Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Curium(III) citrate speciation in biological systems: An europium(III) assisted spectroscopic and quantum chemical study

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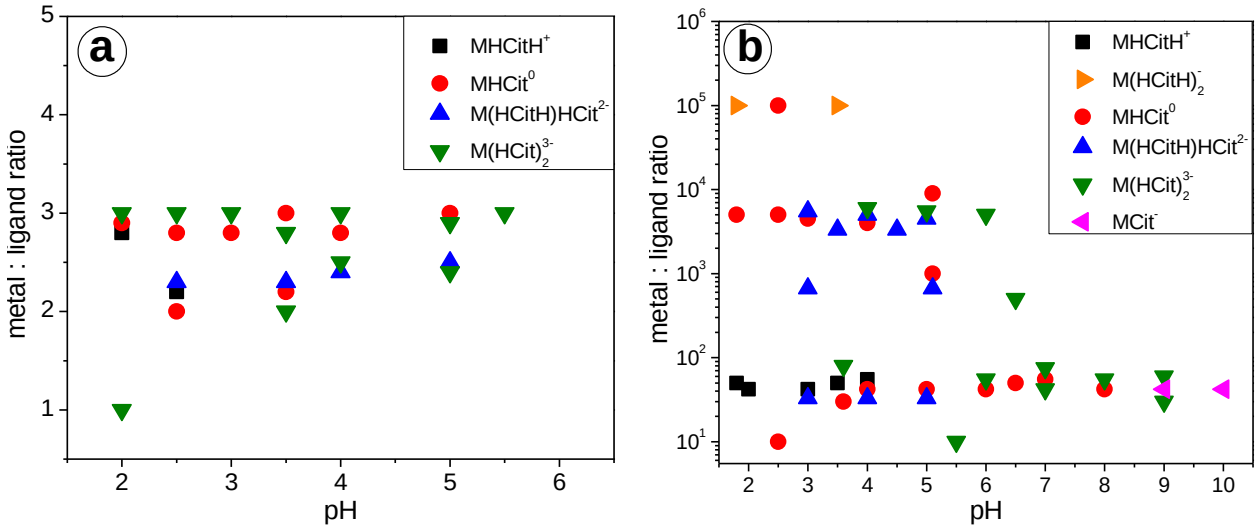

Fig. S1 Overview on the various complex species of M^{3+} (M = An(III), Ln(III)) with different ligand species reported in literature[1, 2-10] for nearly equimolar metal to ligand ratio (a) and ligand excess (b) in dependence on the pH

