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Understanding the Structure of Reversible Coordination Polymers Based on Europium in Electrostatic Assemblies Using Time-Resolved Luminescence

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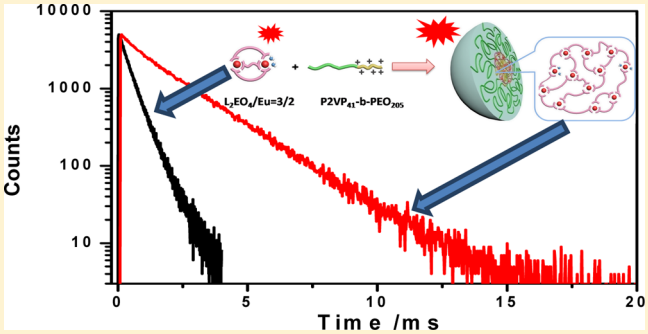
Supporting Information

ABSTRACT: In situ characterization of the structure of reversible coordination polymers remains a challenge because of their dynamic and concentration-responsive nature. It is especially difficult to determine these structures in their self-assemblies where their degree of polymerization responds to the local concentration. In this paper, we report on the structure of reversible lanthanide coordination polymers in electrostatic assemblies using time-resolved luminescence (TRL) measurement. The reversible coordinating system is composed of the bifunctional ligand 1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane (L_2EO_4) and europium ion Eu^{3+}. Upon mixing with the positively charged diblock copolymer poly(2-vinylpyridine)-*b*-poly(ethylene oxide) ($P2VP_{41}$-*b*-PEO_{205}), electrostatic polyion micelles are formed and the negatively charged L_2EO_4–Eu coordination complex simultaneously transforms into coordination "polymers" in the micellar core. By virtue of the water-sensitive luminescence of Eu^{3+}, we are able to obtain the structural information of the L_2EO_4–Eu coordination polymers before and after the formation of polyion micelles. Upon analyzing the fluorescence decay curves of Eu^{3+} before and after micellization, the fraction of Eu^{3+} fully coordinated with L_2EO_4 is found to increase from 32 to 83%, which verifies the occurrence of chain extension of the L_2EO_4–Eu coordination polymers in the micellar core. Our work provides a qualitative picture for the structure change of reversible coordination polymers, which allows us to look into these "invisible" structures.



INTRODUCTION

Recently, reversible coordination polymers have emerged as a novel kind of building blocks for supramolecular self-assemblies owing to their structural and compositional advantages.[1−10] These are equilibrium supramolecular structures with alternatively appearing ligands and metal ions.[1−10] The coordination centers usually carry charges that allow these untraditional polyelectrolytes to interact with oppositely charged species just like their conventional counterparts.[11−16] However, theoretical calculations predict that they respond quickly to changes in the concentration and composition owing to the dynamic formation and breakup of the coordinating bonds.[17] This makes it exceedingly difficult to experimentally characterize these macromolecular structures,[18] and so far, little in situ structural information is available for this type of material.[18,19] The situation becomes even more complicated when the coordination complexes form self-assemblies via electrostatic interactions.[20−24] The local concentration of the coordination complexes may increase in the presence of an oppositely charged polyelectrolyte, which spontaneously leads to a chain growth of the coordination complexes owing to their concentration responsiveness. This means that one may expect a different structure for the coordination complexes before and after the electrostatic self-assembly formation. We have reported several typical examples of the electrostatic assembly of coordination polymers in previous works,[20,21,25−27] from where we infer that the coordination oligomers may grow into polymers owing to the enhancement of their local concentration in the presence of an oppositely charged polyelectrolyte. However, until then, we do not have qualitative proof for such a chain extension because direct measurement of the degree of polymerization and the mass of a single chain is impossible in the electrostatic assemblies.

In the present study, we utilize time-resolved europium luminescence to obtain the information of chain extension of coordination polymers based on europium in electrostatic assemblies. It is well known that the luminescence of europium is very sensitive to water molecules bonded in the first coordination sphere.[28−30] In an aqueous solution, the Eu^{3+} ions show very weak luminescence because of the formation of $Eu(H_2O)_8^{3+}$ and $Eu(H_2O)_9^{3+}$ complexes, which is in an equilibrium owing to the maximum coordinating number of 9

