation peak is at around 360 nm when the broad emission is monitored, and the excitation shape and position are almost the same at different monitored emission wavelengths. The broad emission may be from the MLCT or the d–f transition of Eu<sup>2+</sup>. Eu<sup>2+</sup> is generally not stable in aqueous solution, but it may be stable in DMSO as DMSO is a stronger electron donor than water. Trace Eu<sup>2+</sup> is almost always present in Eu<sup>3+</sup>-containing compounds.<sup>37</sup>

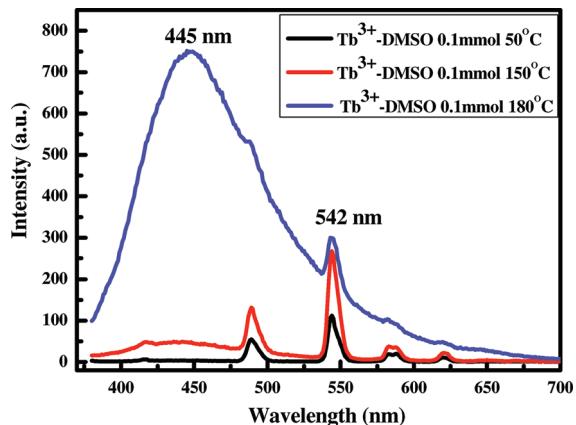
Eu–DMSO is the only solution that shows luminescence following X-ray excitation, and its X-ray luminescence spectrum is shown in Figure 10. The four main peaks at 593, 617, 656, and 700 nm are from the  $^5D_0 \rightarrow ^7F_1$ ,  $^5D_0 \rightarrow ^7F_2$ ,  $^5D_0 \rightarrow ^7F_3$ , and  $^5D_0 \rightarrow ^7F_4$  transitions, respectively. The main emission peaks in the X-ray luminescence spectrum are consistent with the emission peaks in the photoluminescence emission spectra in Figure 8. The intense X-ray luminescence from Eu–DMSO solutions may find applications in biomedical science, radiation detection, and homeland security issues.

#### 4. DISCUSSION

The luminescence properties of Ln–DMSO compounds are interesting not only for fundamental studies but also for potential applications. The luminescence quantum yields from these



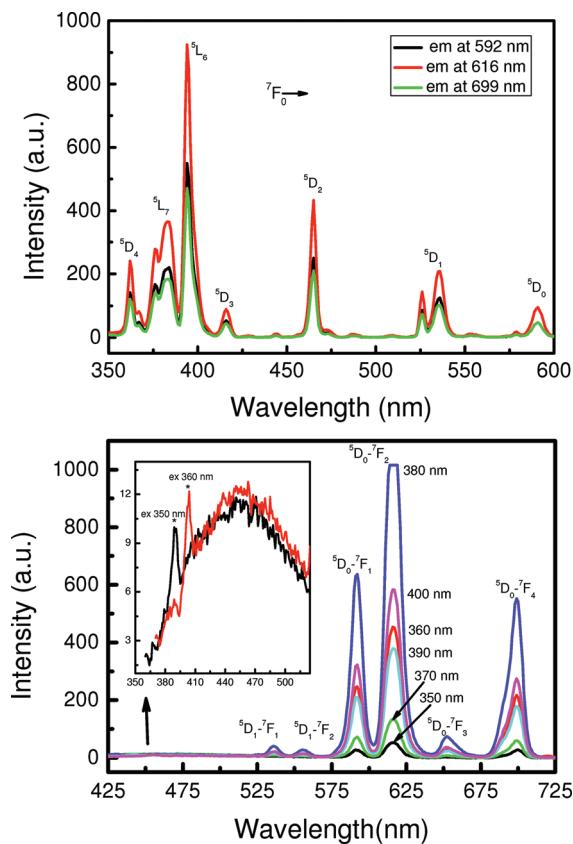
**Figure 6.** Excitation (top) and emission (bottom) spectra of Tb–DMSO solution.



