

# Eu(III)-Fulvic Acid Complexation: Evidence of Fulvic Acid Concentration Dependent Interactions by Time-Resolved Luminescence Spectroscopy.

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The supporting information contains four Figures and one Table. One Figure shows Eu(III)-SRFA normalized luminescence spectra to the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition at 0.1 M NaClO<sub>4</sub> and [Eu]<sub>tot</sub> = 1 μM at pH 4, 6 and 7. One Figure shows luminescence decay times of Eu(III) at pH 4, 6 and 7 depending on fulvic concentration for Eu(III) concentrations of 1 μM and 10 μM. One Figure shows the simulation of Eu bound to SRFA and NICA-Donnan parameters using generic parameters. One Figure shows the transformation of asymmetry ration in proportion of Eu(III) bound to the fulvic acid. One Table is showing the NICA-Donnan generic parameters for simulation, and the NICA-Donnan parameters obtained from modeling.

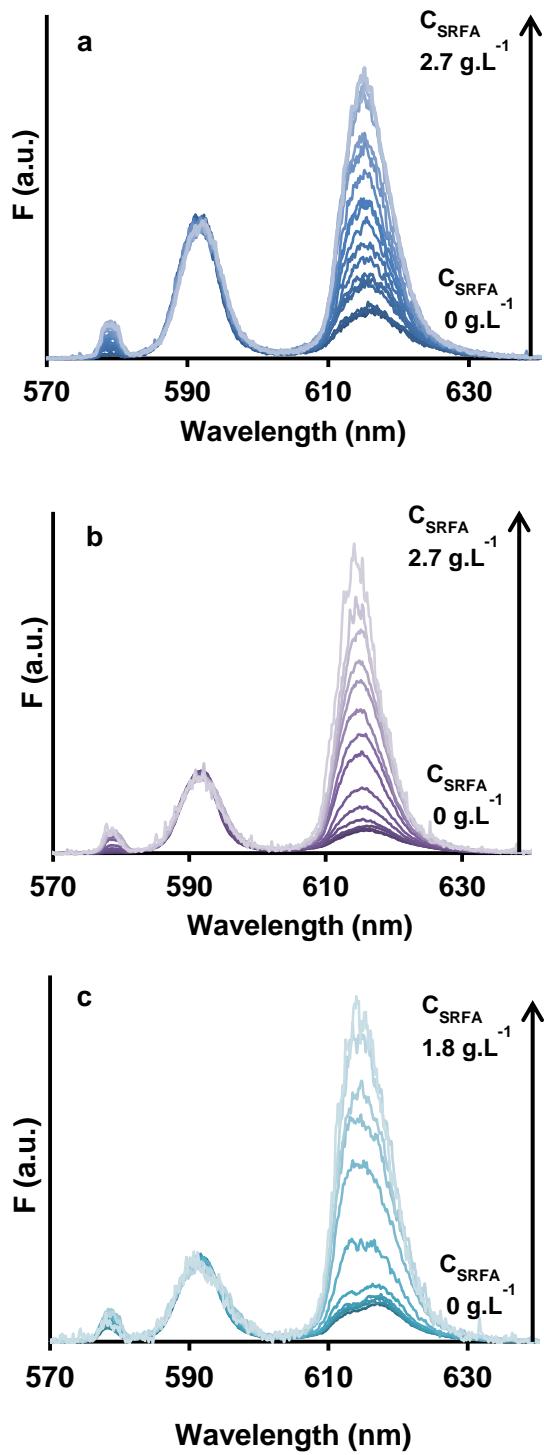


Figure S1. Eu(III)-SRFA normalized luminescence spectra to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition at 0.1 M NaClO<sub>4</sub> and C<sub>Eu(III)</sub> = 1 μM, λ<sub>exc</sub> = 393.7 nm, D = 10 μs, W = 300 μs, 600 lines.mm<sup>-1</sup> grating, pH 4 (a), pH 6 (b), pH 7 (c).