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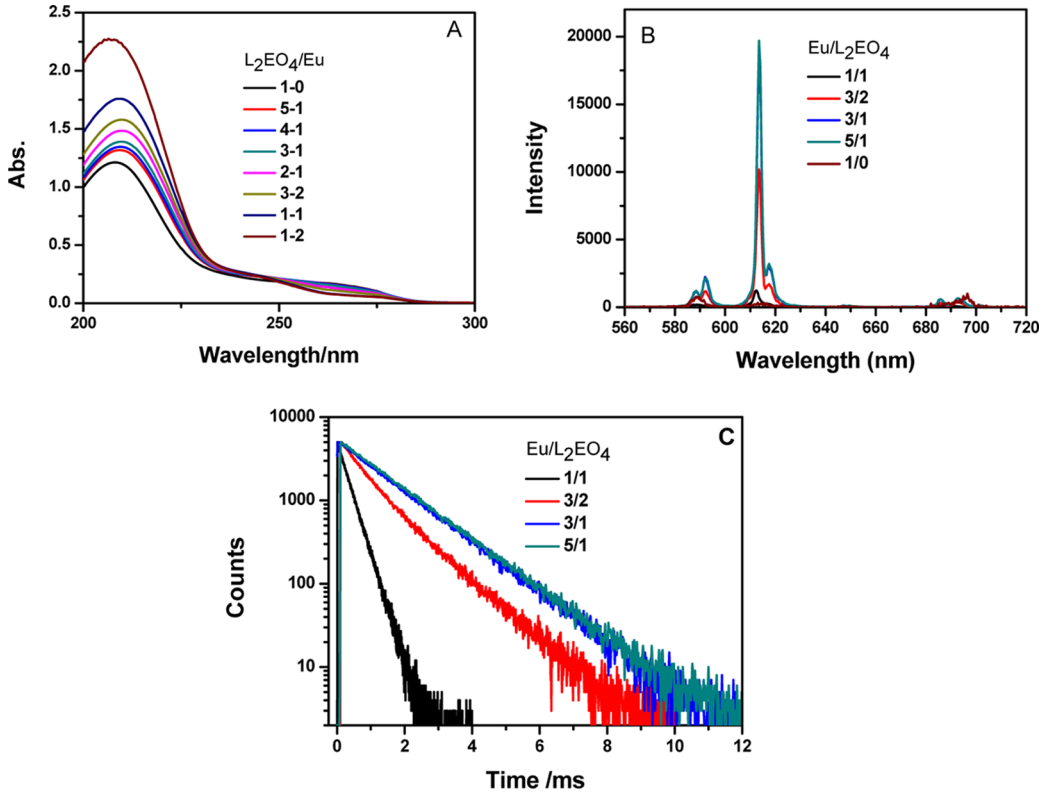

Figure 1. (A) UV−vis absorption spectra, (B) emission spectra, and (C) TRL spectra of L_2EO_4/Eu complexes at various molar ratios. The concentration of L_2EO_4 is fixed at 0.02 mM ([L_2EO_4] = 0.02 mM) in (A) and that of Eu^{3+} varies with the change in the molar ratio; however, in (B, C), the excitation is fixed at 395 nm (λ_{ex} = 395 nm), [Eu^{3+}] = 0.67 mM, pH = 6.9).

for the Eu^{3+}. However, by replacing water molecules with proper ligands, the luminescence of europium can be enhanced significantly.[25,31−36] We have shown that in case the coordination supramolecular polymers are constructed with europium and 1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane (L_2EO_4), the luminescence of europium can be greatly enhanced.[25] Upon combining the coordination complexes and the block copolymer $PMVP_{41}$-PEO_{205}, the luminescence can be further enhanced, which is attributed to the chain extension triggered by the enhanced local concentration of the coordination polymers in the electrostatic assemblies. We have reported the static luminescence enhancement effect of L_2EO_4−Eu in the electrostatic micelles.[25] Here, we show that upon application of time-resolved luminescence (TRL), we are able to infer the most possible structure of the L_2EO_4−Eu complex in a dilute solution. Also, we verified the growth of the chain length of the L_2EO_4−Eu complex in the electrostatic micelles. Our work provides a simple way to probe the in situ structure of dynamic coordination supramolecules, which helps to understand and estimate their behavior and contribution in various applications.

EXPERIMENTAL SECTION

Materials. The bisligand L_2EO_4 used in this work was prepared according to previously reported procedures.[20,37] A diblock polymer, poly(2-vinylpyridine)-*b*-poly(ethylene oxide) ($P2VP_{41}$-*b*-PEO_{205}, M_w = 13.3k, PDI = 1.05), was obtained from Polymer Source. $Eu(NO_3)_3$·$6H_2O$ (99.99%) was obtained from Sigma. Stock solutions of $P2VP_{41}$-*b*-PEO_{205}, L_2EO_4, and $Eu(NO_3)_3$ were prepared at appropriate concentrations. To prepare the Eu coordination complexes, 20 mM L_2EO_4 solution and 50 mM $Eu(NO_3)_3$ solution were mixed at the desired molar ratios. The coordination complexes were added in stoichiometric amounts to a $P2VP_{41}$-*b*-PEO_{205} aqueous solution ([P2VP] = 2 mM, [L_2EO_4] = 1 mM, and [Eu^{3+}] = 0.67 mM). HCl and KOH were used to control the pH instead of buffer to avoid the possible coordination between the buffering components and the europium ion. Ultrapure water was used, and no extra salt was added.

Methods. *Luminescence Measurements.* A steady-state spectrometer FLS920 was used to measure the luminescence emission and decay times of europium in all systems. The excitation wavelength was set at 395 nm because this wavelength allows direct excitation of Eu^{3+}, which avoids the antenna effect of L_2EO_4. Emission spectra were recorded in the range of 500−750 nm. Excitation spectra were recorded in the range of 250−500 nm.

