Isoquinoline-based Eu(III) luminescent probes for citrate sensing in complex matrix

Chiara De Rosa[1], Andrea Melchior[2,*], Martina Sanadar[2], Marilena Tolazzi[2], Axel Duerkop[3], Fabio Piccinelli[1,*]

[1] Luminescent Materials Laboratory, DB, Università di Verona, and INSTM, UdR Verona, Strada Le Grazie 15, 37134 Verona, Italy

[2] Dipartimento Politecnico di Ingegneria e Architettura, Laboratorio di Tecnologie Chimiche, Università di Udine, via Cotonificio 108, 33100 Udine, Italy

[3] Institute of Analytical Chemistry, Chemo and Biosensors, University of Regensburg, Universitätsstrasse 31, D-93040 Regensburg, Germany

* corresponding author's email address: fabio.piccinelli@univr.it and andrea.melchior@uniud.it

Supporting Information

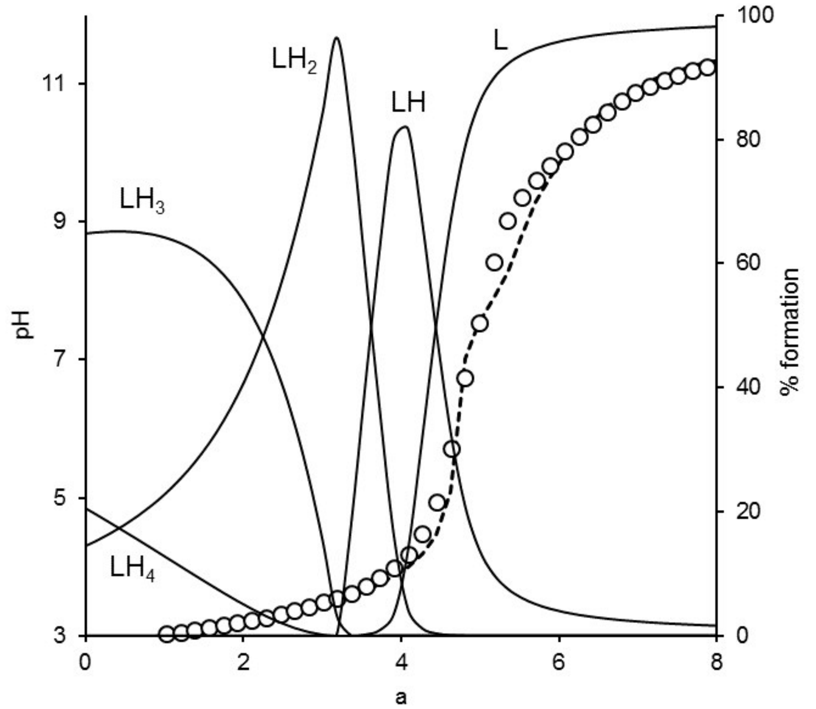


Figure S1. Experimental (O) and calculated (dashed line) pH values of the potentiometric titration of the *iso*QC3A ligand (L) (T= 25°C and μ=0.1 M NaCl); C°_{L} = 0.75 mM; a = (added mol OH^{-}) / (mol/L). Not all the experiment points were used for the graph. Charges were omitted for clarity.

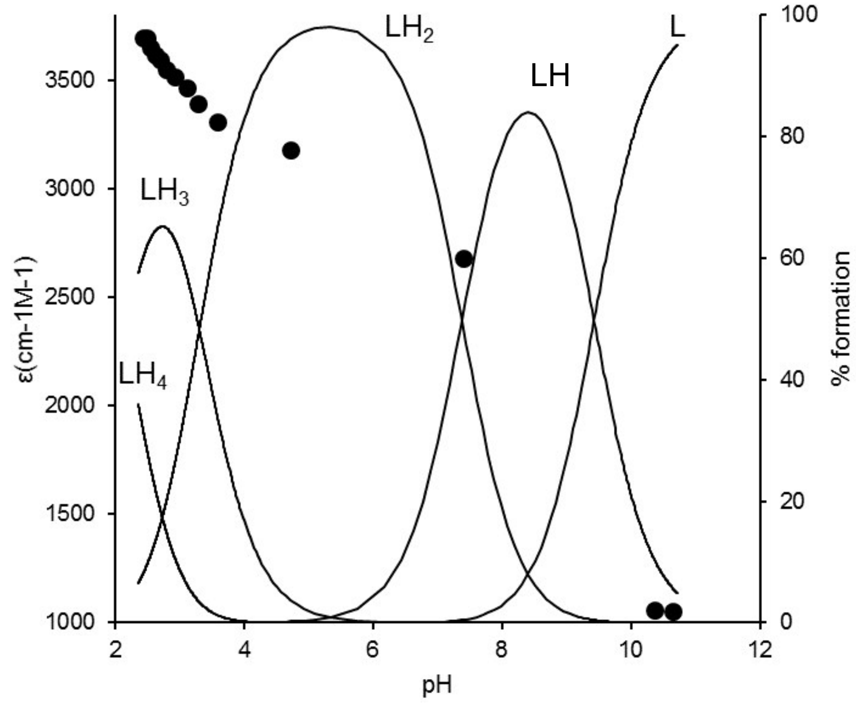


Figure S2. Species distribution of the ligand isoQC3A (C°_{L} = 0.045 mM) with molar absorbance values at λ= 343 nm (●) obtained by acid-base spectrophotometric titration (25 °C, μ = 0.1 M NaCl). The speciation was calculated using the reported protonation constants (Table 1). Charges were omitted for clarity.

