Trivalent *f*-elements in human saliva: A comprehensive speciation study by time-resolved laser-induced fluorescence spectroscopy and thermodynamic calculations

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Electronic Supplementary Information

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Table S1. List of complex stability constants (log β^0) used for speciation calculation.

Species	M = Eu(III)	Reference	M = Cm(III)	Reference
$M[Amy{-}COO]^{2+}$	5.20	S1	5.42	S1
$M[Amy{-}(COO)_3]$	13.31	S1	13.40	S1
MCit	9.46	S2	9.3	S2
$M(HCit)(Cit)^{2-}$	12.7	S2	12.9	S2
$M(Cit)_2^{3-}$	13.2	S2	13.2	S2
$MHCO_3^{2+}$	11.93	S3	12.2	S4
MCO_3^{+}	7.95	S3	8.0	S4
$M(CO_3)_2^{-}$	12.24	S3	12.9	S4
$MH_2PO_4^{2+}$	22.43	S5	22.02	S6
$MHPO_4^{+}$	18.47	S5	18.56	S6
MPO_4	12.2	S7	12.2	S4
MOH^{2+}	-7.9	S3	-7.2	S4
$M(OH)_2^{+}$	-16.38	S3	-15.1	S4
$M(OH)_3$	-25.42	S3	-26.2	S4
$M(OH)_4^{-}$	-34.53	S3	–	
MCl^{2+}	0.28	S3	0.24	S4
MCl_2^{+}	-0.5	S3	-0.74	S4
MCl_3	-0.44	S3	–	

Table S2. Spectroscopic parameters of Eu(III) luminescence in selected single component and combination of single components at 25 °C and 37 °C.

Sample	**I_2/I_1**[a]	**Exponential decay manner**[b]	**Luminescence lifetime, estimated hydration number**[c]			
			τ_1 (µs)	**$n(H_2O)$**	**τ_2 (µs)**	**$n(H_2O)$**
Natural human saliva (average)	1.3–1.7	mono/bi	125 – 302	8.0-2.9	372 – 845	2.6-0.2
Figure S1 (Model C):						
(A) Carb	2.7	mono	102 ± 2	9.9		
(B) Carb + Ca^{2+}	1.8	mono	100 ± 2	10.1		
(C) Phos	1.0	mono	107 ± 2	9.4		
(D) Phos + Ca^{2+}	1.0		n.d.			
(E) Carb + Phos	1.1	mono	312 ± 5	2.8		
(F) Carb + Phos + Ca^{2+}	1.3	mono			445 ± 6	1.8
Figure S2 (Model B):						
(A) SO_4^{2-}	1.1	mono	255 ± 4	3.6		
(B) SCN^-	1.2	mono	209 ± 5	4.5		
(C) Carb	2.2	mono	134 ± 1	7.4		
Figure S3 (Organic components):						
(A) Muc	3.1	bi	267 ± 8	3.4	699 ± 7	0.9
(B) Amy	2.2	bi	412 ± 21	2.0	794 ± 18	0.7
(C) Lac	2.3	mono	176 ± 1	5.5		
(D) Cit	1.2	mono	200 ± 5	4.7		
(E) urea	1.3	mono	155 ± 2	6.3		
(F) uric acid	1.1	mono	172 ± 10	5.6		
Figure S4 (Model B):						
(A) inorganic, 37 °C	1.3	mono			457 ± 7	1.7
(B) inorganic, 25 °C	1.3	mono			494 ± 4	1.5
(C) all, 37 °C	1.4	bi	146 ± 21	6.7	384 ± 35	2.2
(D) all, 25 °C	1.4	bi	146 ± 18	6.7	470 ± 16	1.7
Further data (not pictured):						
Model B:						
Inorganic + Amy, 25 °C	1.4	bi	144 ± 18	6.8	457 ± 11	2.3
Inorganic + Amy, 37 °C	1.4	bi	399 ± 17	2.1	843 ± 37	0.6
Inorganic + Muc, 25 °C	1.4	bi	158 ± 17	6.1	464 ± 20	1.7
Inorganic + Muc, 37 °C	1.4	bi	162 ± 22	6.0	451 ± 43	1.7
Inorganic + Amy + Muc, 25 °C	1.4	bi	173 ± 19	5.6	500 ± 17	1.5
Inorganic + Amy + Muc, 37 °C	1.4	bi	145 ± 18	6.8	450 ± 16	1.8
Model C:						
Carb + Phos + Ca^{2+} + Amy	1.4	bi	256 ± 35	3.6	697 ± 25	0.9
Carb + Phos + Ca^{2+} + Cit	1.4	bi	143 ± 21	6.9	454 ± 16	1.7
Carb + Phos + Ca^{2+} + Muc	1.4	bi	276 ± 16		833 ± 22	
Carb + Phos + Ca^{2+} + Amy + Cit	1.4	bi	275 ± 33	3.3	698 ± 24	0.9
Carb + Phos + Ca^{2+} + Amy + Muc	1.4	bi	295 ± 13		956 ± 22	
Carb + Phos + Ca^{2+} + Cit + Muc	1.4	bi	142 ± 7		672 ± 20	

