Electronic Supplementary Material (ESI) for Soft Matter.

Response of metal-coordination-based polyelectrolyte complex micelles to added ligand and metal

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Experimental section

Materials

Inorganic salts, $Eu(NO_3)_3 \cdot 5H_2O$, $LaCl_3 \cdot 6H2O$ and $Zn(NO_3)_2.4H_2O$, 2-(N-morpholino) ethanesulfonic acid (MES), 4-Hydroxypyridine-2,6-dicarboxylic acid (DPA), 3-(Trimethylsilyl) propanoic-2,2,3,3-d_4 acid sodium salt (TSP, 98% D) and deuterium oxide (99% D) were obtained from Aldrich and used without further purification. The bisligand compound 1,11-bis(2,6-dicarboxypyridin-4-yloxy)-3,6,9-trioxaundecane (L_2EO_4) was prepared according to literature.[1] The diblock copolymer, poly(N-methyl-2-vinyl-pyridinium iodide)-b-poly(ethylene oxide) ($P2MVP_{128}$-*b*-PEO_{477}), was obtained by quaternization of poly(2-vinylpyridine)-b-poly(ethylene oxide) ($P2VP_{128}$-*b*-PEO_{477}) (Polymer Source, Mw/Mn= 1.10, Mn= 34.5 k) following a procedure described elsewhere.[2] The degree of quaternization is about 87% as determined by titration with poly(acrylic acid) (PAA, Polymer Source, Mw/Mn= 1.16, Mn= 2.2 k). All samples were prepared in MES buffer (10 mM, pH 6). For NMR measurements, samples were prepared in D_2O, the pD was adjusted with either DCl (Sigma Aldrich, 35 wt% in D_2O) or NaOD (Sigma Aldrich, 40 wt% in D_2O) to 6.4 ± 0.1, corresponding to the pH 6 in MES buffer.[3]

Methods

The Dynamic light scattering (DLS) measurement was performed with an ALV light scattering apparatus, equipped with a 21 mW He-Ne laser operating at a wavelength of 632.8 nm. Measurements were done at a detection angle of 90°, unless stated otherwise. All measurements were performed at room temperature. The light scattering intensity is expressed as the excess Rayleigh ratio R_θ divided by the total polymer concentration. R_θ is obtained as

$$R_\theta = \frac{I_{sample} - I_{solvent}}{I_{toluene}} \times R_{toluene} \times \frac{n^2_{solvent}}{n^2_{toluene}}$$

where I_{sample} is the scattering intensity of the micellar solution and $I_{solvent}$ is the intensity of the solvent. $I_{toluene}$ is the scattering intensity of toluene, $R_{toluene}$ is the known Rayleigh ratio of toluene ($2.1 \cdot 10^{-2}$ m^{-1}) and n is the refractive of the solvent (1.333) and of toluene (1.497), respectively. The CONTIN method was[4, 5] used to analyze the micellar mean size and distribution. The data were analyzed with the AfterALV program (AfterALV 1.0d, Dullware), which provides $\Gamma_i W_i$ as default output for each size fraction. Here, the intensity weighted contribution W_i is multiplied by Γ, as suggested by Petr Stepanek for the "equal-area representation".[6] To facilitate comparisons, the absolute $\Gamma_i W_i$ was normalized with the highest value of $\Gamma_i W_i$ for each sample.

All the ^{1}H-NMR measurements were carried out at 298 K on a Bruker Avance III 14.1 T NMR spectrometer (400 MHz). The spectra were plotted and analyzed with MestReNova 9.0 software. Steady state luminescence spectra were performed on a Cary-4000 spectrometer. The excitation was set at 275 nm and emission spectra were recorded in the range 570-720 nm. To estimate the free metal concentration in the micellar solution, we put 1 ml of micellar solution in a centrifuge tube with a dialysis membrane (3500 Kd cut-off), and ran a centrifugation at 2000 rpm for 5 minutes. About 0.1 ml of micelle-free solution was filtrated out which was used to measure atomic emission by means of inductively coupled plasma atomic emission spectrometry ICP-AES (Varian, Mulgrave, Australia).

Sample Preparation

Firstly, we prepared different stock solutions in Milli-Q water: $Eu(NO_3)_3 \cdot 5H_2O$, $LaCl_3 \cdot 6H_2O$, $Zn(NO_3)_2.4H_2O$, DPA, L_2EO_4 at 5 mM; 0.1 M MES buffer at pH 6. The concentration of P2MVP$_{128}$-*b*-PEO$_{477}$ stock solution is 0.09 mM, demonstrates a positive charge concentration 10 mM. Then we took different components under the designed amount/volume (Table 1-3) to prepare micelles and study the exchange. In final state, all samples were prepared in 10 mM MES buffer at pH 6, and the total volume was adjusted at 1 ml. Given as an example, for A and A′ samples, we prepared them separately. Sample A was prepared by taking the designed volumes of different components. For samples A′, all the components except for the DPA were mixed first, and the obtained micelle solution was left for 1 hour to equilibrate completely. Then DPA that contained same amount of chelate groups with LEO was added to the solution, followed by 1~2 mins vortex and another hour of equilibration before the analysis. Samples for scenario B, C and D (Table 1), Zn micelles case (Table 2), and Zn-Eu exchange (Table 3) were prepared by the same method. Also, samples for NMR tests were prepared by the similar strategy, only with D_2O as solvent in this case. And the final concentrations of all the components are same with H_2O samples as well. Here we did not use buffer due to the disturbance of the proton from the buffer chemicals. The pD was adjust with either DCl or NaOD to 6.4, corresponding to the pH 6 in MES buffer.[3] 10 mM NaCl was added in order to keep the similar ionic strength with water samples (10 mM buffer), and an internal standard TSP was added to all the samples for the quantitative analysis of the NMR spectra.

/	La	LEO	DPA	BP	MES	H_2O	V_{total}
A	0.08	0.12	0	0.11	0.1	0.59	1 ml
A′	0.08	0.12	0.24	0.11	0.1	0.35	1 ml
B	0.08	0	0.24	0.11	0.1	0.47	1 ml
B′	0.08	0.12	0.24	0.11	0.1	0.35	1 ml
C	0.08	0.12	0.24	0	0.1	0.46	1 ml
C′	0.08	0.12	0.24	0.11	0.1	0.35	1 ml
D	0	0.12	0.24	0.11	0.1	0.43	1 ml
D′	0.08	0.12	0.24	0.11	0.1	0.35	1 ml

Table S1: Designed volume of different components for preparing La-based samples. The green numbers indicated the final added components for study of DPA-LEO exchange.

/	Zn	LEO	DPA	BP	MES	H_2O	V_{total}
A	0.12	0.12	0	0.11	0.1	0.55	1 ml
A′	0.12	0.12	0.24	0.11	0.1	0.31	1 ml
B	0.12	0	0.24	0.11	0.1	0.43	1 ml
B′	0.12	0.12	0.24	0.11	0.1	0.31	1 ml
C	0.12	0.12	0.24	0	0.1	0.42	1 ml
C′	0.12	0.12	0.24	0.11	0.1	0.31	1 ml
D	0	0.12	0.24	0.11	0.1	0.43	1 ml
D′	0.12	0.12	0.24	0.11	0.1	0.31	1 ml

Table S2: Designed volume of different components for preparing Zn-based samples. The green numbers indicated the final added components for study of DPA-LEO exchange.

/	Eu	Zn	LEO	BP	MES	H_2O	V_{total}
X	0.08	0	0.12	0.11	0.1	0.59	1 ml
X′	0.08	0.12	0.12	0.11	0.1	0.47	1 ml
Y	0	0.12	0.12	0.11	0.1	0.55	1 ml
Y′	0.08	0.12	0.12	0.11	0.1	0.47	1 ml
Z	0.08	0.12	0.12	0	0.1	0.57	1 ml
Z′	0.08	0.12	0.12	0.11	0.1	0.47	1 ml

Table S3: Designed volume of different components for preparing Zn-Eu micelles. The green numbers indicated the final added components for study of metal exchange.

