

The advantage of reversible coordination polymers in producing visible light sensitized Eu(III) emissions over EDTA *via* excluding water from the coordination sphere

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In this paper, we report on the impact of the structure of ligands on the luminescence enhancement of Eu(III) by directly exciting Eu(III) with visible light in aqueous media. Upon replacing the water molecules that coordinated around a Eu³⁺ ion with a ditopic ligand 1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane (L₂EO₄) or ethylenediaminetetraacetic acid disodium salt (EDTA), significant luminescence can be obtained. L₂EO₄ may occupy all 9 coordinating sites of a Eu³⁺ ion at proper L₂EO₄/Eu ratios, whereas EDTA only occupies 6 of them with 3 sites left for water at various EDTA/Eu ratios. These coordinated water molecules quench the fluorescence of EDTA–Eu complexes drastically so that the luminescence is about 30 times lower than that of the L₂EO₄–Eu system. Furthermore, the negatively charged L₂EO₄/Eu = 3/2 coordinated complex can be further transformed into coordination ‘polymers’ by mixing with a positively charged block polyelectrolyte, which forms electrostatic micelles with further enhanced luminescence. The emission of the EDTA–Eu complex is not influenced by the addition of polymers due to the formation of stable small 1 : 1 EDTA–Eu complex which doesn’t change with increasing concentration. Our work points out that the L₂EO₄–Eu system is superior to the EDTA–Eu system in creating visible light sensitized Eu(III) luminescence, and the emission of Eu(III) can be indeed significantly enhanced to an applicable level by excluding all the water molecules in the coordination sphere of Eu(III).

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Introduction

The unusual electronic properties of trivalent lanthanide ions make them well suited as luminescent reporters, which have currently attracted intensive attention in developing applications in biotechnology.^{1–4} However, due to the forbidden nature of the f–f transition of the rare earth metals, the direct absorption of Eu³⁺ ions is only very weak, which limits their practical usage.⁵ In order to overcome this bottleneck, the Eu³⁺ ion is often chelated to a chromophore-containing group which functions as an ‘antenna’, absorbing incident light then transferring this excitation to the metal ion, which can then deactivate by undergoing its typical luminescent emission.^{6–9} Unfortunately, due to an energy limit, the excitation of antenna molecules is often in the

UV region, so that antenna sensitized Eu(III) luminescence cannot practically be applied in biological systems.^{1,10}

In the past decade, many efforts were made to shift the excitation window of Eu(III) complexes to the visible region. Two major strategies have been invented, namely to increase the size of the conjugated groups to shift the absorption of the antenna molecules toward the visible region,^{11–14} and to design antenna molecules with twisted and other complicated structures to allow two photon sensitizing.^{15–20} Both strategies require tedious organic synthesis of antenna molecules which is often not applicable to many labs. In addition, antenna molecules in both strategies are often water insoluble,^{12–18} so that organic solvents have to be employed to obtain Eu(III) complexes. Therefore, it still remains a challenge to develop Eu(III) complexes that are soluble in water and meanwhile can be sensitized by visible light.

Among the endeavors for complicated ligand synthesis, it seems that no attempt has been made to study the Eu(III) emission by direct excitation of Eu³⁺ ion when the water molecules coordinated to the first coordination sphere are excluded. It is well-known that the Eu(III) ion in water has weak

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absorptions in the visible region at 395 and 465 nm.⁵ This weak absorbance may produce Eu(III) emissions as well, but in aqueous media the emission was quenched drastically by coupling with the OH vibration of water molecules.²¹ As a result, direct excitation of Eu(III) in water cannot lead to efficient emissions. Therefore, we expect that when quenching from water is avoided, considerable Eu(III) emission may be obtained simply by direct excitation of the central Eu³⁺ ion using visible light.

