

Supporting Information for: Revisiting the assignment of Innocent and Non-Innocent Counter ions in Lanthanide(III) Solution Chemistry:

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Contents

Eu³⁺ : EDTA	S2
Eu³⁺ : AcO⁻	S11
Eu³⁺ : NO₃⁻	S19
Eu³⁺ : HSO₄⁻	S27
Eu³⁺ : SO₄²⁻	S35
Eu³⁺ : Cl⁻	S43
Eu³⁺ : ClO₄⁻	S51
Eu³⁺ : OTf	S59
System Screening	S67
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Eu³⁺ : EDTA

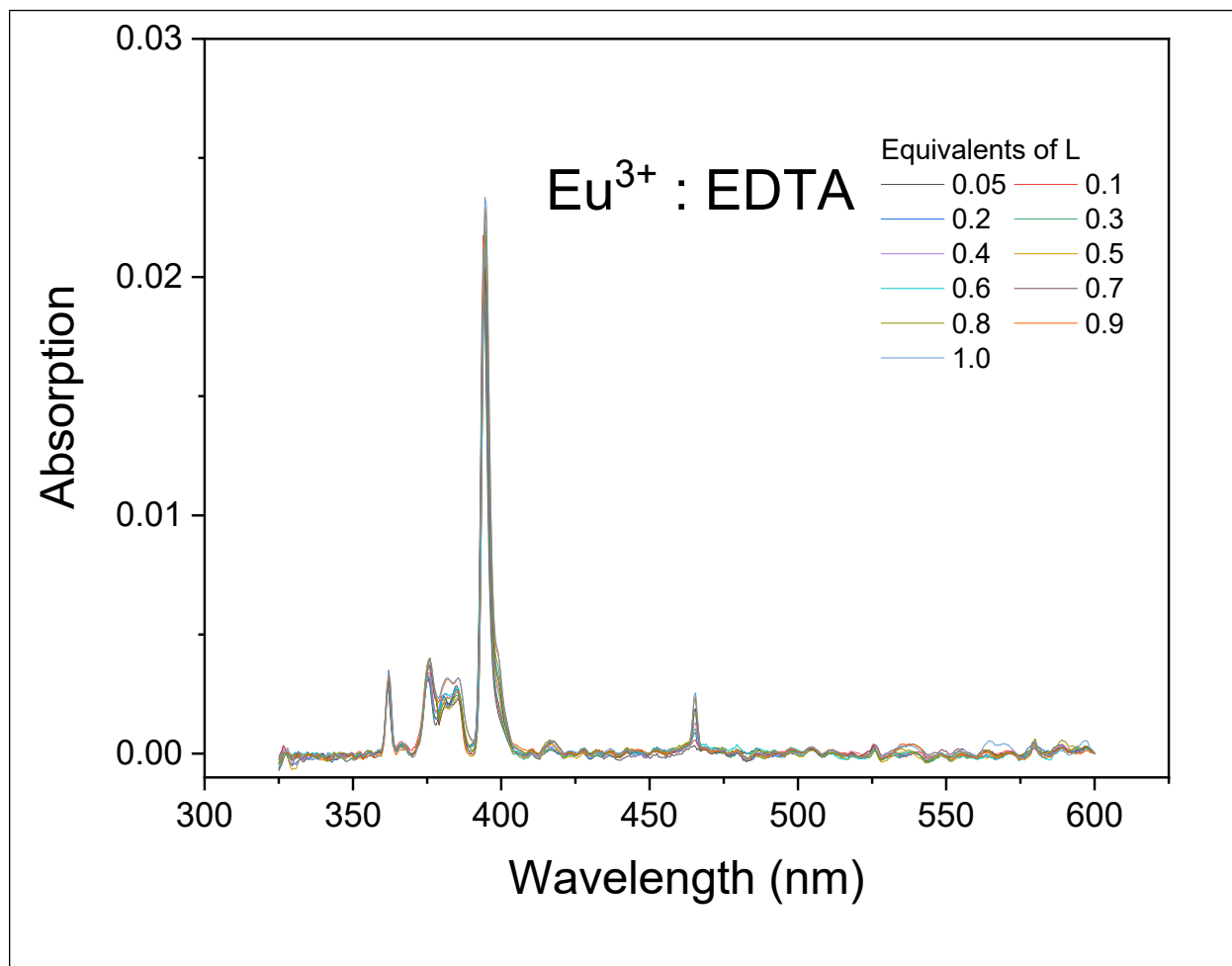


Figure S1. Absorption of Eu³⁺ in NaCl-MES buffer with various equivalents of EDTA.

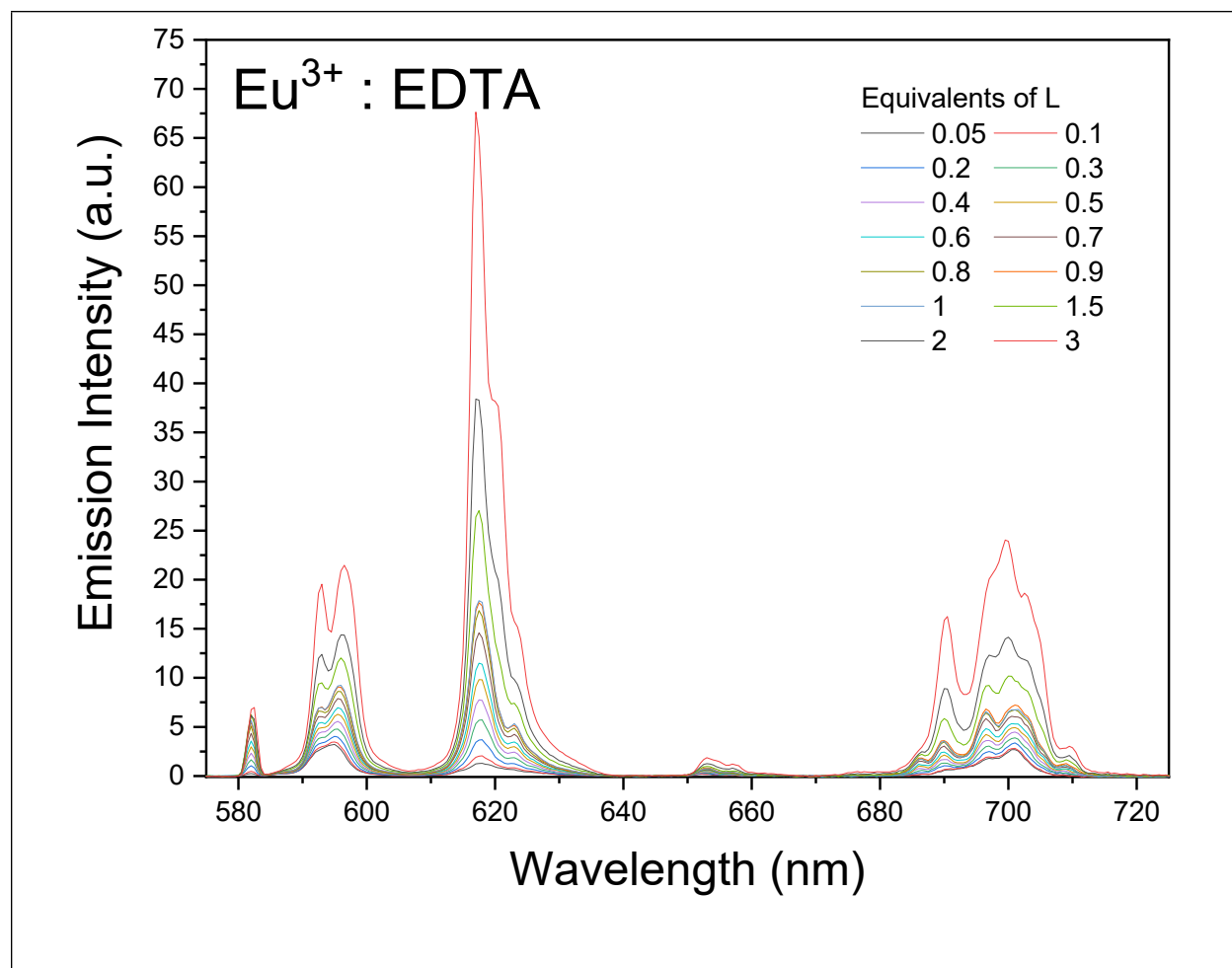


Figure S3. Emission spectrum of Eu³⁺ in NaCl-MES buffer with various equivalents of EDTA.

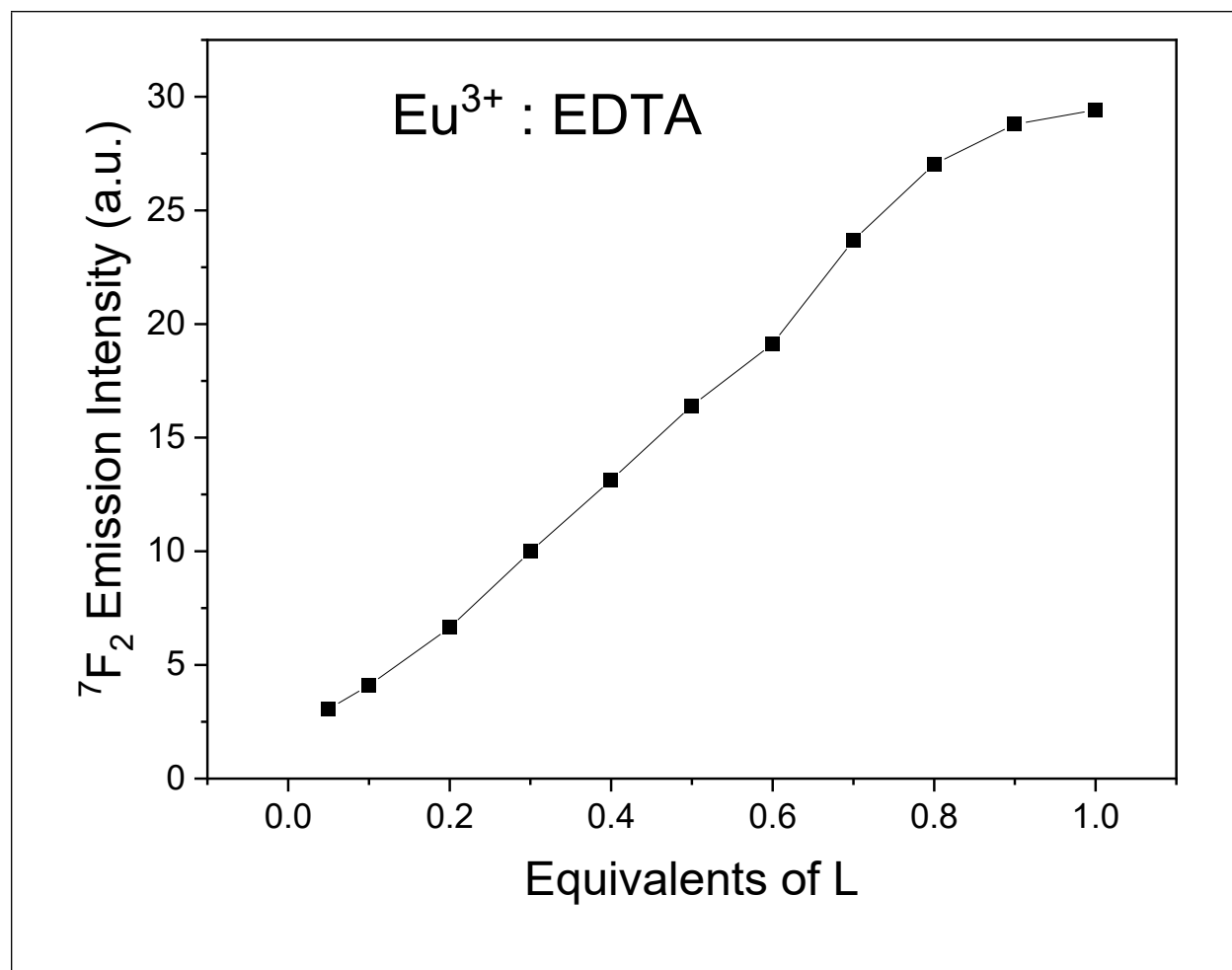


Figure S4. Emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission band of Eu^{3+} in NaCl-MES buffer as a function of equivalents of EDTA. The emission intensity was taken as the integration over the full ${}^7\text{F}_2$ band (606-637 nm).