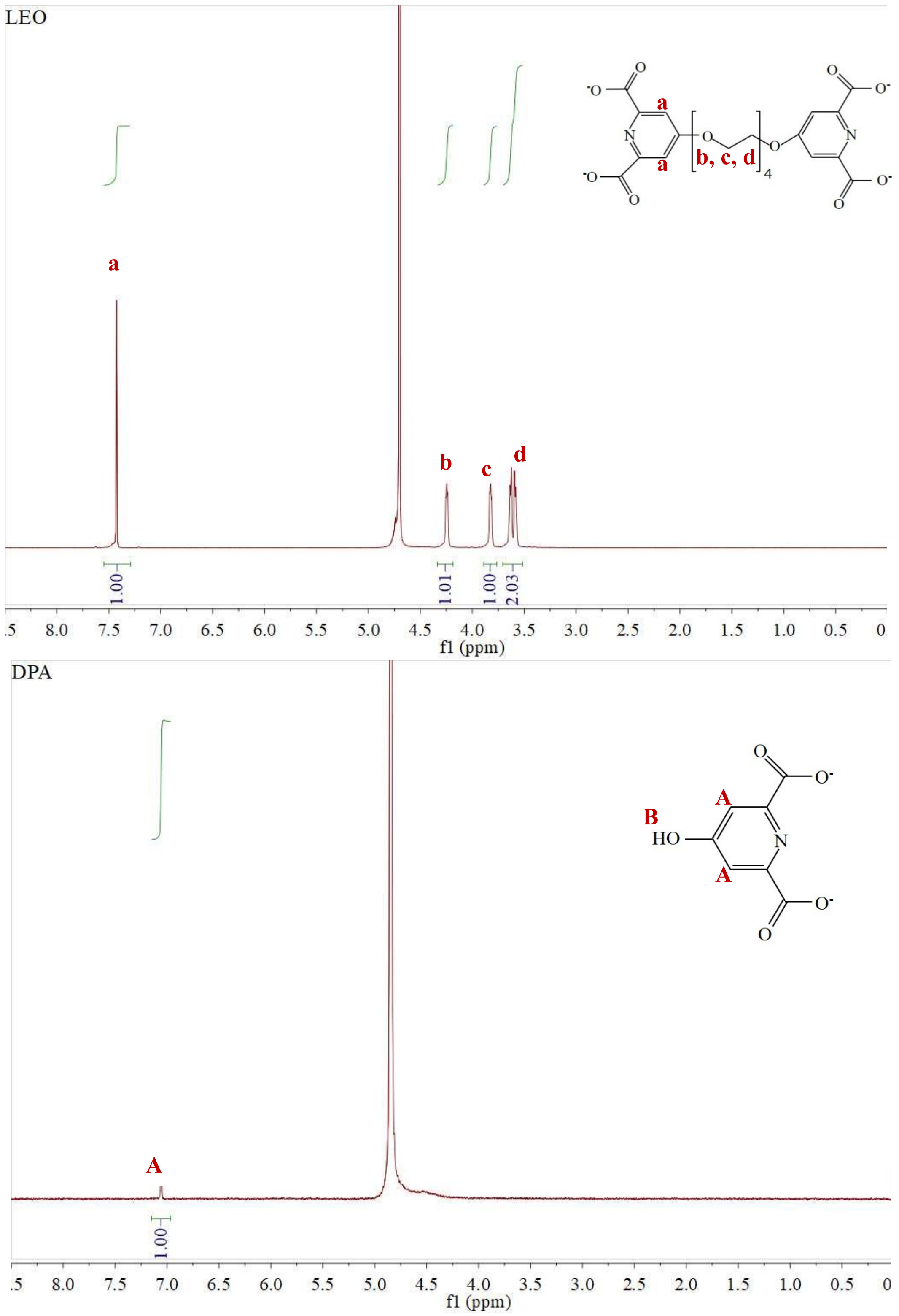


Figure S1: ^{1}H NMR spectrum of LEO and DPA. For LEO spectrum, "b&c" are the methylene groups from the ethylene oxide moiety next to the ring, and the "d" is corresponding to the methylene groups of the two central ethylene oxide moieties.

Figure S2

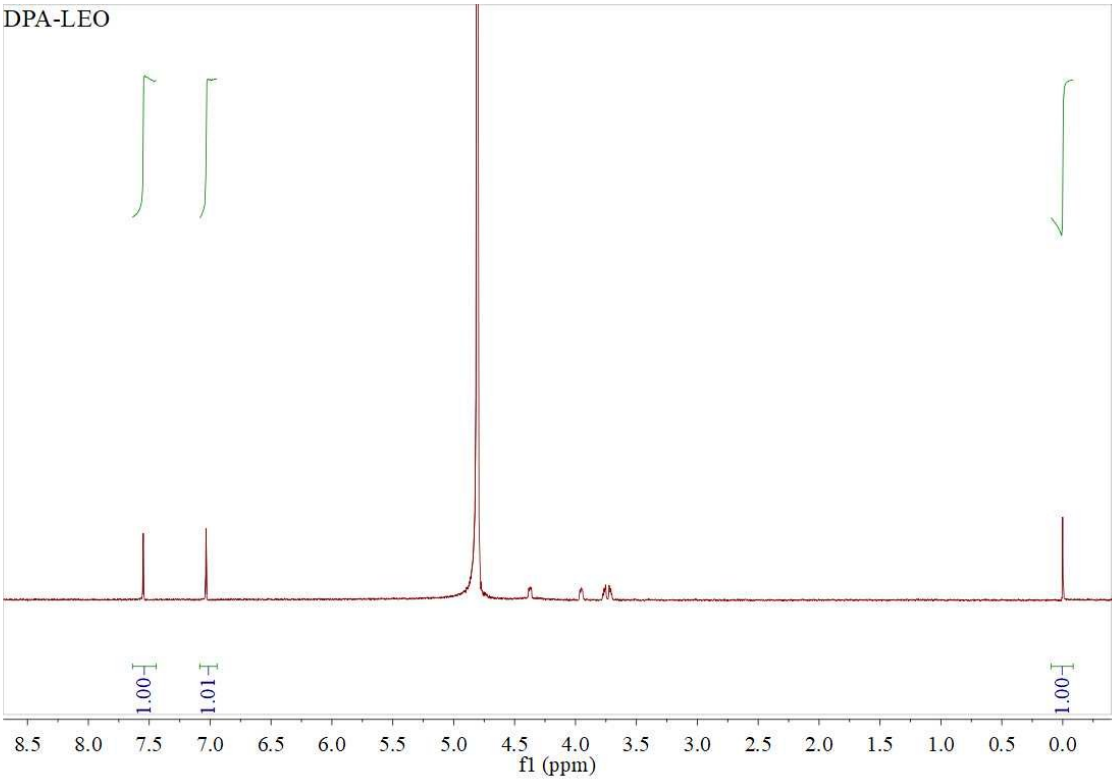


Figure S2: ^{1}H NMR spectrum of DPA-LEO mixture, TSP was added as an internal standard.

As shown in Figure S2, LEO and DPA show typical chemical shift at 7.5 ppm (a, 4H) and 7.0 ppm (A, 2H) from the proton of pyridine groups. We take these two peaks for the quantitative analysis of the LEO and DPA. In each sample there are 0.12ml of 5mM LEO and 0.24ml of 5mM DPA. The total number of H is:

$$a: 4 \times 5mM \times \left(0.12 \times 10^{-3}\right)L = 2.4 \times 10^{-3} \text{ mole}$$

$$A: 2 \times 5mM \times \left(0.24 \times 10^{-3}\right)L = 2.4 \times 10^{-3} \text{ mole}$$

In each sample there are 0.053ml of 5mM TSP. Each TSP molecular has 9 H that can be detected by ^{1}H-NMR. The total number of detectable H of TSP is:

$$9 \times 5mM \times \left(0.053 \times 10^{-3}\right)L = 2.39 \times 10^{-3} \text{ mole}$$

Therefore, in the free case, the integral ratio of TSP/LEO and TSP/DPA in the ^{1}H NMR spectrum is approximately equal to 1/1. The aggregation or micellization of the coordination complexes leads to the decay or disappear of the characteristic peaks of LEO and DPA. In other words, only the free LEO or DPA in solution could be detected, and the analysis of the integral, with TSP as internal standard, allows to calculate the amount of the LEO or DPA in the solution.