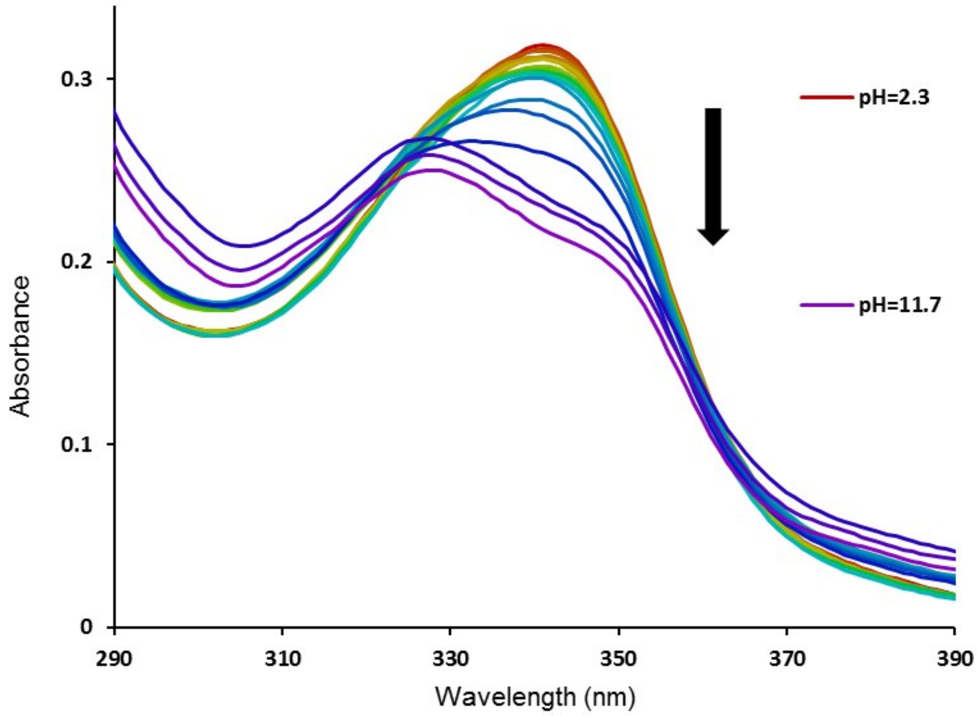
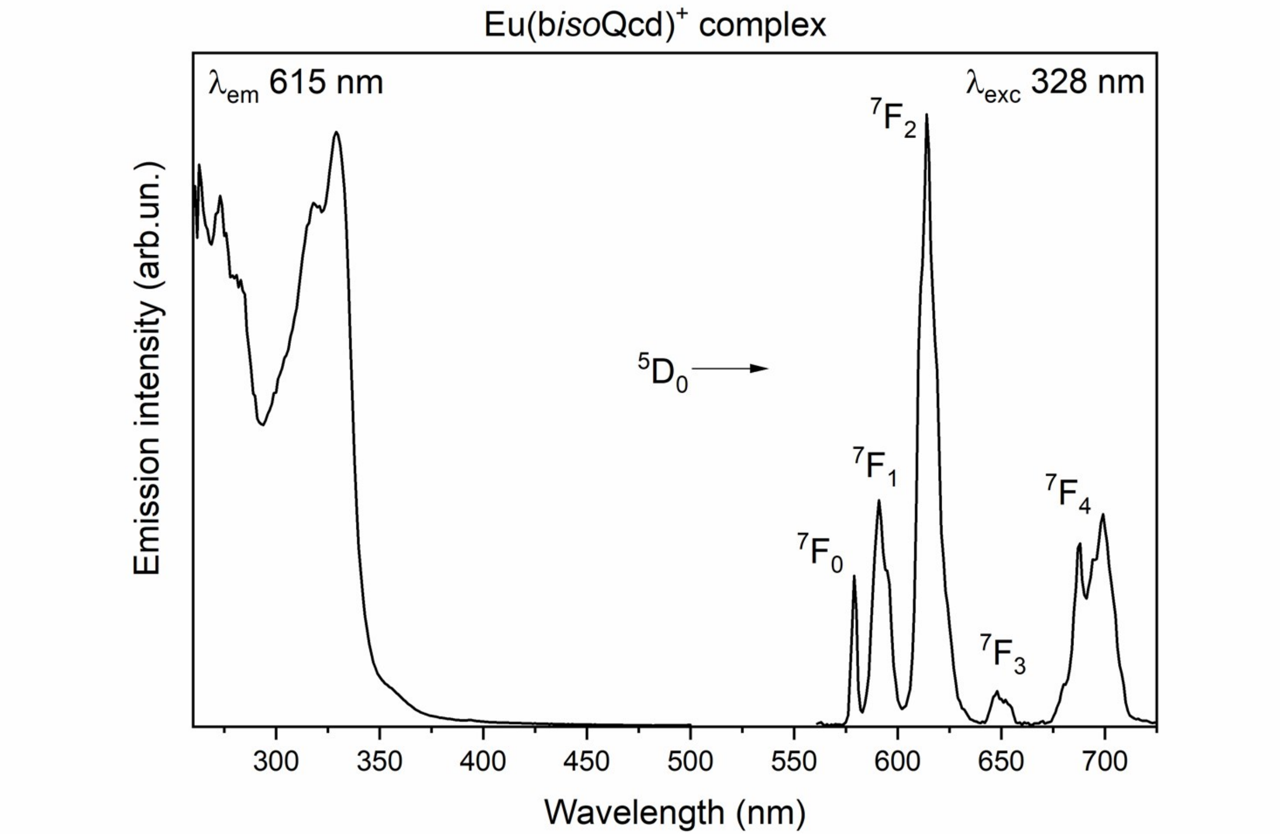