Analysis of TRL Data. The luminescence intensity I_t can be expressed by eqs 1 and 2 for single- and double-exponential decays, respectively,[38]

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

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

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

where I_t is the emission intensity at time t. In the case of single exponential decay, only one decay time can be obtained. If a single luminophore displays two decays, I_i (i = 1, 2) is the emission intensity of luminophores in different environments at time 0 and τ_i (i = 1, 2) is the decay time of luminescence for luminophores in different environments. In this case, α_i (i = 1, 2) values represent the fraction of the luminescence of Eu^{3+} in the ith environment. Because the fraction of Eu^{3+} at the chain end will be decreased when chain extension occurs in the electrostatic micelles, we are able to calculate the average chain length simply from α. Meanwhile, control experiments were carried out in deuterium oxide (D_2O), which does not quench the emission of europium,[39] to calculate the number of

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water molecules that are still in the coordination sphere by using eq 4[28]

$$q = 1.2 \times (k_{H_2O} + k_{D_2O} - 0.25) \quad (4)$$

Here, k_{H_2O} and k_{D_2O} represent the rate constants of luminescence decay, which are measured in H_2O and D_2O, respectively. The re-evaluated proportionality constant of 1.2 ms signifies the sensitivity of the lanthanide ion to vibronic quenching by the OH oscillators. A correction factor of −0.25 ms^{-1} is applied to allow for the effect of closely diffusing OH oscillators.

As lanthanide ions are known to coordinate with 8−9 water molecules in an aqueous solution,[40,41] the number of coordinating sites occupied by ligands can be obtained upon subtracting the coordinated water molecules.

The photophysical properties of the Eu^{3+} complexes, including the 4f−4f emission quantum yield (Φ_{ln}), the radiative lifetime (τ_{rad}), the radiative constant (k_r), and the nonradiative constant (k_{nr}), were estimated from the observed lifetimes (τ_{obs}) and emission spectra using the following equations[42,43]

$$\Phi_{ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}} \quad (5)$$

$$\frac{1}{\tau_{rad}} = A_{MD,0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right) \quad (6)$$

$$k_r = \frac{1}{\tau_{rad}} \quad (7)$$

$$k_{nr} = \frac{1}{\tau_{obs}} - \frac{1}{\tau_{rad}} \quad (8)$$

where $A_{MD,0}$ is the spontaneous emission probability for the $^5D_0-{}^7F_1$ transition in vacuum (14.65 s^{-1}), n is the refractive index of the medium (an average index of refraction equal to 1.5 was employed), and (I_{tot}/I_{MD}) is the ratio of the total area of the corrected Eu(III) emission spectrum to the area of the $^5D_0-{}^7F_1$ band.

pH Measurements and pH Titration Experiments. pH was measured using a pH meter S40 produced by Mettler-Toledo. The electrode is from InLab Semi-Micro. Before measurements, technical buffer solutions with pH 4.01, 7.00, and 9.21 made by Mettler-Toledo were used to calibrate the pH meter. The degree of quarternization of $P2VP_{41}$-*b*-PEO_{205} at various pH values was determined using pH titration experiments. A pH titration curve for $P2VP_{41}$-*b*-PEO_{205} was obtained by recording the variation of solution pH with the volume of added 0.1 M HCl. Then, the pK_b for $P2VP_{41}$-*b*-PEO_{205} was obtained. The concentration of protonated $P2VP_{41}$-*b*-PEO_{205} was calculated based on the following equilibrium

$$A + 41H^+ \overset{K_b}{\rightleftharpoons} AH^{41+}$$

Light-Scattering Measurements. Dynamic light-scattering (DLS) measurements were carried out using a laser light scattering spectrometer ALV/DLS/SLS-5022F of standard design (ALV-5000/E/WIN Multiple Tau Digital Correlator) with a 22 mW He−Ne laser (wavelength: 632.8 nm). The scattering angle was 90°, and the CONTIN method was used to analyze the distribution of the radii of micelles. Nonweighed data were recorded for all experiments.

Transmission Electron Microscopy (TEM). A JEOL 2100F TEM was employed to observe the morphology of micelles. Drops of samples were put onto 230 mesh copper grids coated with a carbon film. Excess water was removed using filter paper, and the samples were then allowed to dry in ambient air at room temperature before TEM observation.

RESULTS AND DISCUSSION

TRL Technique in Probing the Structure of the Free Coordination Complex. Because theoretical calculations have predicted the structure of the free coordination complex in a solution,[17,19] we first studied the structure of the free coordination complex at various metal-to-ligand ratios to evaluate the reliability of the TRL technique in determining the structure of the coordination complex.

Figure 1A shows an increase of UV absorbance with increase in the amount of L_2EO_4 in the Eu^{3+} solution, suggesting stepwise coordination of L_2EO_4 to Eu^{3+}. Meanwhile, the luminescence in Figure 1B also gives a stepwise increase at 593, 613, and 693 nm, which corresponds to the $^5D_0-{}^7F_1$, $^5D_0-{}^7F_2$, and $^5D_0-{}^7F_4$ transitions, respectively. Because the excitation wavelength is set at 395 nm, which excited only the central europium ion rather than the ligand (Figure S1), the luminescence intensity is related only to the water molecules that coordinated with Eu^{3+} ions. Therefore, it is obvious that L_2EO_4 has gradually replaced the water molecules in the first coordination sphere of the coordination of Eu^{3+}.