Figure S3

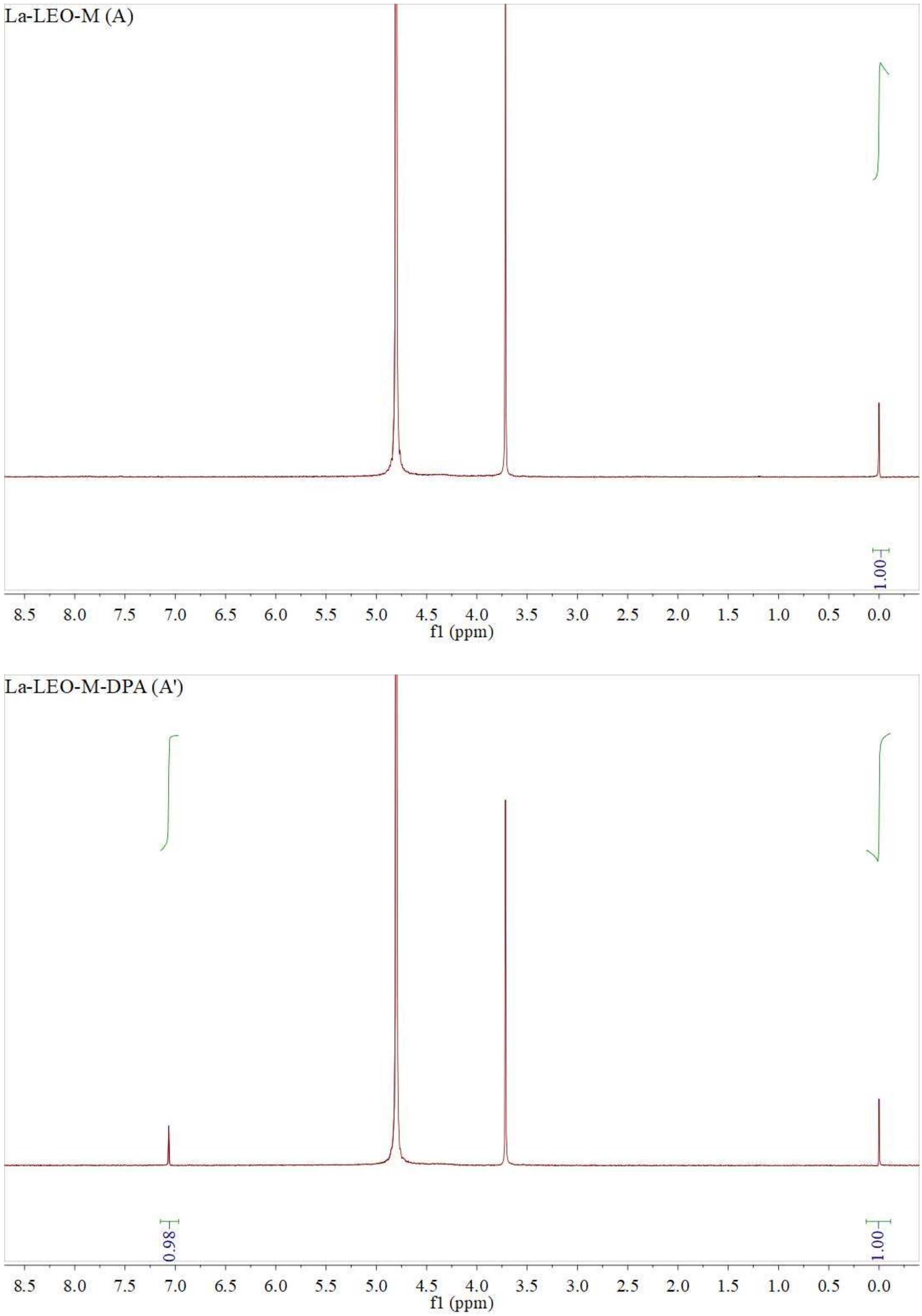
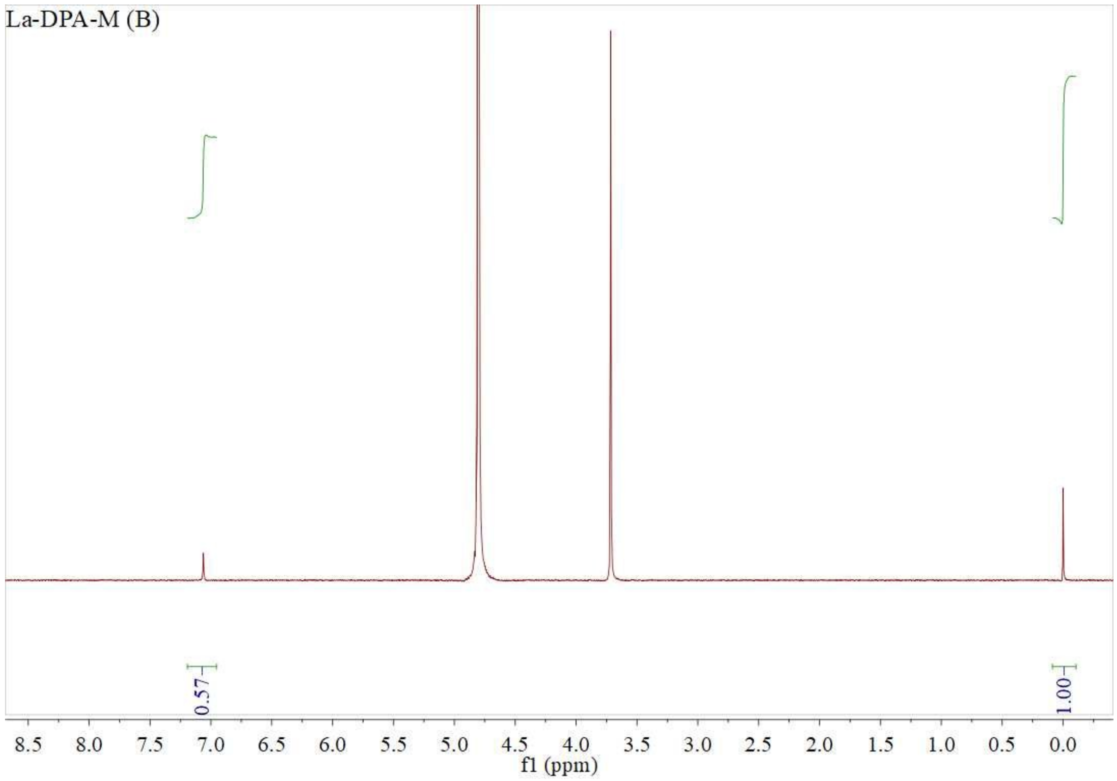


Figure S3: ^{1}H NMR spectrum of La-LEO-BP micelles (top, A) and the micelles with added DPA (bottom, A′). Signal at 3.5 is from the methylene groups of PEO.