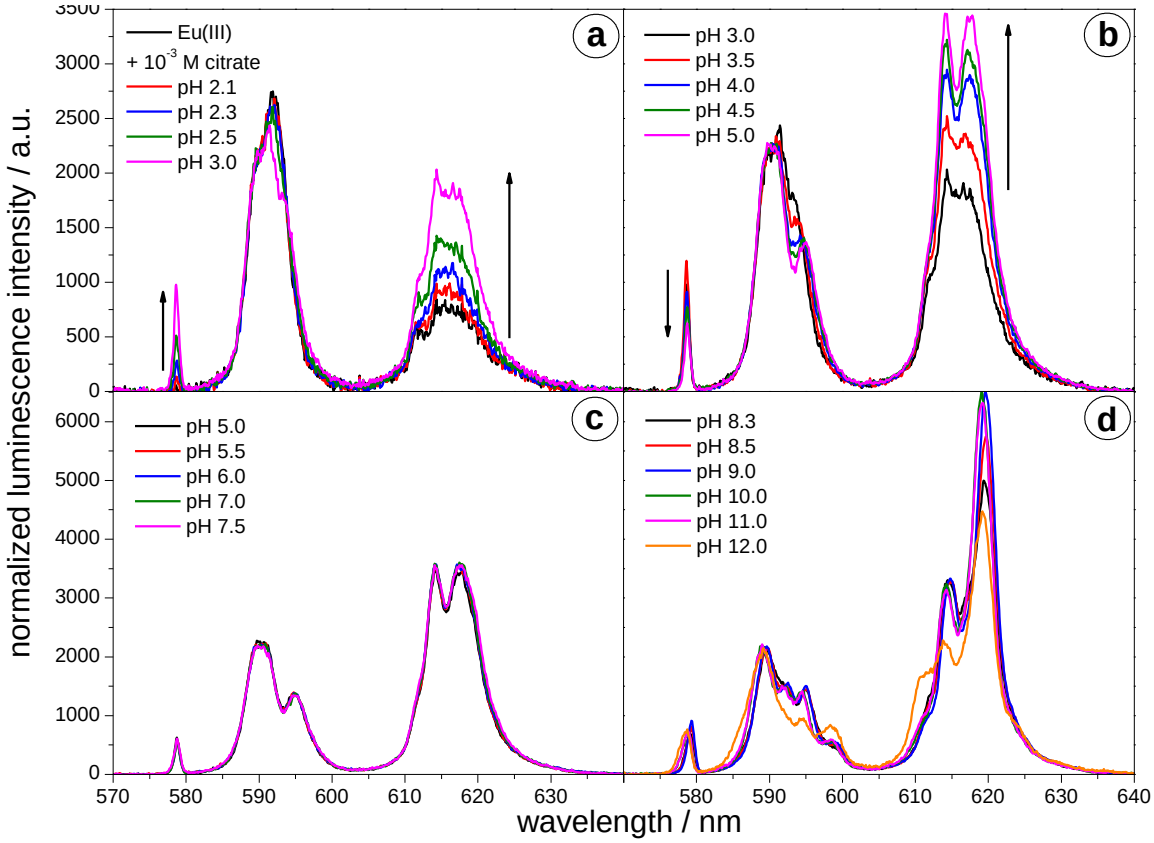

Fig. S2 Normalized steady-state luminescence spectra of $3 \cdot 10^{-5}$ M europium(III) + 10^{-3} M citrate at I = 0.1 M and room temperature in dependence on the pH