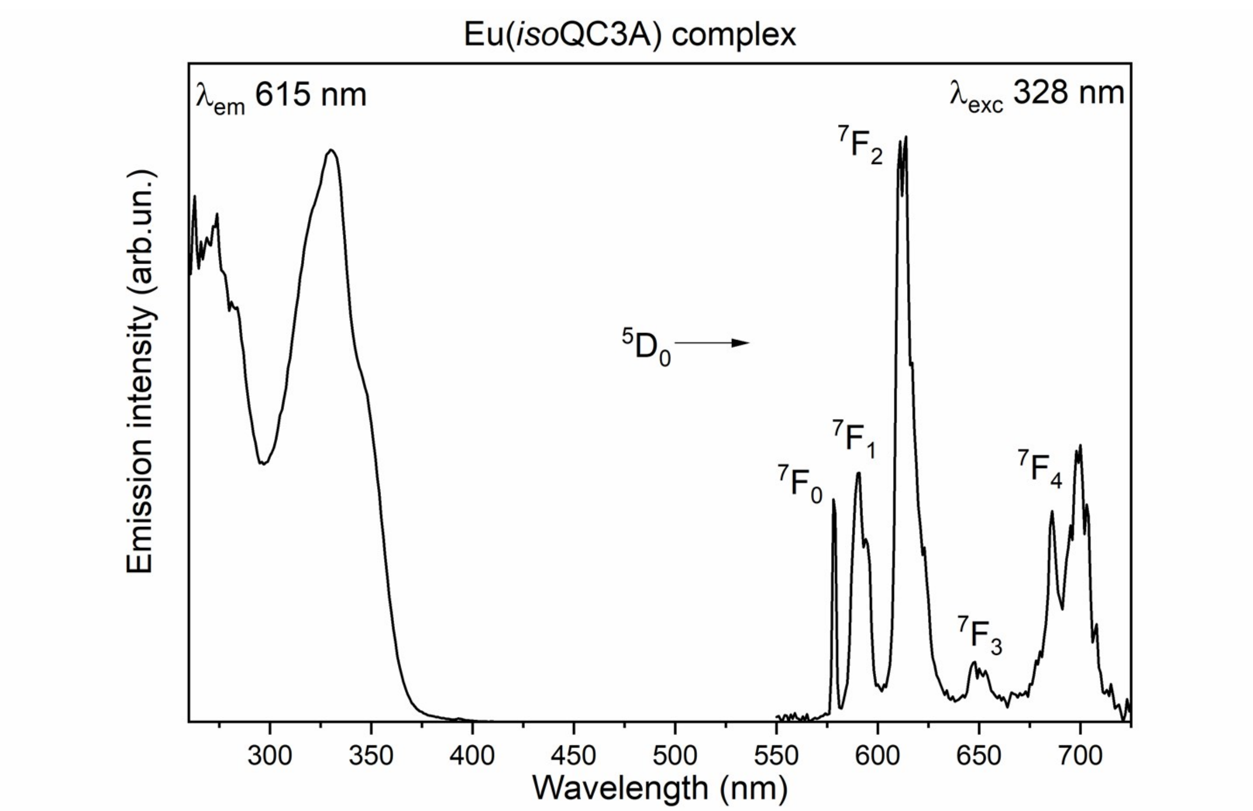
Figure S3. UV-Vis absorption spectra changes during the acid-base titration (pH 2.3 - 11.7) of the ligand *iso*QC3A (0.045 mM) in the presence of equimolar Eu(III).

(a)



Eu(bisoQcd)+ complex
λem 615 nm
λexc 328 nm
7F2
5D0
7F1
7F0
7F3
7F4
Emission intensity (arb.un.)
300
350
400
450
500
550
600
650
700
Wavelength (nm)

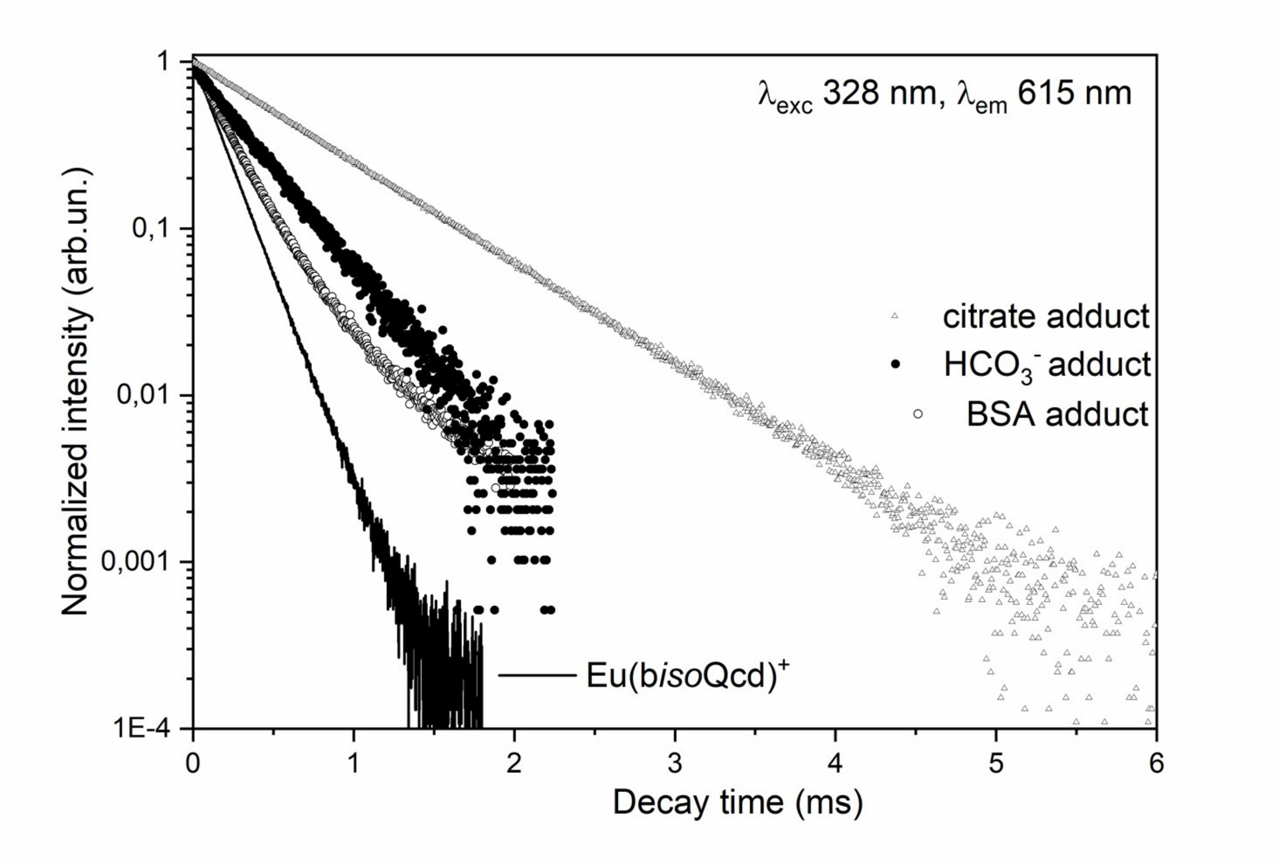
(b)



Eu(isoQC3A) complex
λem 615 nm
λexc 328 nm
7F2
5D0
7F1
7F0
7F3
7F4
Emission intensity (arb.un.)
300
350
400
450
500
550
600
650
700
Wavelength (nm)

Figure S4. Excitation and emission luminescence spectra of the *iso*quinoline-based complexes: (a) Eu(b*iso*Qcd)OTf and (b) Eu(*iso*QC3A).