In this work we report a systematic study of the emissions of Eu(III) excited at its own absorbance wavelength when water was excluded from the first coordination sphere with water soluble ligands. Two ligands with different numbers of chelating points and topologies were employed to study the impact of the remaining coordinated water molecules on the Eu(III) emissions. One is a ditopic ligand L₂EO₄ where each head has 3 chelating points, and 3 of such heads were expected to exclude all the coordinated water molecules from the first coordination sphere of Eu(III).^{22–26} The other is EDTA, which is a strong chelating agent with 6 chelating points.²⁷ In aqueous media, the practical coordination number and coordination topology of Eu(III)–L₂EO₄ complexes depends on the mixing ratio between Eu³⁺ and L₂EO₄. At stoichiometric mixing of L₂EO₄/Eu = 3/2, chain extension may occur to form coordination polymers where, except from the Eu³⁺ ion located at the end of the chain, all the other Eu³⁺ ions are supposed to be coordinated with 3 chelating heads, so that there should be no coordinated water molecules in the coordination sphere of these Eu(III) ions. This readily occurs by mixing the L₂EO₄/Eu = 3/2 coordination complex with a positively charged block polyelectrolyte, which forms electrostatic micelles with further enhanced luminescence. However, the emission of the EDTA–Eu complex cannot be influenced by the addition of polymers due to the formation of a stable small 1:1 EDTA–Eu complex which doesn't change with increasing concentration. We expect that the different chelating number and topology of these two ligands may have a different impact on the emission of Eu(III) under visible light. The results showed that when all the 9 chelating points are taken by ligand molecules, the emission of Eu(III) luminescence can be indeed significantly enhanced. *In vitro* bioimaging measurements revealed that this emission may be applicable. In contrast, if only 6 sites among the 9 were taken, where the others sites are left for water molecules, the luminescence can barely be improved to an applicable level.

Experimental section

Materials

The bis-ligand 1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane (L₂EO₄) used in this work was prepared according to previously reported procedures.^{28,29} Diblock polymer poly-(2-vinylpyridine)-*b*-poly(ethylene oxide) (P2VP₄₁-*b*-PEO₂₀₅, MW = 13.3 k, PDI = 1.05) were obtained from Polymer Science. Eu(NO₃)₃·6H₂O (Sigma, 99.99%), D₂O (J&K) and EDTA (Beijing Chemicals Company, AR) were used without further purification. Ultra-pure water was used and no extra salt was added. Stock solutions of P2VP₄₁-*b*-PEO₂₀₅, L₂EO₄, EDTA and Eu(NO₃)₃ were prepared at appropriate concentrations. 50 mM EDTA solution

and 50 mM Eu(NO₃)₃ solution were mixed at desired molar ratios to prepare EDTA–Eu complexes. To prepare the Eu coordination complexes, a 20 mM L₂EO₄ solution and 50 mM Eu(NO₃)₃ solution were mixed at the desired molar ratios. The coordination complexes were added in stoichiometric amounts to a P2VP₄₁-*b*-PEO₂₀₅ aqueous solution ([P2VP] = 2 mM, [L₂EO₄] = 1 mM, [Eu³⁺] = 0.67 mM). HCl and KOH were used to control the pH.

Luminescence spectrometer measurements

A lifetime and steady state spectrometer FLS920 was used to measure the luminescence emission and lifetimes of europium(III)-containing solutions. The excitation wavelength was set at 395 nm to directly excite the europium ions. Emission spectra were recorded in the range of 500–750 nm. Excitation spectra were recorded in the range of 250–500 nm. The slit was set at 5 mm for the Eu–L₂EO₄ system, whereas that for the Eu–EDTA system was set as 10 mm in separate measurements to get spectra of sufficient intensity. However, for comparison of the emission intensities in these two systems, the slit was set at 5 mm for both. The lifetimes were measured at 395 nm since the excitation wavelength doesn't affect the lifetime.