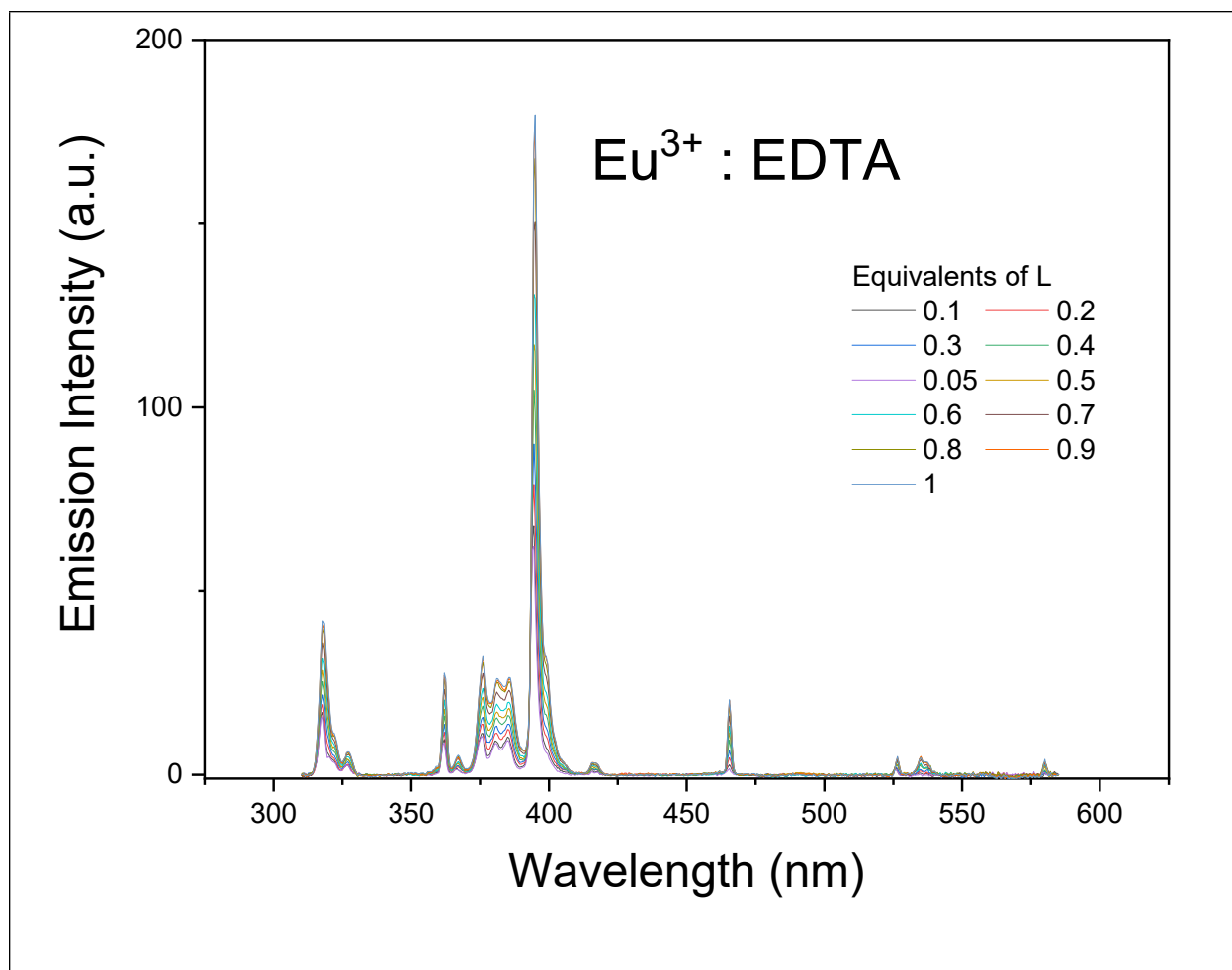


Figure S5. Excitation spectra of Eu³⁺ in NaCl-MES buffer with various equivalents of EDTA

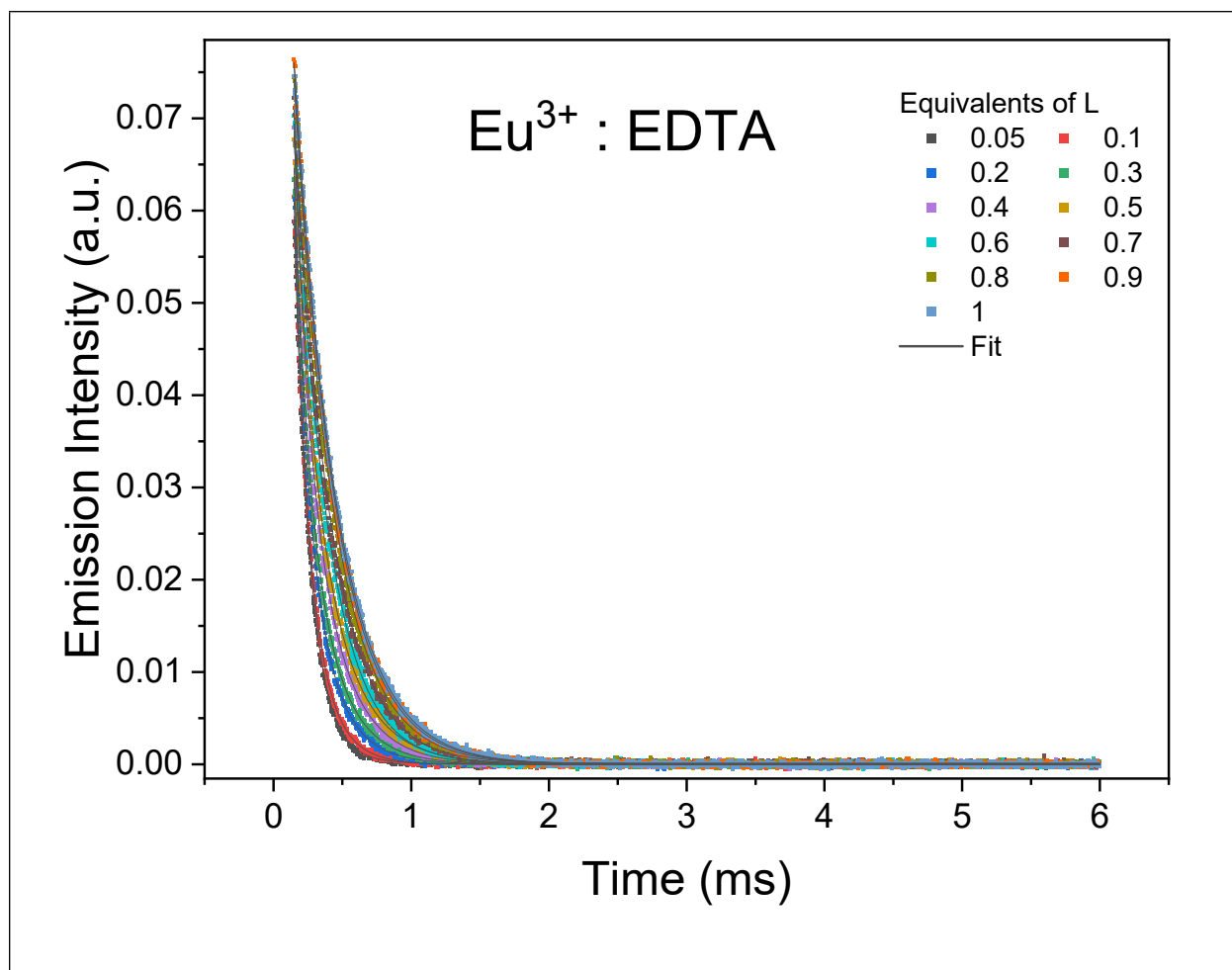


Figure S6. Time-resolved emission decay trace of Eu^{3+} in NaCl-MES buffer with various equivalents of EDTA. The decay traces has been fit with a bi-exponential (0.05-0.5 eq.) or mono-exponential (0.5-1 eq.) decay function.

Table S1. Fitting parameters for emission decay traces of Eu^{3+} : EDTA. Note that the 0.05-0.5 eq. traces have been fit with a bi-exponential function

$y = A1*\exp(-x/t1) + A2*\exp(-x/t2) + y0$						
Trace	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
0.05	2.77746E-5	4.33681E-6	0.2097	0.00196	112.1435	1.27065
0.1	-3.66695E-5	4.48631E-6	0.18808	0.00345	101.44463	1.95507
0.2	5.141E-6	4.75709E-6	0.15137	0.00179	100.5097	1.95021
0.3	3.84374E-6	4.91936E-6	0.12724	0.00135	103.99027	2.03351
0.4	-9.91226E-6	5.5693E-6	0.10405	0.00139	111.77184	2.57198
0.5	2.23623E-5	5.4108E-6	0.07909	0.00198	132.81916	3.49278
Trace			A2	A2 (Error)	t2	t2 (error)
0.05			0.00817	0.003	235.58143	24.18941
0.1			0.03873	0.00514	198.84566	6.60211
0.2			0.05872	0.00316	220.01497	3.40661
0.3			0.06439	0.00241	240.66595	2.78712
0.4			0.07383	0.00239	260.67886	2.66747
0.5			0.0722	0.00276	283.34426	3.1816
$y = A1*\exp(-x/t1) + y0$						
Trace	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
0.6	5.78785E-5	6.7356E-6	0.1272	1.89374E-4	247.13064	0.31496
0.7	1.2453E-4	6.99623E-6	0.12316	1.71581E-4	268.80265	0.33428
0.8	5.97184E-5	6.16966E-6	0.12457	1.34812E-4	289.3119	0.28961
0.9	3.41393E-6	6.16791E-6	0.12461	1.25888E-4	302.4841	0.28865
1	-2.052E-5	5.89362E-6	0.12322	1.15499E-4	310.73524	0.27858
1.5	5.50488E-5	7.76593E-6	0.11879	1.09634E-4	390.03251	0.38108
2	1.03164E-4	8.98538E-6	0.10338	8.47943E-5	525.91178	0.51852
3	-1.06215E-5	1.17413E-5	0.08808	6.28974E-5	801.66684	0.83823

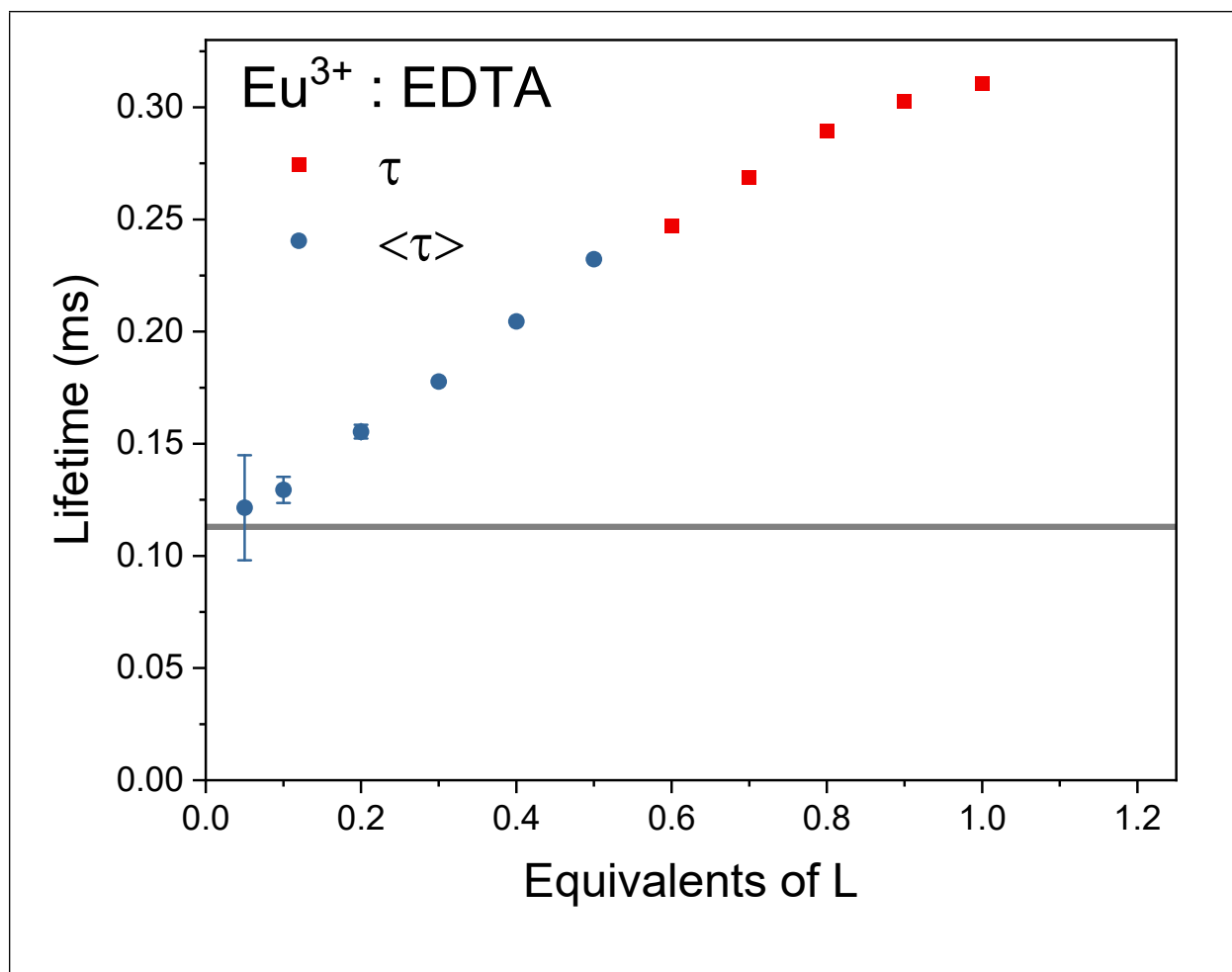


Figure S7. Excited state lifetime of Eu³⁺ in NaCl-MES buffer as a function of equivalents of EDTA. The lifetimes has been determined from either a mono-exponential decay function (red) or an average of a bi-exponential decay function. The grey bar indicates the excited state lifetime of Eu³⁺ in water. Error bars not shown are smaller than the data point