[a] Intensity ratio of the transitions into the $^7F_2$ and $^7F_1$ ground states (intensity of the $^5D_0 \rightarrow {}^7F_1$ transition band is fixed as 1). [b] Corresponds to index *i* in eq. (1) [c] Number of water molecules ± 0.5 according to eq. (2).
n.d. = not determined.

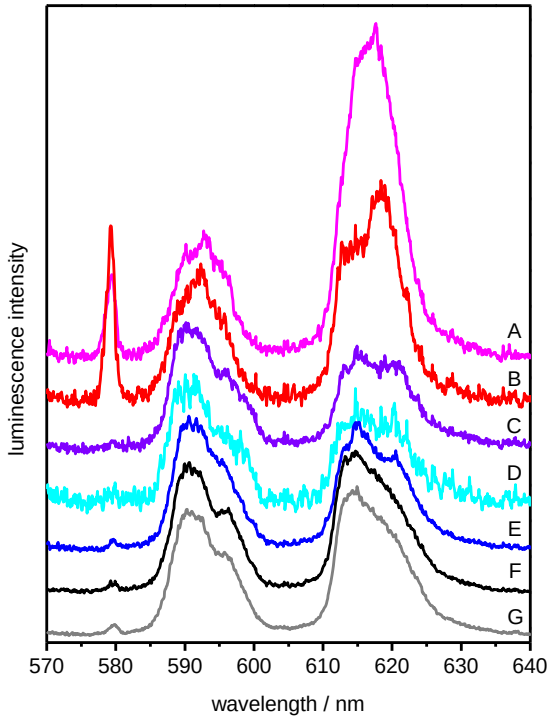

Figure S1. Normalized luminescence spectra of 3×10^{-5} M Eu(III) with single inorganic components and different combinations of components based on Model C (4.5 mM Carb, 4 mM Phos, 1 mM Ca^{2+}; pH = 7.0 ± 0.1, T = 25 °C):
(A) Carb, (B) Carb + Ca^{2+}, (C) Phos, (D) Phos + Ca^{2+}, (E) Carb + Phos, (F) Carb + Phos + Ca^{2+}, and (G) natural saliva (average of 10 samples).