Solution fluorescence

Aqueous solutions of L₂EO₄/Eu = 5/1, 3/1 and Eu-micelles ([Eu³⁺] = 3.33 mM, L₂EO₄/Eu = 3/2) were imaged by a Maestro EX *in vivo* spectral imaging system under the excitation of a 455 nm laser. A 500 nm short pass emission filter was used to prevent disturbance of the excitation light with the charge coupled device (CCD) camera. The solution fluorescence imaging from 500 nm to 720 nm (in 10 nm steps) was conducted with an exposure time of 6000 ms in virtue of the long lifetime of rare earth metals. Background was removed using the spectral unmixing software.

Results and discussion

Emissions in L₂EO₄–Eu and EDTA–Eu systems

The aqueous solution of Eu(NO₃)₃ exhibits negligible emission under 395 nm irradiation due to the quenching by water. Upon mixing with EDTA or L₂EO₄ at various mixing ratios, the emission increases significantly, suggesting that excluding water molecules from the coordination sphere occurs in both systems. The luminescence intensities for the EDTA–Eu system reach a plateau at EDTA/Eu around 1/1 (Fig. 1B), suggesting one europium ion maximally coordinates with 1 EDTA. It is well-known that each EDTA molecule has 6 chelating points whereas one Eu³⁺ has 9 chelating sites in its first coordination sphere. This means that 3 coordination sites of Eu(III) are still taken by water molecules. It is worth noting that although there are still remaining sites for chelation, additional EDTA cannot coordinate with Eu³⁺ any more at EDTA/Eu > 1/1. It is probably the steric hindrance that hinders further binding. In contrast, in the L₂EO₄–Eu system, the plateau occurs at L₂EO₄/Eu = 3/1. Because each head of L₂EO₄ contributes 3 chelating group (Scheme 1D), this means L₂EO₄ uses one head to coordinate with one Eu³⁺ ion so that 3 of such heads from three L₂EO₄ molecules may occupy all 9 chelating points of Eu³⁺.