(a)


λexc 328 nm, λem 615 nm
citrate adduct
HCO3- adduct
BSA adduct
Eu(bisoQcd)+
Normalized intensity (arb.un.)
1
0,1
0,01
0,001
1E-4
0
1
2
3
4
5
6
Decay time (ms)

(b)

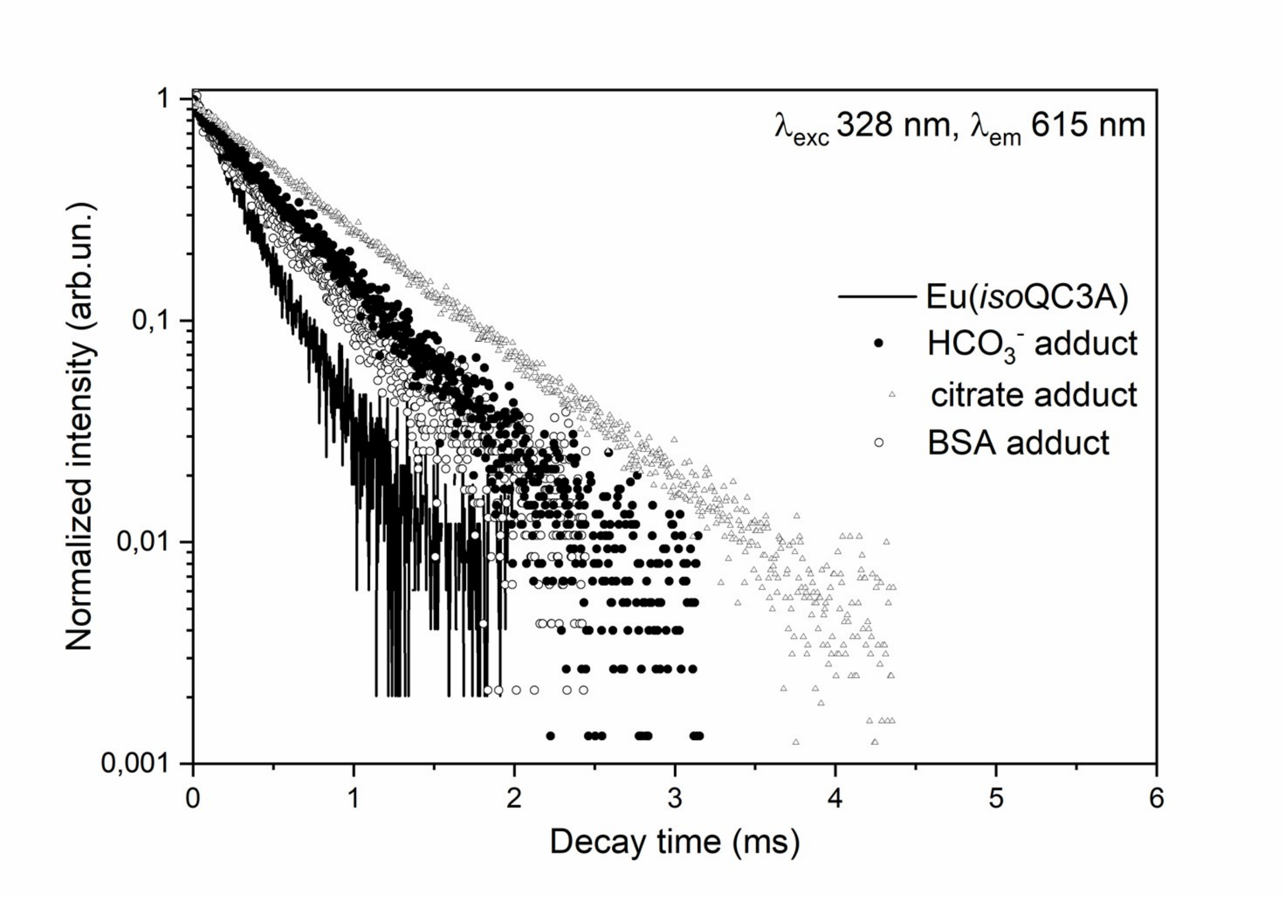


Figure S5. Decay curves of the luminescence from $^5D_0$ level of Eu(III) in the case of aqueous solution of (a) Eu(bisoQcd)$^+$ and its adducts and (b) Eu(isoQC3A) and its adducts. All the decay curves can be well fitted by a single exponential function, except in the case of the BSA adduct with Eu(bisoQcd)$^+$ complex: in this case, the 1/*e* folding time is used as τ_{obs}. The quality of the fits is always excellent ($R^2 > 99.5$ %).