In Figure 1C, we show the TRL of Eu^{3+} for the L_2EO_4/Eu coordinating complexes at various L_2EO_4/Eu ratios. It is found that the decay rate becomes slower with increase in the ratio (Figure 1C), indicative of increased decay times. The decay times obtained using eqs 1 and 2 are listed in Table 1. It is clear that the decay time reaches a constant value as L_2EO_4/Eu > 3/1, suggesting that all nine coordinating sites of one Eu^{3+} ion are occupied by L_2EO_4 at L_2EO_4/Eu > 3/1. This is in line with the conclusion obtained with steady-state luminescence (Figure 2B).[31] The decay times and the number of remaining coordinating water molecules q for the L_2EO_4−Eu systems at all ratios are also given in Table 1. Clearly, q decreases with increasing fraction of L_2EO_4. Without the addition of L_2EO_4, the number of water molecules coordinated to a central Eu^{3+} ion is 8.8, which is in good agreement with the literature results, which suggests that 8−9 water molecules can be coordinated to one Eu^{3+} in water.[40,41]

As indicated in Table 1, only one decay time is obtained for the coordination complexes of the L_2EO_4−Eu system at various ratios except for the L_2EO_4/Eu = 3/2 system, suggesting the presence of only one detectable coordinating environment for Eu^{3+}. It is noticed that the q value is about 3 for the L_2EO_4/Eu = 1/1 coordination complexes, which implies that six coordination sites of Eu^{3+} are occupied by L_2EO_4. Because previous studies have shown that the spacer length of L_2EO_4 is not long enough to form an intramolecular complex,[19] this result indicates that a closed ring structure with the composition of $(L_2EO_4)_2Eu_2$ is formed, as has been verified in the L_2EO_4−Zn system.[19] This is rather unexpected for the

Table 1. Summary of Decay Times, Fractions of Long Decay Time Luminophores (α_2), and the Number of Coordinating Water Molecules (q) of the L_2EO_4−Eu Complexes in H_2O (τ_1, τ_2) and in D_2O (τ)[a]

	H_2O				D_2O		
L_2EO_4/Eu	τ_1/ms	τ_2/ms	α_2	χ^2	τ/ms	χ^2	q
0/1	0.11		0	1.10	2.38	1.20	8.81
1/1	0.33		0	1.16	2.71	1.18	2.94
3/2	0.59	1.25	0.47	1.17	2.69	1.29	0.21
2/1		1.33	1	1.20	2.59	1.25	0.14
5/2		1.41	1	1.15	2.59	1.16	0.09
3/1		1.43	1	1.26	2.57	1.15	0.07
4/1		1.45	1	1.13	2.57	1.23	0.06
5/1		1.46	1	1.18	2.56	1.25	0.06

[a]The quality of data fitting is expressed as χ^2 (λ_{ex} = 395 nm, [Eu^{3+}] = 0.67 mM, pH = 6.9).

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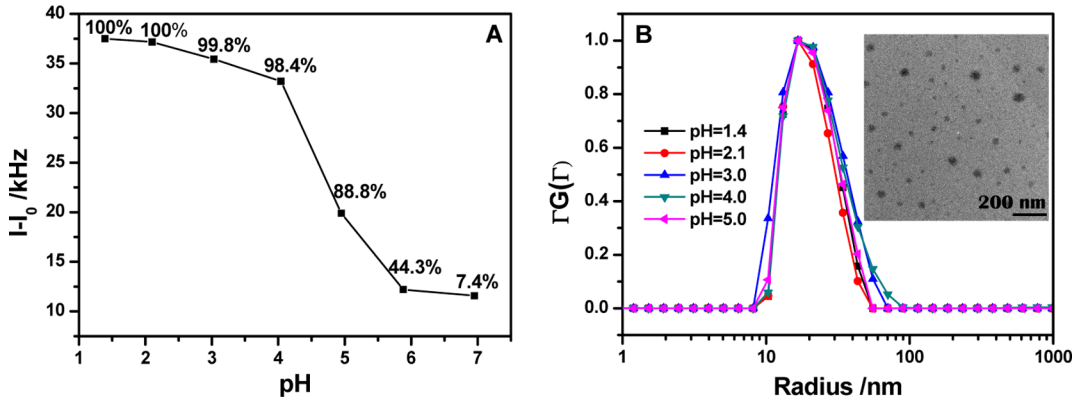
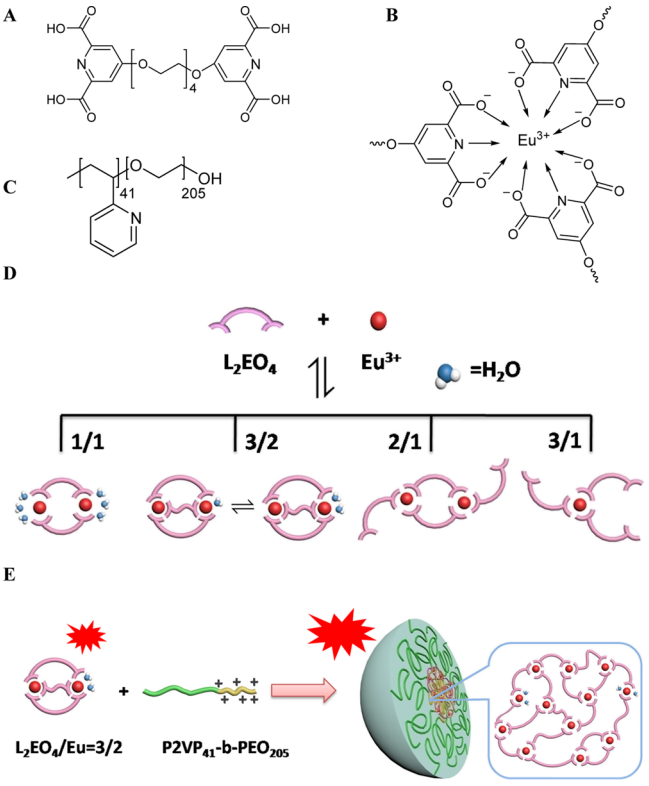