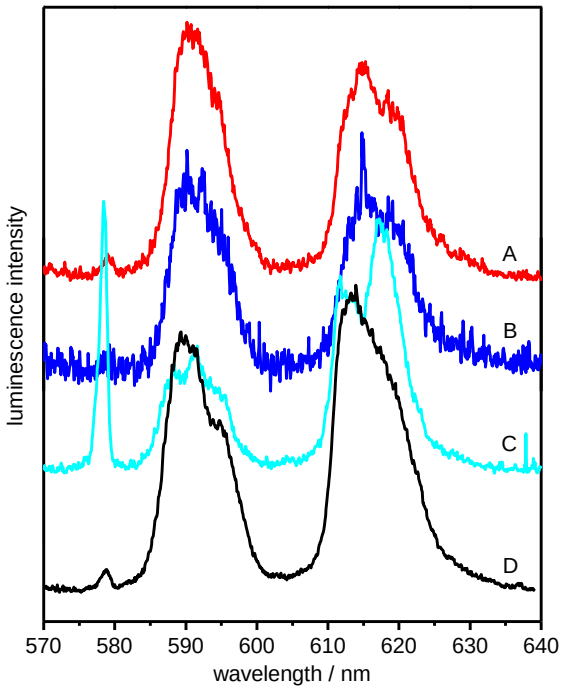

Figure S2. Normalized luminescence spectra of 1×10^{-5} M Eu(III) with single inorganic components based on Model B (pH = 7.0 ± 0.1, T = 25 °C): (A) 8 mM SO_4^{2-}, (B) 4 mM SCN^-, (C) 15 mM Carb, and (D) natural saliva (average of 10 samples).

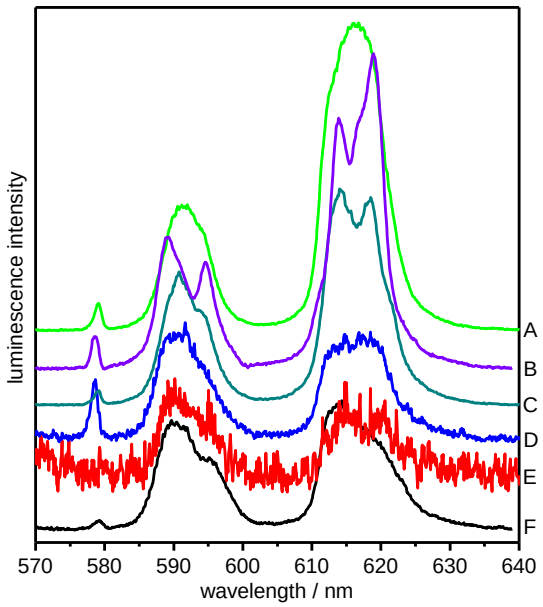

Figure S3. Luminescence spectra of 1×10^{-5} M (A, D, E) or 3×10^{-5} M (B, C, F) Eu(III) with single organic components based on Models B, and C (pH = 6 – 7, T = 25 °C):
(A) 0.5 g/L Muc, (B) 1 mM Cit, (C) 1 g/L Amy, (D) 0.1 mM urea, (E) 6.6 mM uric acid, (F) natural saliva (average of 10 samples).

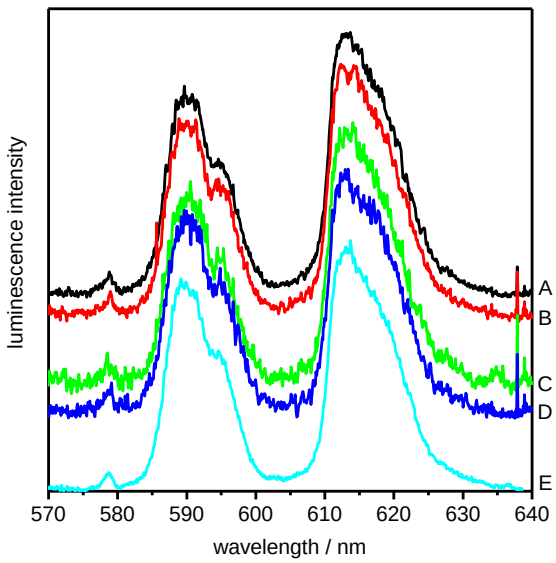

Figure S4. Luminescence spectra of 1×10^{-5} M Eu(III) in artificial human saliva (Model B) at 37 °C compared to 25 °C: (A) inorganic components, 37 °C, (B) inorganic components, 25 °C, (C) complete components of Model B, 37 °C, (D) complete components of Model B, 25 °C, and (E) natural saliva (average of 10 samples), 25 °C .

