Electronic Supplementary Material (ESI) for Dalton Transactions.

Interaction of europium and curium with alpha-amylase

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Electronic Supplementary Information

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Determination of Eu-Amy excitation spectra

1. Experimental

Suspensions of 5 g/L Amy in 0.1 M NaCl with 1×10^{-4} M Eu(III) were prepared and the pH was adjusted to 5.2 and 7.2. The mixtures were shaken for 24 hours at ambient temperature and afterwards centrifuged for 20 min at 4000 rpm. The Eu-Amy solids were separated from the aqueous solutions and dried at ambient temperature. Measurements were performed at < 20 K using a pulsed flash lamp pumped Nd:YAG-OPO laser system from Spectra Physics (Mountain View, USA), combined with a spectrograph M270 and an ICCD camera system Spectrum One (Horiba-Jobin Yvon). The excitation wavelength was varied between 577 and 582 nm, that cover the range of the $^7F_0 \rightarrow {}^5D_0$ transition, with a precision of 0.01 nm, and the luminescence emission was recorded between 585 and 780 nm.

2. Results

Since the $^7F_0$ transition of Eu(III) is a non-degenerate transition, every non-equivalent Eu(III) species yields a single emission line. Therefore the direct excitation of the $^7F_0 \rightarrow {}^5D_0$ transition enables us to determine the number of existing Eu(III) species. The excitation spectra of Eu(III)-Amy samples at pH 5.2 and 7.2 exhibit two peak maxima at 578.70 nm (pH 5.2) / 578.90 nm (pH 7.2) and 579.30 nm, indicating the presence of two different Eu(III)-Amy complexes at both pH values (Figure S1, left). The intensities of these peaks vary depending on the pH. At pH 5.2 both excitation maxima are pronounced similarly, while at pH 7.2 the peak at 579.30 nm becomes dominant. The species distribution in Figure 4 shows that at pH ~ 5 both 1:1 and 1:3 complexes are formed with similar fractions. On the other hand at pH ~ 7 the 1:3 complex is the dominating species with ~90% fraction, while the 1:1 complex represents only about 10% fraction. Therefore, the excitation maximum at 579.30 nm can be assigned to the 1:3 complex and that at 578.70 nm to the 1:1 complex.

However, the luminescence spectra of the single species could not be extracted from the data collected at the relevant excitation wavelengths. The luminescence decay remains mostly bi-exponential, except for the excitation of the pH ~ 7 sample at 579.70 nm, which shows mono-exponential luminescence decay. The static luminescence spectrum in Figure S1 (right) is similar to the spectra with the highest pH and Amy concentration at ambient and physiological temperature (see Figures 3, S2 and S3). Also the luminescence lifetime of 580 ± 10 µs is comparable to that measured at ambient temperature for the 1:3 species. All other static spectra seem to be sum spectra of both species. Nevertheless, the average values of the shorter and longer lifetimes (280 ± 20 µs and 700 ± 50 µs) are comparable to those measured at ambient temperature for the 1:1 and 1:3 species.

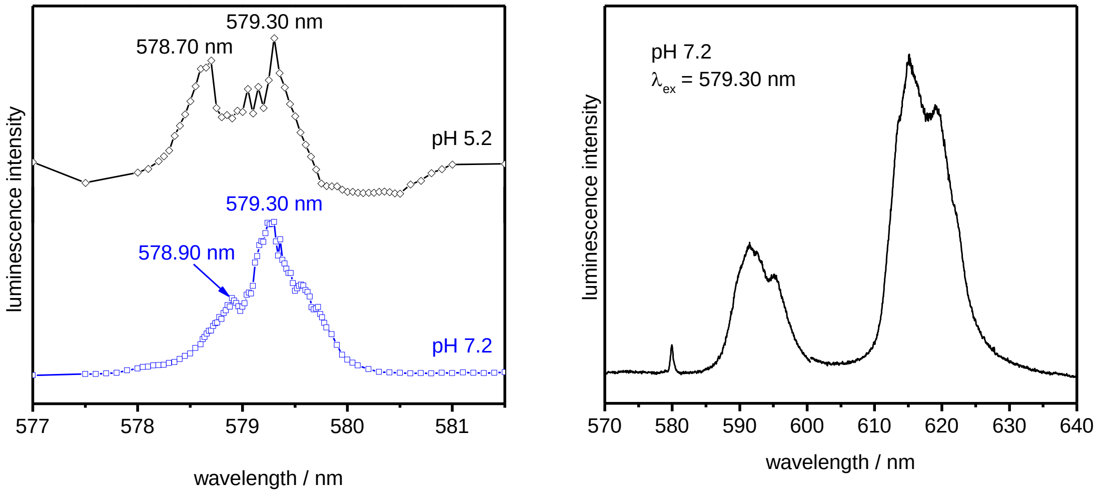

Figure S1. Left: Excitation spectra of Eu-Amy at pH 5.2 and 7.2. Right: Emission spectra of Eu-Amy at pH 7.2 after direct excitation at 579.30 nm.