**Figure 7.** Photoluminescence spectra of Tb–DMSO formed at 50, 150, and 180 °C. The excitation is at 370 nm.

compounds are shown in Table 1. For most of these compounds, the quantum yield is about 1%, which is low for practical applications. However, it has been observed that the luminescence of these compounds, such as the emissions of Eu–DMSO, is very sensitive to addition of molecules such as water.<sup>10</sup> The potential applications of these compounds for chemical sensing are worthy of further investigation.

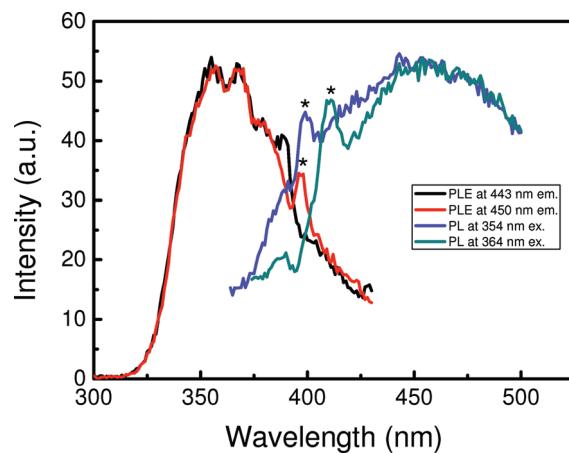
The f–f emissions from Tb<sup>3+</sup>, Yb<sup>3+</sup>, Gd<sup>3+</sup>, and Nd<sup>3+</sup> are usually spectrally narrow and are significantly different from what



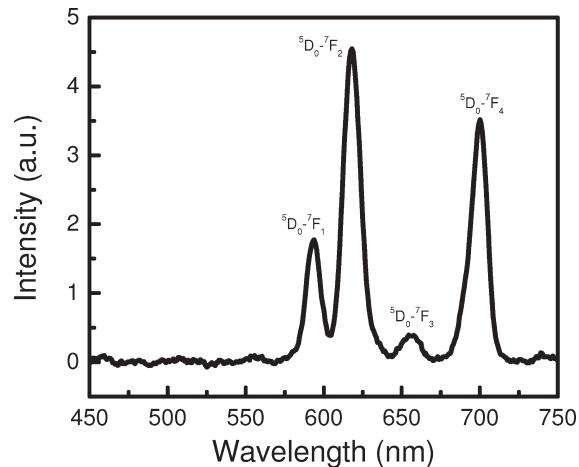
**Figure 8.** Excitation (top) and emission (bottom) spectra of Eu–DMSO solution.

is observed in Figures 1 and 4–6. The emission of the Ce–DMSO solution is similar to the f–d emission for  $\text{Ce}^{3+}$  ions, but there are several differences between the emission spectra shown in Figure 2 and the emission spectrum for  $\text{Ce}^{3+}$  ions. First, the emission and excitation bands shown in Figure 2 are broader than those of  $\text{Ce}^{3+}$  ions. Second, the excitation or emission spectra of  $\text{Ce}^{3+}$  usually do not change with the monitored emission or excitation wavelength. In addition, the luminescence lifetimes of d–f transitions of  $\text{Ce}^{3+}$  are typically about 20–25 ns. However, the luminescence lifetimes of the solution samples are much shorter (0.3 and 2.8 ns; see Figure 11). Therefore, it is likely that the Ce–DMSO solution emission is not from  $\text{Ce}^{3+}$  ions. Figure 11 shows the luminescence lifetime curve for the Nd<sup>3+</sup>–DMSO solution. Once again, the lifetime is distinctly different from that expected for a rare-earth ion. For La–DMSO, it is unlikely that the emission is due to La<sup>3+</sup> ions because it is well-known that La<sup>3+</sup>, Y<sup>3+</sup>, Lu<sup>3+</sup>, and Sc<sup>3+</sup> ions have no 4f electrons; therefore, they have no electronic energy levels that can induce excitation and luminescence processes in or near the visible region.<sup>2</sup> Therefore, it may be concluded that the emissions of lanthanide–DMSO compounds I and II are not from the intrinsic transitions of the lanthanide ions.

