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LETTER

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Hypersensitive Luminescence of Eu^{3+} in Dimethyl Sulfoxide As a New Probing for Water Measurement

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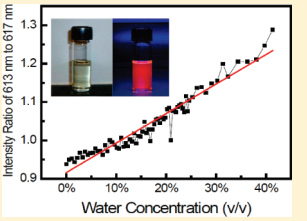
Supporting Information

ABSTRACT: Dimethyl sulfoxide (DMSO) is a well-known organic solvent that can be used for biological applications. DMSO is miscible with water, and it is very common that the two solvents are mixed for some applications. It is important to detect water in DMSO, and this has been done using the luminescence decay lifetimes from Eu^{3+} ions. We observed that the emissions of Eu^{3+} in DMSO are very strong and very sensitive to water. The emission band from the $^5D_0 \rightarrow {}^7F_2$ transition has two peaks at 613 and 617 nm, respectively, and these two peaks change in the opposite ways when water is added into DMSO. The intensity ratio of the two peaks follows nearly perfect linear dependence on the water concentration added in DMSO. This linear relationship provides a new and convenient method for water measurement in DMSO.



The emission from lanthanide ions has been studied extensively in these years because of their wide applications in various areas such as luminescence imaging,[1,2] luminescent labels, and the detection of cellular functions,[3,4] etc. Luminescence of Ln(III) ions, characterized by sharp, narrow emission spectroscopic bands corresponding to the f−f transitions of the metal ion, has proven useful as a sensitive detection method in biological systems. The luminescence from lanthanide excited states can be quenched through nonradiative energy transfer to stretching vibrations of nearby or coordinated solvent molecules, especially in aqueous media where there are abundant of O−H oscillators resulting in Franck−Condon overlap of energy levels and stretching vibrations.[5−8] Europium was the first lanthanide that has been studied in solution due to its more efficient luminescence compared with other lanthanide ions.[9] Freed et al. found that the intensities of the spectral emission lines of europium(III) were affected by the solvent in which it was studied.[10] Furthermore, the changes in the intensity of the Eu(III) luminescence upon binding to proteins and enzymes have been utilized to examine the ligation sphere within the active site;[9,11−13] therefore, the luminescence quenching rates have become valuable data in evaluating hydration in the primary coordination sphere of complexes of the Eu ion.[12,14−16]

Lanthanide-DMSO compounds may find some new and interesting applications due to their unique properties. However, little attention has been paid to luminescence of lanthanide-DMSO compounds.[17] DMSO is a clear, colorless to yellowish 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.[18−20] 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.[20] DMSO itself is also a drug which was approved by the Food and Drug Administration (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.[21] DMSO has many other clinical properties by itself. It has been used successfully as an adjuvant, for its analgesic properties, in the treatment of pulmonary adenocarcinoma, rheumatologic, and dermatologic diseases, chronic prostatitis, and as a topical analgesic.[18−20] DMSO has been used for the local treatment of extravasation in chemotherapy,[22] it can reduce the ulcer size from Adria extravasation, and is a cure for necrosis.[23,24] It was reported that DMSO increases radioiodination yield for radiopharmaceuticals.[25] It can be used as an adjunct to tissue expansion for breast reconstruction.[26] At the central nervous system, it has been used in the treatment of traumatic brain edema and schizophrenia, and it has been suggested for the treatment of Alzheimer's disease.[27] 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 at various concentrations. The process is revisible, and the integrity of most membranes is not affected except at extremely high concentrations of 90−100% employed.[28] This property has been exploited as an indicator or probe to study changes in the barrier properties of human skin in certain disease states like atopic dermatitis[29] or damage due to exposure of skin to ultraviolet radiation.[30] 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.[20] These properties plus its unique membrane penetration make DMSO potentially useful for bacteria decontamination. It is well-known that luminescence

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Figure 1. Pictures of Eu-DMSO solution in room light (left) and under a UV lamp excitation (right).

has been widely applied in biological investigations. DMSO based luminescence materials may find some interesting applications in biological and biomedical investigations due to its above unique properties

DMSO is miscible with water, and it is very common that the two solvents are mixed for some specific applications. In a sense, it is important to detect water in DMSO, and this has been done using the luminescence decay lifetimes from Eu^{3+} ions.[9] Barthelemy et al calculated the degree of hydration of Eu(III) from the luminescence decay rate constants to determine the water amount in DMSO,[11] and Stefan and Gregory measured the lifetimes of Eu(III) and found the linearity of the response to the water concentration in DMSO solution.[31] Here we report that the emissions of Eu(III) in DMSO are very strong and very sensitive with encounters with water, which provides a new and convenient method for water measurement in DMSO.