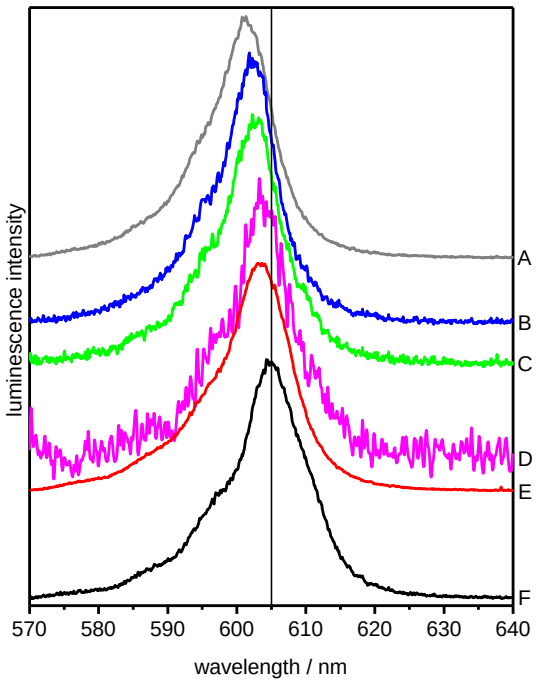

Figure S5. Normalized luminescence spectra of 3×10^{-7} M Cm(III) with single inorganic and organic components and component mixtures based on Models B and C (4.5 mM Carb, 4 mM Phos, 1 mM Ca^{2+}; 1 g/L Amy, 0.5 g/L Muc; pH = 7.0 ± 0.1, T = 25 °C):
(A) Carb, (B) Carb + Phos, (C) Carb + Phos + Ca^{2+}, (D) Amy, (E) Muc, and (F) natural saliva (average of 5 samples).