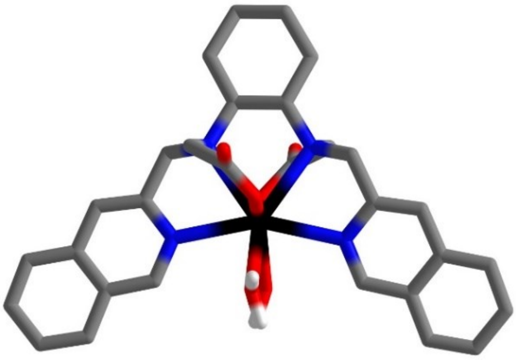
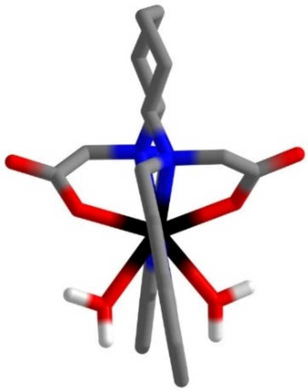
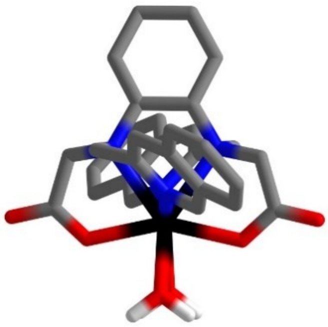
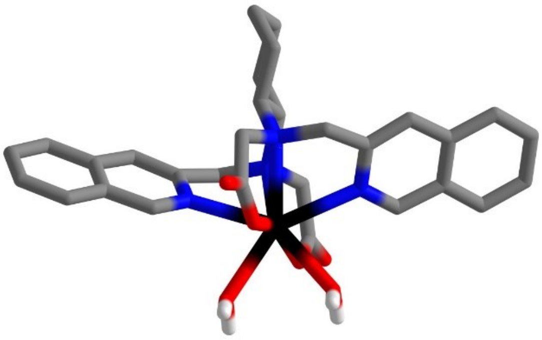
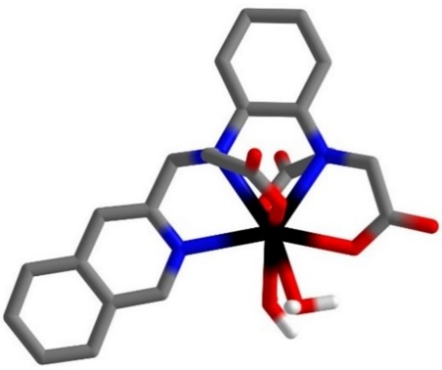
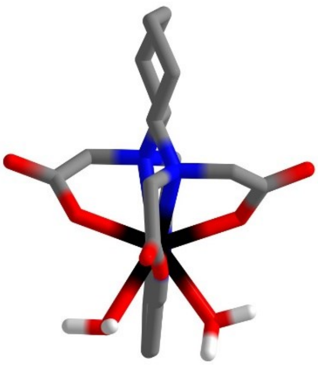
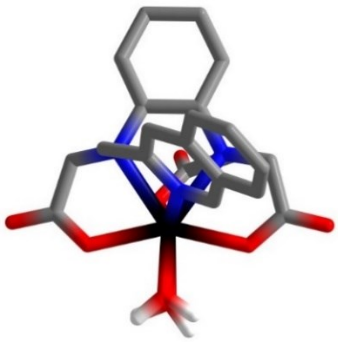
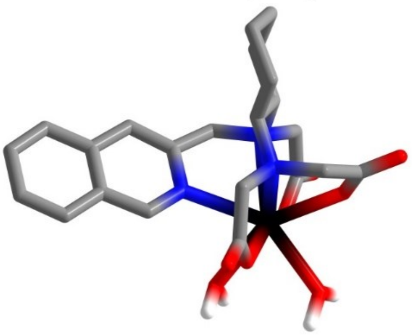
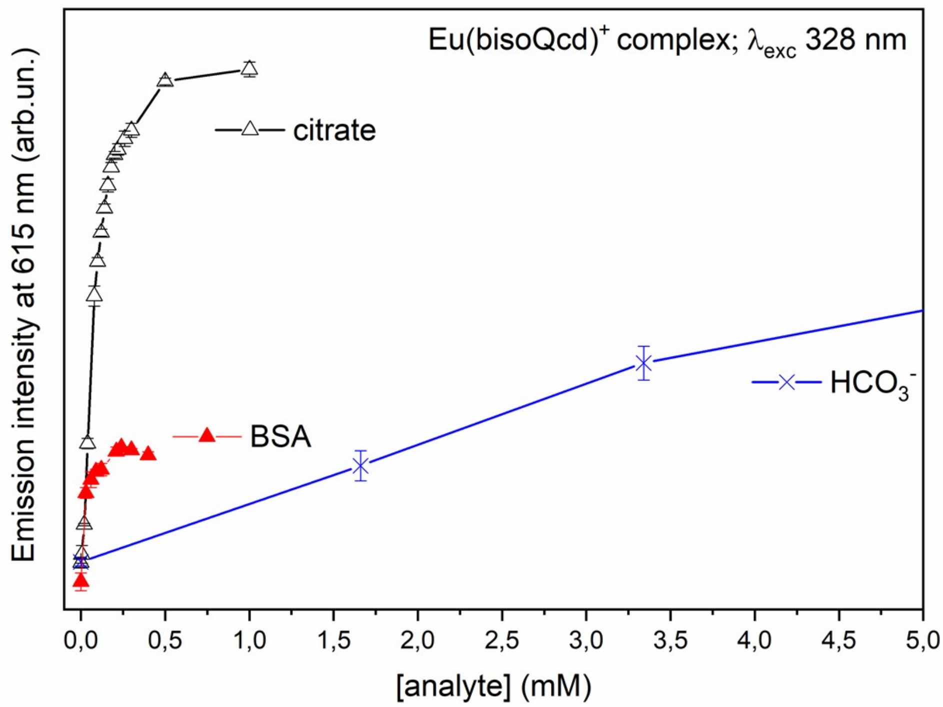
	front	side
Y(bisoQcd)$^+$		
trans O,O		
trans N,N		
Y(isoQC3A)		
trans O,O		
trans N,N		

Figure S6. Minimum energy structures (front and side views) of the Y(L)$^{3-n}$ complexes with L = bisoQcd (n = 2) and L = isoQC3A (n=3).

(a)



(b)

