Europium based coordination polyelectrolytes enable core-shell-corona micelle as luminescent probe

Cheng Wei, Peng Ding, Xiran Nie, Martien A. Cohen Stuart and Junyou Wang*

State-Key Laboratory of Chemical Engineering, and Shanghai Key Laboratory of Multiphase

Materials Chemical Engineering, East China University of Science and Technology, Shanghai

200237, People's Republic of China

*To whom correspondence should be addressed:

E-mail: junyouwang@ecust.edu.cn

This file includes:

1. Luminescence measurements

2. Figure S1: Life time measurements of $Eu-L_2EO_4$ loaded in CSC micelles with different Cu^{2+} and S^{2-} concentration

3. Table S1: Photophysical properties of the Eu-L₂EO₄ loaded in CSC micelles with different Cu^{2+} and S^{2-} concentration

Luminescence measurements

Lifetime of the Eu-L₂EO₄ loaded in CSC micelles was measured with an Agilent Cary Eclipse spectrophotometer. Solution was put in 1.0 cm quartz cells and the excitation was set at 277 nm. The photophysical properties of the Eu-L₂EO₄ loaded CSC micelles, including the 4f-4f emission quantum yield (Φ_{In}), 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 equations¹⁻³:

$$\Phi_{\rm In} = \frac{k_{\rm r}}{k_{\rm r} + k_{\rm nr}} = \frac{\tau_{\rm obs}}{\tau_{\rm rad}} \tag{1}$$

$$\frac{1}{\tau_{\rm rad}} = A_{\rm MD,0} n^3 \left(\frac{I_{\rm tot}}{I_{\rm MD}}\right) \tag{2}$$

$$k_{\rm r} = \frac{1}{\tau_{\rm rad}} \tag{3}$$

$$k_{\rm nr} = \frac{1}{\tau_{\rm obs}} - \frac{1}{\tau_{\rm rad}} \tag{4}$$

Where $A_{MD,0}$ is the spontaneous emission probability for the ${}^{5}D_{0}{}^{-7}F_{1}$ transition in vacuum (14.65 s⁻¹), n is the refractive index of the medium (1.5). Values are obtained from previous study which investigated the Eu-L₂EO₄ coordination structures loaded in similar coacervate complexes¹. (I_{tot}/I_{MD}) is the ratio of the total area of the three peaks located at 592, 615 and 694 nm in the emission spectra to the area of the peak at 592 nm.

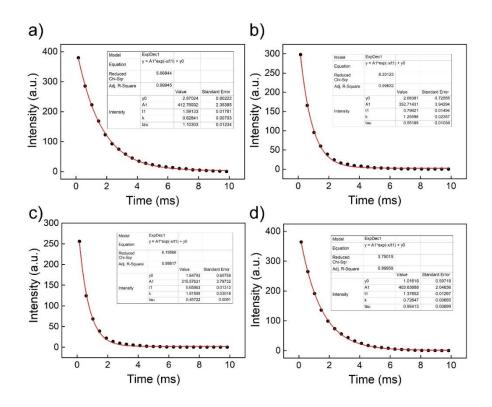


Figure S1. a, b: Life time measurements of Eu-L₂EO₄ loaded in CSC micelles with the concentration of Cu²⁺ at 0 μ M (a) and 10 μ M (b). c, d: Life time measurements of copper quenched Eu-L₂EO₄ loaded CSC micelles with the concentration of S²⁻ at 30 μ M (c) and 80 μ M (d). All the tests are performed in 10 mM Tris-HCl buffer at pH 7.0, at a fixed Eu³⁺ concentration of 10 μ M.

Table S1. Photophysical properties of the Eu-L₂EO₄ loaded in CSC micelles at different Cu²⁺

Ion concentration	$\tau_{rad}\!/ms$	$ au_{obs}/ms$	k_r/s^{-1}	k_{nr}/s^{-1}	Φ_{In}
0 µM Cu ²⁺	3.88	1.59	2.6×10 ²	3.7×10 ²	0.41
$10 \ \mu M \ Cu^{2+}$	4.04	0.79	2.5×10^{2}	1.0×10^{3}	0.20
$^{a}30 \ \mu M \ Cu^{2+}$	/	/	/	/	/
$30 \ \mu M \ Cu^{2+} + 30 \ \mu M \ S^{2-}$	4.09	0.65	2.4×10^{2}	1.2×10 ³	0.16
$30 \ \mu M \ Cu^{2+} + 80 \ \mu M \ S^{2-}$	3.87	1.37	2.6×10 ²	4.7×10^{2}	0.35
^a The Luminescence intensity was too low to measure the life time of the $Eu-L_2EO_4$.					

Reference:

- 1. Xu, L.; Xie, M.; Huang, J. and Yan, Y., *Langmuir* 2016, **32**, 5830-7.
- 2. Moreau, P.; Colette-Maatouk, S.; Vitorge, P.; Gareil, P. and Reiller, P. E., *Inorg. Chim. Acta* 2015, **432**, 81-88.
- Marmod ée, B.; de Klerk, J.; Kumke, M. U.; Ariese, F. and Gooijer, C., *J. Alloys Compd.* 2008, 451, 361-364.