Figure 2. (A) Scattering light intensity of P2VP$_{41}$-*b*-PEO$_{205}$/L$_2$EO$_4$–Eu (3/2) micelles at different pH values (I_0: scattering light intensity of the solvent); the numbers are the protonation rates of P2VP$_{41}$-*b*-PEO$_{205}$ at different pH values. [Eu^{3+}] = 0.67 mM, and λ_{ex} = 395 nm. (B) DLS size distribution of P2VP$_{41}$-*b*-PEO$_{205}$/L$_2$EO$_4$–Eu (3/2) micelles at different pH values and the TEM image (inset) of the micelles at pH = 4.0.

Scheme 1. (A) Structure of L$_2$EO$_4$, (B) Demonstration of the Coordination between the Head of L$_2$EO$_4$ and Eu^{3+}, (C) Structure of P2VP$_{41}$-*b*-PEO$_{205}$, (D) Schematic Illustration of the Dominant Coordination Complexes in the L$_2$EO$_4$/Eu System at pH 6.9, (E) Illustration of the Chain Extension of the L$_2$EO$_4$/Eu = 3/2 System upon Formation of PIC Micelles.



L$_2$EO$_4$–Eu^{3+} system because the nine coordinating sites of Eu^{3+} may accommodate three heads from L$_2$EO$_4$, which is expected to form branched structures. It is noticed that the decay time for Eu^{3+} ions in water is 0.11 ms, whereas it slightly increases to 0.33 ms in the L$_2$EO$_4$/Eu = 1/1 system where six of the nine sites in the coordination sphere are chelated with the ligand. This implies that quenching by water is very significant even in the presence of a small fraction of water, as can be revealed again in the following section.

When the ratio of L$_2$EO$_4$/Eu reaches 3/2, two decay times appear, which indicates that the europium ions are in two different coordinating states.[16] These two states can be ascribed to the europium ions that partially and fully coordinated with L$_2$EO$_4$, respectively. For Eu^{3+} with long decay times, the q value is about zero, and the fraction for such Eu^{3+} is about 47%. This means that the quantity of Eu^{3+} ions that are partially and fully coordinated with L$_2$EO$_4$ is nearly equal. It is worth noting that the short decay time in the 3/2 system increases to 0.59 ms, which is nearly double as that in the 1/1 system, suggesting that the coordinating numbers for the partially coordinated Eu^{3+} are higher than 6. Because each coordinating head may contribute three chelating points, this means that the partially coordinated Eu^{3+} may be in equilibrium between the two structures, as demonstrated in Scheme 1. In line with this, the q value of the partially coordinated Eu^{3+} is 1.3 instead of 3, which probably indicates that the third ligand coordinates to the central Eu^{3+} ion in a more labile way.

As the L$_2$EO$_4$/Eu ratio reaches 2/1 or beyond, only one decay time appears. The q value is about zero, which suggests that all nine coordinating sites of Eu^{3+} are occupied by L$_2$EO$_4$. It is worth noting that all Eu^{3+} are already fully coordinated with L$_2$EO$_4$ at L$_2$EO$_4$/Eu = 2/1 instead of 3/1. We infer that the possible structure is as shown in Scheme 1D. However, the decay time in the 2/1 system is shorter than that in the 3/1 system, suggesting that the chance of the quenching by water in the 2/1 system is larger than that in the latter.

Furthermore, the 4f–4f emission quantum yield (Φ_{ln}) and the radiative (k_r) and nonradiative (k_{nr}) constants were estimated and are listed in Table 2. By adding L$_2$EO$_4$ to the Eu^{3+} solution, k_{nr} reduced from 8.9 × 10^3 to 3.6 × 10^3 s^{-1} and k_r increased from 1.6 × 10^2 to 3.3 × 10^2 s^{-1}. The significant reduction in k_{nr} and slight increase in k_r suggest that the main effect of the ligand is replacing coordinated water and reducing the quenching effect.[42,43]

TRL Technique in Probing the Structure of the Coordination Complex in Micelles. Next, we used the TRL technique to probe the possible structure of coordination complexes in electrostatic micelles. As discussed previously, the L$_2$EO$_4$/Eu = 3/2 complex may form well-defined micelles upon addition of an oppositely charged block polyelectrolyte. The block polyelectrolyte used in this work is P2VP$_{41}$-*b*-PEO$_{205}$, which is positively charged at pH < 6 according to the pH titration experiments (Figure S2). In Figure 2A, we see that strong scattering occurs at pH 1–5, where DLS measurements

