Optimization of Eu$^{3+}$ Luminescence in DMSO as a Multiparameter Method for Trace Water Detection

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**ABSTRACT:** Photoluminescence of Eu$^{3+}$ in DMSO is intense and ultrasensitive to water, thereby providing a novel method for water detection. Herein, for the first time, we investigated the effects of Eu$^{3+}$ concentration on luminescence and developed a multiparameter method for trace water detection based on a single luminescence agent. To further extend its practical applications, we explored its performance for water detection in ethanol and gasoline. Our findings demonstrate that it is a sensitive and reliable probe for the detection of a wide concentration range of water in ethanol (0–24.24%) and gasoline (0–32.43%), making Eu–DMSO a promising candidate to detect water in a wide concentration range. These phenomena not only make Eu–DMSO a sensitive agent for in situ water detection in real time but also provide scientifically interesting mechanisms behind its application as a water sensing probe.

**INTRODUCTION**

Earth is the only place that we know for sure supports life because of the cozy temperature, plenty of water, and oxygen. As the earth is becoming hotter, the earth might become inhabitable in the future. As a result, humans may need to immigrate to other planets, such as Mars. Scientists all over the world are looking for new habitable planets, and determining the water content on the surface of the planets is a crucial step to achieve this goal.

Water is not only an extremely important part of life for all living beings but it also plays a vital role in chemistry and industrial processes. Despite its ubiquitous importance, water content plays a detrimental role in many routine laboratory and industrial applications; therefore, detecting and quantifying water content is of crucial importance in chemical reactions and industrial processes. For example, the presence of water in organometallic reagents may lead to fire and explosions under some conditions. Besides, water impurity adversely affects the yield and selectivity of the final products in many chemical reactions, such as the foods produced in photosynthesis. Furthermore, the presence of water in petroleum-based fuels lowers the performance of the engine. When the temperature is sufficiently low, emulsification and phase separation may lead to damage and failure of the engine. As water can influence torque characteristics and wear resistance, the trace amount of water in wet clutch systems can be problematic. Moreover, the presence of free water can cause corrosion and cavitation inside or throughout the clutch systems, thereby leading to iron and lead corrosion. Additionally, water can disturb the generation of friction modifying boundary film on the friction interfaces. The presence of water also disrupts the friction-increasing substances, including detergents and dispersants. Furthermore, fibers can loosen from the diluted binder in the water-contained lubricant, resulting in the degradation of the material. Studies have found that 1000 ppm water in petroleum-based transmission and hydraulic oils and in synthetic engine-lubricating oil can have a detrimental effect. Premature oil change causes financial burden and generates additional disposal costs, whereas changing oil too late results in wear and possible engine failure. Therefore, knowledge of the condition of the oil is necessary to replace it in a timely manner. Accordingly, a probe that is suitable for accurate, real-time, and in situ early detection of water contents in oil is highly desirable.

The determination of the humidity level in the atmosphere is vital for human health. For example, joint pain and rheumatoid arthritis are profoundly affected by temperature and humidity. In addition, many industrial applications are substantially affected by trace water content in ambient air. Therefore, monitoring trace water has been a hot topic investigated extensively. There are some well-established techniques to estimate water content in organic solvents, including Karl Fischer titration, chromatography, and other
spectroscopic techniques. Even though the Karl Fischer method\textsuperscript{14} can detect trace amounts of water up to the ppm level, it has some limitations, such as involving toxic reagents, specialized instruments, time-consuming, requiring well-trained personnel, chemical interference, and complicated sample preparation, which limit its application.\textsuperscript{15–17} Consequently, cost-effective, reliable, and highly efficient alternative methods are required for the real-time and in situ estimation of water in routine laboratory works and industrial processes.

Fluorescent and colorimetric probes could be an alternative option to monitor water content, primarily in organic solvents and raw foods. Since water is an effective quencher of luminescence, luminescent probes for monitoring water content have been extensively studied and developed.\textsuperscript{7–10,18,19} It has been reported that ratiometric fluorescence measurement method, based on the ratio of the photoluminescence (PL) intensities of two wavelengths, can be suitable for detecting analytes as this method is independent of interference from the environment and eliminates the most likely variabilities.\textsuperscript{20–22} Consequently, it is highly desirable to develop an effective ratiometric probe that can respond to water impurity in various organic solvents.