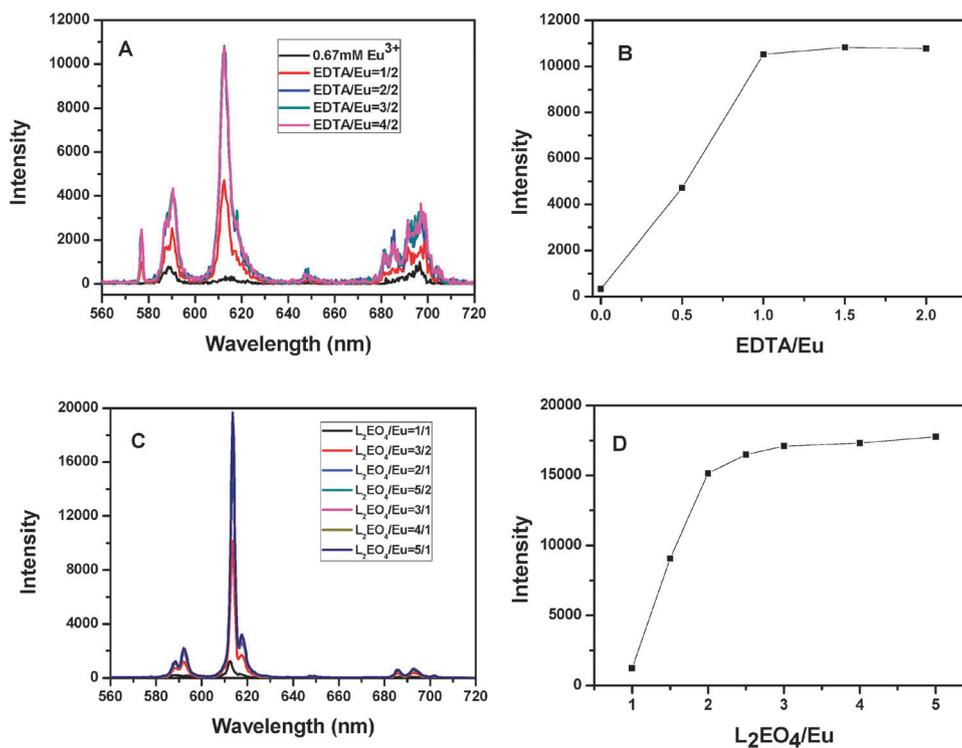


Fig. 1 (A) The emission spectra of EDTA–Eu complexes. (B) The emission intensity at 613 nm of EDTA–Eu complexes in (A) formed at various molar ratios ($[\text{Eu}^{3+}] = 0.67 \text{ mM}$, $\lambda_{\text{ex}} = 394 \text{ nm}$); (C) the emission spectra of L_2EO_4 –Eu complexes. (D) The emission intensity at 614 nm of L_2EO_4 –Eu complexes formed at various molar ratios ($[\text{Eu}^{3+}] = 0.67 \text{ mM}$, $\text{pH} = 6.9$, $\lambda_{\text{ex}} = 395 \text{ nm}$ for all the systems).

Since no water exists in the coordination sphere at this ratio, the plateau emission is much stronger than that for the EDTA system. It can be read in Fig. 1C that the plateau emission for the L_2EO_4 –Eu system, namely, emission at $\text{L}_2\text{EO}_4/\text{Eu} > 3$, is 14 times higher than that at $\text{L}_2\text{EO}_4/\text{Eu} = 1$, whereas even the latter is more than two fold of that in the EDTA–Eu system (Fig. 2). These results suggest: (1) the quenching effect of water in the EDTA system is indeed very significant, 3 water molecules in the coordination sphere leads to nearly 30 times lower emission; (2) the coordination between L_2EO_4 is stronger than that between EDTA.

Time-resolved luminescence intensity measurements

The above results clearly indicate that the L_2EO_4 –Eu system is superior in creating visible light sensitized $\text{Eu}(\text{III})$ luminescence, therefore time resolved luminescence measurements were conducted to gain more physical insight into the change of emission lifetime and the number of water molecules coordinated under various conditions. The luminescence intensity I_t can be expressed by eqn (1) and (2) for single and doubly exponential decays, respectively:³⁰

$$I_t = I_1 e^{-t/\tau_1} \quad (1)$$

$$I_t = I_1 e^{-t/\tau_1} + I_2 e^{-t/\tau_2} \quad (2)$$

$$\alpha_i = \frac{I_i}{I_1 + I_2} \quad (3)$$

where I_t is the emission intensity at time t , I_i ($i = 1, 2$) is the emission intensity of luminophores in different environments