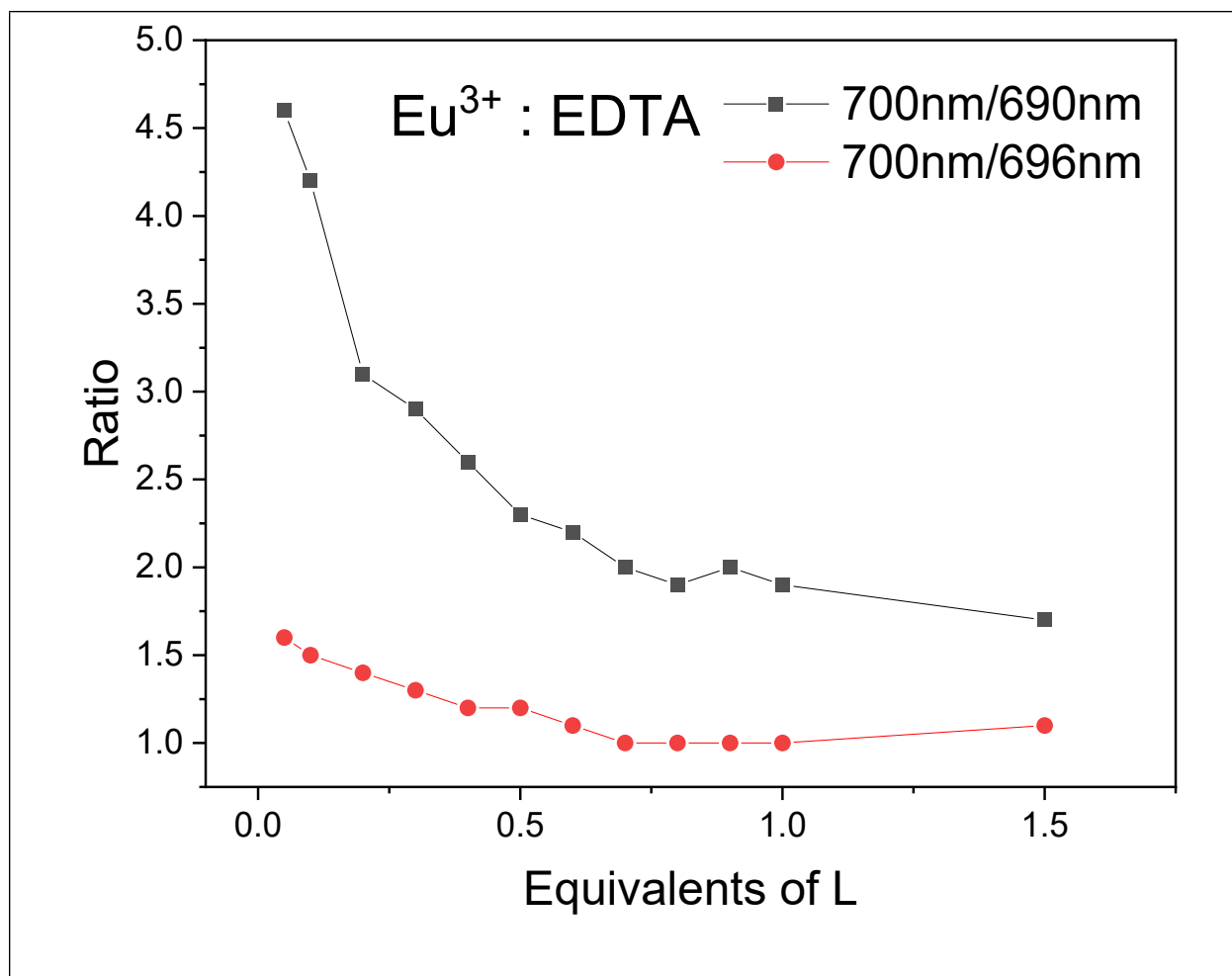


Figure S8. Ratios of emission intensity of Eu³⁺ in NaCl-MES buffer as a function of equivalents of EDTA. The ratios give an indication of the changes in LF-splitting (see main text).

Eu³⁺ : AcO⁻

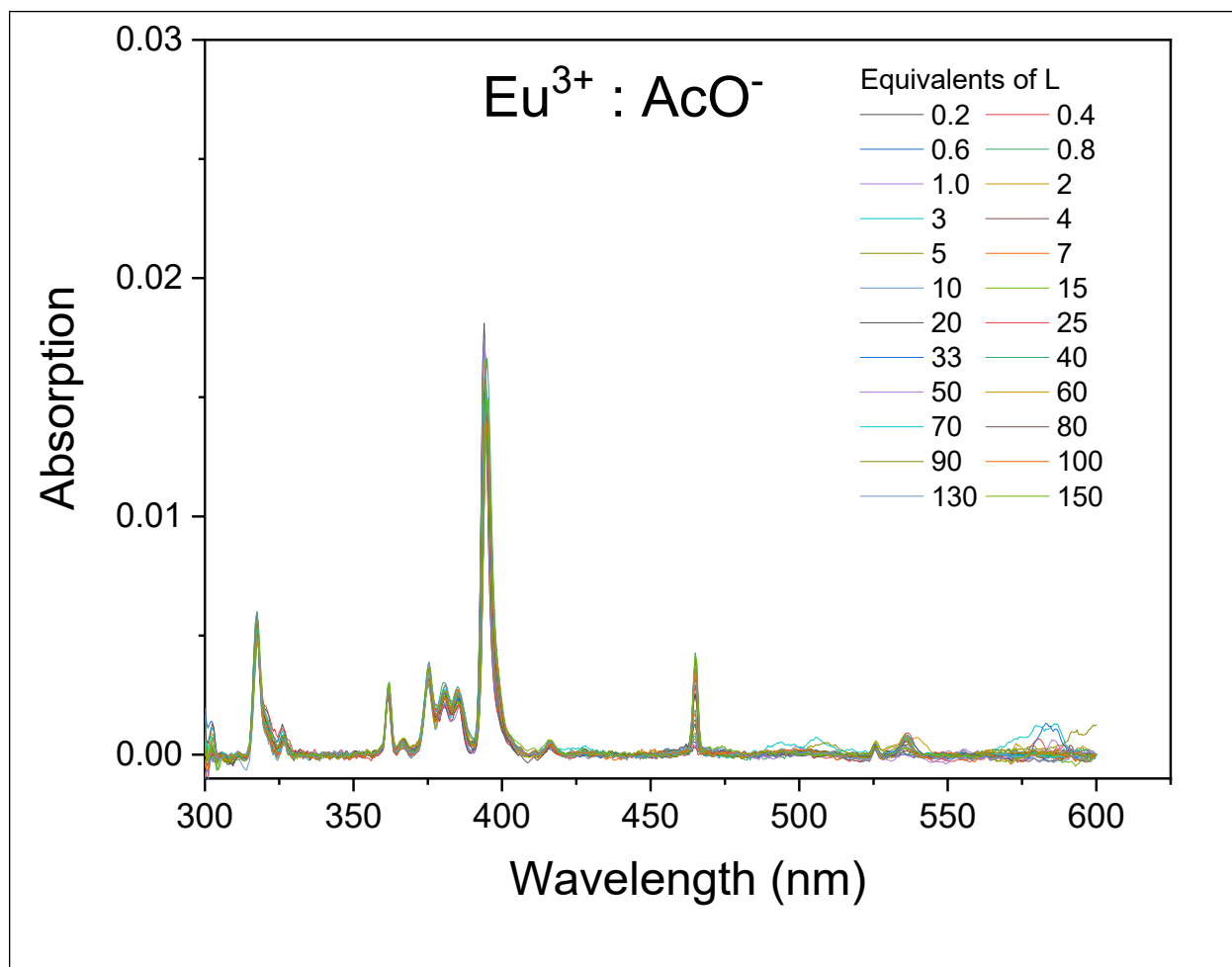


Figure S9. Absorption of Eu³⁺ in KCl-MES buffer with various equivalents of AcO⁻.

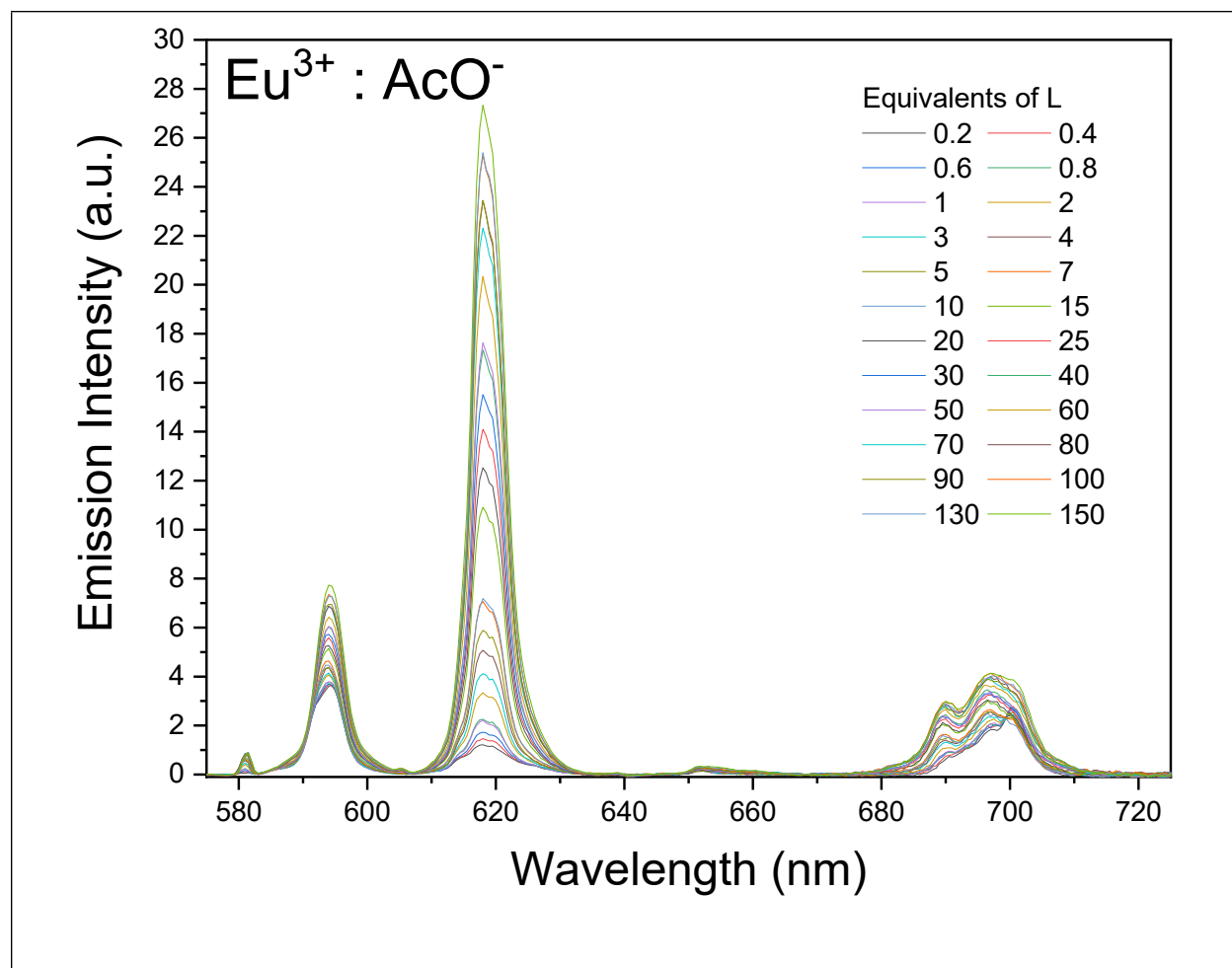


Figure S10. Emission spectrum of Eu³⁺ in KCl-MES buffer with various equivalents of AcO⁻.