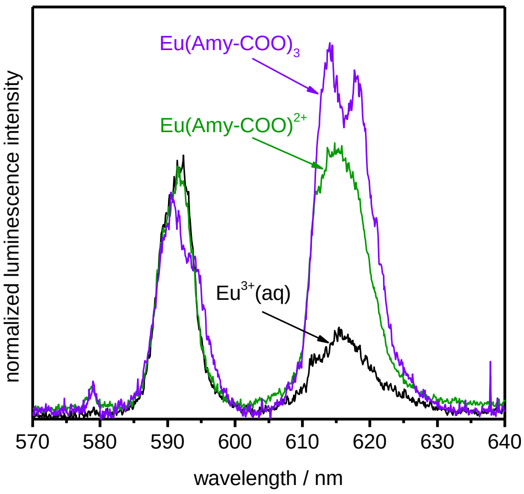

Figure S2. Deconvoluted luminescence spectra of individual Eu(III) species in the Eu(III)-Amy complexation system as obtained from SPECFIT.

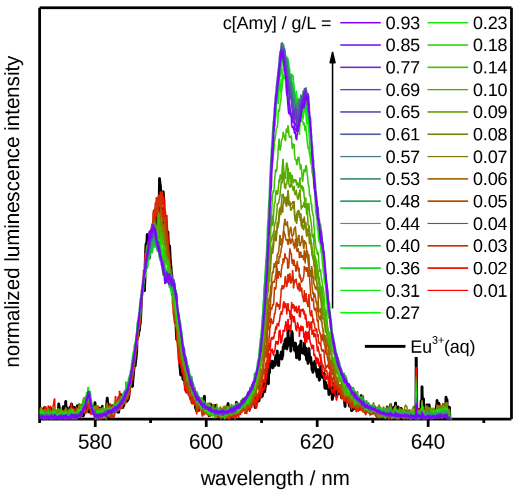

Figure S3. Spectrophotometric titration of 1×10^{-5} M Eu(III) at 37 °C as a function of Amy concentration (pH = 5.5, I = 0.1 M with NaCl).

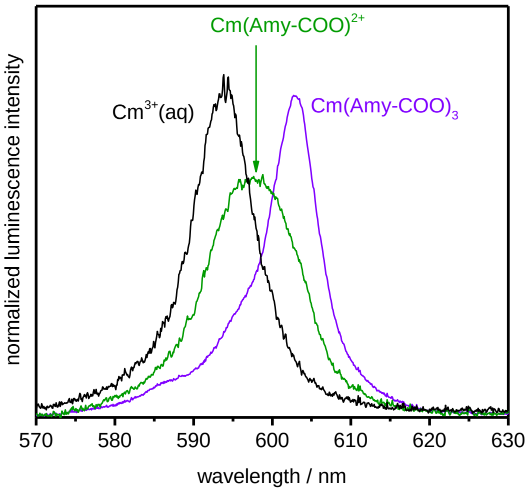

Figure S4. Deconvoluted luminescence spectra of individual Cm(III) species in the Cm(III)-Amy complexation system as obtained from SPECFIT.

Table S1. Luminescence lifetimes of Eu(III) obtained from spectrophotometric titration experiments at different pH values, 1×10^{-5} M Eu^{3+} and 1 g/L Amy (25 °C, I = 0.1 M with NaCl)

pH	τ_1 (μs)		τ_2 (μs)		
	Eu^{3+}(aq)	Mixture	$Eu(Amy{-}COO)^{2+}$	Mixture	$Eu(Amy{-}COO)_3$
3.2		122 ± 1			
3.5		130 ± 2			
3.8		197 ± 6			
4.0	110 ± 9		313 ± 81		
4.2	120 ± 7		384 ± 94		
4.4	118 ± 6		422 ± 53		
4.6	117 ± 18		390 ± 24		
4.8	118 ± 25		371 ± 40		
5.1	114 ± 13			427 ± 14	
5.3		206 ± 20			568 ± 7
5.8		184 ± 22			688 ± 9
6.0		172 ± 9			575 ± 15
6.4		179 ± 14			599 ± 19
6.7		167 ± 15			602 ± 21
7.0		168 ± 16			614 ± 18
7.4		170 ± 18			693 ± 26
7.8		148 ± 23			650 ± 16
8.6		213 ± 18			664 ± 15
9.1		169 ± 19			654 ± 17