DMSO is miscible in many solvents, such as water, ethanol, acetone, ether, and chloroform, and is a solvent for unsaturated, nitrogen-containing, and aromatic compounds,\textsuperscript{23–27} making it a versatile solvent to be used in a probe. Despite the enormous potential of lanthanide—DMSO compounds to meet novel applications, only a handful of probes. Despite the enormous potential of lanthanide—DMSO compounds to meet novel applications, only a handful of probes has been developed to elucidate and exploit its luminescence.\textsuperscript{18,19,26,28,29} Luminescence of rare earth ions in DMSO is a new phenomenon that has been reported only recently and is still in its infancy.\textsuperscript{18,19,30} Consequently, more research on DMSO-based luminescence water-detecting sensors needs to be conducted to realize them in practical use.

In the present work, for the first time, we explored the effect of Eu\textsuperscript{3+} concentration on the luminescence of Eu—DMSO samples and used the results to develop a multiparameter method for trace water detection based on a single probe. Additionally, we attempted to detect water content in ethanol and gasoline using the ratiometric fluorescence measurement method, based on the ratio of the PL intensities of two wavelengths (613 and 617 nm) of the same sample.

## RESULTS AND DISCUSSION

Effect of Eu\textsuperscript{3+} Concentration on Photoluminescence (PL) of Eu—DMSO. Eu—DMSO shows a strong red photoluminescence (PL) upon UV exposure, as depicted in Figure 1 (left) for various concentrations of Eu\textsuperscript{3+} (0.02, 0.1, 0.2, 0.3, and 0.5 M). The emission spectra of all samples, when excited by 394 nm, are presented in Figure 1 (right). The sharp and narrow emissions of the Eu\textsuperscript{3+} ion originate from f–f transitions, and the emissions in the range of 575–725 nm are attributed to 5D\textsubscript{0} – 7F\textsubscript{j} (j = 0, 1, 2, 3, and 4) transitions of Eu\textsuperscript{3+}.\textsuperscript{31}

As can be seen in Figure 1 (right), the PL intensity of Eu\textsuperscript{3+} showed a gradual increase with an increase in concentration and attained the highest intensity at the concentration of 0.2 M, and then decreased gradually with further increase in concentration (see inset in Figure 1 (right) for the emission of 617 nm). This result shows that 0.2 M is the optimum concentration of Eu—DMSO, whereas it suffers from a concentration quenching effect beyond 0.2 M.

The molecular structure of Eu—DMSO is still unclear due to the lack of extensive characterization as no crystals or precipitates could be obtained from the solutions. Nevertheless, the luminescence phenomenon may provide some critical information about the environments of Eu\textsuperscript{3+} ions in the solution. In fact, the luminescence spectroscopy of the europium ion has been exploited to elucidate the structure of natural and synthetic compounds.\textsuperscript{32} The fact that 5F\textsubscript{0} and 4D\textsubscript{0} levels are nondegenerate, its number of components suggests the number of different metal—ion sites.\textsuperscript{33–36} As shown in Figure 2 (left), the 5D\textsubscript{0} – 7F\textsubscript{0} emission is a single peak in DMSO, indicating that Eu\textsuperscript{3+} ions occupy an equivalent site. The 5D\textsubscript{0} – 7F\textsubscript{0} transition of Eu\textsuperscript{3+} is forbidden by both electric dipole transitions (EDT) and magnetic dipole transition (MDT) mechanisms, thereby resulting in very weak luminescence. It has also been reported that the 5D\textsubscript{0} – 7F\textsubscript{0} transition normally appears when the site symmetry around europium ion is very low and is generally seen for 10 site symmetries: C\textsubscript{4v}, C\textsubscript{2v}, C\textsubscript{2}, C\textsubscript{s}, C\textsubscript{1}, C\textsubscript{1v}, C\textsubscript{1}, C\textsubscript{i}, C\textsubscript{1}, C\textsubscript{3}, C\textsubscript{3v}, C\textsubscript{3}, C\textsubscript{2}, C\textsubscript{2}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1}, C\textsubscript{1} based on the electric dipole selection rule. In many phosphors, the emissions of 5D\textsubscript{0} – 7F\textsubscript{0} can be attributed to the presence of oxygen in the crystals, which lowers the site symmetry of Eu\textsuperscript{3+} ions.\textsuperscript{37,38} Accordingly, it is reasonable to believe that the occurrence of oxygen in DMSO is one likely reason for the 5D\textsubscript{0} – 7F\textsubscript{0} emissions.