Figure S4



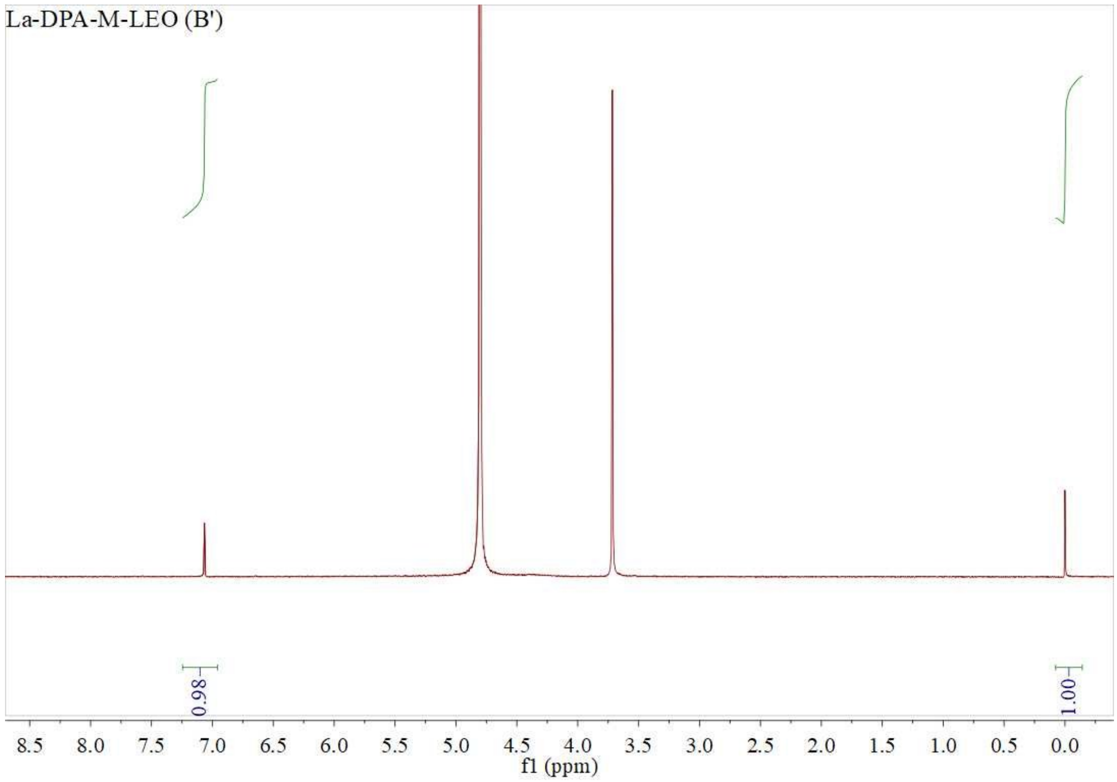
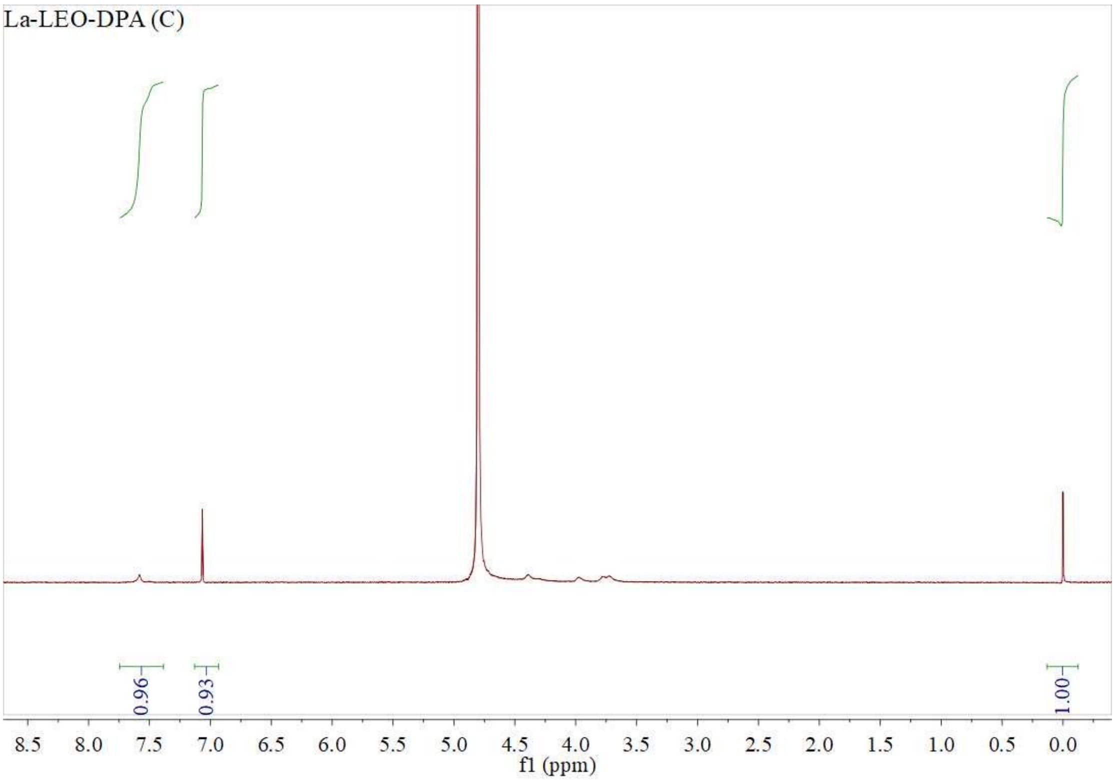


Figure S4: ^{1}H NMR spectrum of La-DPA-BP mixture (top, B) and the mixture with added LEO (bottom, B′)

Figure S5



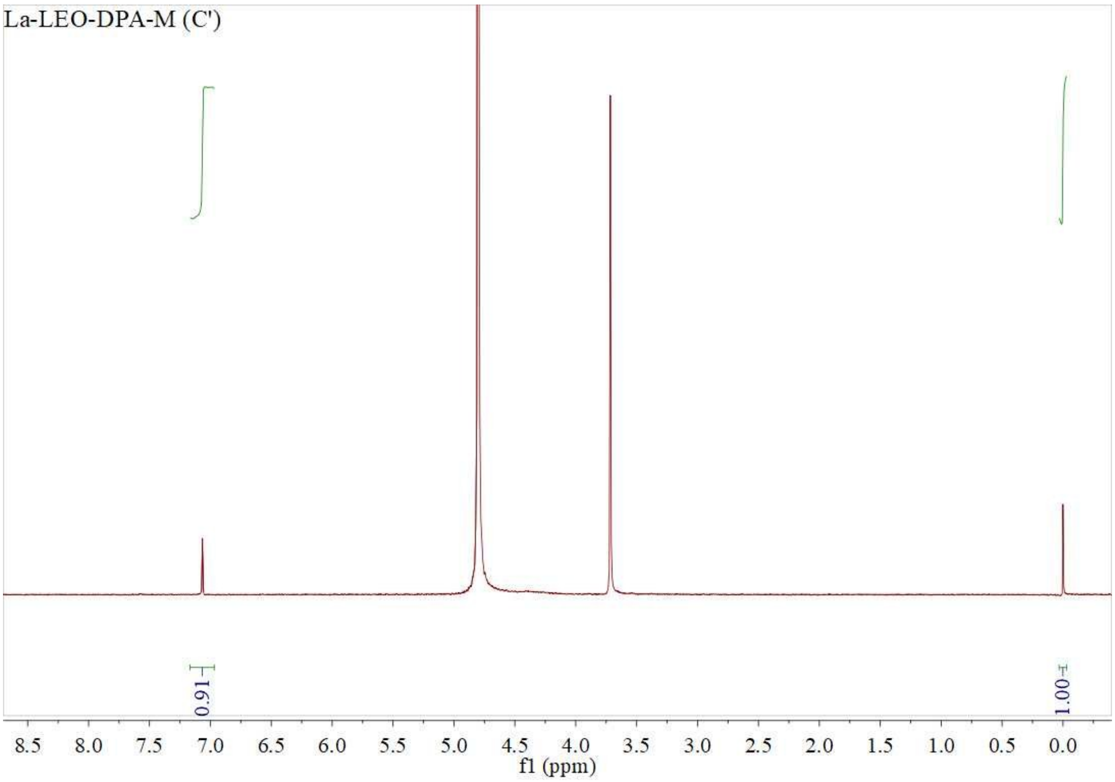
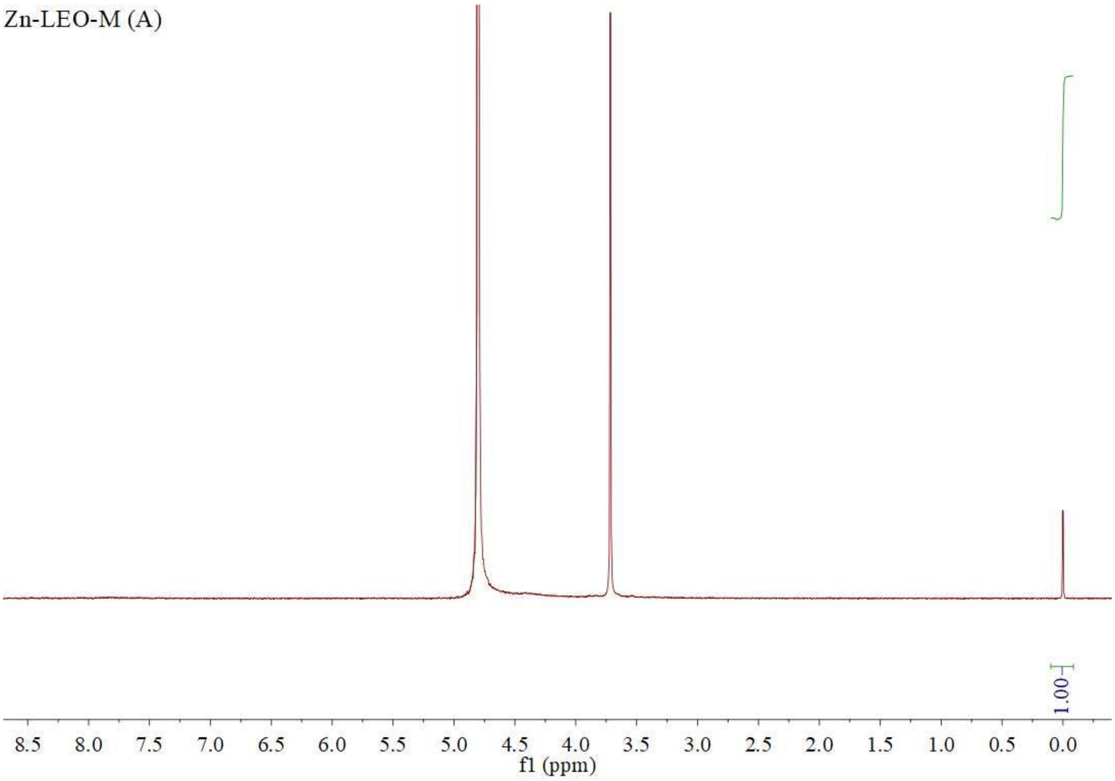