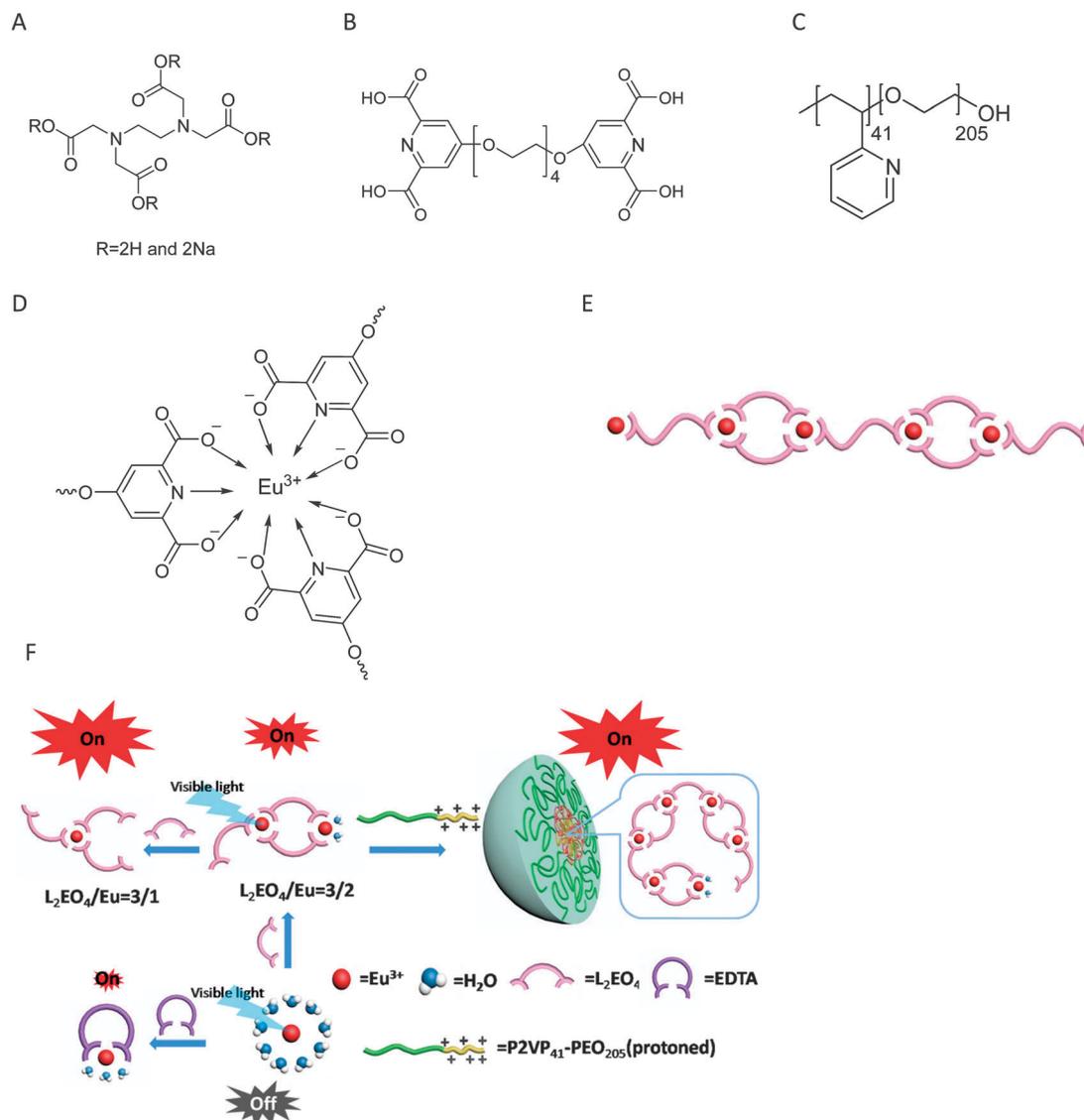
at time 0, τ_i ($i = 1, 2$) is the lifetime of luminescence for luminophores in different environments, whereas the pre-exponential factors α_i ($i = 1, 2$) represent their fraction.

As indicated in Table 1, only one lifetime is obtained for the coordination complexes of the EDTA–Eu system at various ratios, suggesting the presence of only one coordinating environment for Eu^{3+} . The lifetime for Eu^{3+} ions in water is 114 μs , whereas it is slightly increased to 310 μs in the EDTA–Eu coordination complexes. This indicates that quenching from water is still very significant. For coordination complexes formed between rare earth metal and multidendate ligands, the number of water molecules still in the coordination sphere can be calculated using eqn (4).³¹

$$q = 1.2 \times (k_{\text{H}_2\text{O}} - k_{\text{D}_2\text{O}} - 0.25) \quad (4)$$

Here, $k_{\text{H}_2\text{O}}$ and $k_{\text{D}_2\text{O}}$ represent the rate constants of luminescence decay, namely, the slopes obtained in the time-resolved fluorescence intensity curves, which are measured in H_2O and D_2O , respectively. The q values for EDTA–Eu systems at all ratios are listed in Table 1. Clearly, q decreases with the increasing fraction of EDTA. Without addition of EDTA, the number of water molecules coordinated to the central Eu^{3+} ion is 8.8, which is in good agreement with the literature result and suggests the presence of 8–9 water molecules in the coordinating sphere of Eu^{3+} .^{21,32}