As displayed in Figure 2 (left), the intensities of the 5D\textsubscript{0} – 7F\textsubscript{0} emissions are dependent on the concentration of Eu\textsuperscript{3+} and followed a similar trend to f–f emissions, as illustrated in Figure 1 (right). The luminescence intensity of the 5D\textsubscript{0} – 7F\textsubscript{0} transition increased with the concentration of Eu\textsuperscript{3+} and
reached the maximum at 0.2 M and then decreased with further increase in the concentration. The change in the intensity ratios of the $^{3}D_{0}\to^{7}F_{J}$ ($J = 1, 2, 3, \text{ and } 4$) transition to the $^{3}D_{0}\to^{7}F_{2}$ transition (i.e., 592/579, 613/579, 617/579, 652/579, and 700/579) with an increase in the Eu$^{3+}$ concentration is shown in Figure 2 (right). It is particularly interesting to observe that the trend is similar for all of the transitions, suggesting the effects of concentration are similar to all of the $^{3}D_{0}\to^{7}F_{J}$ ($J = 0, 1, 2, 3, \text{ and } 4$) transitions.

The two peaks at 592 ($^{3}D_{0}\to^{7}F_{2}$) and 615 nm ($^{3}D_{0}\to^{7}F_{1}$) are ascribed to the magnetic dipole and electric dipole transitions, respectively. The strong peak at 615 nm, which corresponds to the $^{7}F_{2}$ level in a low-symmetry site. In theory, the $^{7}F_{2}$ level splits into three crystal field levels of A1 and 2E with a low-symmetry site. Due to the close energy levels of A1 and one of the two E levels, these energy levels can be overlapped in the emission spectra, resulting in only two energy levels A1 and E. Here, we assign the 613 nm emission to A1 and the 617 nm emission to E.

The peak at 592 nm, which corresponds to the $^{3}D_{0}\to^{7}F_{2}$ transition, is due to the allowed magnetic dipole transition. According to the Laporte selection rule (equal parity), if an Eu$^{3+}$ ion is situated in a symmetry center, the electric dipole transitions between the 4E levels are strictly forbidden, whereas the magnetic dipole transition is still possible. On the other hand, the electric dipole transition intensity should be stronger than the magnetic dipole transition intensity in an asymmetric environment, as stated by the Judd–Ofelt theory. The intensity at 615 nm (electric dipole transition) is stronger than that at 592 nm (magnetic dipole transition), which signifies that Eu$^{3+}$ occupied sites have low inversion symmetry or asymmetric environment. The intensity ratio of the $^{3}D_{0}\to^{7}F_{1} \text{ to } ^{3}D_{0}\to^{7}F_{2}$ transitions (617/592 and 613/592 nm), called the symmetry ratio, can provide information about the structural quality of the material. As presented in Figure 3, the intensity ratios of various Eu–DMSO samples (0.02, 0.1, 0.2, and 0.5 M of Eu$^{3+}$) are from 1.4 to 2.8, suggesting a low inversion symmetry of Eu$^{3+}$ sites. Notably, the symmetry ratios (617/592 and 613/592 nm) enhanced with increasing Eu$^{3+}$ concentrations (Figure 3), most likely due to the increase in the symmetry for the Eu$^{3+}$-occupying sites.