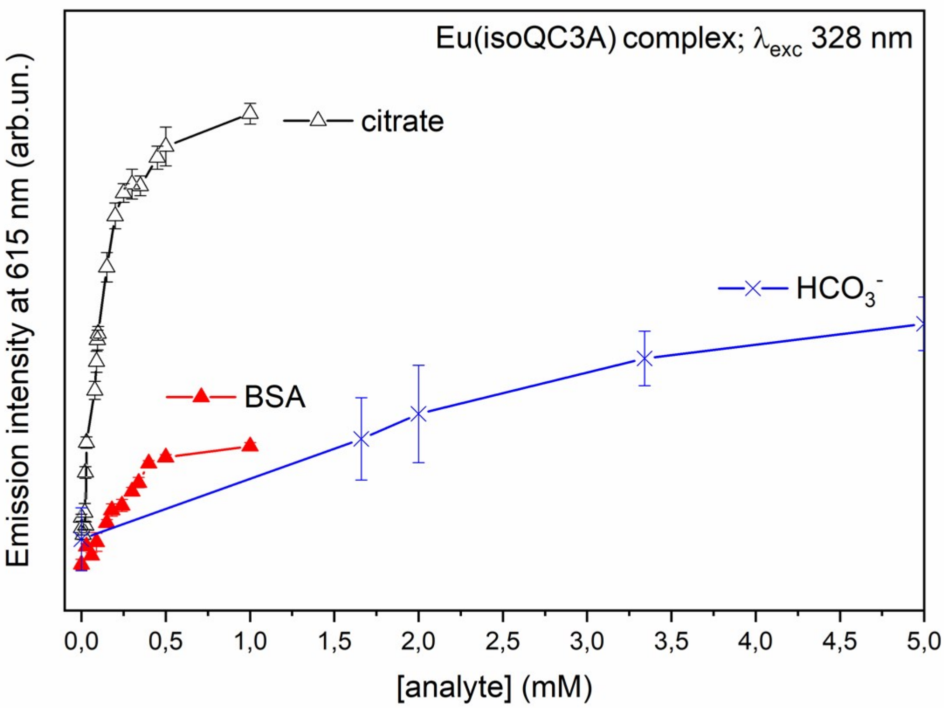
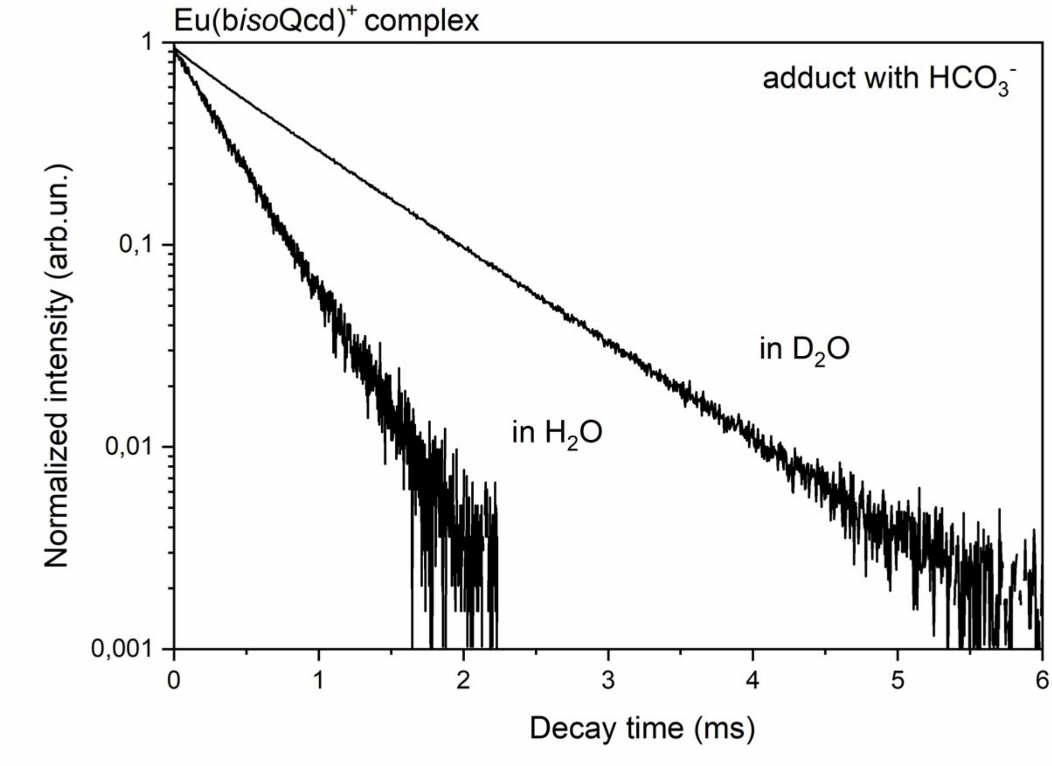


Figure S7. Evolution of the Eu(III) luminescence emission intensity at 615 nm upon addition of HCO_3^-, BSA and citrate for (a) Eu(b*iso*Qcd)OTf and (b) Eu(*iso*QC3A) complexes. The concentration of the