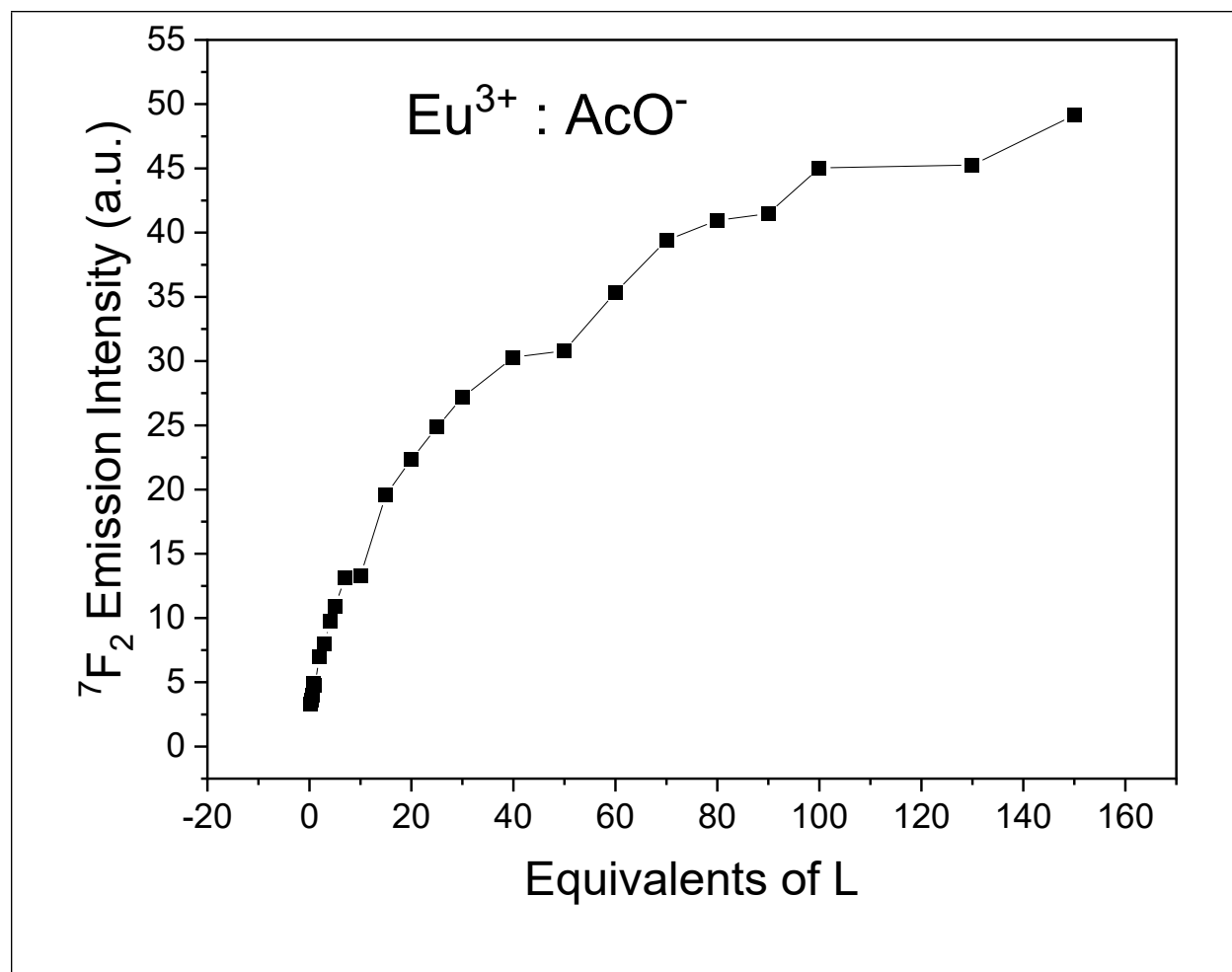


Figure S11. Emission intensity of the $^5D_0 \rightarrow ^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of AcO^- . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

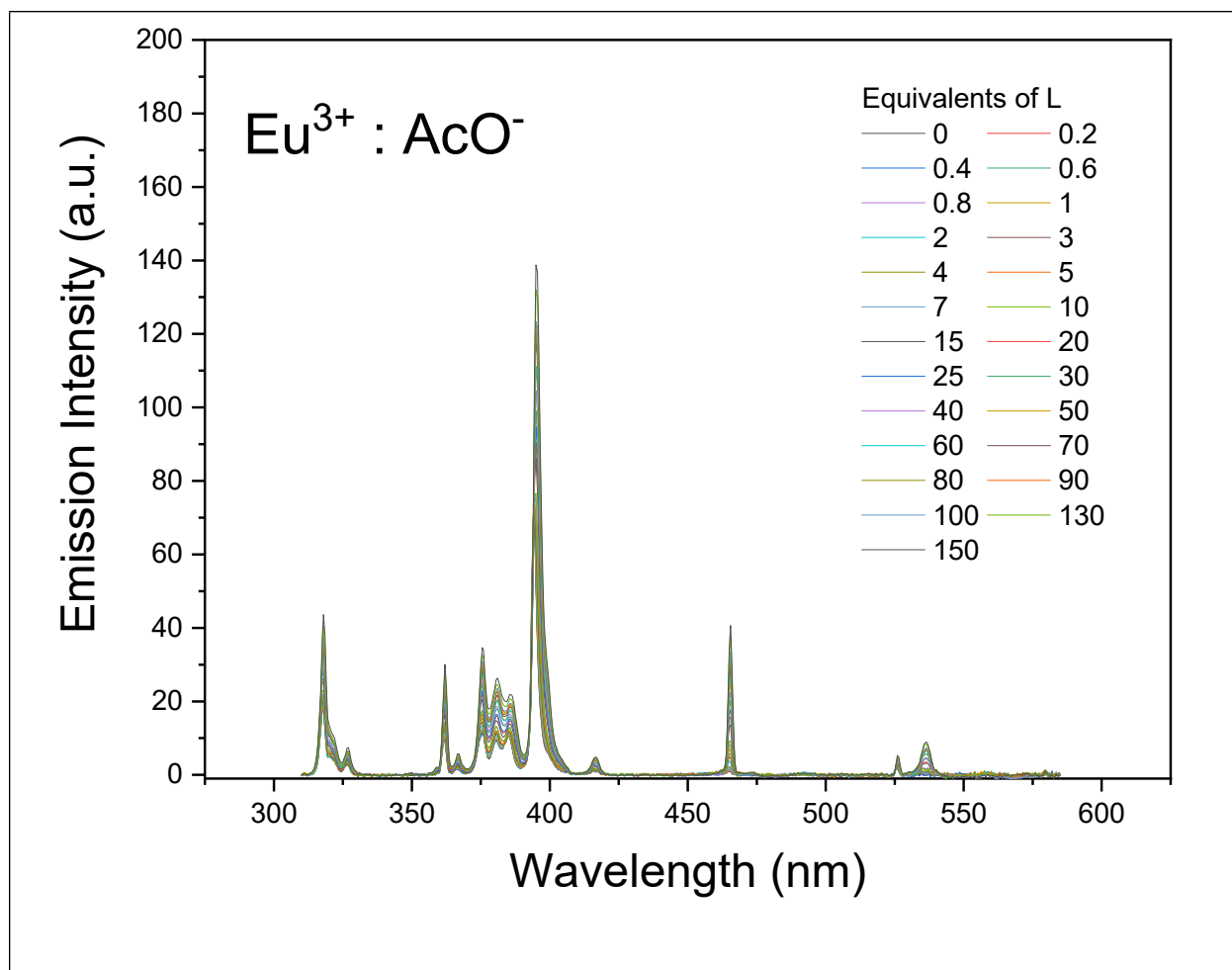


Figure S12. Excitation spectra of Eu^{3+} in KCl-MES buffer with various equivalents of AcO^- .

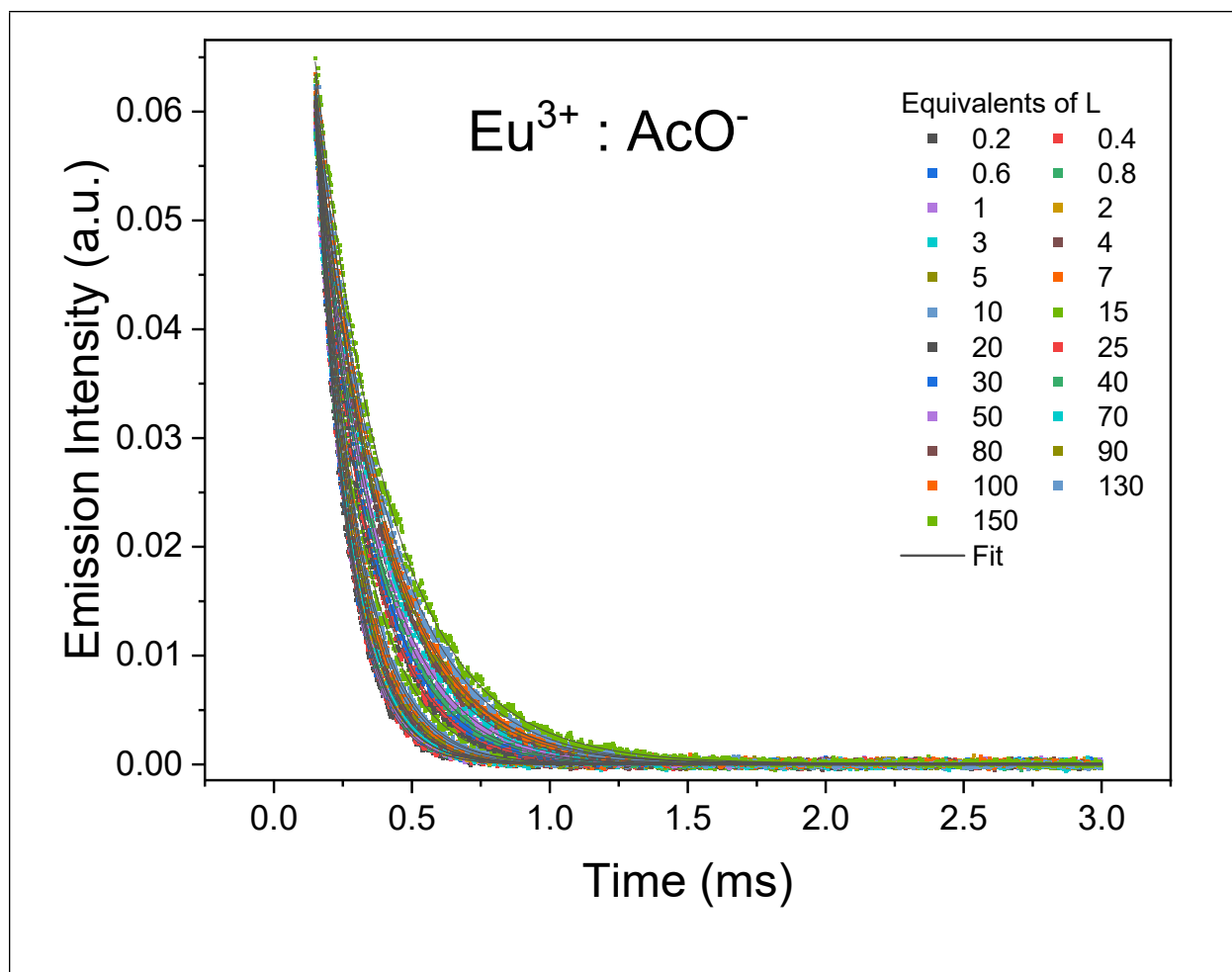


Figure S13. Time-resolved emission decay trace of Eu^{3+} in KCl-MES buffer with various equivalents of AcO^- . The decay traces has been fit with a mono-exponential decay function.