FTIR, NMR Spectra, and UV–Vis Absorption. To elucidate the interaction of Eu$^{3+}$ ions with DMSO and water, FTIR, $^1$H NMR, $^{13}$C NMR, and UV–vis absorption spectra were acquired. Figures S1–S3 depict the FTIR spectra of DMSO alone, Eu–DMSO, and water-added Eu–DMSO samples, respectively. As shown in Figure S1, the S=O stretch in pure DMSO sample appeared at 1048 cm$^{-1}$. This peak shifted to the lower wavenumber of 1041 cm$^{-1}$ in the Eu–DMSO sample (Figure S2), indicative of the oxygen atom of DMSO in interaction with Eu$^{3+}$ ions. Upon interaction, the S=O bond gets more polarized to lose double-bond character, thus providing a lower energy transition during infrared interaction. Furthermore, the Eu–DMSO sample containing water relaxed the S=O stretch to 1045 cm$^{-1}$ (Figure S3). This is probably due to an increased interaction between added water and Eu$^{3+}$ ions, which competes with the DMSO interaction with Eu$^{3+}$ ions, thereby releasing more DMSO in its native free state.

To further understand the interaction of Eu$^{3+}$ with DMSO, $^1$H NMR and $^{13}$C NMR spectra were also collected. Figure S4 demonstrates the results of the $^1$H NMR spectra of Eu–DMSO and DMSO alone. The results reveal that the proton signal of the methyl group in DMSO appears as a singlet peak at 2.584 ppm. However, in the Eu–DMSO sample, the same proton signal appears to shift to the low-field region of 2.588 ppm. This minimal deshielding effect could arise from the interaction between DMSO and Eu$^{3+}$ ions through the S=O group of DMSO. A similar effect is observed in the carbon signal, where the chemical shift value of carbon in DMSO shifted to a low-field region in the Eu–DMSO sample (Figure 4). Upon the addition of water in the Eu–DMSO sample, the carbon signal moves back to the high-field region, potentially due to competitive interaction between water and Eu$^{3+}$ ions in the presence of water. Both FTIR and NMR results show the interaction between DMSO and Eu$^{3+}$ ions, although the exact mode of interaction or complexation is currently not known.

Figure 5 depicts the UV–vis absorption spectra of the Eu–DMSO sample after diluting with an equal volume of DMSO (left) and water (right). As can be seen in Figure 5 (left), the absorption peak of the Eu–DMSO sample at about 264 nm decreased after the gradual addition of DMSO, which can be attributed to the dilution effect. On the other hand, as displayed in Figure 5 (right), after adding the same amount of water to the Eu–DMSO sample, not only peak intensity decreased but also wavelength shifted. As water is considered as a competitive agent for complexation in lanthanide complexes, the peak wavelength shift after diluting with water can be ascribed to the possible interaction of water with Eu$^{3+}$. The results of the UV–vis absorption spectra are consistent with the results of the FTIR and NMR spectra.

Water Sensing in DMSO. As reported in our previous work, the photoluminescence (PL) of the Eu–DMSO compound can be exploited as a highly sensitive probe for water detection. Particularly, the emission corresponding to the $^{3}D_{0}\to^{7}F_{2}$ transition of Eu$^{3+}$ in Eu–DMSO is ultrasensitive with water. Due to $J$-mixing in the crystal field expansion and the spin–orbit interaction, the $^{3}D_{0}\to^{7}F_{2}$ transition band splits into two emission peaks (613 (A1) and 617 nm (E)). When water was added to the as-synthesized sample, the ratio of the intensities of 613 to 617 nm peaks ($I_{613}/I_{617}$) showed a remarkable change. Interestingly, the 617 nm peak suffered from a more rapid quenching effect than the 613 nm peak in the presence of water. The quenching effect after adding water can be ascribed to the loss of some energy of excited state of Eu$^{3+}$ to O–H oscillators of water molecules. An alternative mechanism of fluorescence quenching could be the photo-
induced electron transfer (PET) process. On the other hand, both 613 and 617 nm peaks showed similar quenching effect with the addition of DMSO, which can simply be attributed to the dilution of the sample.

The systematic changes in the two emission peaks (613 and 617 nm) with water are shown in Figure 6 for the four samples with Eu$^{3+}$ concentrations of 0.02, 0.1, 0.2, and 0.5 M. For the original samples, the emission at 617 nm is always higher in intensity than the emission at 613 nm. When water was added to the Eu–DMSO samples, both the emissions at 617 and 613 nm saw a reduction in intensity, but the decrease of the peak at 617 nm with water was faster than that of the 613 nm peak, which might be caused by changes in the Eu$^{3+}$ environment and symmetry of the complex. Even though the results of FTIR, NMR, and absorption spectra suggest the interaction of water with Eu$^{3+}$, the exact mechanism of faster intensity decrease at 617 nm is still mysterious. Since the decrease in intensity at 617 nm is faster than that of 613 nm, the two peaks should have an equal intensity at a certain concentration of water, named as “turning point”. It is worthwhile mentioning that this turning point is different for the samples of different concentrations, as shown in Table 1 and Figure 7 (left). For the 0.02 M sample, the turning point is at 1.0%, while for the 0.5 M sample, the turning point is at 13%. This means the