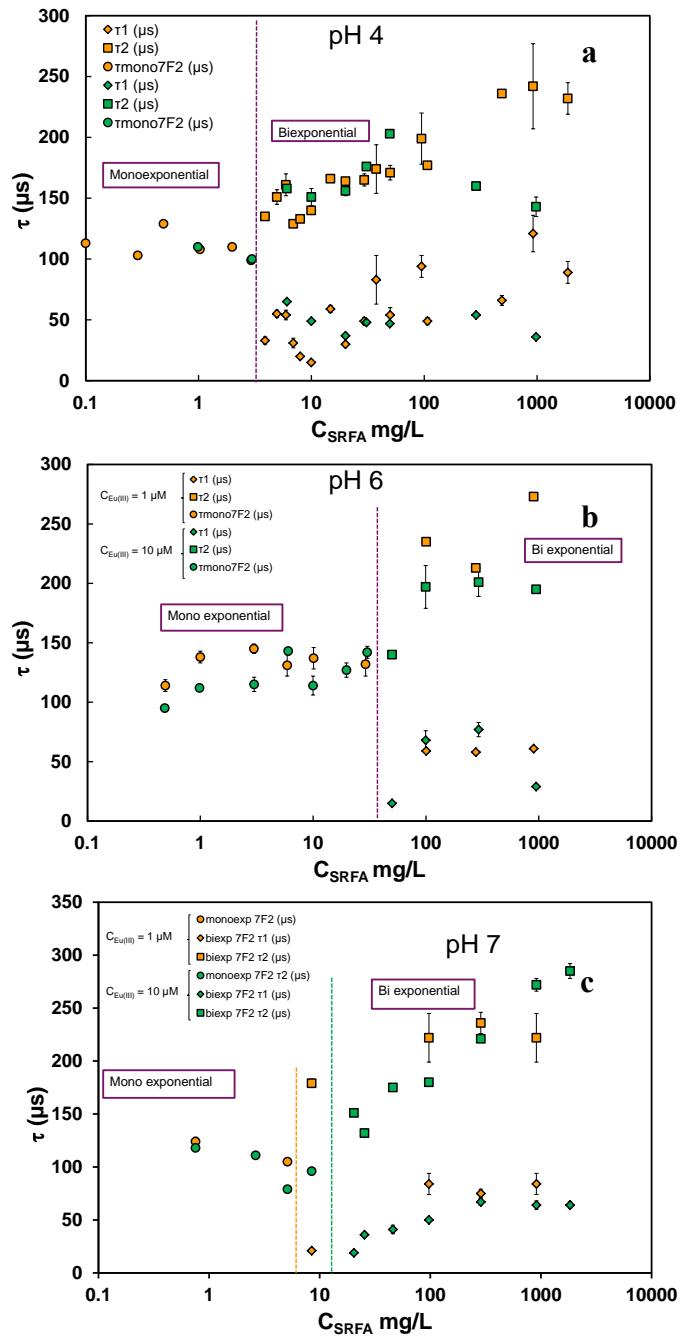


Figure S2. Luminescence decay times of Eu(III) at pH 4 (a), 6 (b) and 7 (c) depending on  $C_{\text{SRFA}}$  concentration for  $C_{\text{Eu(III)}}$  of  $1 \mu\text{M}$  (orange symbols), and  $10 \mu\text{M}$  (green symbols) and  $I = 0.1 \text{ M NaClO}_4$ . Circles symbols correspond to mono exponential decay times, diamonds and squares correspond to bi-exponential decay times. Dashed lines correspond to the transition between mono and bi exponential decay times (in purple when the transition is the same for the two  $C_{\text{Eu(III)}}$ , in orange for the transition of  $C_{\text{Eu(III)}}$  of  $1 \mu\text{M}$ , and in green for the transition of  $C_{\text{Eu(III)}}$  of  $10 \mu\text{M}$ .