It is clear that the number of coordinated water molecules decreases to 3 and keeps constant at $\text{EDTA}/\text{Eu} > 1/1$,



Scheme 1 Structure of (A) EDTA. (B) L_2EO_4 . (C) $P2VP_{41}\text{-}b\text{-}PEO_{205}$. (D) Demonstration of coordination between the head of L_2EO_4 and Eu^{3+} . (E) Demonstration of the linear structure formed between Eu^{3+} and L_2EO_4 in the $L_2EO_4/Eu = 3/2$ system. (F) Illustration of the mechanism of emission in the EDTA–Eu system and the enhancement of the luminescence emission of L_2EO_4 –Eu coordination complexes with and without $P2VP_{41}\text{-}b\text{-}PEO_{205}$.

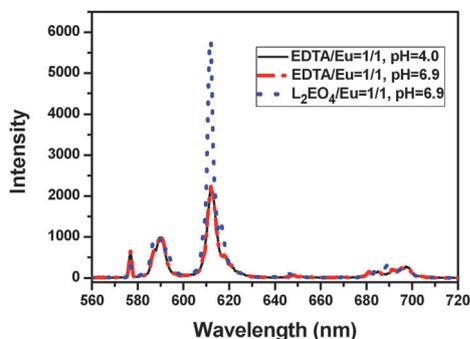


Fig. 2 The emission spectra of EDTA–Eu ($\lambda_{ex} = 394$ nm) and L_2EO_4 –Eu ($\lambda_{ex} = 395$ nm) complexes. The variation of pH in the EDTA system suggests that pH has no obvious influence on the coordination.

Table 1 Summary of lifetimes of EDTA–Eu complexes in H_2O and in D_2O ($\lambda_{ex} = 394$ nm, $[Eu^{3+}] = 0.67$ mM)

EDTA/Eu	τ/ms (H_2O)	τ/ms (D_2O)	q
0/2	0.11	2.38	8.81
1/2	0.28	2.09	3.46
2/2	0.31	2.35	3.11
3/2	0.31	2.39	3.07
4/2	0.31	2.44	3.08

which confirms that all 6 chelating groups in EDTA have coordinated to the Eu^{3+} ion, and additional EDTA doesn't bind. This result is in good agreement with the variation of emission intensity with EDTA/Eu ratios in Fig. 1B.

Table 2 Summary of lifetimes and fractions of long lifetime luminophores α_2 of L_2EO_4 -Eu complexes in H_2O and in D_2O ($\lambda_{ex} = 395$ nm, $[Eu^{3+}] = 0.67$ mM, pH = 6.9)

L_2EO_4/Eu	H_2O			D_2O τ/ms	q	
	τ_1/ms	τ_2/ms	α_2			
1/1	0.33	—	0	2.71	—	2.94
3/2	0.59	1.25	0.47	2.69	1.29	0.21
2/1	—	1.33	1	2.59	—	0.14
5/2	—	1.41	1	2.59	—	0.09
3/1	—	1.43	1	2.57	—	0.07
4/1	—	1.45	1	2.57	—	0.06
5/1	—	1.46	1	2.56	—	0.06

However, the results for L_2EO_4 -Eu systems are different. As shown in Table 2, with increasing the L_2EO_4/Eu ratio, the lifetime increases significantly. In the 1/1 solution, only one τ (0.33 ms) is obtained, indicating the coordinating states of the measurable emissive europium ions are the same. This lifetime is similar to that in EDTA-Eu system at this ratio, suggesting that only part of the coordinating sites of one $Eu(III)$ ion is occupied by L_2EO_4 and the remaining sites are still taken up by water molecules. At L_2EO_4/Eu ratios beyond 3/2, a long lifetime > 1 ms appeared in all solutions. In line with this, the number of coordinated water molecules keeps decreasing from 2.94 to 0.06. Clearly, water molecules have been excluded more efficiently in the L_2EO_4 -Eu system than in EDTA-Eu system.