Figure S5: ^1H NMR spectrum of La-LEO-DPA mixture (top, C) and the mixture with added BP (bottom, C′)

Figure S6



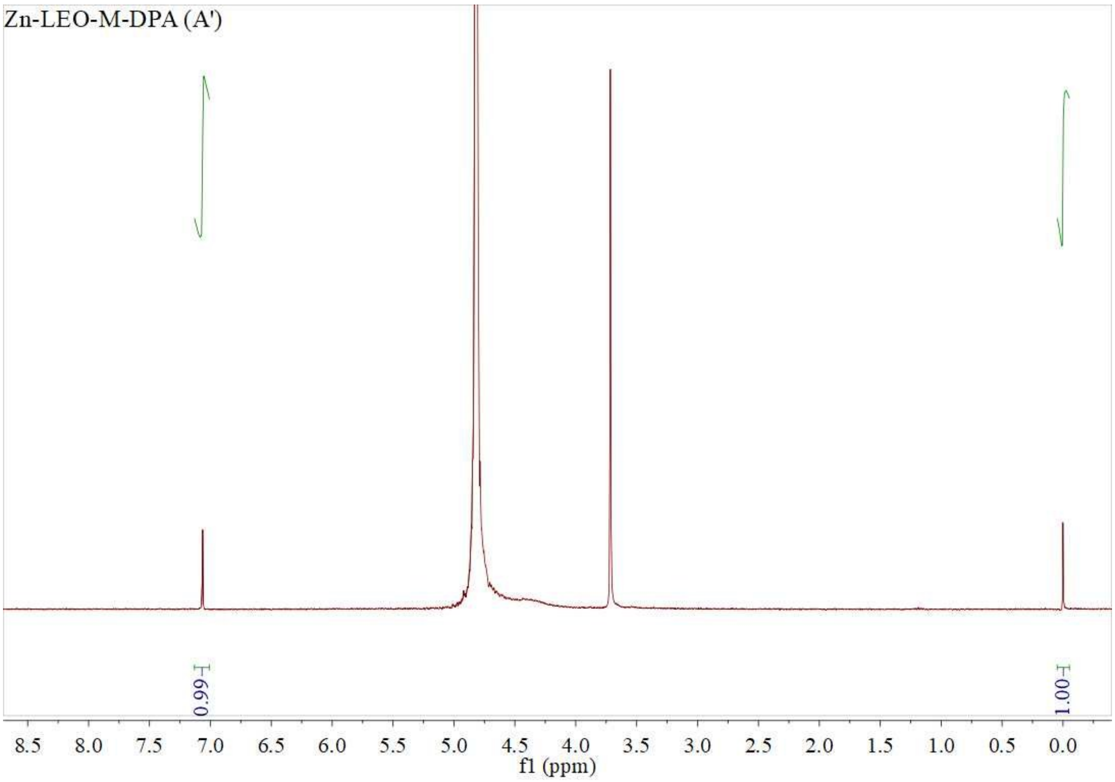


Figure S6: ^{1}H NMR spectrum of Zn-LEO-BP micelles (top, A) and the micelles with added DPA (bottom, A′)

Figure S7

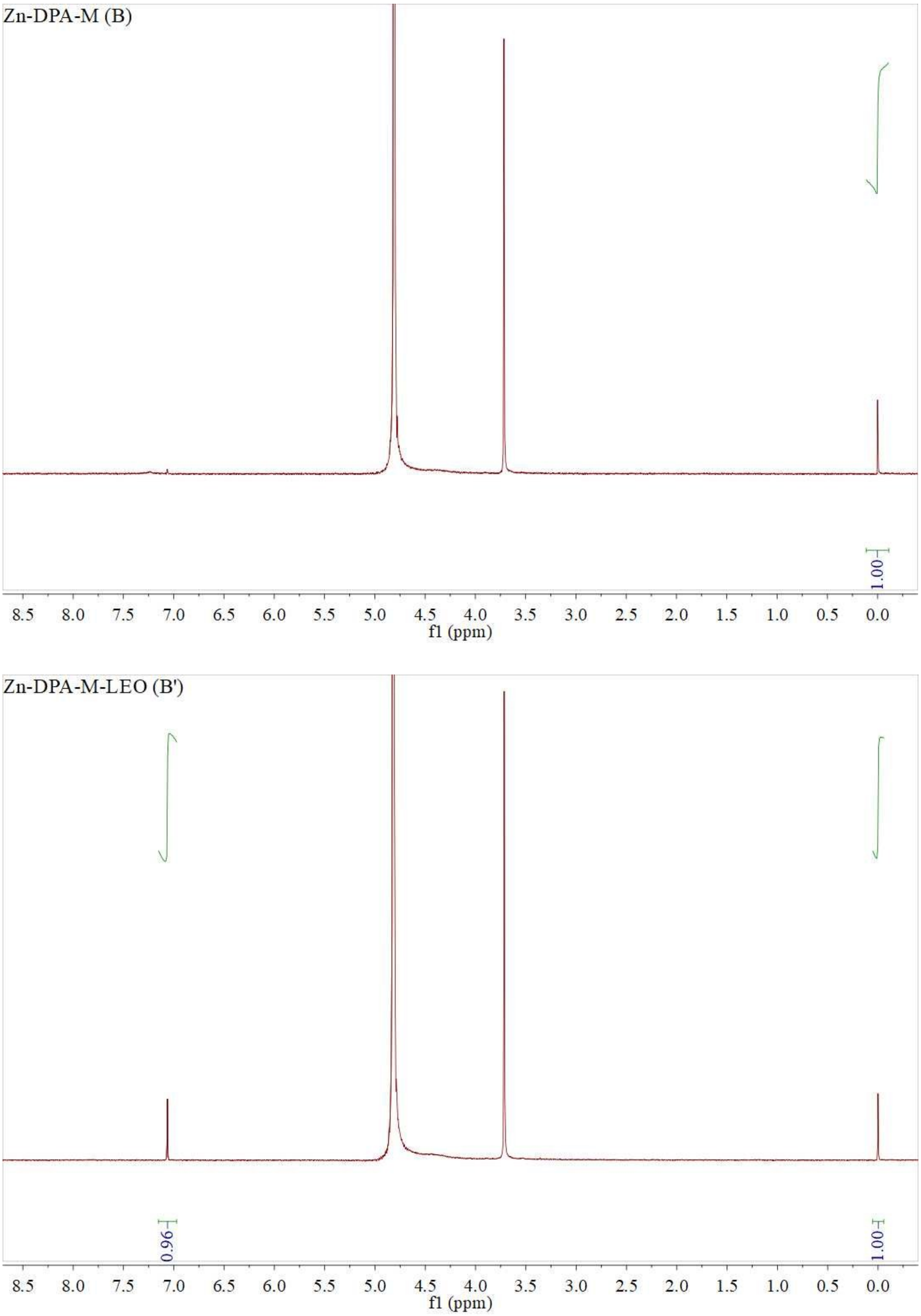
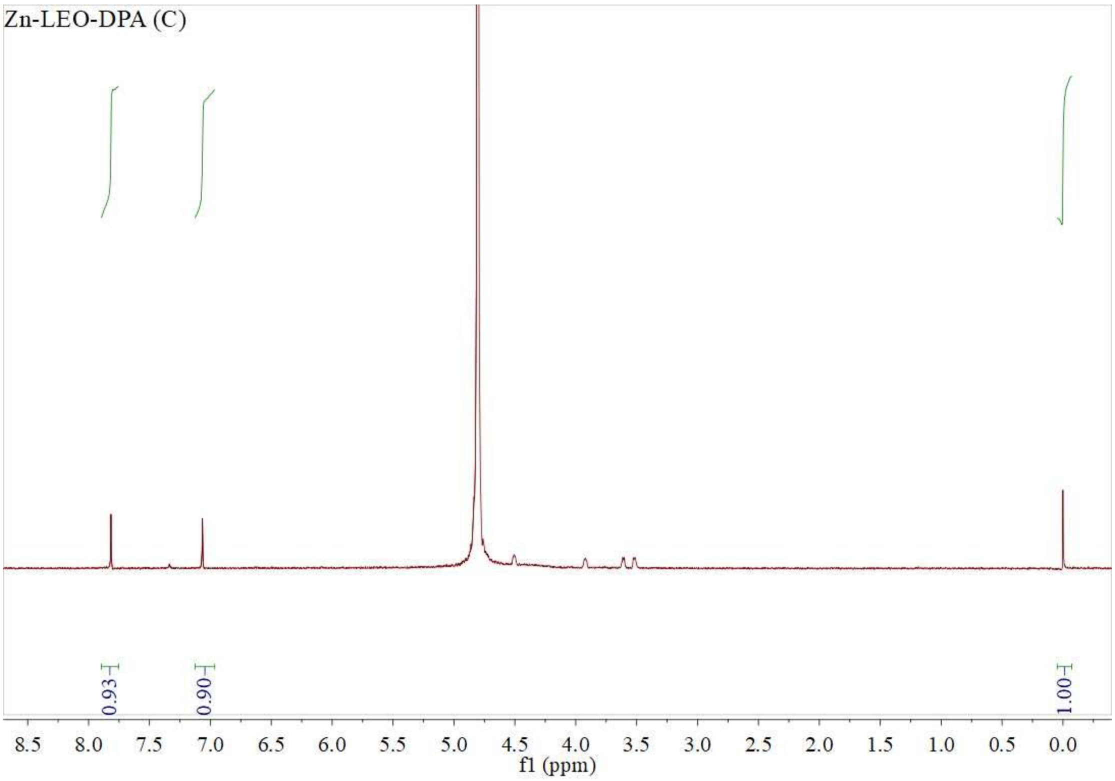