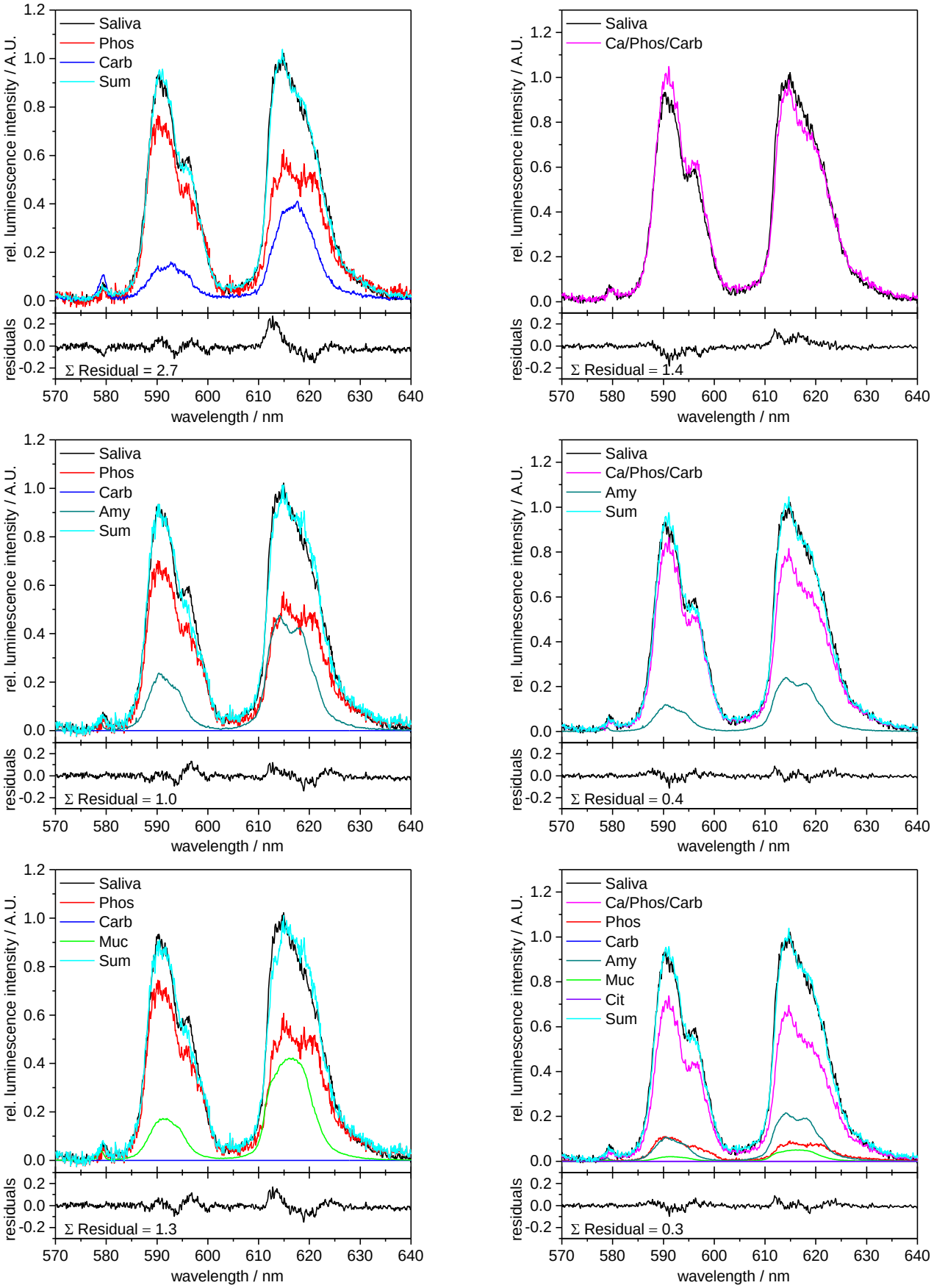

Figure S6. Linear combination fitting on the luminescence spectrum of Eu(III) in human saliva (sample S9) based on the reference spectra of Eu(III) with single components.