Table S2. Luminescence lifetimes of Eu(III) obtained from spectrophotometric titration experiments with different Amy concentrations, 1×10^{-5} M Eu^{3+} at pH 5.5 (25 °C, I = 0.1 M with NaCl)

c(Amy) (g/L)	τ_1 (μs)		τ_2 (μs)		
	Eu^{3+}(aq)	Mixture	$Eu(Amy{-}COO)^{2+}$	Mixture	$Eu(Amy{-}COO)_3$
0	104 ± 2				
0.03	125 ± 3				
0.06	103 ± 13		345 ± 113		
0.09	111 ± 13		387 ± 123		
0.10	107 ± 9			453 ± 133	
0.16	120 ± 11			519 ± 105	
0.20	105 ± 8			435 ± 36	
0.23	99 ± 19			393 ± 51	
0.27	108 ± 10			422 ± 10	
0.31	109 ± 9			479 ± 21	
0.36	121 ± 20			532 ± 40	
0.40		161 ± 16			738 ± 63
0.44		160 ± 14			700 ± 41
0.48		151 ± 20			591 ± 34
0.57		149 ± 18			590 ± 28
0.65		143 ± 20			591 ± 27
0.73		145 ± 20			576 ± 21
0.81		156 ± 18			624 ± 24
0.91		166 ± 24			622 ± 27
1.00		132 ± 27			599 ± 22
Average (Table S1 / S2)			**380 ± 40**		**630 ± 50**

Table S3. Luminescence lifetimes of Cm(III) obtained from spectrophotometric titration experiments with different Amy concentrations, 3×10^{-7} M Cm^{3+} at pH 5.5 (25 °C, I = 0.1 M with NaCl)

c(Amy) (g/L)	τ_1 (µs) Cm^{3+}(aq)	τ_1 (µs) $Cm(Amy{-}COO)^{2+}$	τ_2 (µs) $Cm(Amy{-}COO)^{2+}$	τ_2 (µs) $Cm(Amy{-}COO)_3$
0	65 ± 2			
0.03	61 ± 10		113 ± 3	
0.06	63 ± 13		126 ± 11	
0.09		107 ± 1		
0.18		88 ± 5		182 ± 12
0.27		98 ± 3		243 ± 9
0.36		101 ± 5		277 ± 22
0.44		107 ± 4		312 ± 24
0.53		96 ± 5		281 ± 19
0.61		85 ± 4		276 ± 12
0.69		94 ± 4		576 ± 21
0.77		96 ± 4		624 ± 24
0.85		91 ± 4		622 ± 27

Table S4. Luminescence lifetimes of Cm(III) obtained from spectrophotometric titration experiments at different pH values, 3×10^{-7} M Cm^{3+} and 1 g/L Amy (25 °C, I = 0.1 M with NaCl)

pH	τ_1 (µs)		τ_2 (µs)	
	Cm^{3+}(aq)	**mixture**	**Cm[Amy−COO]$^{2+}$**	**Cm[(Amy−(COO)]$_3$**
3.1		81 ± 1		
3.3		84 ± 1		
3.4		87 ± 1		
3.5		89 ± 1		
3.7		90 ± 1		
3.8		95 ± 2		
3.9	58 ± 14		103 ± 5	
4.0	57 ± 12		112 ± 6	
4.2	59 ± 11		123 ± 9	
4.4	57 ± 10		140 ± 14	
4.7			81 ± 3	223 ± 11
4.8			90 ± 6	220 ± 6
4.9			88 ± 9	180 ± 27
5.1			86 ± 6	270 ± 5
5.4			86 ± 9	187 ± 16
5.6			90 ± 5	184 ± 13
6.0			91 ± 4	216 ± 20
6.2			93 ± 7	215 ± 12
6.5			92 ± 12	173 ± 10
6.8			114 ± 10	190 ± 13
7.0			97 ± 8	196 ± 9
7.3			115 ± 6	284 ± 20
7.7			123 ± 6	326 ± 15
8.0			121 ± 7	304 ± 13
8.3			88 ± 6	231 ± 8
8.5			98 ± 7	242 ± 12
8.7			99 ± 7	245 ± 13
8.8			83 ± 4	205 ± 7
8.9			98 ± 7	241 ± 13
9.1			99 ± 6	259 ± 15
9.2			82 ± 6	209 ± 10
9.5			95 ± 6	219 ± 10
Average (Table S3 / S4)			**120 ± 10**	**240 ± 40**