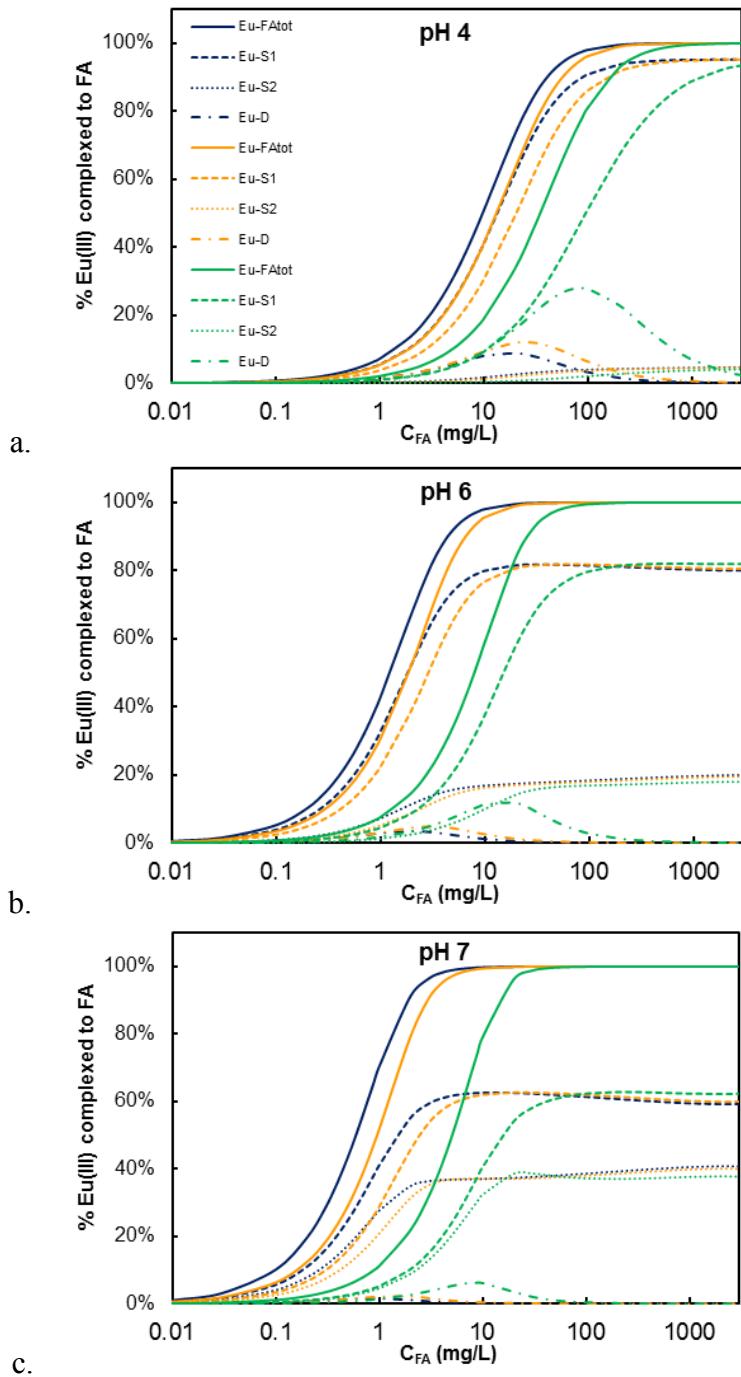


Figure S3. Simulation of the proportion of Eu(III) bound to a generic fulvic acid for  $C_{\text{Eu(III)}}$  of 0.5  $\mu\text{M}$  (blue lines), 1  $\mu\text{M}$  (orange lines) and 10  $\mu\text{M}$  (green lines) at pH 4 (a), 6 (b), and 7 (c). Simulation of Eu(III) distribution on  $S_1$  sites (dashed lines) and  $S_2$  sites (dotted lines) of SRFA. Solid lines are the sum of  $S_1$  and  $S_2$  sites. Generic NICA-Donnan parameters are given in Table S1.