It is likely that lanthanide–DMSO organometallic compounds are formed during the process when lanthanide nitrates are heated in DMSO. The structures of these compounds cannot be determined as only small amounts of solid samples could be obtained from the solutions. In lanthanide–organic compounds, generally there are three types of emissions, from the  $\pi-\pi^*$  transition of the organic ligands, the MLCT state, and the



**Figure 9.** Excitation (top) and emission (bottom) spectra of Eu–DMSO solution for the MLCT emission.

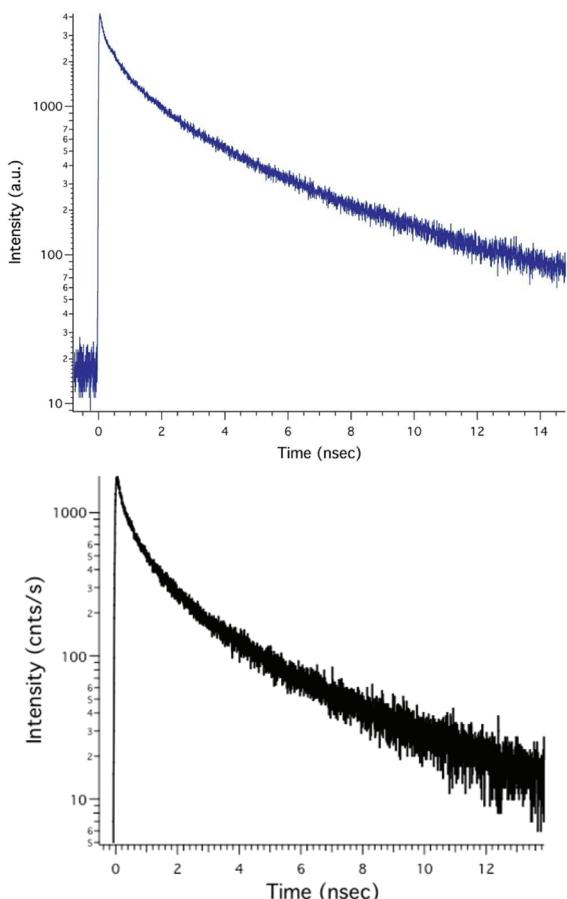


**Figure 10.** X-ray luminescence of Eu–DMSO solution.

intrinsic f–f or f–d transitions of the lanthanide ions.<sup>7,38,39</sup> It has been reported that the MLCT states in organometallic compounds are usually located between the singlet state and the triplet state.<sup>7,38,40</sup> On the basis of this assumption, the three broad peaks shown in the emission spectra of the lanthanide–DMSO compounds can be assigned to the singlet, MLCT, and triplet states. On the basis of the emission spectra, the lowest energy levels of these states in the lanthanide–DMSO compounds can be approximately estimated as shown in Table 2 along with the typical emission wavelengths from the lanthanide ions. In the cases of Ce–DMSO and Gd–DMSO, the energies of the intra-ion emitting states are much higher than the energies of the MLCT and triplet states. Therefore, intra-ion emission is unlikely. In La–DMSO only the emissions from the MLCT and triplet states can be detected because La<sup>3+</sup> has no singlet luminescence.<sup>2</sup> In Tb–DMSO, the Tb<sup>3+</sup> emitting state is higher than the triplet state but within the MLCT state in energy. Therefore, it is understandable that the narrow-line-type emissions from Tb<sup>3+</sup> are suppressed and the MLCT emission is dominant. This is particularly likely because the lifetimes of the MLCT states measured in Figure 11 are on the order of nanoseconds or shorter while the lifetimes of the Tb<sup>3+</sup> ion states are typically much longer ( $\sim 3$  ms). Therefore, any energy