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Table 2. Photophysical Properties of L_2EO_4–Eu Complexes in H_2O at Different Molar Ratios[a]

L_2EO_4/Eu	τ_{rad}/ms	τ_{obs}/ms	k_r/s^{-1}	k_{nr}/s^{-1}	Φ_{ln}
0/1	6.11	0.11	1.6×10^2	8.9×10^3	0.018
1/1	4.07	0.33	2.4×10^2	2.8×10^3	0.081
3/2	3.19	0.59/1.25	3.1×10^2	$1.4 \times 10^3/4.9 \times 10^2$	0.18/0.39
2/1	3.05	1.33	3.3×10^2	4.2×10^2	0.44
5/2	3.08	1.41	3.2×10^2	3.8×10^2	0.46
3/1	3.06	1.43	3.3×10^2	3.7×10^2	0.47
4/1	2.99	1.45	3.3×10^2	3.6×10^2	0.48
5/1	3.05	1.46	3.3×10^2	3.6×10^2	0.48

[a] τ_{rad} and τ_{obs} are the radiative and observed lifetimes, respectively, and k_r and k_{nr} are the radiative and nonradiative constants, respectively; Φ_{ln} is the quantum yield. Experimental conditions: λ_{ex} = 395 nm, $[Eu^{3+}]$ = 0.67 mM, pH = 6.9.

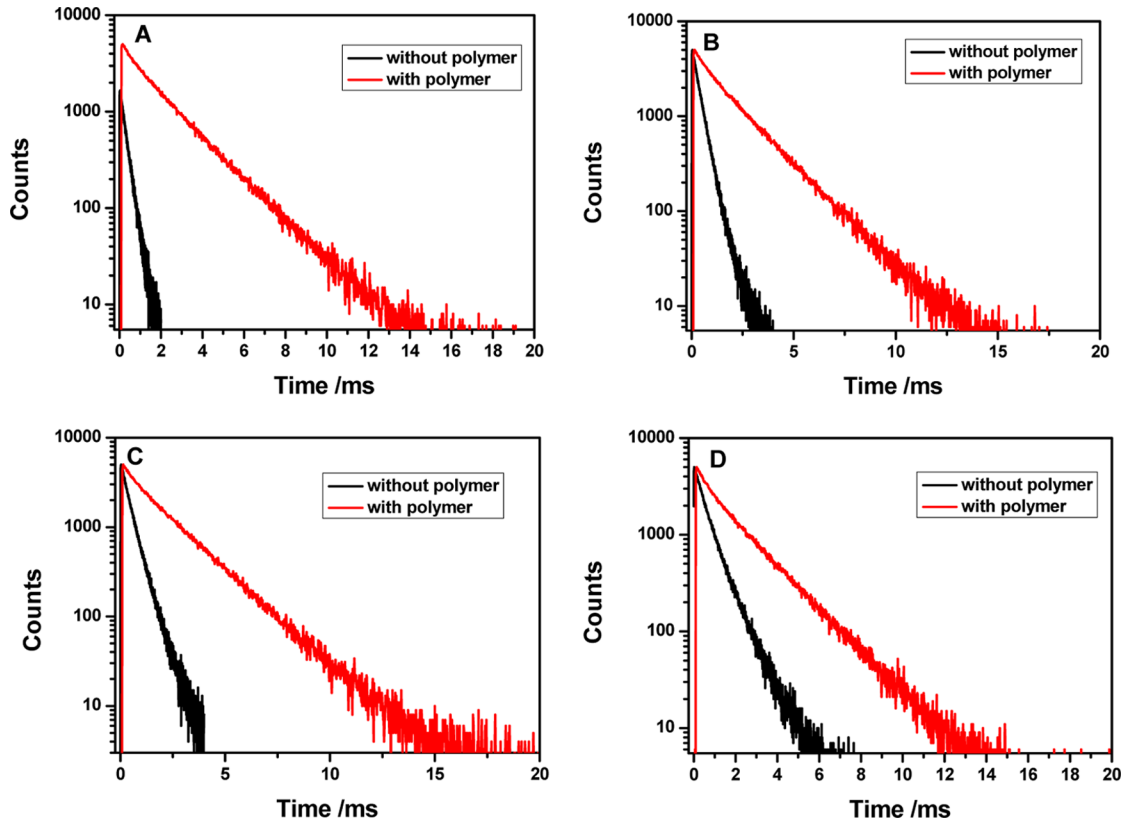

Figure 3. TRL measurement for L_2EO_4–Eu complexes at 3/2 with and without polymer P2VP$_{41}$-*b*-PEO$_{205}$: (A) pH = 1.4, (B) pH = 3.0, (C) pH = 4.0, and (D) pH = 4.9 ($[Eu^{3+}]$ = 0.67 mM, λ_{ex} = 395 nm).