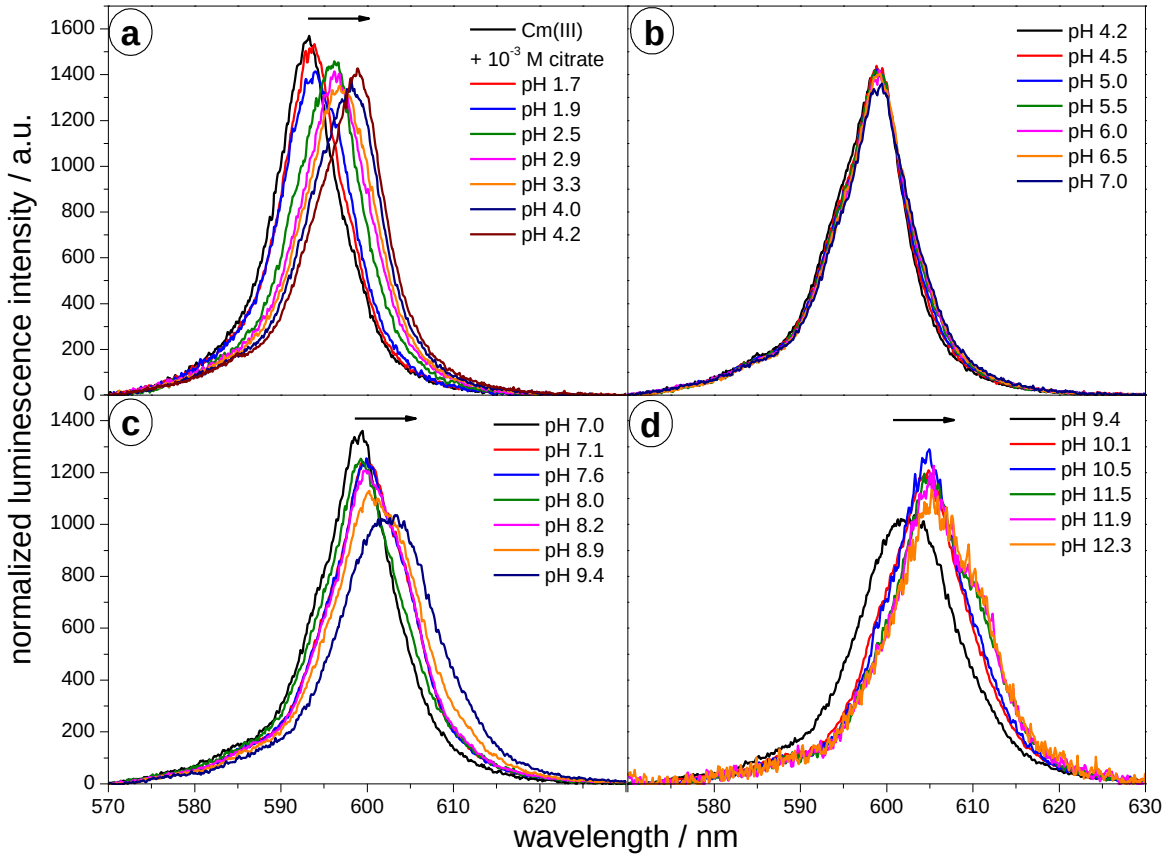

Fig. S3 Normalized steady-state luminescence spectra of $3 \cdot 10^{-7}$ M curium(III) + 10^{-3} M citrate at I = 0.1 M and room temperature in dependence on the pH

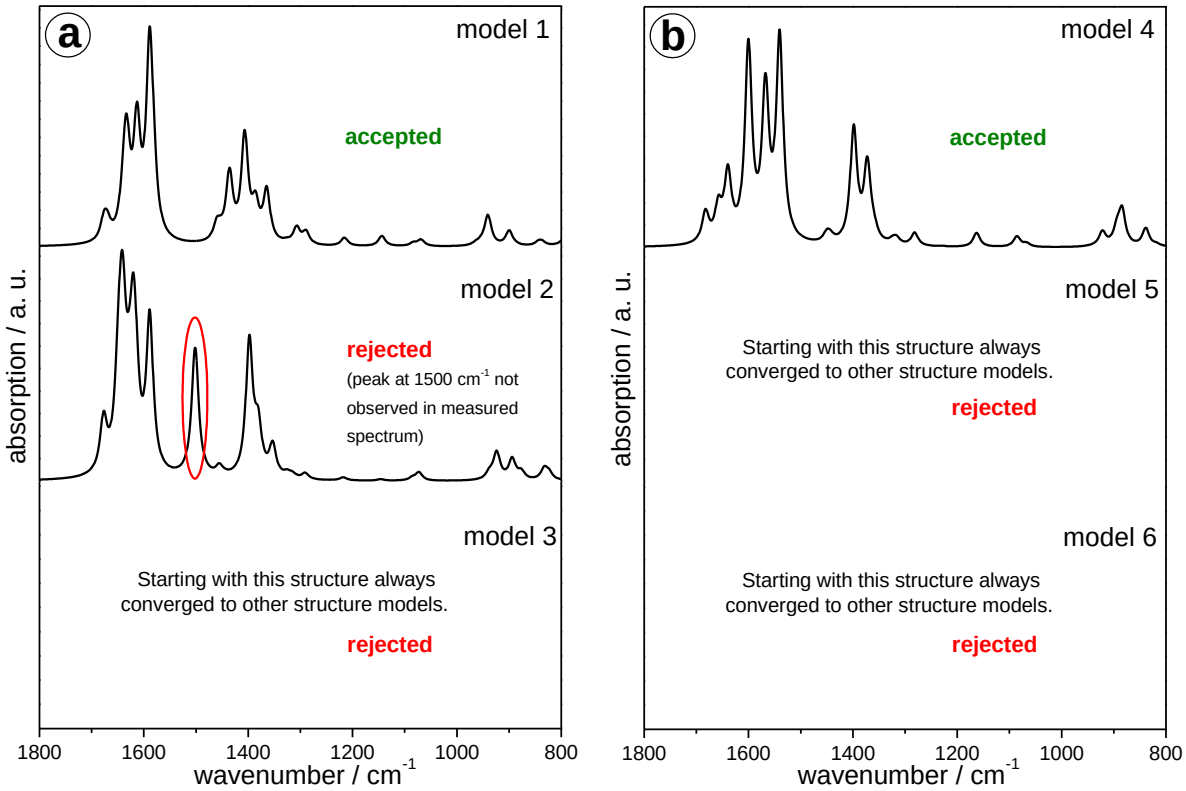

Fig. S4 DFT calculated absorption spectra of different $EuCitH^0$ (a) and $EuCit^-$ (b) structure models