EXPERIMENTAL METHODS AND MATERIALS

Europium nitrate pentahydrate, ($Eu(NO_3)_3 \cdot 5H_2O$, 99.9%) and dimethyl sulfoxide were both purchased from Sigma-Aldrich. The reagents were used as received, without further purification. The synthesis of europium-DMSO compounds is straightforward. A total of 2.14 g of $Eu(NO_3)_3 \cdot 5H_2O$ was first dissolved into 25 mL of DMSO and then boiled at 150 °C with vigorously stirring for 2 h under the protection of nitrogen. In order to find out the luminescence quenching effect of Eu-DMSO on coordinating solvent containing an OH group, the sample was diluted with the same calculated amount of DMSO and deionized (DI) water, respectively, with different sets of concentrations for comparison. The excitation and emission spectra were measured on a Shimadzu RF-5301PC fluorometer. All measurements were conducted at room temperature.

RESULTS AND DISCUSSION

Our previous research found that some of the lanthanide-DMSO compounds such as Ce-DMSO and La-DMSO showing very strong emissions in longer wavelength area other than their characteristic emissions, which have been considered as the emissions induced by metal to ligand charge transfer (MLCT);[17] however, the situation is totally different for Eu-DMSO. Eu-DMSO compounds show the typical luminescence of Eu^{3+}, which is similar to that of Eu(III) ions in aqueous

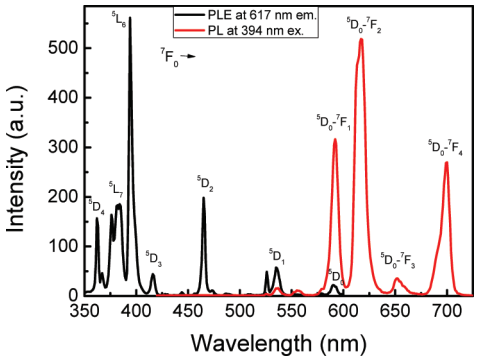

Figure 2. Excitation and emission spectra of Eu-DMSO solution. The excitation spectrum was recorded by monitoring the emission at 617 nm, and the emission spectrum was taken by excitation at 394 nm.

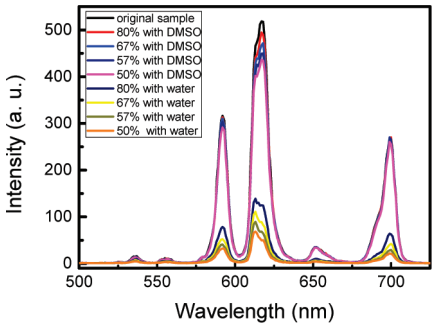

Figure 3. Emission spectra of the original Eu-DMSO solution and dilutions (v/v) with water and DMSO. The excitation is at 394 nm.

solution or other solid phosphors, and no obvious MLCT emissions were observed. However, unlike the weak luminescence from the aqueous solution of Eu(III) due to the low absorption cross section of the ions in the UV−visible region, Eu-DMSO has very strong luminescence as displayed in Figure 1. The excitation and emission spectra of Eu-DMSO are shown in Figure 2. The sharp and narrow bands in the excitation and emission spectra are corresponding to the f−f transitions of the Eu ion, and the emissions within the range of 575−725 nm are due to $^5D_0 \rightarrow {}^7F_{1-4}$ transitions of Eu^{3+}.[32,33] The two weak emission peaks at 536 and 555 nm originated from transitions of $^5D_1 \rightarrow {}^7F_1$ and $^5D_1 \rightarrow {}^7F_2$ of Eu^{3+}.[34] The absorption peaks in the excitation spectrum are from the ground state of $^7F_0$ to the high energy levels of Eu^{3+}, and their assignments are labeled in the spectrum in Figure 2.

Figure 3 shows emission spectra of DMSO-Eu solution in comparison with the spectra when different amounts of water and DMSO were dropped into the compound. Clearly, the emission intensity of Eu^{3+} in DMSO is decreased when water or DMSO is added into the solution. However, the intensity decrease caused by adding water is almost 5 times greater than that by the same amount of DMSO. It is more interesting to see that the emission of $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} in Eu-DMSO is hypersensitive when encountering water. The $^5D_0 \rightarrow {}^7F_2$ emission band is split into two peaks at 613 and 617 nm as a result of J-mixing in the crystal field expansion and the spin−orbit interaction.[35] In the original Eu-DMSO compound, the peak at 617 nm is stronger than that at 613 nm. After a different amount of DMSO is being added into the compound, the emission intensity of $^5D_0 \rightarrow {}^7F_2$ transition is decreased gradually but the

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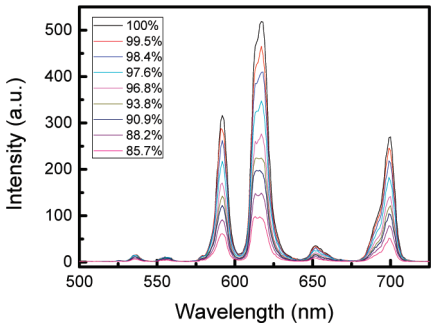

Figure 4. Emission spectra of Eu-DMSO dilutions (v/v) with water. The excitation is at 394 nm.