Table S2. Fitting parameters for emission decay traces of Eu³⁺ : AcO.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
0.2	-2.49647E-5	6.05282E-6	0.23158	5.98309E-4	110.82767	0.15312
0.4	-6.72781E-5	6.90522E-6	0.22266	6.2808E-4	114.45941	0.17668
0.6	1.30635E-4	6.23495E-6	0.21418	5.3962E-4	116.71849	0.16317
0.8	-4.99712E-5	7.07855E-6	0.20757	5.65756E-4	120.4849	0.18634
1	5.08292E-5	7.57766E-6	0.20939	6.30542E-4	118.55568	0.20029
2	6.11809E-5	7.50846E-6	0.2066	5.59607E-4	123.94984	0.19432
3	-3.5316E-5	7.72802E-6	0.18948	5.21204E-4	129.17782	0.21162
4	-3.08636E-5	7.66779E-6	0.19099	4.87345E-4	132.44527	0.20476
5	-3.17756E-5	7.45318E-6	0.17815	4.16792E-4	139.93788	0.2059
7	6.02524E-5	8.83932E-6	0.17436	4.63954E-4	143.88834	0.24533
10	-9.09468E-6	8.10866E-6	0.16555	3.88827E-4	149.81998	0.23161
15	-2.60939E-5	8.11049E-6	0.14662	3.10425E-4	166.30946	0.24809
20	-2.09934E-5	9.32502E-6	0.14395	3.17137E-4	176.03965	0.28337
25	5.56065E-5	8.5598E-6	0.13607	2.68914E-4	183.04177	0.2709
33	4.41245E-5	9.1438E-6	0.12995	2.56748E-4	193.65593	0.29678
40	-3.23022E-5	8.91394E-6	0.12605	2.26604E-4	203.79343	0.29329
50	6.98088E-5	1.10835E-5	0.1238	2.6218E-4	211.60217	0.36709
60	3.92326E-5	7.1595E-6	0.05987	1.53558E-4	222.89247	0.48338
70	-3.88514E-5	1.00449E-5	0.12096	2.11226E-4	225.27013	0.33474
80	9.12452E-5	1.00143E-5	0.11529	1.96025E-4	234.17269	0.34682
90	9.53848E-5	1.08702E-5	0.11281	1.99829E-4	242.35938	0.38177
100	7.06623E-5	9.86731E-6	0.11793	1.82415E-4	241.61147	0.33173
130	-4.91215E-5	1.12128E-5	0.11133	1.81749E-4	259.90975	0.39347
150	6.86499E-5	1.17069E-5	0.11207	1.75588E-4	271.52543	0.40497

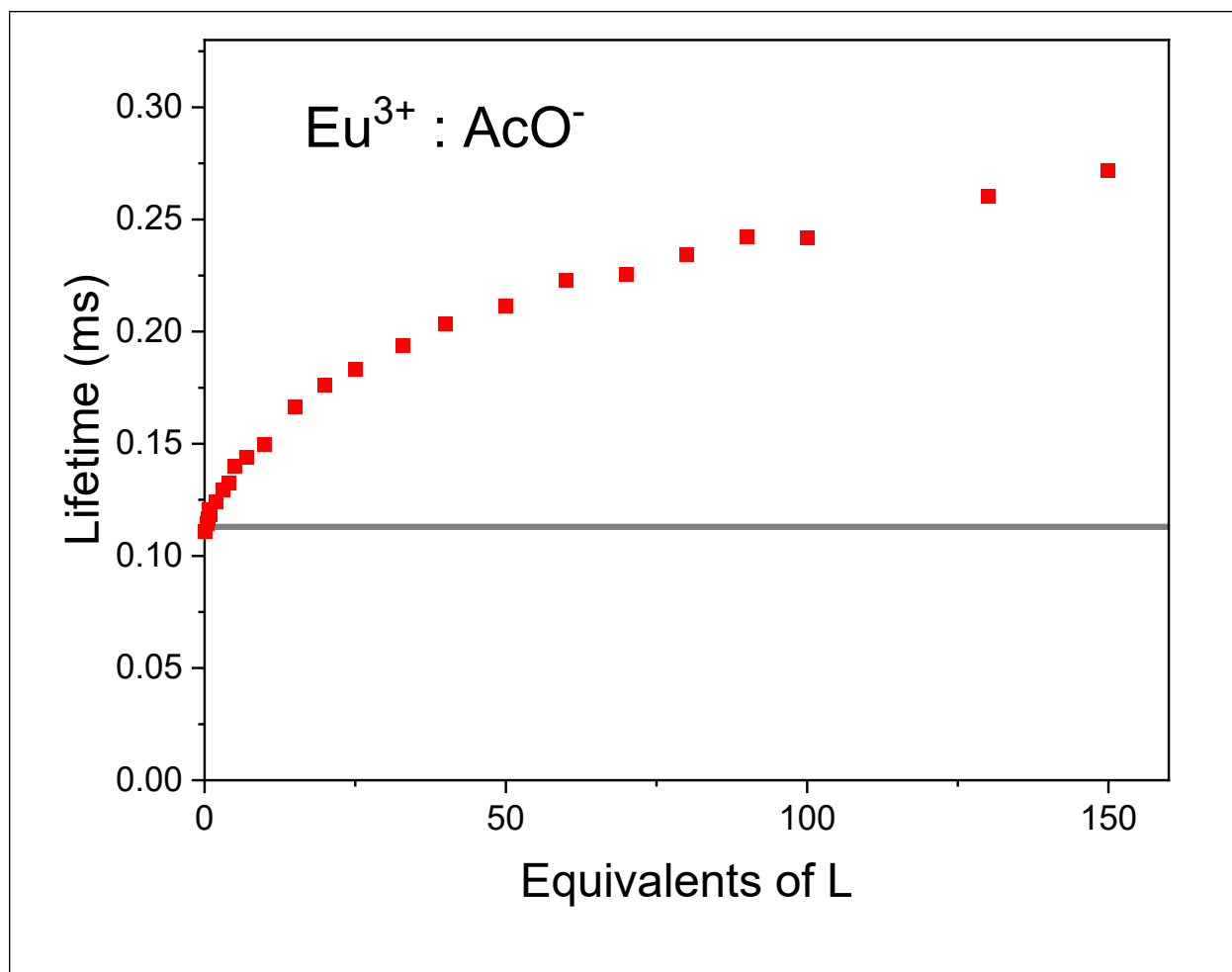


Figure S14. Excited state lifetime of Eu³⁺ in KCl-MES buffer as a function of equivalents of AcO⁻. The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu³⁺ in water.

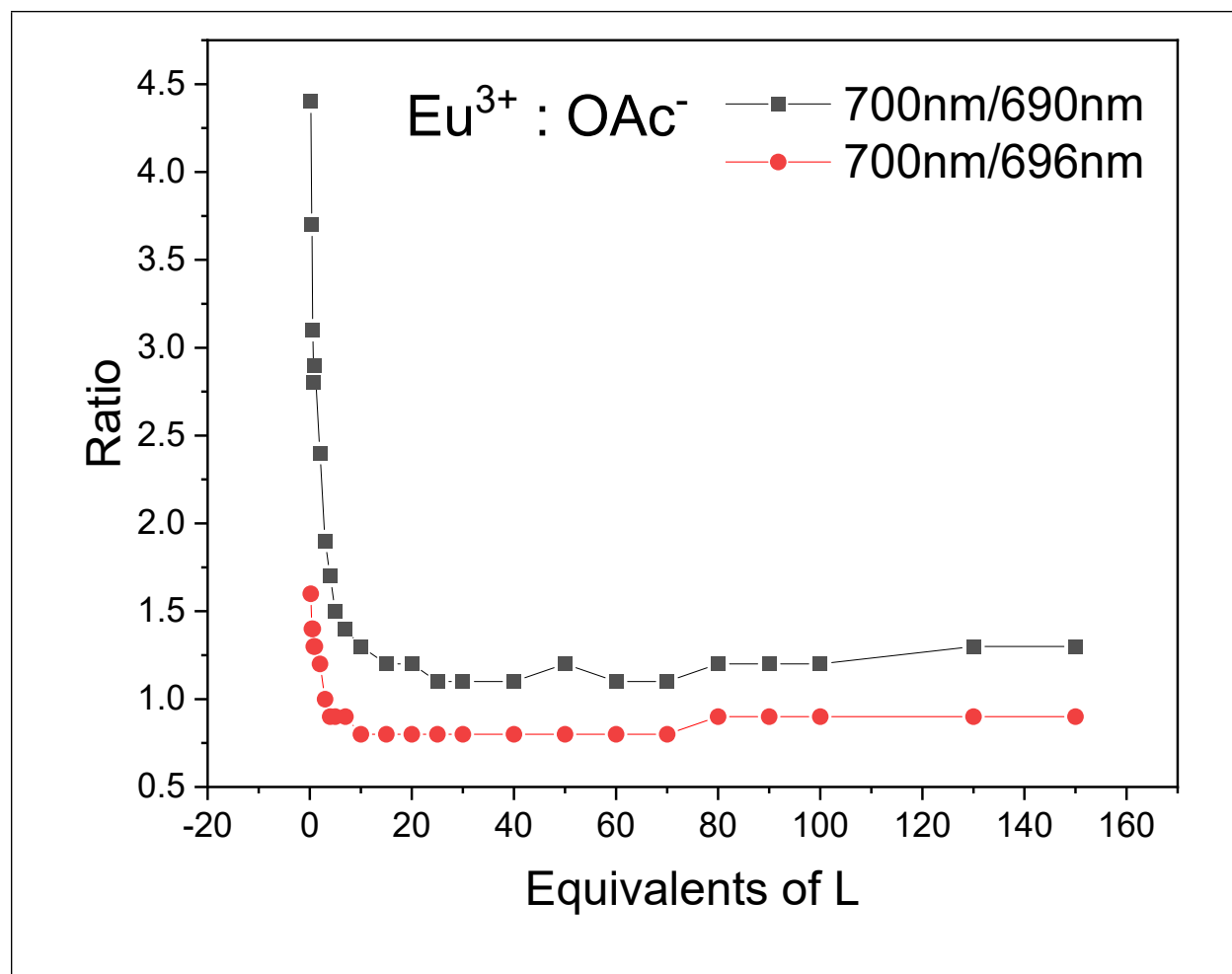


Figure S15. Ratios of emission intensity of Eu³⁺ in KCl-MES buffer as a function of equivalents of AcO⁻. The ratios give an indication of the changes in LF-splitting (see main text).

$\text{Eu}^{3+} : \text{NO}_3^-$

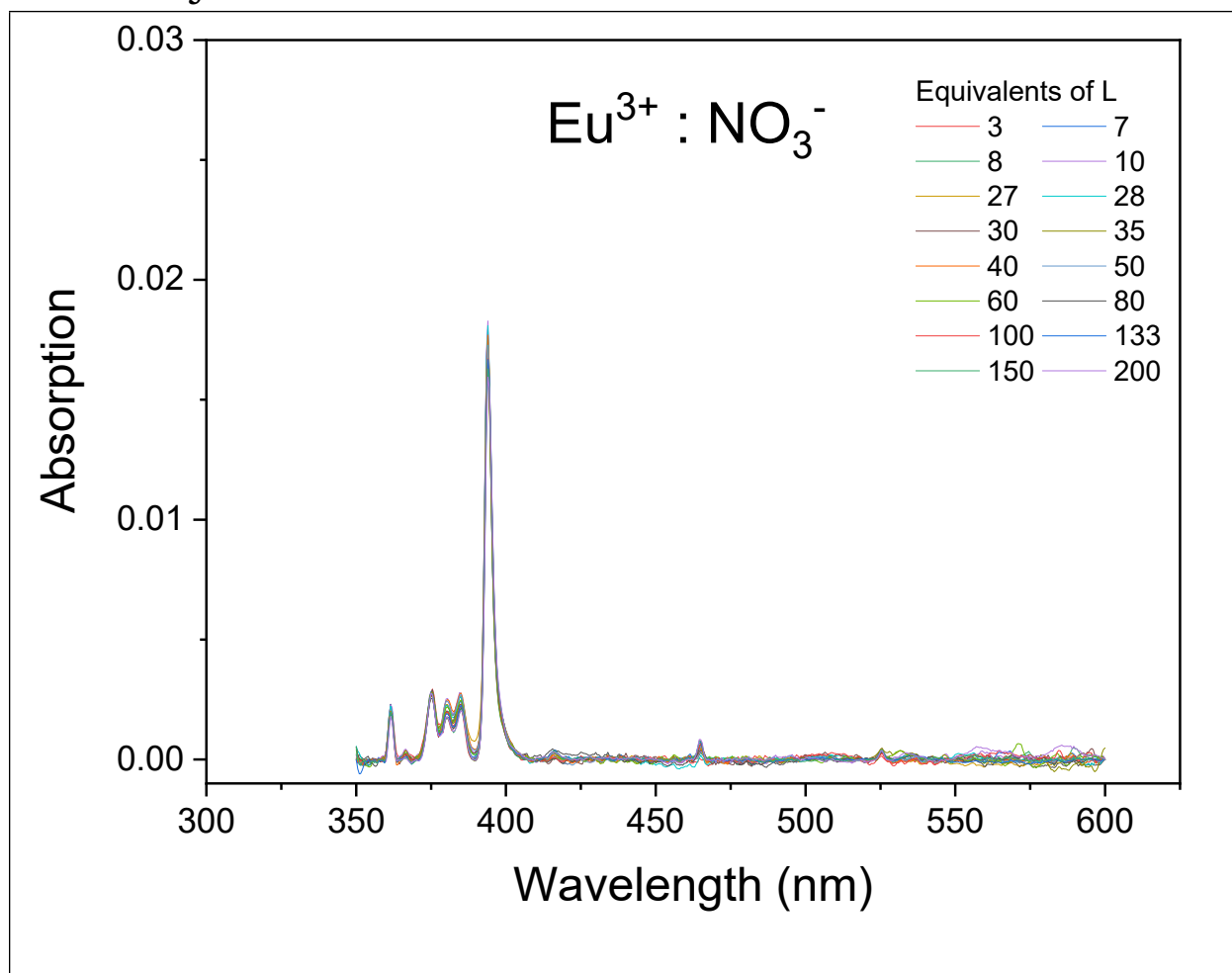


Figure S16. Absorption of Eu^{3+} in KCl-MES buffer with various equivalents of NO_3^- .