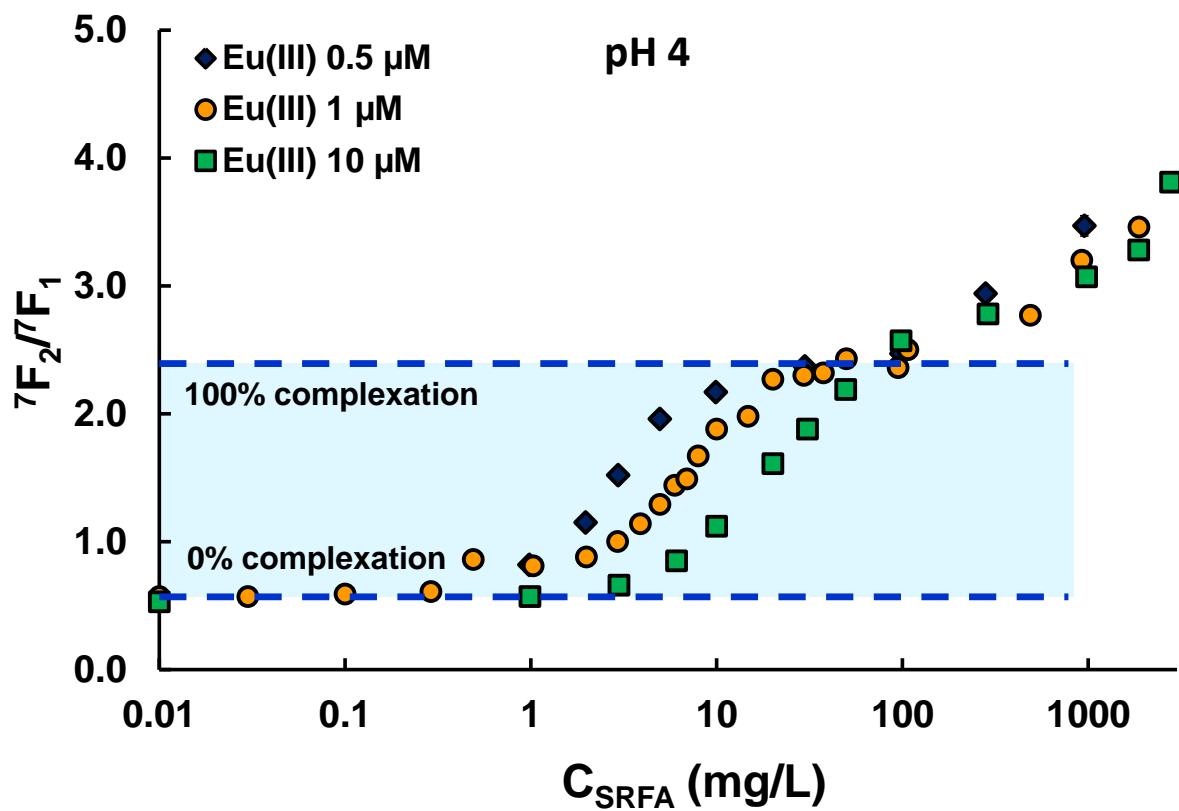


Figure S4. Evolution of asymmetry ratio of Eu(III)-SRFA spectra at pH 4 depending on  $C_{\text{SRFA}}$  for  $C_{\text{Eu(III)}}$  of 0.5 (blue diamonds), 1 (orange circles), and 10  $\mu\text{M}$  (green squares) and  $I = 0.1 \text{ M NaClO}_4$ .

Table S1. NICA-Donnan parameters for proton and Eu(III) binding to a fulvic acid.

	$Q_{max,1}$ (mol.kg <sub>FA</sub> <sup>-1</sup> )	$n_{M,1}$	$\log_{10}\tilde{K}_{M,1}$	$n_1 \times \log_{10}\tilde{K}_{M,1}$	$p_1$	$Q_{max,2}$ (mol.kg <sub>FA</sub> <sup>-1</sup> )	$n_{M,2}$	$\log_{10}\tilde{K}_{M,2}$	$n_{M,2} \times \log_{10}\tilde{K}_{M,2}$	$p_2$	b	Ref.
<b>H<sup>+</sup></b>	5.88	0.66	2.34		0.59	1.86	0.76	8.60		0.70	0.57	(I)
<b>Eu<sup>3+</sup></b>		0.47	-1.92	-0.90			0.45	5.87	2.64			(I)
<b>Eu<sup>3+</sup></b>		0.53	-1.11	-0.83			0.40	6.92	2.77			This work

## **REFERENCES**

- (1) Milne, C. J.; Kinniburgh, D. G.; Van Riemsdijk, W. H.; Tipping, E. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environ. Sci. Technol.* **2003**, *37*, 958-971.