Table 3. Summary of Decay Times τ_1 and τ_2 and Fractions of Long Decay Time Fluorophore α_2 of L_2EO_4–Eu Complexes with and without the Diblock Copolymer at Different pH Values[a]

	L_2EO_4–Eu				L_2EO_4–Eu/P2VP$_{41}$-*b*-PEO$_{205}$			
system pH	τ_1/ms	τ_2/ms	χ^2	α_2	τ_1/ms	τ_2/ms	χ^2	α_2
1.4	0.28		1.19	0	0.68	1.98	1.10	0.80
2.1	0.35		1.20	0	0.68	1.99	1.15	0.79
3.0	0.37		1.19	0	0.54	1.95	1.14	0.79
4.0	0.35	0.62	1.20	0.32	0.46	1.98	1.20	0.83
4.9	0.45	0.91	1.16	0.36	0.49	1.93	1.16	0.74

[a] The quality of data fitting is expressed as χ^2 (λ_{ex} = 395 nm, $[Eu^{3+}]$ = 0.67 mM, L_2EO_4/Eu = 3/2).

revealed the presence of particles with an average radius of 18 nm. This is consistent with the size of micelles formed in our previous observations and again confirmed using TEM observation in Figure 2B,[20,25] suggesting that micelles are indeed formed in these systems. It is remarkable that the scattering intensity increases as pH decreases (Figure 2B), suggesting that more micelles are formed at acidic pH. This is because the diblock polymer carries more positive charges under acidic conditions owing to the protonation of the pyridine groups, which facilitates the electrostatic interaction with the negatively charged L_2EO_4/Eu complexes.

In Table 2 and Figure 3, we show the TRL results of the L_2EO_4/Eu = 3/2 system at various pH values with and without the presence of the block copolymer. It is remarkable that without the presence of the polymer, the L_2EO_4/Eu = 3/2 system at pH < 4 forms only a short-life coordinating complex, which indicates that all Eu^{3+} ions are partially coordinated. This is because both the N atom and the COO^- groups in the L_2EO_4 molecule are protonated at acidic pH, so that the ligand cannot form an effective coordination bond with Eu^{3+} ions. As

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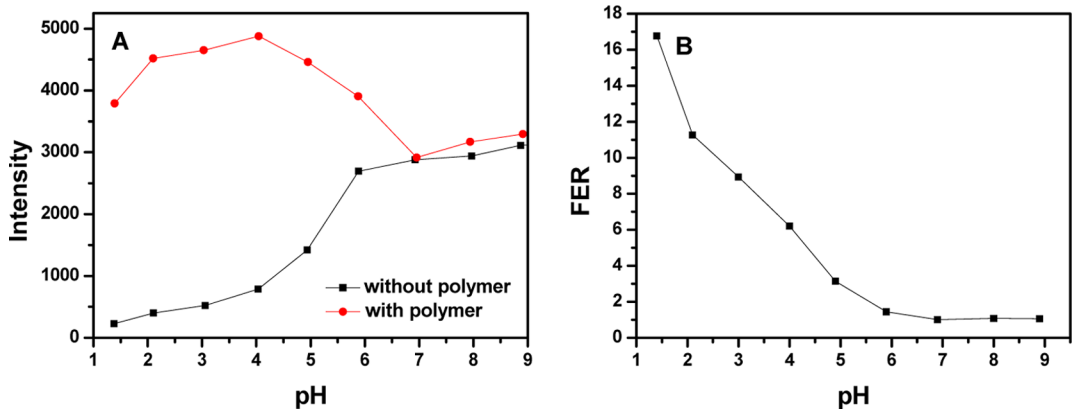

Figure 4. (A) The emission intensity at 614 nm of the L_2EO_4/Eu = 3/2 system with and without diblock copolymer P2VP$_{41}$-*b*-PEO$_{205}$ at different pH values. (B) The luminescence enhancement ratios at different pH values (FER, defined as the ratio of intensities in the presence and in the absence of the diblock copolymer) at L_2EO_4/Eu = 3/2 ([Eu^{3+}] = 0.67 mM, λ_{ex} = 395 nm).

Table 4. Photophysical Properties of L_2EO_4/Eu = 3/2 Complexes in H_2O at Different pH Values[a]

pH	τ_{rad}/ms	τ_{obs}/ms	k_r/s^{-1}	k_{nr}/s^{-1}	Φ_{ln}
1.4	4.08	0.28	2.4×10^2	3.3×10^3	0.068
2.1	3.87	0.35	2.6×10^2	2.6×10^3	0.090
3.0	3.94	0.37	2.5×10^2	2.4×10^3	0.094
4.0	3.58	0.35/0.62	2.8×10^2	$2.4 \times 10^3/1.3 \times 10^3$	0.098/0.17
4.9	3.20	0.45/0.91	3.1×10^2	$1.9 \times 10^3/7.8 \times 10^2$	0.14/0.28

[a] τ_{rad} and τ_{obs} are the radiative and observed lifetimes, respectively, and k_r and k_{nr} are the radiative and nonradiative constants, respectively; Φ_{ln} is the quantum yield (λ_{ex} = 395 nm, [Eu^{3+}] = 0.67 mM).