Effect of oppositely charged polymers on the emissions

Because all these coordination complexes are negatively charged, an oppositely charged block copolymer was added into the EDTA-Eu and L_2EO_4 -Eu systems to examine the effect of electrostatic interaction on the emission. It can be clearly seen in Fig. 3A that the emission in the EDTA-Eu system is not influenced by the addition of polymers, suggesting the coordinating state is not changed. As mentioned in the previous text, this is probably because of the steric hindrance that prevents further binding of extra EDTA to the 1 : 1 EDTA-Eu coordination complexes. In accordance with this, the lifetime is measured to be 308 μs , and the number of coordinated water molecules is 3, which is exactly the same as the situation where no polymer is added.

Similar results occur for the $L_2EO_4/Eu > 3/1$ systems;³³ however, the emissions for the L_2EO_4/Eu ratio below 3 are significantly enhanced, suggesting more emissive Eu^{3+} are formed.³³ Among which, the enhancement for emission in the $L_2EO_4/Eu = 3/2$ system is the largest.³³ This is attributed to the ditopic nature of the ligand which allows chain extension. As reported in our previous work, coordination complexes of L_2EO_4 with metal ions at stoichiometric ratios may grow into polymers at high concentrations.³⁴ For the L_2EO_4 -Eu system, this ratio is 1.5. Before the addition of polymer, the concentration of the system is very low; however, in the presence of a positively charged polymer, the local concentration of L_2EO_4/Eu can be considerably enhanced, which may lead to chain extension. In our previous work we have reported that the simultaneously occurring chain extension and electrostatic interaction lead to formation of polyion type micelles.²⁸ For convenience, we show the TEM image of the micelles as well in this paper in the inset of Fig. 3B.

Chain extension in the micellar core decreases the number of partly coordinated Eu^{3+} ions, and increases it for fully coordinated ions, as illustrated in Scheme 1E. It can be imagined that as mixing ratios deviate from the stoichiometric ratios, the formation of coordinating ends do not allow chain extension. That's why no emission enhancement can be observed at $L_2EO_4/Eu > 3/1$.

It is noticeable that two lifetimes occurred in the $L_2EO_4/Eu = 3/2$ solution, which indicates that the europium ions are in two different coordination states.^{9,35} If we assume that these two states can be ascribed to the europium ions at the end and middle of the bridged chains as illustrated in Scheme 1E, the long lifetimes, corresponding to europium ions that are fully coordinated with europium, account for 47%. According to the simple model in Scheme 1E, the number of fully coordinated europium ions n per chain in the $L_2EO_4/Eu = 3/2$ system can be estimated to be 1 using eqn (5), suggesting the complex has a structure as we illustrated in Scheme 1F. However, in the presence of polymer, n is increased to 5, indicating chain extension indeed occur in the micelles.