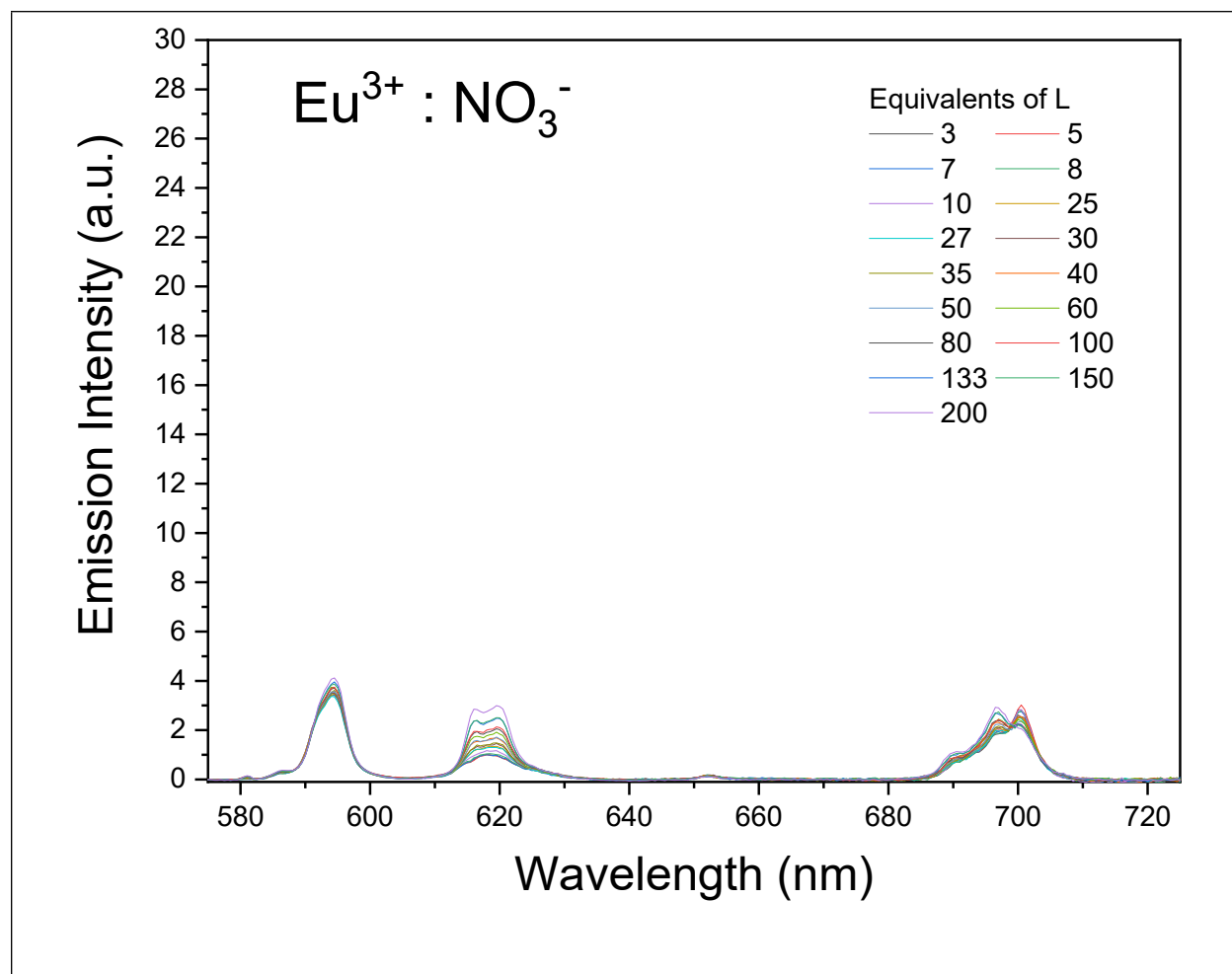


Figure S17. Emission spectra of Eu^{3+} in KCl-MES buffer with various equivalents of NO_3^- .

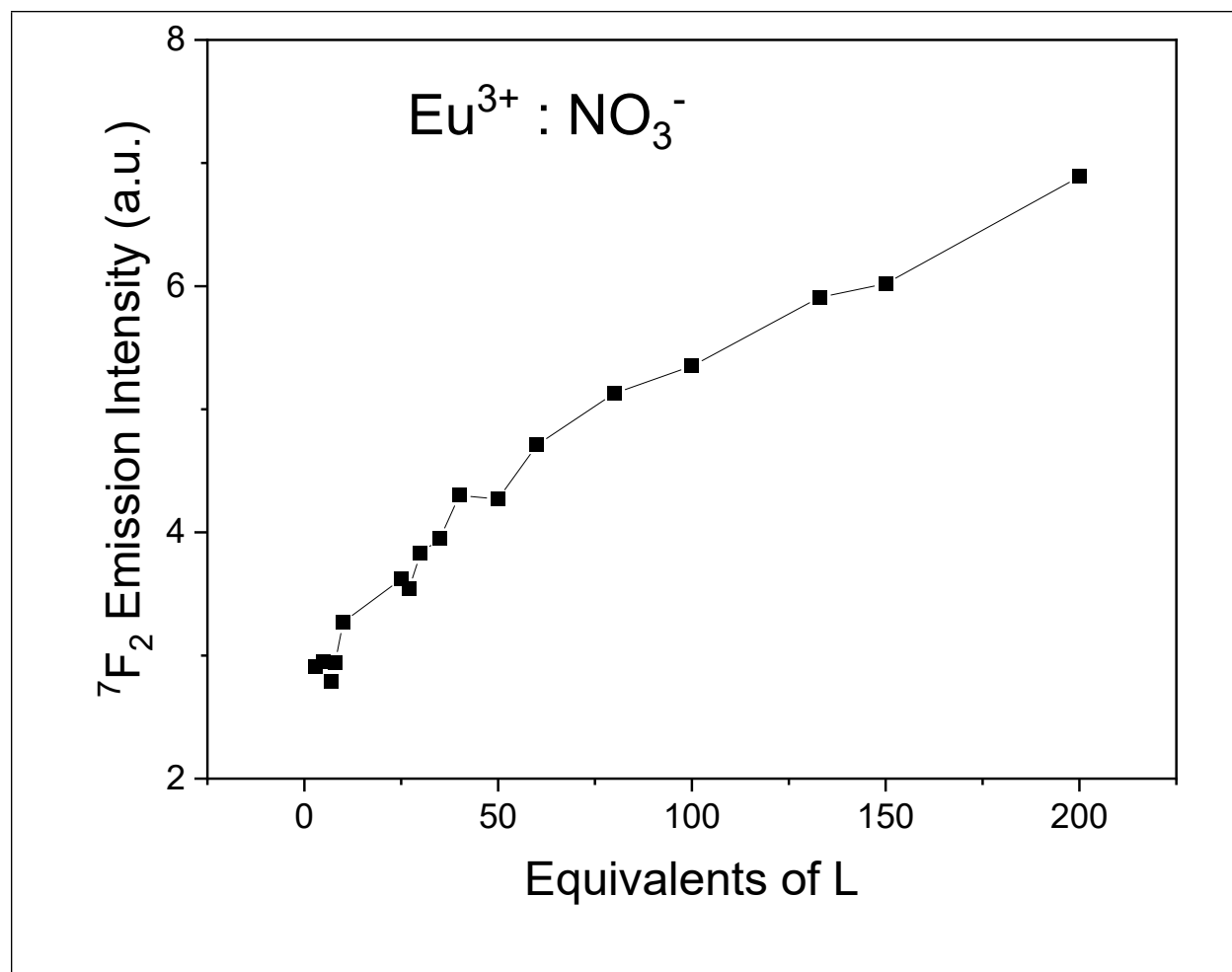


Figure S18. Emission intensity of the $^5D_0 \rightarrow ^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of NO_3^- . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

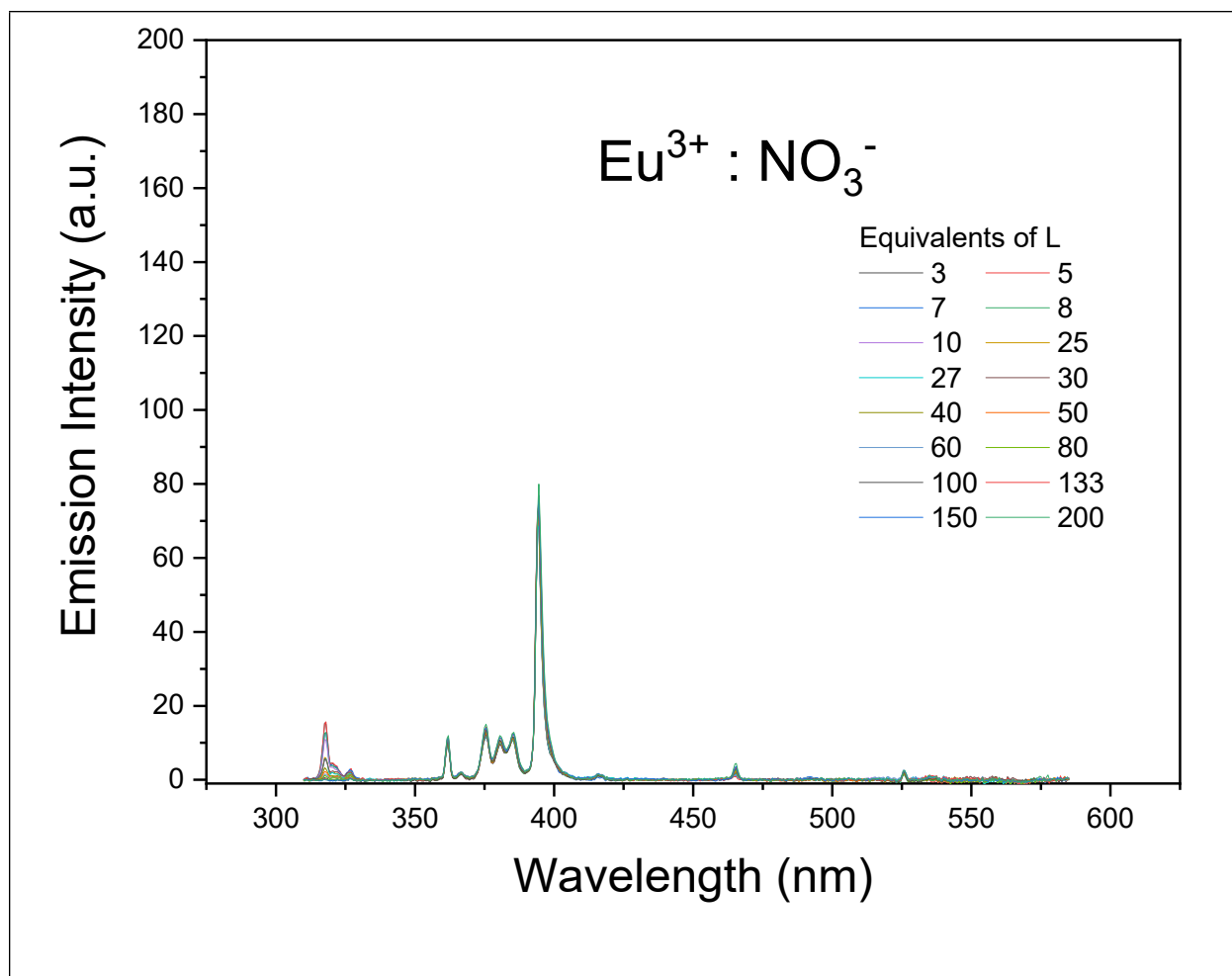


Figure S19. Excitation spectra of Eu^{3+} in KCl-MES buffer with various equivalents of NO_3^- .