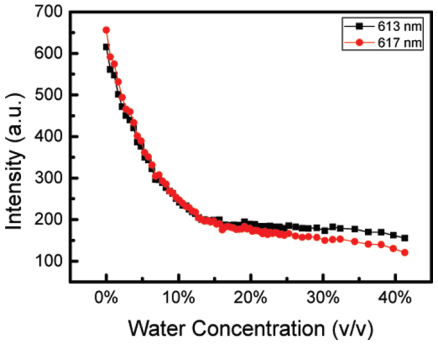

Figure 5. The intensity trends of emission peaks at 613 and 617 nm in Eu-DMSO solution with the concentration of water added.

relative intensities of the two peaks at 613 and 617 nm are not varied. However, when the same amount of water is dropped into the Eu-DMSO compound, the relative intensities of the two peaks at 613 and 617 nm are changed remarkably. That is the emission peak at 617 nm becomes weaker than that at 613 nm, which is opposite to that in the Eu-DMSO compound. This indicates that the quenching mechanisms by water and DMSO are different. By addition of water, the quenching on the peak at 617 nm is much faster than that on the peak at 613 nm. While the addition of DMSO quenches the two peaks at 613 and 617 nm in the same step, it is obvious that the quenching by adding DMSO is simply due to the decrease of the concentration. However, the quenching mechanism by water is more complicated. The quenching of emission intensities is due to coupling of the Eu excited state to O−H oscillators of water molecules where some of the energy from the Eu excited state has been transferred to the O−H oscillators of bound water molecules.[14,36]

In order to observe the gradual variation in the two peaks at 613 and 617 nm, reduced amounts of water were added into the Eu-DMSO compound. It was found that as the water concentration is at 6.2%, the two peaks have almost equal intensity, and then as water is increased, the 617 nm peak is gradually quenched and becomes weaker than the peak at 613 nm. The changes in the emission spectra can be seen in Figure 4 when the water is changed from 0.5% to 14.3%. The changes of the two peaks at 613 and 617 nm with the water percentage added are displayed in Figure 5, and the change of the intensity ratio of the two peaks with water is shown in Figure 6. A linear fitting shows that the intensity ratio is changed linearly with the water concentrations added to the Eu-DMSO solution as

$$R_I = 0.769P_v + 0.916$$

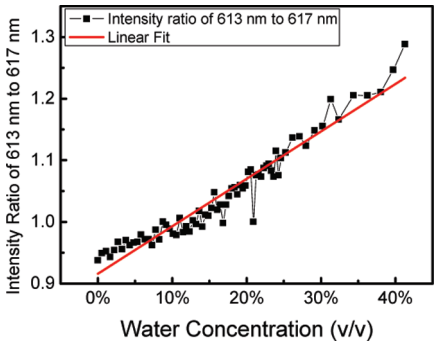

Figure 6. The dependence of intensity ratio of 613 to 617 nm emissions on the water concentration in DMSO.

or

$$P_v = (R_I - 0.916)/0.769$$

where P_v stands for the volume concentration of water in Eu-DMSO in percentage, R_I stands for the intensity ratio of two emission peaks at 613 to 617 nm. This relationship provides a new method for the measurement of water in DMSO, and this method is much easier and more convenient than the lifetime measurement because the measurement of the emission spectra is much easier than the lifetime measurement. In addition, the cost by using the method described here is much cheaper than that by lifetime methods. It is believed that the reported method can be used for other solvent detection in DMSO such as ethanol, acetone, diethyl ether, benzene, chloroform, phosphate buffered saline (PBS) buffer solutions, and cell culture media which are under investigation. However, we need to point out that when the concentration of water is higher than 50%, the emission peak at 617 nm disappears, so the method of using the ratio of the 613 and 617 nm peaks is limited to the concentrations from 0 to 50%. For water concentrations higher than 50%, the Eu^{3+}-emission intensities are still decreased gradually with the increasing of water, so the intensity change is still reliable for water determination in DMSO.

CONCLUSIONS

In summary, the luminescence of Eu^{3+} in DMSO is strong and very sensitive to water. The emission of $^5D_0 \rightarrow {}^7F_2$ transition has two peaks at 613 and 617 nm which are changed in the opposite ways when water is added into DMSO. The intensity ratio of the two peaks changes linearly with the concentration of water, and this provides a new and convenient method for water measurement in DMSO.

ASSOCIATED CONTENT

Supporting Information. Additional information about the changes of the excitation spectra of Eu-DSMSO encountering water and the changing behaviors of the emissions when water and DMSO were added to the Eu-DMSO solutions, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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