| Eu$^{3+}$ concentrations in Eu–DMSO (M) | turning point (%) for equal intensity at 613 and 617 nm | linearity $R$ | ratio of 613 to 592 nm ($I_{613}/I_{592}$) |
|----------------------------------------|-------------------------------------------------------|---------------|-----------------------------------|
| 0.02                                   | 1.0                                                   | 0.9675        | 1.441                             |
| 0.10                                   | 4.8                                                   | 0.9925        | 1.540                             |
| 0.20                                   | 6.5                                                   | 0.9973        | 1.596                             |
| 0.50                                   | 13.0                                                  | 0.9945        | 1.801                             |

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Figure 4. $^{13}$C NMR spectral figure showing a comparison between pure DMSO, Eu–DMSO sample, and Eu–DMSO + water sample taken in deuterated chloroform (CDCl$_3$) at room temperature under identical instrumental conditions.

Figure 5. UV–vis absorption spectra of the Eu–DMSO solution before and after diluting with different amounts of DMSO (left) and water (right).

Figure 6. Representative photoluminescence spectra (Exi = 394 nm) of Eu–DMSO at different concentrations of Eu$^{3+}$ before and after dilution with water (% v/v).

Figure 7. Left: Intensity trends of emission peaks at 613 and 617 nm of different concentrations of Eu$^{3+}$ in Eu–DMSO solution with increase an in water content. Right: Plot of intensity ratios of 613 to 617 nm peaks with water content in various Eu–DMSO samples.
interaction of water with Eu\textsuperscript{3+} in Eu—DMSO is related to the Eu\textsuperscript{3+} concentration, which affects the sensitivity for water detection.

The change in the intensities of the 613 and 617 nm peaks with water content can be used for water detection. A linear plot of \(I_{613}/I_{617}\) with respect to water content is shown in Figure 7 (right). The results demonstrate that the linearity is related to the Eu\textsuperscript{3+} concentrations and that the 0.2 M Eu—DMSO sample has the strongest luminescence and highest slope.

As labeled in Figure 1 (right), the two sharp peaks at 592 and 615 nm are ascribed to the magnetic dipole (\(\tilde{D}_0 \rightarrow \tilde{T}_F\)) and electric dipole (\(\tilde{D}_0 \rightarrow \tilde{F}_3\)) transitions, respectively. As the symmetry ratio (\(\tilde{D}_0 \rightarrow \tilde{T}_F/\tilde{D}_0 \rightarrow \tilde{T}_F\)) can provide information about the quality structure of the material,\textsuperscript{33–36,39} the intensity ratio of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) to \(\tilde{D}_0 \rightarrow \tilde{T}_F\) might be sensitive to water too. However, the ratios of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) (613 and 617 nm) to \(\tilde{D}_0 \rightarrow \tilde{F}_I\) (592 nm) transitions are not really sensitive to water, as shown in Figure S5.

On the contrary, the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) emission is very sensitive to water concentrations, as seen in Figure S6, even though it is a forbidden transition by both EDT and MDT mechanisms. As pointed out earlier, in many phosphors, the emissions of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) are due to the presence of oxygen in the crystals, which lowers the site symmetry of Eu\textsuperscript{3+} ions. Accordingly, the presence of oxygen in DMSO is one likely reason for observing the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) emissions. The sensitivity of the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) emissions to water further indicates that the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) transition is involved with the disturbance of external ions.