complexes was 80 μM; bandwidth in excitation = 2 nm, in emission = 1.5 nm. The 0-5 mM concentration range for hydrogen carbonate and the 0-1 mM concentration range for citrate and BSA are reported.

(a)



(b)

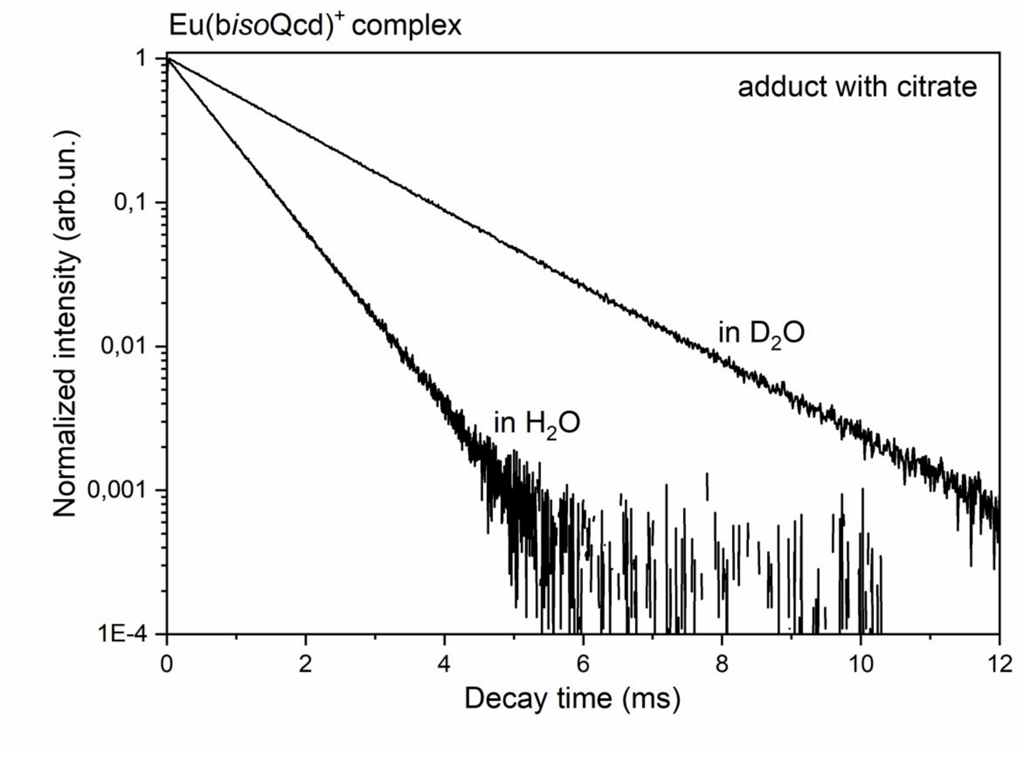
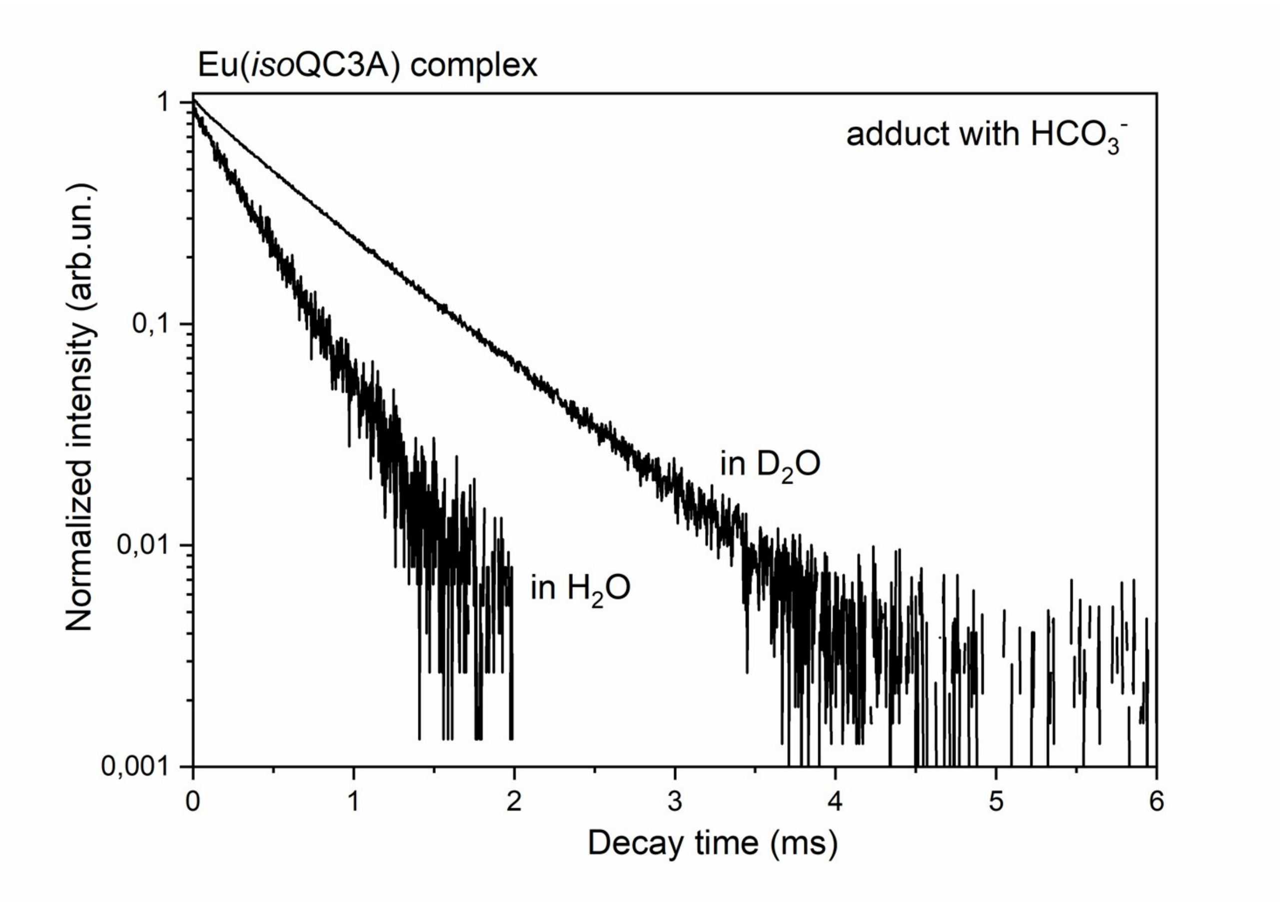