$$\frac{n}{n+1} = \alpha_2 \quad (5)$$

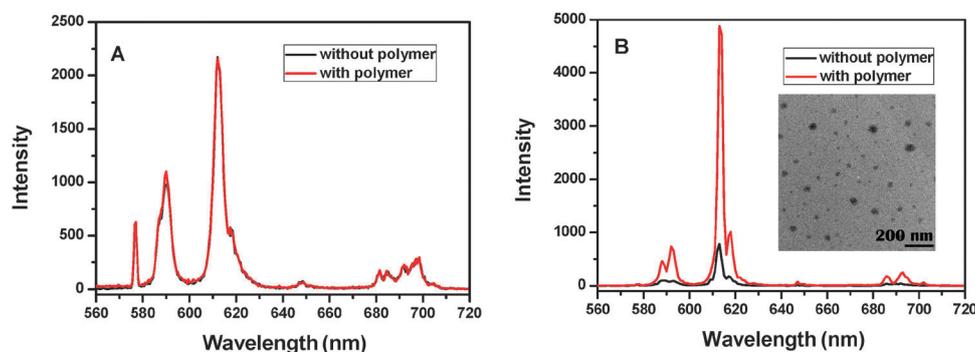


Fig. 3 (A) Emission spectra of EDTA-Eu(1/1) complexes with and without P2VP_{41-b}-PEO₂₀₅. ($\lambda_{ex} = 394$ nm, $[Eu^{3+}] = 0.67$ mM, pH = 4.0). (B) Emission spectra of L_2EO_4 -Eu(3/2) complexes with and without PVP_{41-b}-PEO₂₀₅ ($\lambda_{ex} = 395$ nm, $[Eu^{3+}] = 0.67$ mM, pH = 4.0). The inset in (B) is the TEM image for the micelles formed in the L_2EO_4 -Eu(3/2)/PVP_{41-b}-PEO₂₀₅ system.

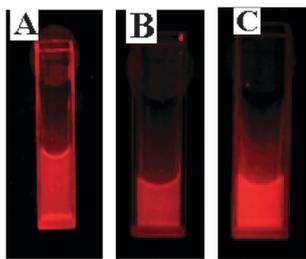


Fig. 4 Fluorescent images of (A) $L_2EO_4/Eu = 5/1$. (B) $L_2EO_4/Eu = 3/1$ complexes and (C) micelles formed at $L_2EO_4/Eu = 3/2$ (pH 4.0). These images were taken by a Maestro *in vivo* fluorescence imaging system under 455 nm irradiation.

Spectra unmixing of Eu(III) luminescence sensitized by visible light

The above results indicate that direct excitation of Eu(III) in the $L_2EO_4/Eu > 3/1$ or P2VP₄₁-*b*-PEO₂₀₅/ L_2EO_4 -Eu (3/2) micelle system may indeed produce applicable emission. In Fig. 4 we demonstrate the feasibility of fluorescence imaging with luminescent europium coordination complexes and Eu-micelles. A distinguished red color was obtained for solutions of $L_2EO_4/Eu = 5/1$, 3/1 and $L_2EO_4/Eu = 3/2$ in the presence of polymer. The emission intensity of the $L_2EO_4/Eu = 5/1$ system is stronger than that of the 3/1 system, suggesting the coordination between L_2EO_4 and Eu(III) is more efficient in excess of L_2EO_4 . However, in the presence of polymer to form micelles, the emissions can be the strongest even at a low L_2EO_4/Eu ratio of 1.5. Although these colors were obtained by spectral unmixing, it points out that the emission intensity in directly excited systems may be applicable, because these long lifetimes facilitate 'time-gated' emission experiments which result in a drastic improvement in signal to noise ratios.

Conclusion

In conclusion, we have compared the effect of ligand topology on the ability of achieving Eu(III) luminescence without using any antenna effect. Significant luminescence of Eu(III) can be obtained in water if all 9 coordinating sites in the first coordinating sphere of Eu(III) are occupied by chelating groups. This can be achieved by chelating Eu(III) ions with 3 ligand groups each bearing 3 chelating sites. In the case that such a ligand group was linked together with a spacer group to form a bisligand, reversible coordination polymers can be formed in the presence of an oppositely charged block copolyelectrolyte owing to chain extension. This simultaneously leads to formation of core-shell type micelles which show significant luminescence upon directly exciting the Eu(III) ions. In contrast, if the topology of the ligand, such as EDTA, doesn't allow effective occupation of the coordinating sites around a Eu(III) ion, only weak luminescence can be obtained. In this case, chain extension cannot occur in the presence of oppositely charged polyelectrolytes, so that the luminescence intensity cannot be promoted further. Spectra unmixing analysis suggests the emission of Eu(III) can be enhanced to an applicable level by excluding all the water molecules in the coordination sphere of the Eu(III). However, EDTA can only occupy 6 coordinated sites of Eu(III) and the

remaining 3 sites are occupied by water molecules, which means the luminescence can barely be improved to an applicable level.

Acknowledgements

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