To further explore other parameters for water probing, we investigated the changes in the intensity ratios of \(\tilde{D}_0 \rightarrow \tilde{T}_F\), \(\tilde{D}_0 \rightarrow \tilde{T}_F\), \(\tilde{D}_0 \rightarrow \tilde{T}_F\) to \(\tilde{D}_0 \rightarrow \tilde{T}_F\) with water (Figures S7, S8, S9, and S10, respectively). Interestingly, all of the ratios of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) (\(\tilde{D}_0 \rightarrow \tilde{T}_F\)) are sensitive to water and to \(\tilde{D}_0 \rightarrow \tilde{T}_F\) with water (Figures S7, S8, S9, and S10, respectively). Interestingly, all of the ratios of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) (\(\tilde{D}_0 \rightarrow \tilde{T}_F\)) are sensitive to water and to \(\tilde{D}_0 \rightarrow \tilde{T}_F\) with water (Figures S7, S8, S9, and S10, respectively). Among these ratios, the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) transition is the most sensitive, while the \(\tilde{D}_0 \rightarrow \tilde{T}_F\) transition is the least sensitive. These observations indicate that the intensity ratios of \(\tilde{D}_0 \rightarrow \tilde{T}_F\) (\(\tilde{D}_0 \rightarrow \tilde{T}_F\)) can also be used for water detections, as illustrated in Figure 8. These findings also suggest that the changes of the intensity ratios are not merely due to the concentration changes but as a result of the intrinsic interactions of water with the Eu\textsuperscript{3+} ions; however, the details of the interaction mechanisms are still unknown. For each ratio, the 0.2 M Eu—DMSO sample has the best sensitivity, demonstrating that 0.2 M Eu\textsuperscript{3+} is the optimized concentration for water detection as well as the luminescence intensity.

**Detection of Water in Ethanol.** Real-time monitoring of water content in ethanol is of utmost importance for alcoholic beverage, fuel, and solvent industries.\textsuperscript{17} Ethanol is considered as an alternative to fossil fuels such as gasoline and diesel and has gained immense interest owing to the limited amount of available fossil fuels, the ever-increasing petroleum cost, and pollution concerns. While producing ethanol from grains, water is removed by distillation, and only ethanol with a purity of approximately 93% or higher is suitable to be used as a biofuel. Consequently, a cost-effective, in situ, reliable, and real-time analysis method to determine the water contained in ethanol is essential for its usage as a fuel.\textsuperscript{35,46}

On the other hand, with the addition of the same amounts of ethanol, both intensities decreased to a substantially lesser extent (Figure 9 (right)). For the purpose of comparison, we plotted \(I_{613}/I_{617}\) of the Eu—DMSO—ethanol probe as a function of water/ethanol concentration in ethanol. As can be seen in Figure 10 (left), the \(I_{613}/I_{617}\) ratio almost remained constant after diluting the probe with ethanol. Conversely, after adding DI water, \(I_{613}/I_{617}\) was found to increase, indicating that our sample can be used as a ratiometric water detection probe. Furthermore, \(I_{613}/I_{617}\) is plotted as a function of water content in ethanol to obtain a calibration curve. The
DI water is linear with gasoline to the probe. The result demonstrates that purpose of a comparison between the dilution effect of water and gasoline (%, v/v).

Figure 10. Left: Ratiometric fluorescence response of the Eu–DMSO–ethanol probe to various water or ethanol content in ethanol. Right: Calibration plot for determining the linear relationship between $I_{613}/I_{617}$ and water content in ethanol (0–24.24%, v/v).

Detection of Water in Gasoline. To further extend the possibility of the as-prepared Eu–DMSO sample, we attempted to detect water content in gasoline using the same ratiometric fluorescence measurement method, based on the ratio of the PL intensities of two wavelengths (613 and 617 nm) of the same sample. To achieve this goal, a Eu–DMSO–gasoline probe was prepared by mixing 500 μL of gasoline and 2 mL of Eu–DMSO. The Eu–DMSO–gasoline probe was then diluted with various amounts of water or gasoline. Finally, $I_{613}/I_{617}$ was plotted as a function of water concentrations in gasoline to quantify the amount of water in gasoline.