Table 5. Photophysical Properties of L_2EO_4/Eu Complexes with the Diblock Copolymer at Different pH Values[a]

pH	τ_{rad}/ms	τ_{obs}/ms	k_r/s^{-1}	k_{nr}/s^{-1}	Φ_{ln}
1.4	3.61	0.68/1.98	2.8×10^2	$1.2 \times 10^3/2.3 \times 10^2$	0.19/0.55
2.1	3.53	0.68/1.99	2.8×10^2	$1.2 \times 10^3/2.2 \times 10^2$	0.19/0.56
3.0	3.53	0.54/1.95	2.8×10^2	$1.6 \times 10^3/2.3 \times 10^2$	0.15/0.55
4.0	3.44	0.46/1.98	2.9×10^2	$1.9 \times 10^3/2.1 \times 10^3$	0.13/0.58
4.9	3.45	0.49/1.93	2.9×10^2	$1.8 \times 10^3/2.3 \times 10^2$	0.14/0.56

[a] τ_{rad} and τ_{obs} are the radiative and observed lifetimes, respectively, and k_r and k_{nr} are the radiative and nonradiative constants, respectively; Φ_{ln} is the quantum yield (λ_{ex} = 395 nm, L_2EO_4/Eu = 3/2, [Eu^{3+}] = 0.67 mM).

pH increases, the coordinating ability of L_2EO_4 increases as well. It is remarkable that upon addition of the block copolymer into these systems, the decay time increases to about 2 ms in all solutions. Control experiments suggest that the number of coordinating water molecules q in these states is zero (obtained using the parameters τ_{D_2O} = 2.95 ms and $\tau_{micelle}$ = 2.95 ms). This implies that in the micelles, all of the coordinating sites of the Eu^{3+} ion are taken by L_2EO_4. According to eq 3, the fraction of long decay time Eu^{3+} amounts to the maximum value of 83% at pH 4 (Table 3), suggesting that at this pH the degree of "polymerization" for the L_2EO_4–Eu coordinating system is the largest. This is in line with the observation of the maximum luminescence intensity at the same pH (Figure 4A). The long decay time is contributed by the europium ions that are fully coordinated with L_2EO_4, verifying that the chain extension for the L_2EO_4/Eu coordinating complex indeed occurs in the micellar core. It is remarkable that even under the very acidic conditions of pH 1–3, the fraction for Eu^{3+} ions fully coordinated with L_2EO_4 is about 80% in the micelles, whereas that for the free coordination complexes under the same conditions is zero. Meanwhile, the emission intensity is enhanced by a factor of 9 and 16 for systems at pH 3.0 and 1.4 (Figures 4B, S3, and S4), respectively, suggesting that micellization facilitates coordination between L_2EO_4 and Eu^{3+}. This indicates that the formation of micelles and coordination supramolecular polymer occurs synergistically. It can be inferred from the TRL results that in the presence of oppositely charged block copolymers, L_2EO_4 prefers coordination with Eu^{3+} instead of protonation.

Table 3 tells that the number of coordinating water molecules q of partially coordinated Eu^{3+} in the micellar system at pH = 4 is 1.9 (≈2) instead of 3. Each head of L_2EO_4 contributes three chelating points, indicating that three heads have participated in chelation, but probably the third head chelated to the Eu^{3+} with only one site, as illustrated in Scheme 1E, because of steric hindrance. Most importantly, the TRL results indicate that on average, there were no Eu^{3+} ions chelating 6 or 3 water molecules, suggesting that there are no coordinating ends in the micellar core. In other words, the Eu^{3+} and L_2EO_4 exist in the micellar core in the form of one whole network. This is the first qualitative analysis for the extent of chain extension enhanced by electrostatic micellization, which we were not able to know before this study.

Also, we calculated Φ_{ln}, k_r, and k_{nr} of L_2EO_4/Eu = 3/2 complexes with and without the diblock copolymer and listed the data in Tables 4 and 5. As expected, the k_{nr} of L_2EO_4/Eu =

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3/2 complexes is large because of the protonation of ligands, which weakens the coordination effect. By adding the diblock polymer, k_{nr} was reduced significantly. The k_r values of the L_2EO_4/Eu = 3/2 complex with and without the polymer under different conditions are almost the same, which suggests that this value probably depends on the properties of ligands. These results confirm that the main effect of ligands is reducing the quenching by water molecules.

CONCLUSIONS

In conclusion, we have employed the TRL technique to probe the in situ structure of reversible coordination polymers in their electrostatic micelles. Upon analyzing the luminescence intensity decay rate, we obtained the coordination information of the europium ions, which directly correlates with the structure of the coordinating system. In this way, we are able to know the polymerization degree of the coordinating complex. We expect that the method established in this work may provide fundamental information on the structure change in reversible coordination polymer systems and may help to explain, understand, and predict relevant properties and functions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b00967.

Additional experimental results for the excitation spectra of the L_2EO_4−Eu complex, pH titration, the emission spectra for the L_2EO_4−Eu complexes at various pH values, the emission spectra of L_2EO_4−Eu/$P2VP_{41}$-PEO_{205} at fixed pH, and the comparison between these two groups Figures S1−S5; the summary of evolutions of the transitions of L_2EO_4−Eu complexes in H_2O at different molar ratios and the summary of evolutions of the transitions of L_2EO_4−Eu complexes with and without the polymer in H_2O at different pH values Tables S1 and S2 (PDF)

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Notes

The authors declare no competing financial interest.

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