**Table 1. Quantum Yields of Ln–DMSO Compounds**

	Tb–DMSO	La–DMSO	Ce–DMSO	Eu–DMSO	Nd–DMSO	Yb–DMSO	Gd–DMSO
quantum yield (%)	0.9 ± 0.05	0.9 ± 0.05	0.7 ± 0.05	1.5 ± 0.05	0.3 ± 0.05	0.9 ± 0.05	0.8 ± 0.05



**Figure 11.** (Top) Ce–DMSO sample luminescence lifetime following 305 nm excitation. The biexponential decay can be fit to components of 0.3 and 2.8 ns. (Bottom) Nd<sup>3+</sup>–DMSO sample luminescence lifetime following 290 nm excitation. The biexponential decay can be fit to components of 0.3 and 2.1 ns.

coupling between the ion states and the charge transfer states will quickly deplete the excited state via MLCT emission. In Yb–DMSO and Nd–DMSO, in principle, the emissions from Yb<sup>3+</sup> and Nd<sup>3+</sup> should be observed but the infrared emissions are beyond the detection range of our spectrophotometer. In the Eu–DMSO compound, the emissions from the f–f transitions of Eu<sup>3+</sup> ions are dominant, and it is the only compound that exhibits X-ray luminescence. The broad emission at 450 nm from Eu–DMSO is likely from some trace Eu<sup>2+</sup> ions rather than MLCT because MLCT is not likely possible in Eu<sup>3+</sup> compounds.

The intense luminescence observed from lanthanide–DMSO compounds is interesting not only to basic research but also for practical applications. For example, blue, green, and red emissions can be easily obtained in these compounds. Therefore, these compounds may find potential applications for full-color displays. The strong X-ray luminescence from Eu–DMSO solution is particularly interesting because X-ray luminescence is very difficult to detect from solution samples.<sup>41–44</sup> Due to the strong X-ray luminescence and the unique properties of DMSO for cell

**Table 2. Emitting States (nm) in Lanthanide–DMSO Compounds and Typical Emission Wavelengths (nm) of the Lanthanide Ions**

compd	S state	MLCT state		lanthanide ion typical emission
		(av)	T state	
Tb–DMSO	370	480	640	540
Yb–DMSO		476	640	980
Ce–DMSO	365	460	640	390
La–DMSO		455	640	
Gd–DMSO		490	640	312
Nd–DMSO	330	440		890
Eu–DMSO		450 (Eu <sup>2+</sup> ) <sup>a</sup>		

<sup>a</sup>The 450 nm broad emission band in Eu–DMSO is likely from Eu<sup>2+</sup> ions rather than MLCT.

penetration as well as its miscibility with water, Eu–DMSO may find applications in dirty bomb detection for water security, in vivo dosimetry, in vivo imaging, and cell labeling and as a new light source for photodynamic therapy.<sup>1,42,45–47</sup>

#### 4. CONCLUSION

In summary, lanthanide–DMSO compounds were prepared by heating lanthanide nitrates in DMSO, and their luminescence was investigated. All the compounds except Eu–DMSO show broad emissions that are attributed to MLCT states. For the compounds containing Yb, Ce, and La, the excitation and emission spectra are very broad and their excitation or emission peaks shift to longer wavelengths if the monitored emission or excitation wavelength increases. For the compounds containing Gd and Nd, both the excitation and emission are very broad but their emission wavelengths change very little at different excitation wavelengths. For Tb–DMSO compounds, both MLCT and f–f emissions are observed. For the compounds formed at temperatures lower than 150 °C, the f–f emissions are dominant, while for the compound formed at 180 °C, the MLCT emission is dominant. For Eu–DMSO compounds, the dominant emissions are from the f–f transitions of Eu<sup>3+</sup> and only a weak broad emission is observed, which is likely from the d–f emission of Eu<sup>2+</sup> ions. In addition to photoluminescence, Eu–DMSO solution shows intense X-ray luminescence. White color emission as well as blue, green, and red emissions can be easily obtained from these compounds. The observations indicate that lanthanide–DMSO compounds may find applications in lighting, full-color displays, imaging, labeling, and radiation detection and as a light source for photodynamic therapy and disease treatment.

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