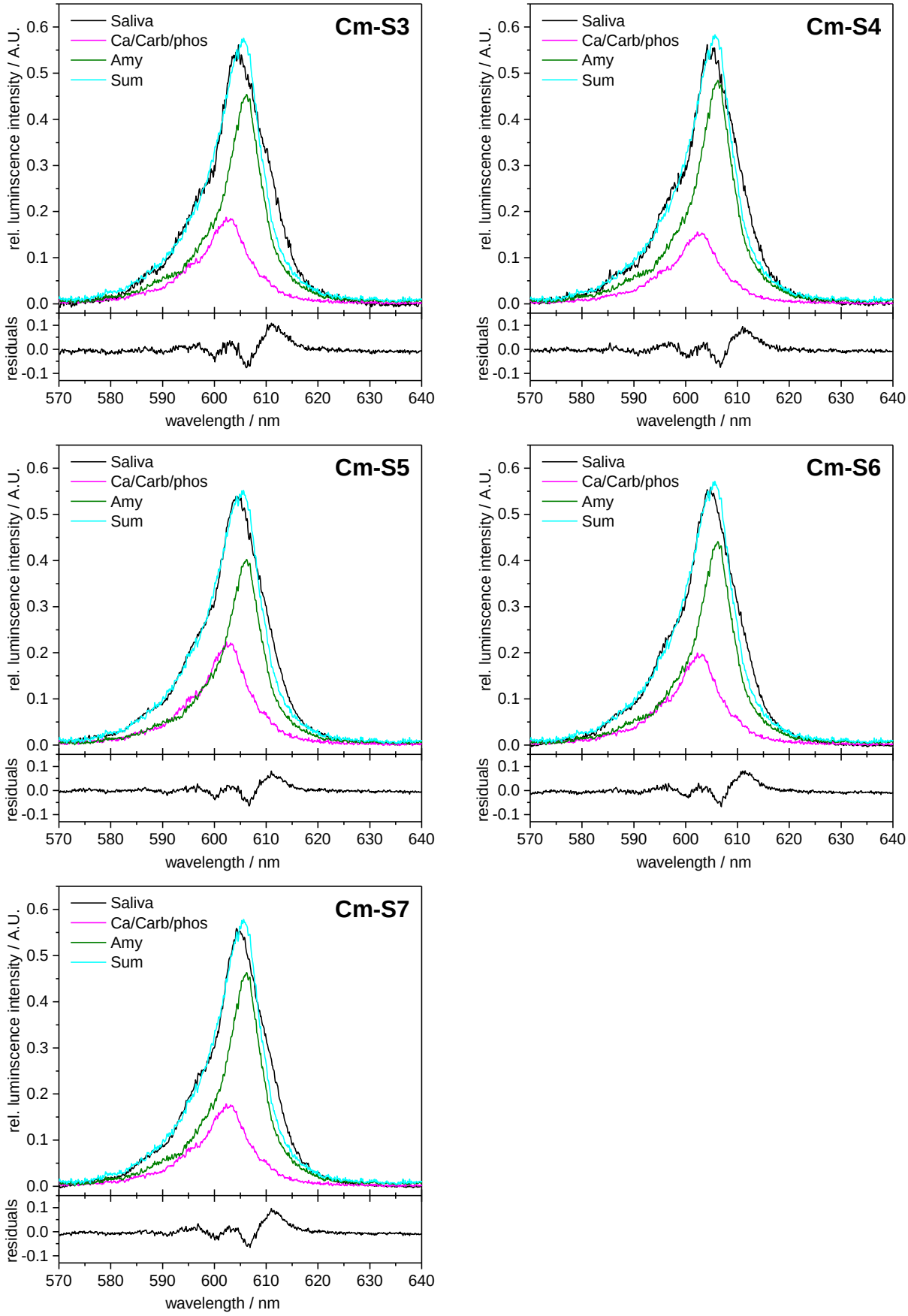

Figure S7. Linear combination fitting on the luminescence spectra of Cm(III) in human saliva (samples S3-S7) based on the reference spectra of Cm(III) with single components.

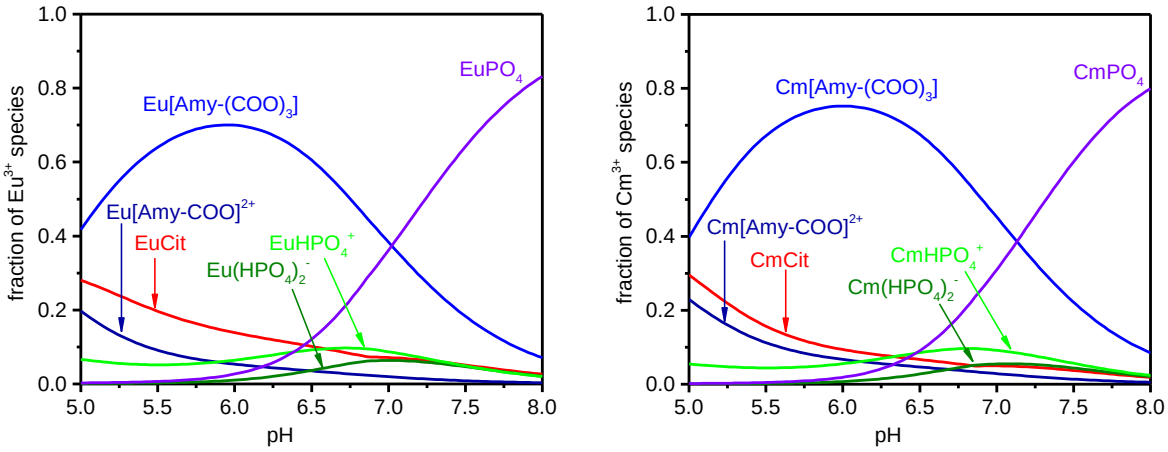

Figure S8. Speciation of 3×10^{-5} M Eu(III) (left) and 3×10^{-7} M Cm(III) (right) in artificial saliva (Model C without consideration of ternary species) as a function of pH. Concentrations of inorganic/organic components are given in Table 1 (main text). Complex stability constants used for speciation calculation are summarized in Table S2.

References:

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