As can be seen in Figure 11 (left), after adding water to the probe, the PL intensities at 613 and 617 nm were found to decrease significantly compared to the gasoline-added sample (Figure 11 (right)). Figure 12 (left) was plotted for the purpose of a comparison between the dilution effect of water and gasoline to the probe. The result demonstrates that $I_{613}/I_{617}$ almost remained constant after diluting the probe with gasoline. In contrast, $I_{613}/I_{617}$ was found to increase with the addition of DI water, corroborating our hypothesis that the sample could be used to detect water in gasoline. The linear fitting (Figure 12 (right)) displays that the sample diluted with DI water is linear with $R^2 = 0.9969$ ($R_l = 0.334P_V + 0.8448$, where $R_l$ and $P_V$ stand for $I_{613}/I_{617}$ and volume fraction of water in gasoline, respectively) in a wide concentration range (0–32.43%), indicating that the sample is suitable to detect water in gasoline from a small amount to a high amount.

Determination of Detection Limits. The detection limit (DL) was calculated based on the equation: $DL = 3\sigma/s$, where $\sigma$ is the standard deviation of the y-intercept and $s$ is the slope of the calibration curve. The detection limits of water in DMSO, ethanol, and gasoline were found to be 0.17, 0.63, and 1.36% (v/v), respectively. Although it might not be fully justified to compare our results with the previously published results due to some differences in the calculation and experimental methods, a comparison of detection of water in DMSO and ethanol using the Eu–DMSO probe with some of the previously reported probes is presented in Table 2. As can be seen in Table 2, the detection limit of the Eu–DMSO probe is comparable to most of the probes for detecting water in ethanol, and DMSO. Considering the facile synthesis method, good detection limit, wider detection range, and large Stokes shift, we anticipate that the Eu–DMSO sample could be one of the deserving candidates for further investigation in the study of the detection of water in various organic solvents.

CONCLUSIONS

We demonstrated, for the first time, a multiparameter method for trace water detection using the robust and water-sensitive luminescence of Eu$^{3+}$ in DMSO. This one probe with several output parameters can be constructed with the ratio of the two $^5D_0 \rightarrow F_i$ emissions at 613 and 617 nm along with the intensity ratios of $^5D_0 \rightarrow F_{1/2}, ^5D_0 \rightarrow F_{0}, ^5D_0 \rightarrow ^7F_{2}/^7D_0 \rightarrow F_{0}$, $^5D_0 \rightarrow ^7F_{1/2}/^7D_0 \rightarrow F_{0}$, and $^5D_0 \rightarrow ^7F_{3/2}/^7D_0 \rightarrow F_{0}$. This multiparameter method provides reliable yet accurate detection as four parameters can be used for water detection based on a single agent. The concentration at 0.2 M has the best sensitivity and linearity for each parameter, demonstrating that 0.2 M is the optimized concentration for water detection. Furthermore, to extend its practical applications, water detections in ethanol and gasoline have been carried out, and the results demonstrate that $I_{613}/I_{617}$ increased linearly over a wide range of water content, signifying it as a promising method for water detection in ethanol and gasoline. Our future work will focus on a better understanding of the luminescence quenching mechanism of the sample and the attempt to extend our knowledge to detect water in other organic solvents. Overall, considering its straightforward synthesis method, large Stokes shift, and sensitivity over a wide concentration range, this ratiometric fluorescent probe could provide a new accessible tool for the quantitative determination of water content in organic solvents and be a deserving candidate for further study.
Table 2. Comparison of Eu–DMSO Probe with Different Probes for Water Detection in Ethanol and DMSO