Table S1 Comparison of log K values for curium(III), americium(III), and europium(III) citrate species

complex	metal	method[a]	ionic strength / M	log K[b]	referencec
$MHCit^0$	Eu	TRLFS	0.1 ($NaClO_4$)	7.5 ± 0.2	p.w.
		SOLVEX	0.1	7.4	4
		SOLVEX	0.1	7.75 ± 0.08	7
		SOLVEX	0.1 ($NaClO_4$)	7.78 ± 0.06	10
		POT	0.1 (KNO_3)	7.98 ± 0.03	8
	Cm	TRLFS	0.1 ($NaClO_4$)	7.4 ± 0.2	p.w.
		SOLVEX	0.1	7.6	4
		SOLVEX	0.1	7.74 ± 0.08	7
		SOLVEX	0.1 ($NaClO_4$)	7.69 ± 0.07	10
	Am	SOLVEX	0.1	7.6	4
		SOLVEX	0.1	7.74 ± 0.08	7
		SOLVEX	0.1 ($NaClO_4$)	7.64 ± 0.06	10
		SOLVEX	0.1 (NaCl)	6.74 ± 0.08	3
		SOLVEX	0.1 ($LiClO_4$)	8.0	5
		POT	0.1 ($LiClO_4$)	8.69	5
		UV/VIS	1.0 ($NaClO_4$)	6.96 ± 0.06	2
$M(HCitH)HCit^{2-}$	Eu	TRLFS	0.1 ($NaClO_4$)	10.8 ± 0.5	p.w.
		SOLVEX	0.1	13.6	4
		SOLVEX	0.1	10.25 ± 0.1	7
		SOLVEX	0.1 ($LiClO_4$)	11.11	9
	Cm	TRLFS	0.1 ($NaClO_4$)	11.0 ± 0.3	p.w.
		SOLVEX	0.1	13.4	4
		SOLVEX	0.1 ($LiClO_4$)	10.69 ± 0.2	6
		SOLVEX	0.1	10.24 ± 0.1	7
	Am	SOLVEX	0.1	13.4	4
		SOLVEX	0.1 ($LiClO_4$)	10.76 ± 0.2	6
		SOLVEX	0.1	10.24 ± 0.1	7
		SOLVEX	0.1 ($LiClO_4$)	10.6	5
		POT	0.1 ($LiClO_4$)	13.25	5
$M(HCit)_2^{3-}$	Eu	TRLFS	0.1 ($NaClO_4$)	11.4 ± 0.4	p.w.
		SOLVEX	0.1	10.95 ± 0.2	7
		SOLVEX	0.1 ($NaClO_4$)	11.12 ± 0.07	10
		POT	0.1 (KNO_3)	12.84 ± 0.07	8
	Cm	TRLFS	0.1 ($NaClO_4$)	11.3 ± 0.7	p.w.
		SOLVEX	0.1	10.94 ± 0.2	7
		SOLVEX	0.1 ($LiClO_4$)	11.93 ± 0.2	6
		SOLVEX	0.1 ($NaClO_4$)	11.94 ± 0.07	10
	Am	SOLVEX	0.1	10.94 ± 0.2	7
		SOLVEX	0.1 ($LiClO_4$)	12.16 ± 0.2	6
		SOLVEX	0.1 ($NaClO_4$)	11.89 ± 0.06	10
		SOLVEX	0.1 (NaCl)	11.55 ± 0.08	3
		SOLVEX	0.1 ($LiClO_4$)	12.1	5
		POT	0.1 ($LiClO_4$)	14.29	5
		UV/VIS	1.0 ($NaClO_4$)	10.3 ± 0.2	2
$MCit^-$	Am	POT	0.1 ($LiClO_4$)	10.53	5
		UV/VIS	1.0 ($NaClO_4$)	12.95 ± 0.02	2
$M(Cit)_2^{5-}$	Eu	TRLFS	0.1 ($NaClO_4$)	21.0 ± 0.2	p.w.

[a] TRLFS = Time-Resolved Laser-Induced Fluorescence Spectroscopy, SOLVEX = Solvent Extraction, POT = Potentiometric Titration. [b] log K-values corresponding to equations 5 – 8 from the original paper. [c] p.w. = present work

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