Figure S7: ^{1}H NMR spectrum of Zn-DPA-BP mixture (top, B) and the mixture with added LEO (bottom, B′)

Figure S8



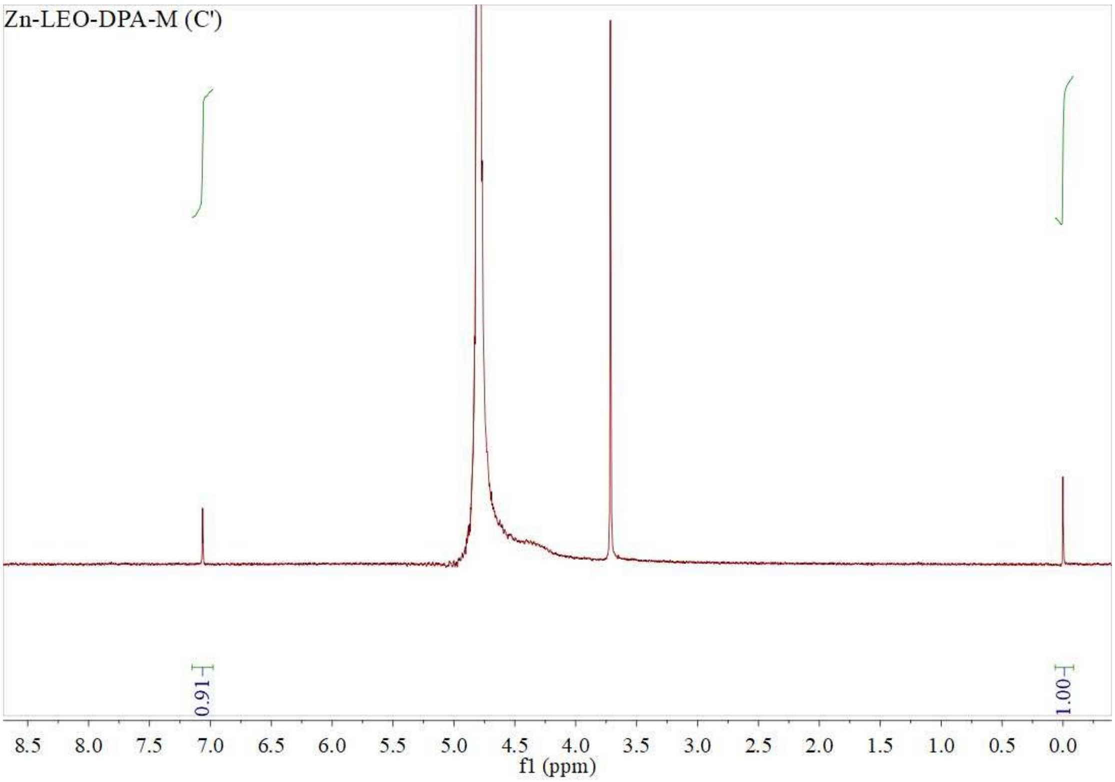
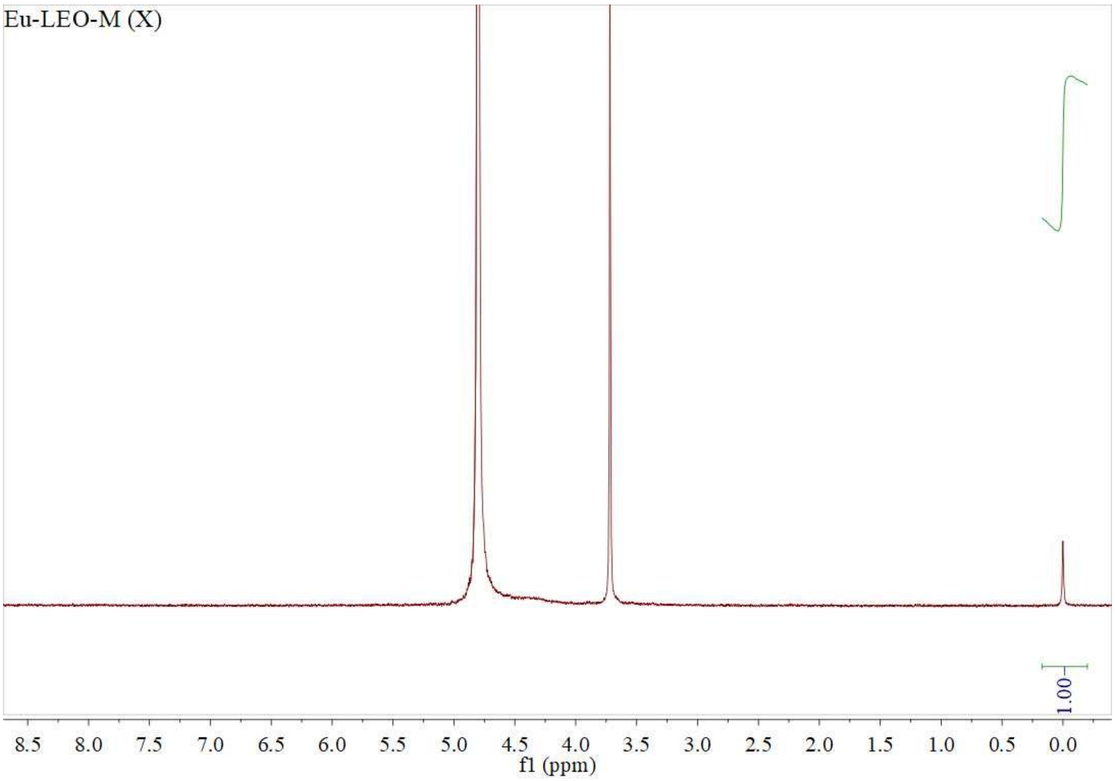