| S.No. | probe                        | detection limit | detection mode | references |
|-------|------------------------------|-----------------|----------------|------------|
| 1.    | poly(3-aminobenzoic acid)    | 0.1 wt %        | turn-off       | 48         |
| 2.    | anthracene-amino acid        | 0.1 wt %        | turn-on        | 49         |
| 3.    | carbon dots-imidazole nanoprobe | 0.28% (ethanol) | turn-on         | 50         |
| 4.    | Tb4+/p-CDs/MOF               | 0.28% (ethanol) | ratiometric    | 51         |
| 5.    | M1 membrane                  | 0.42% (ethanol) | turn-on         | 52         |
| 6.    | OU-1                         | over 1.0 wt %   | turn-on         | 53         |
| 7.    | LiTaO3 coated with ITO       | 1.3% (ethanol)  | photothermal spectroscopy | 54         |
| 8.    | LiTaO3 coated with ITO       | 1.6% (ethanol)  | photothermal spectroscopy | 54         |
| 9.    | LiTaO3 crystal coated with ITO| 1.6% (ethanol) | photothermal spectroscopy | 55         |
| 10.   | copper electrodes            | 10% (ethanol)   | capacitance    | 56         |
| 11.   | triangular silver (Ag)       | 1.2% (ethanol)  | surface plasmon resonance | 57         |
| 12.   | PPQ-CDs                      | 0.092% (ethanol)| turn-on         | 58         |
| 13.   | merocyanine dye 1            | 0.63 wt %       | ratiometric absorbance | 59         |
| 14.   | merocyanine dye 2            | 1.1 wt %        | ratiometric absorbance | 59         |
| 15.   | M1 membrane                  | 8.05% (DMSO)    | turn-on         | 52         |
| 16.   | PPQ-CDs                      | 0.023% (DMSO)   | turn-on         | 58         |
| 17.   | coumarin conjugate (DC)       | 0.095% (DMSO)   | turn-off        | 60         |
| 18.   | coumarin based Schiff base   | 0.18% (DMSO)    | turn-on         | 61         |
| 19.   | Eu–DMSO                      | 0.63% (ethanol) | ratiometric fluorescence | this work |

**EXPERIMENTAL SECTION**

Materials. Europium nitrate pentahydrate (Eu(NO3)3·5H2O, 99.9%) and DMSO were received from Sigma-Aldrich. Anhydrous ethanol was purchased from Decon Labs, Inc. Gasoline was obtained from a local gas station. All of the chemicals were used without purification.

**Synthesis of Eu–DMSO Compound.** The Eu–DMSO sample was synthesized following a previously reported method. Typically, 2.14 g of Eu(NO3)3·5H2O and 25 mL of DMSO were mixed in a 125 mL three-neck round-bottom flask. The reaction mixture was then heated at 150 °C for 2 h under a nitrogen environment with vigorous magnetic stirring. Finally, the solution was cooled to room temperature naturally under a nitrogen environment.

**Investigation of Effects of Eu3+ Concentration on Luminescence.** To investigate the luminescence quenching effect of the as-prepared Eu–DMSO sample in the presence of water, the sample was diluted with desired amounts of DI water. The emission spectra (excitation wavelength = 394 nm) of all of the samples were recorded on a Shimadzu RF-5301PC spectrophotofluorometer at room temperature. To serve as a control, the sample (Eu–DMSO) was diluted with equal amounts of DMSO.

**FTIR, UV–Vis Absorption, and NMR Spectra.** FTIR spectra were obtained using a Bruker Alpha-P FT-IR spectrometer using attenuated total reflectance on a diamond sample plate. 1H NMR spectroscopic data were recorded on a 500 MHz JEOL spectrometer and referenced to the internal solvent signal (7.26 ppm in CDCl3).

13C NMR spectroscopic data were recorded on a 125 MHz JEOL spectrometer and referenced to the internal solvent signal (central peak 77.00 ppm in CDCl3). The UV–vis absorption spectra of the Eu–DMSO sample after adding DMSO or DI water were measured using a Shimadzu UV-2450 UV–vis spectrophotometer.

**Detection of Water in Ethanol and Gasoline.** To detect the water impurity in ethanol, the Eu–DMSO–ethanol probe was prepared by mixing 500 μL of anhydrous ethanol and 2 mL of the Eu–DMSO sample. After measuring its PL intensity, the probe was diluted with various amounts of DI water to investigate its luminescence quenching effect. For the purpose of comparison, the probe was diluted with an equal volume of ethanol instead of DI water. Similarly, to detect water in gasoline, the Eu–DMSO–gasoline probe was prepared by adding 500 μL of gasoline to 2 mL of the Eu–DMSO sample and all other experimental conditions were the same except gasoline was used instead of ethanol. Finally, a calibration curve of I613/I617 was established as a function of water/ethanol or water/gasoline content to quantify water contents. All measurements were carried out right after adding DI water, ethanol, or gasoline in the respective probes, suggesting its very fast response rate and capability for real-time monitoring of trace water in organic solvents.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00270.

FTIR spectra and 1H NMR spectra of Eu–DMSO samples; study of relationships of various intensity ratios of Eu–DMSO with water concentrations (PDF)

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Notes

The authors declare no competing financial interest.

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