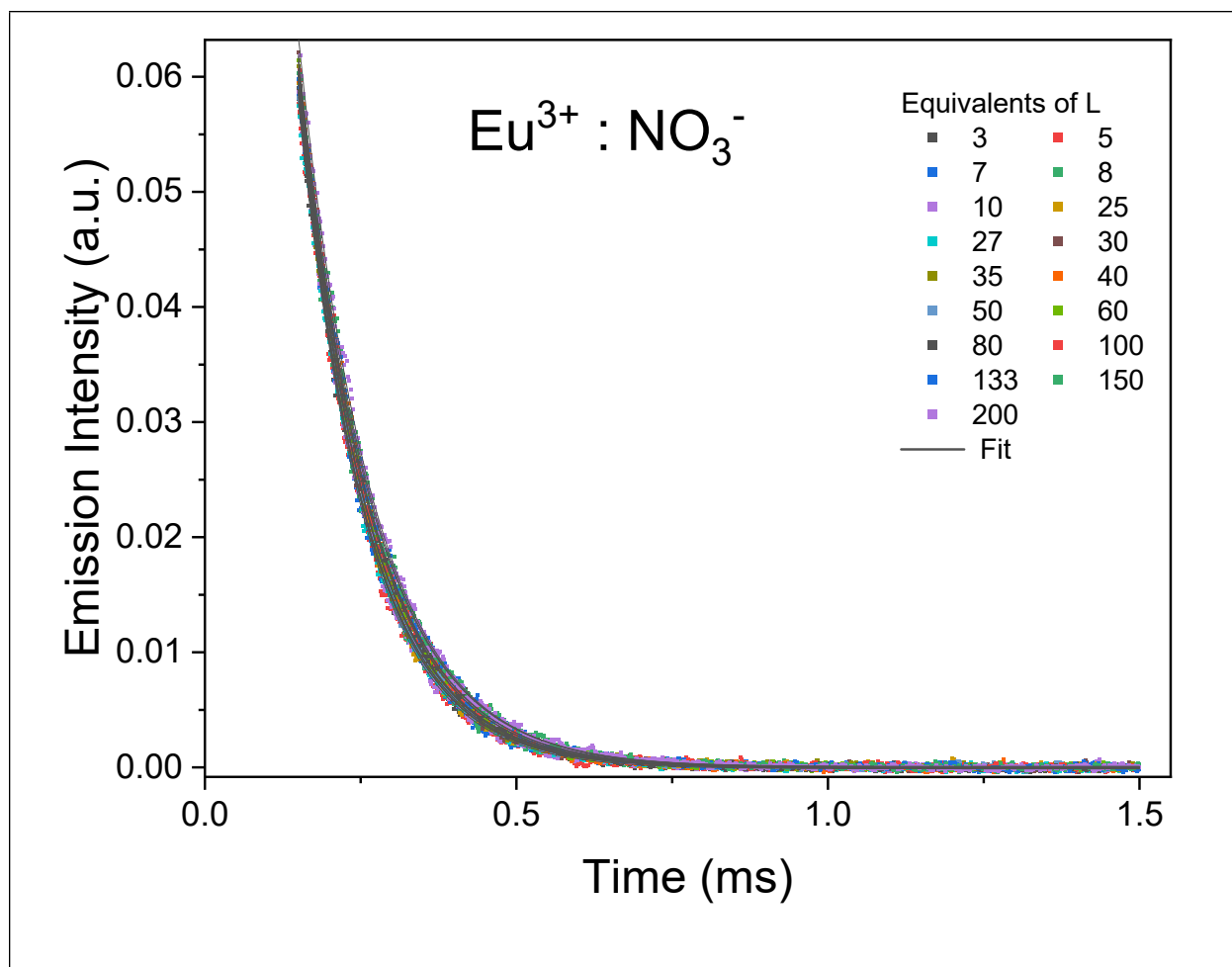


Figure S20. Time-resolved emission decay trace of Eu^{3+} in KCl-MES buffer with various equivalents of NO_3^- . The decay traces has been fit with a mono-exponential decay function.

Table S3. Fitting parameters for emission decay traces of $\text{Eu}^{3+} : \text{NO}_3^-$.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
3	-6.10966E-5	1.54932E-5	0.23175	0.00101	109.55214	0.25959
5	-1.2103E-4	1.43897E-5	0.23793	0.001	106.78968	0.24075
7	-9.0178E-6	1.54097E-5	0.24231	0.00107	106.89502	0.2529
8	2.14328E-5	1.36274E-5	0.24277	9.44309E-4	106.9612	0.22309
10	-2.15456E-5	1.39593E-5	0.23658	9.45372E-4	107.85304	0.23261
25	2.40856E-5	1.59653E-5	0.23673	0.00103	109.70589	0.26152
27	-3.78839E-5	1.39909E-5	0.22376	8.80096E-4	110.79793	0.24019
30	2.49096E-5	1.49761E-5	0.2377	9.6491E-4	109.82939	0.24405
35	6.19089E-5	1.65116E-5	0.23235	0.00103	110.97539	0.27257
40	-9.4274E-5	1.3722E-5	0.23021	7.97373E-4	114.09612	0.22285
50	1.304E-5	1.31783E-5	0.23076	8.24857E-4	111.00121	0.219
60	3.62526E-7	1.47433E-5	0.22442	8.53904E-4	114.23615	0.24534
80	-6.42485E-5	1.51861E-5	0.21761	8.23461E-4	117.09152	0.25493
100	7.69573E-5	1.47529E-5	0.22631	8.44236E-4	114.75	0.24246
133	-2.17635E-5	1.46394E-5	0.21068	7.38558E-4	120.33804	0.24793
150	8.5243E-6	1.58412E-5	0.2171	8.135E-4	119.52769	0.26185
200	-1.2736E-5	1.57835E-5	0.22347	8.14618E-4	119.29954	0.25388

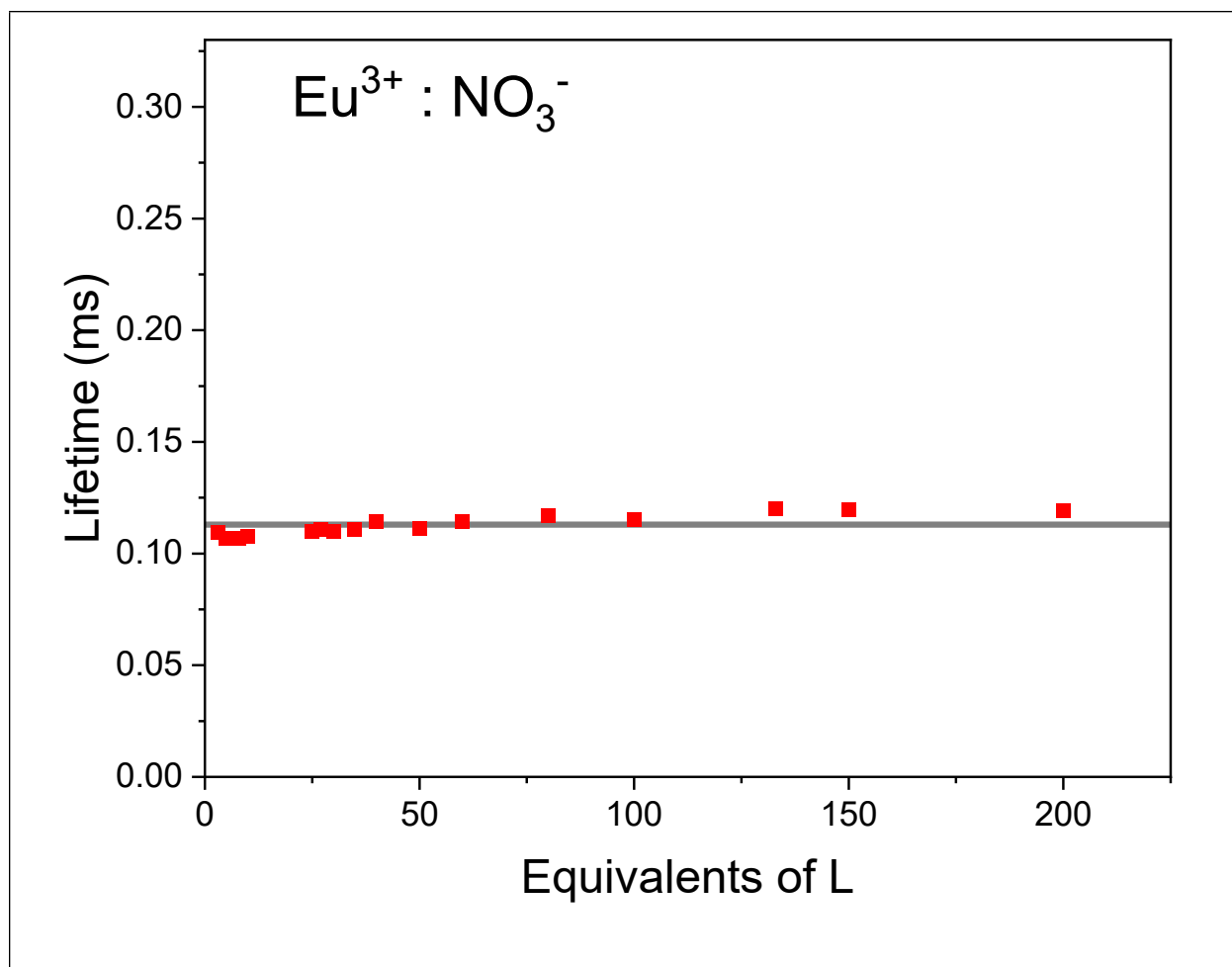


Figure S21. Excited state lifetime of Eu^{3+} in KCl-MES buffer as a function of equivalents of NO_3^- . The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu^{3+} in water.

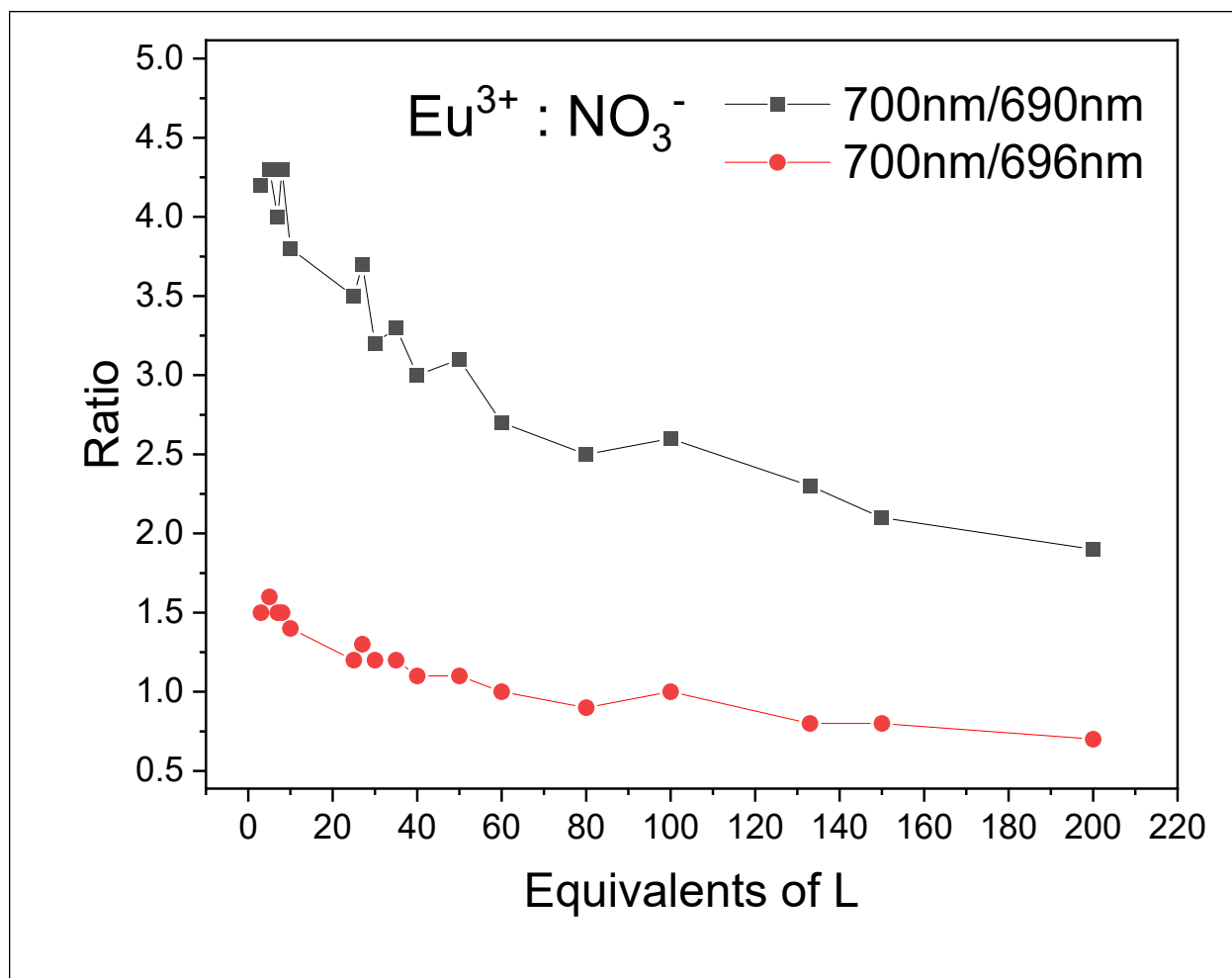


Figure S22. Ratios of emission intensity of Eu^{3+} in KCl-MES buffer as a function of equivalents of NO_3^- . The ratios give an indication of the changes in LF-splitting (see main text).