Figure S8. Decay curves of the luminescence from $^5D_0$ level of Eu(III) in H_2O and D_2O, in the case of the adducts of $Eu(bisoQcd)^+$ complex with HCO_3^- (a) and citrate (b). λ_{exc} was 328 nm, λ_{em} was 615 nm. All the decay curves can be well fitted by a single exponential function and the quality of the fits is always excellent ($R^2 > 99.8$ %).

(a)



(b)

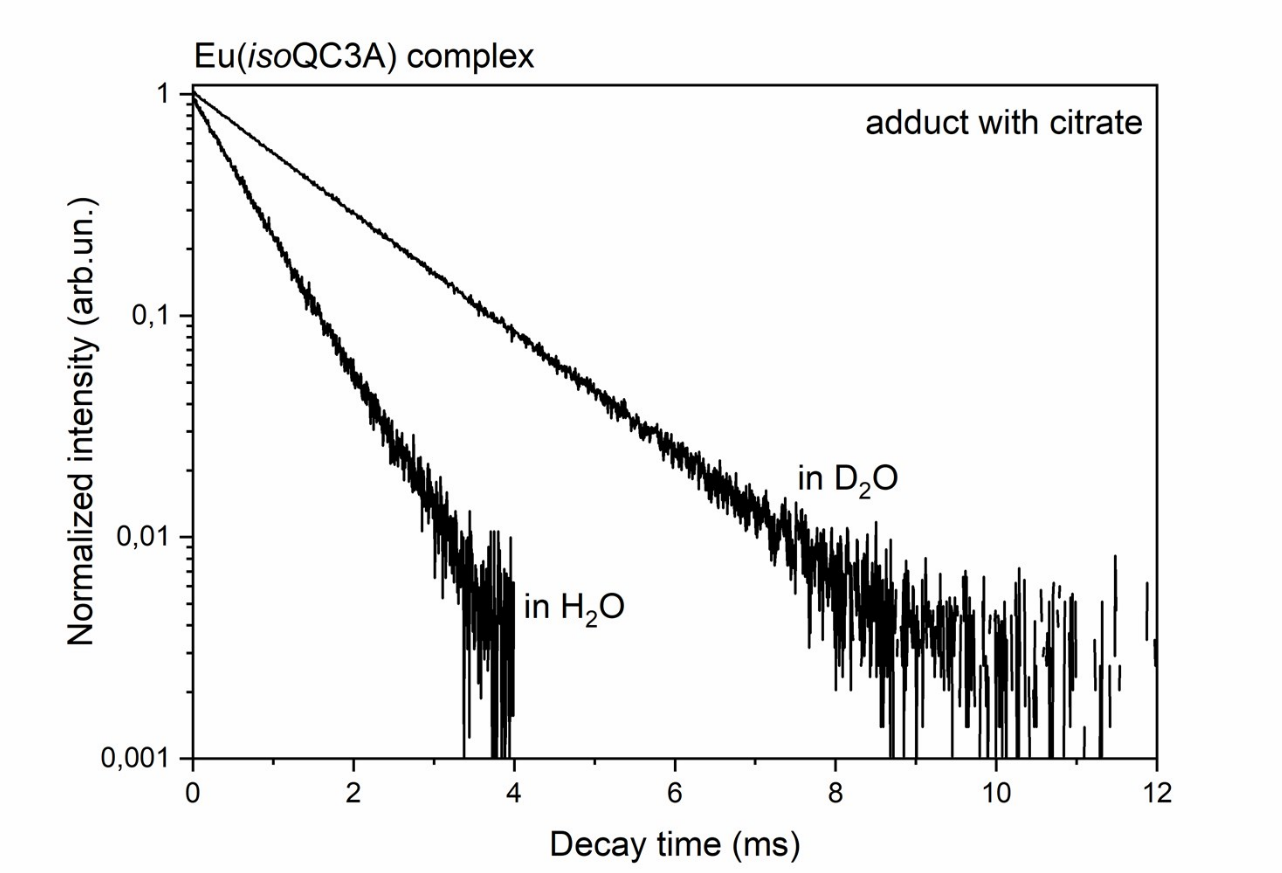


Figure S9. Decay curves of the luminescence from $^5D_0$ level of Eu(III) in H_2O and D_2O, the case of the adducts of Eu(*iso*QC3A) complex with HCO_3^- (a) and citrate (b). λ_{exc} was 328 nm, λ_{em} was 615 nm. All the decay curves can be well fitted by a single exponential function and the quality of the fits is always excellent ($R^2 > 99.8$ %).

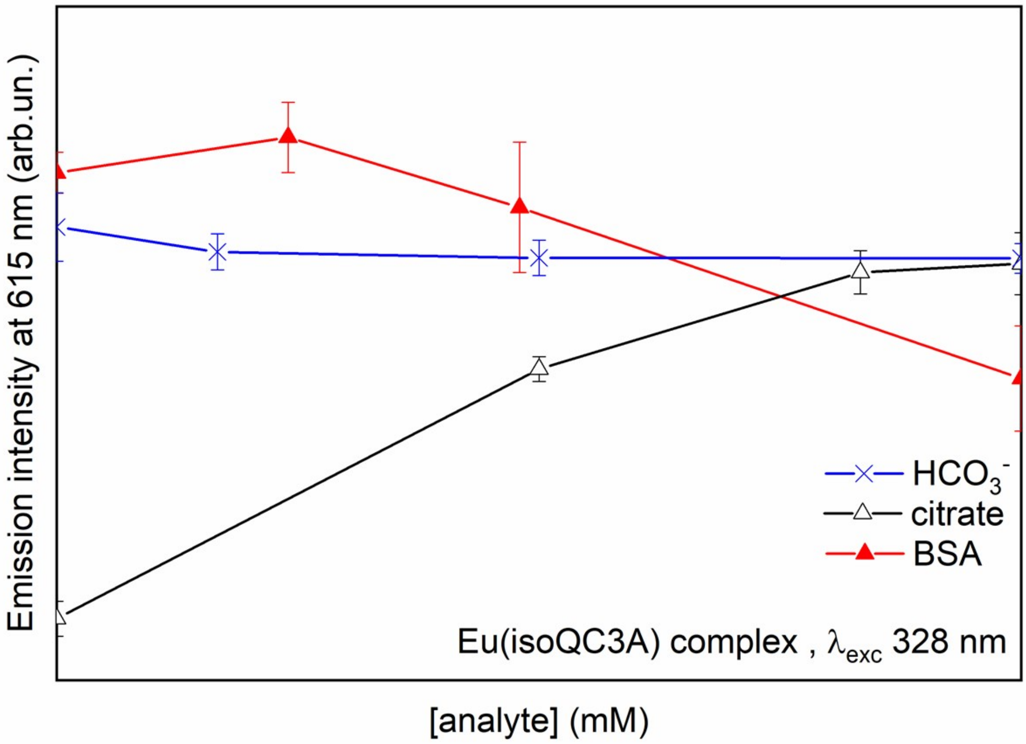


Figure S10. Evolution of the Eu(III) emission intensity upon titration (in the presence of interfering species) of Eu(*iso*QC3A) with: HCO_3^- (experiment 1, blue line, crosses, 0-25 mM HCO_3^- concentration range; 0.4 mM BSA and 0.3 mM citrate as interferents); BSA (experiment 2, red line, triangle, 0-0.4 mM BSA concentration range; 25 mM HCO_3^- and 0.3 mM citrate as interferents) and citrate (experiment 3, black line, open triangle, 0-0.3 mM citrate concentration range; 25 mM HCO_3^- and 0.4 mM BSA as interferents). The concentration of the complex was 80 μM. λ_{exc} was 328 nm, λ_{em} was 615 nm.

Table S1. Concentrations (mmol L^{-1}) and the relative formation percent (X_i) of each luminescence species upon titration of Eu(b*iso*Qcd)OTf with HCO_3^-, BSA and citrate, at the beginning, in the middle and at the end of the titrations, referred to total EuL concentration. The total concentration of the Eu(III) is 0.1 mM. The total concentration of the interfering analytes is the typical extracellular one (25 mM for HCO_3^-, 0.4 mM for BSA and 0.3 mM for citrate). In all solutions, the concentration of the $[Eu(bisoQcd)]_2 \cdot BSA$ adduct is negligible.

$[HCO_3^-]_{TOT}$	[free complex]	[BSA adduct]	[HCO_3^- adduct]	[citrate adduct]	%HCO_3^- adduct	%BSA adduct	%citrate adduct	% free EuL
0	0.0134	0.0383	0	0.0442	**0**	**38.3**	**44.2**	**13.4**
12.5	0.00723	0.0217	0.0443	0.0255	**44.3**	**21.7**	**25.5**	**7.23**
25	0.00308	0.00954	0.0756	0.0114	**75.6**	**9.54**	**11.4**	**3.08**
$[BSA]_{TOT}$	[free complex]	[BSA adduct]	[HCO_3^- adduct]	[citrato adduct]	%HCO_3^- adduct	%BSA adduct	%citrate adduct	% free EuL
0	0.00342	0	0.0839	0.0127	**83.9**	**0**	**12.7**	**3.42**
0.2	0.00324	0.00502	0.0795	0.0120	**79.6**	**5.02**	**12.0**	**3.24**
0.4	0.00308	0.00954	0.0756	0.0114	**75.6**	**9.54**	**11.4**	**3.08**
$[citrate]_{TOT}$	[free complex]	[BSA adduct]	[HCO_3^- adduct]	[citrate adduct]	%HCO_3^- adduct	%BSA adduct	%citrate adduct	% free EuL
0	0.00348	0.0108	0.0855	0	**85.5**	**10.8**	**0**	**3.48**
0.15	0.00327	0.0101	0.0802	0.00606	**80.2**	**10.1**	**6.06**	**3.27**
0.3	0.00308	0.00954	0.0756	0.0114	**75.6**	**9.54**	**11.4**	**3.08**