Figure S8: ^{1}H NMR spectrum of Zn-LEO-DPA mixture (top, C) and the mixture with added BP (bottom, C′)

Figure S9



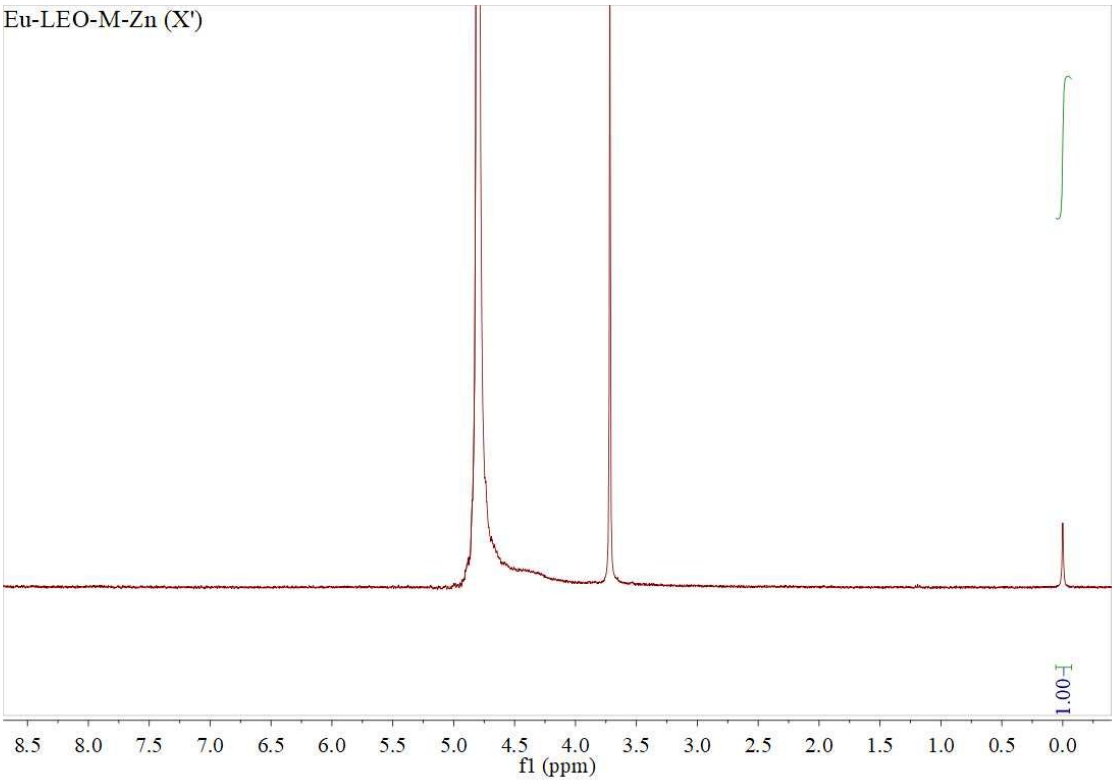
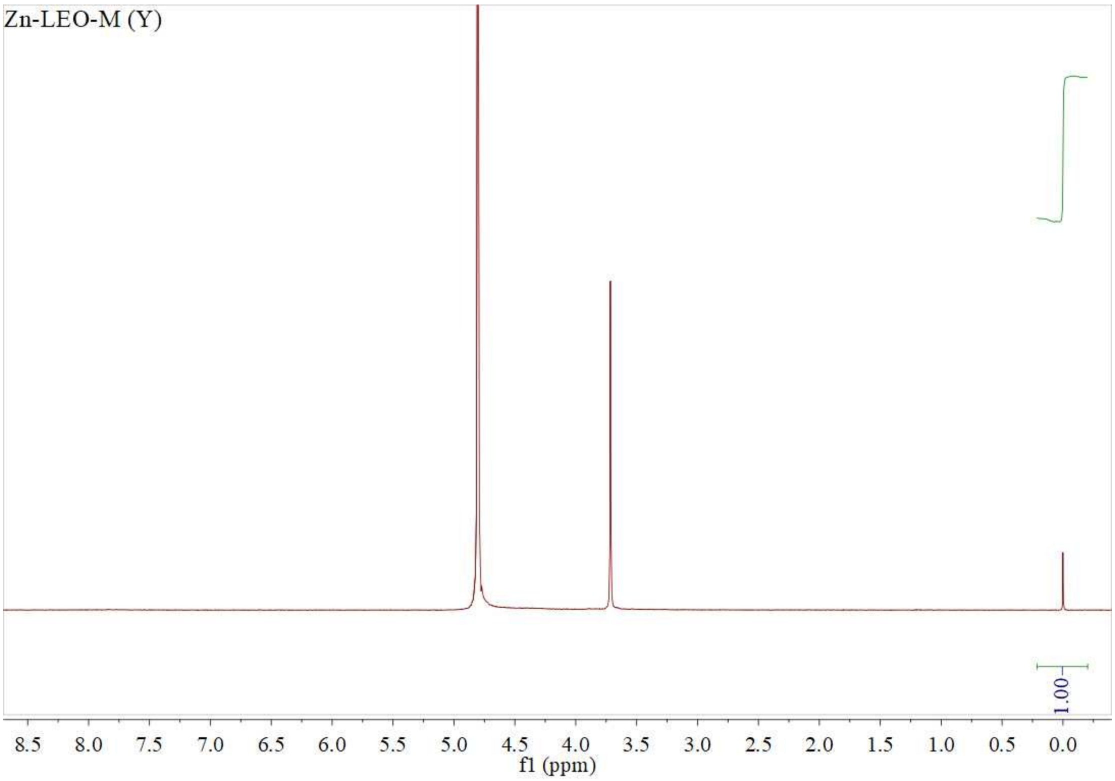


Figure S9: ^{1}H NMR spectrum of Eu-LEO-BP micelles (top, X) and the micelles with added Zn (bottom, X′)

Figure S10



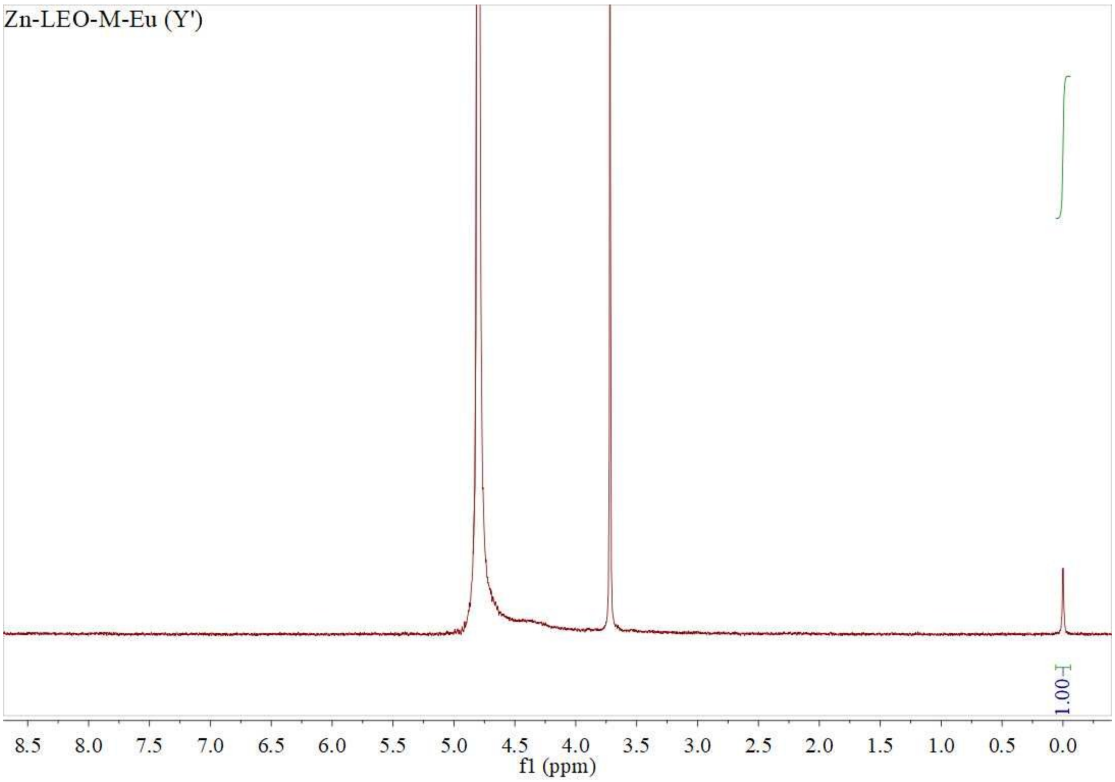
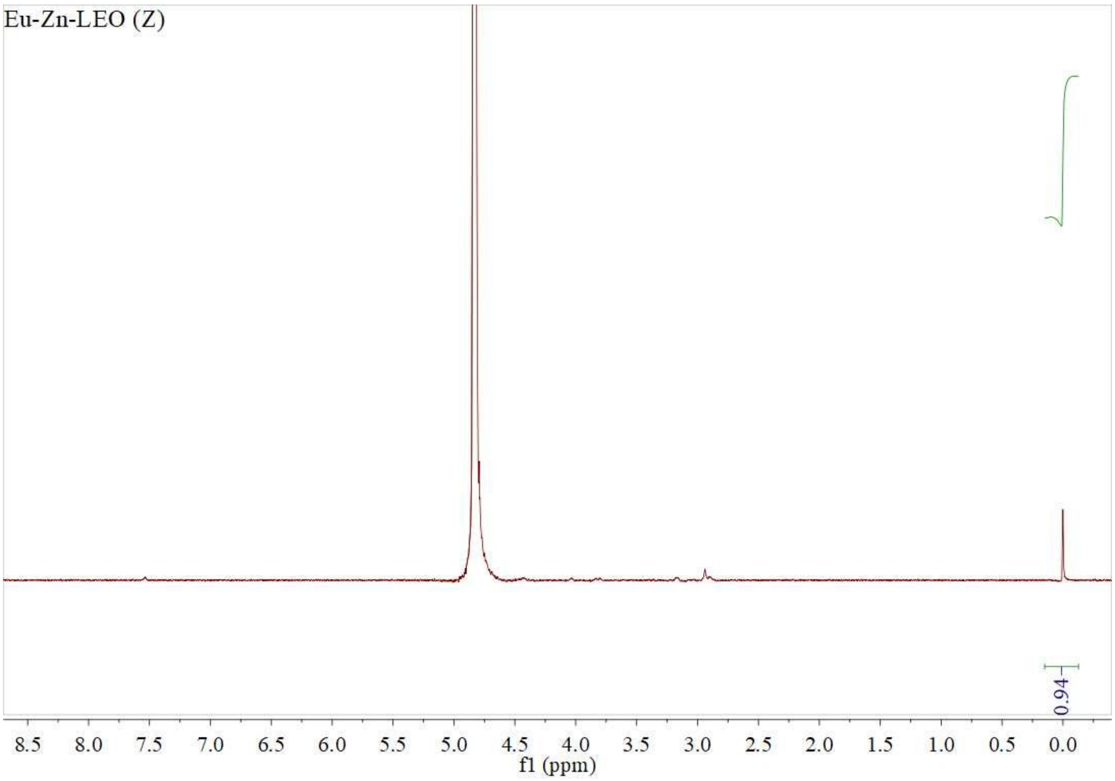


Figure S10: ^{1}H NMR spectrum of Zn-LEO-BP micelles (top, Y) and the micelles with added Eu (bottom, Y′)

Figure S11



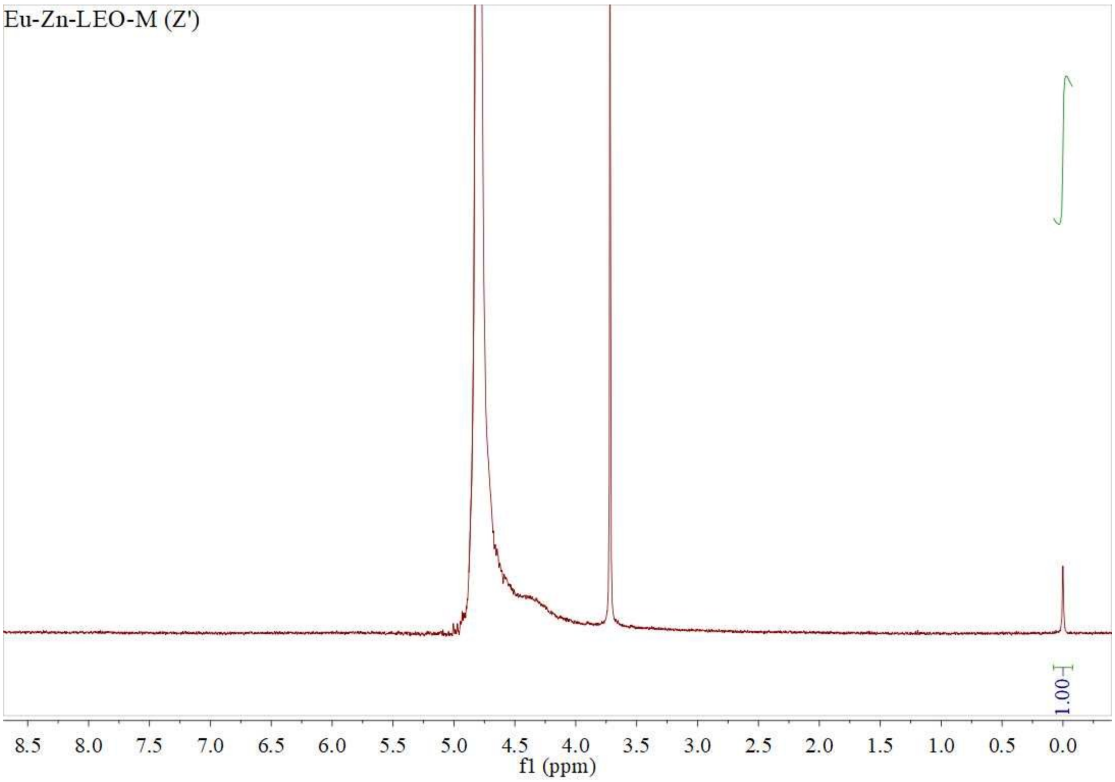


Figure S11: ^{1}H NMR spectrum of Eu-Zn-LEO mixture (top, Z) and the micelles with added BP (bottom, Z′)

Figure S12

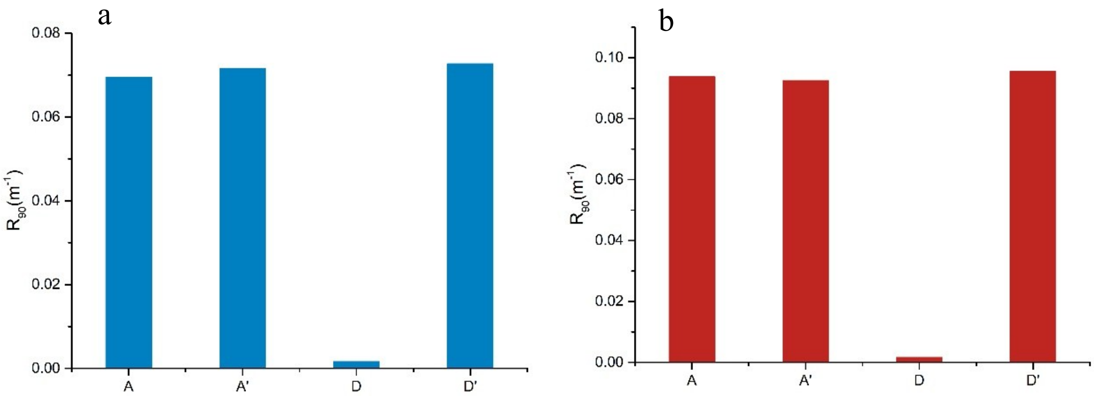


Figure S12: Light scattering intensity of La-C3Ms and mixtures (a), and Zn-C3Ms and mixtures (b).

The light scattering data in manuscript clearly prove that micelles always select the LEO bis-ligand. To avoid any further speculation, we add additional preparation route D and D′, that is, we first mix DPA, LEO and BP together, then add metal ions, La or Zn into the mixture. Samples were prepared by the same strategy with previous scenarios (A, B, C, see experimental part). As shown in Figure S12, mixture D indicates no micelle formation, and D′ display comparable intensity with A′, for both La- and Zn-based micelles, confirming the results from A, B and C scenarios, which is that the LEO is indeed essential for the micelle formation.

References:

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