$\text{Eu}^{3+} : \text{HSO}_4^-$

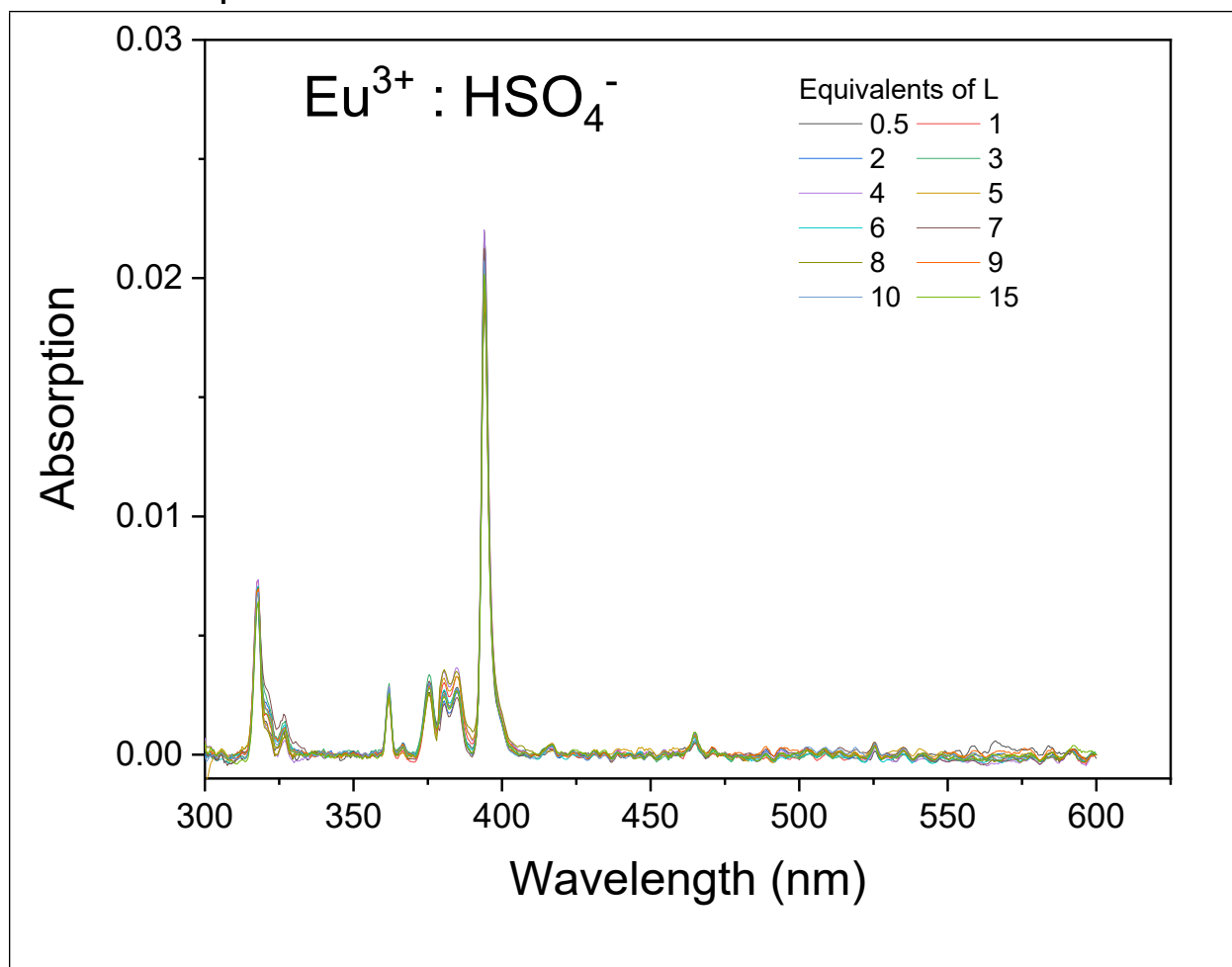


Figure S23. Absorption of Eu^{3+} in KCl-MES buffer with various equivalents of HSO_4^- .

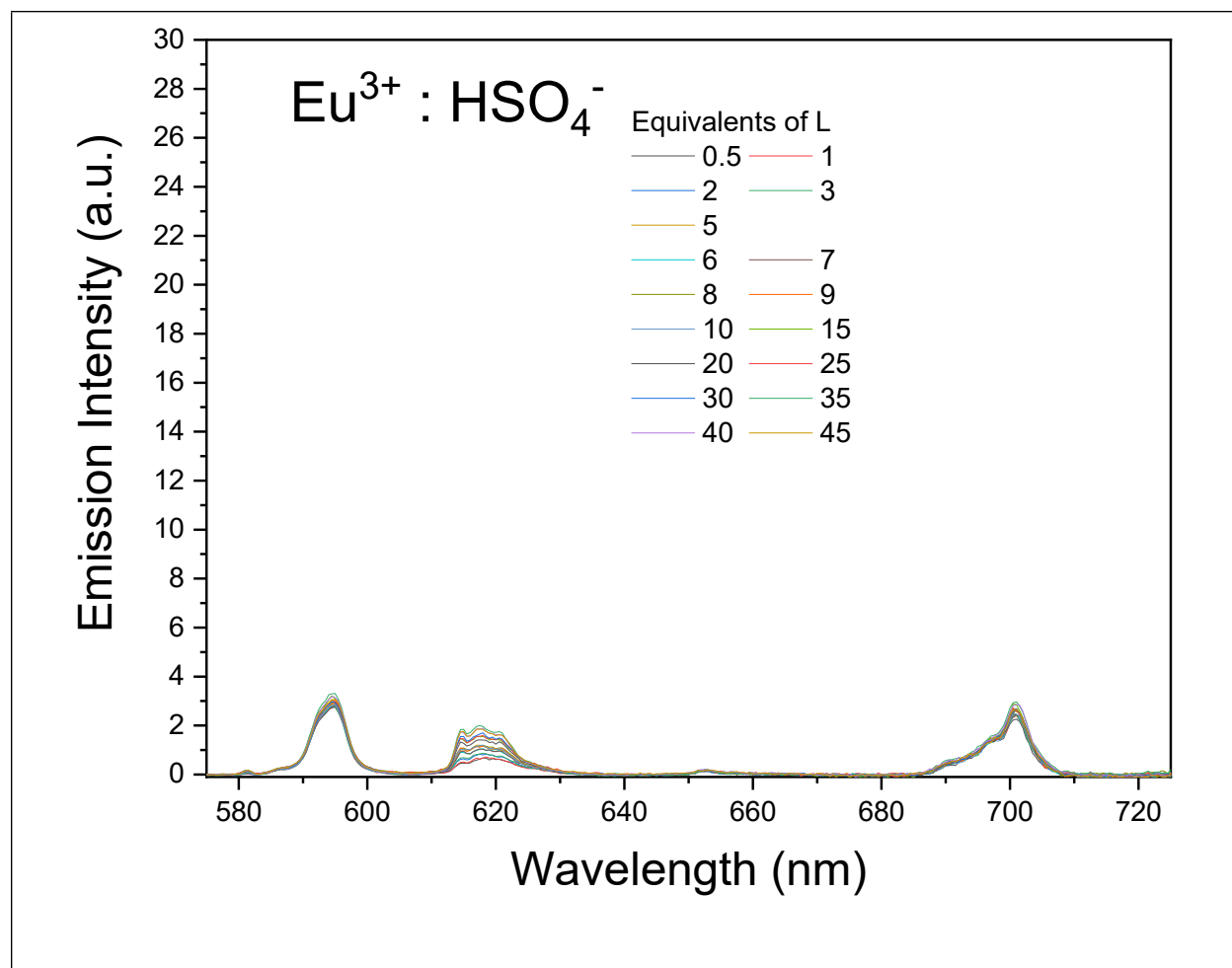


Figure S24. Emission spectrum of Eu^{3+} in KCl-MES buffer with various equivalents of HSO_4^- .

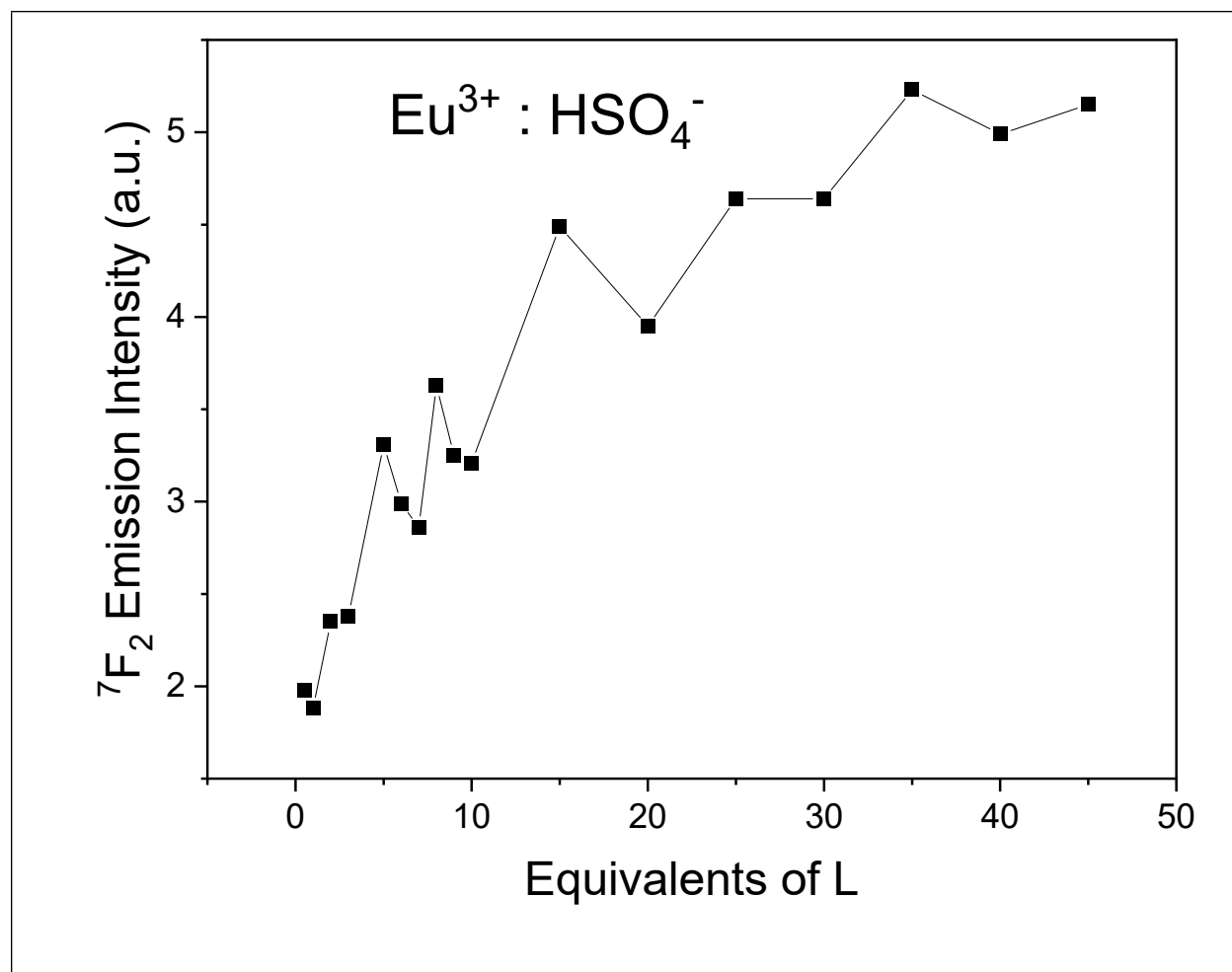


Figure S 25. Emission intensity of the ${}^5D_0 \rightarrow {}^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of HSO_4^- . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

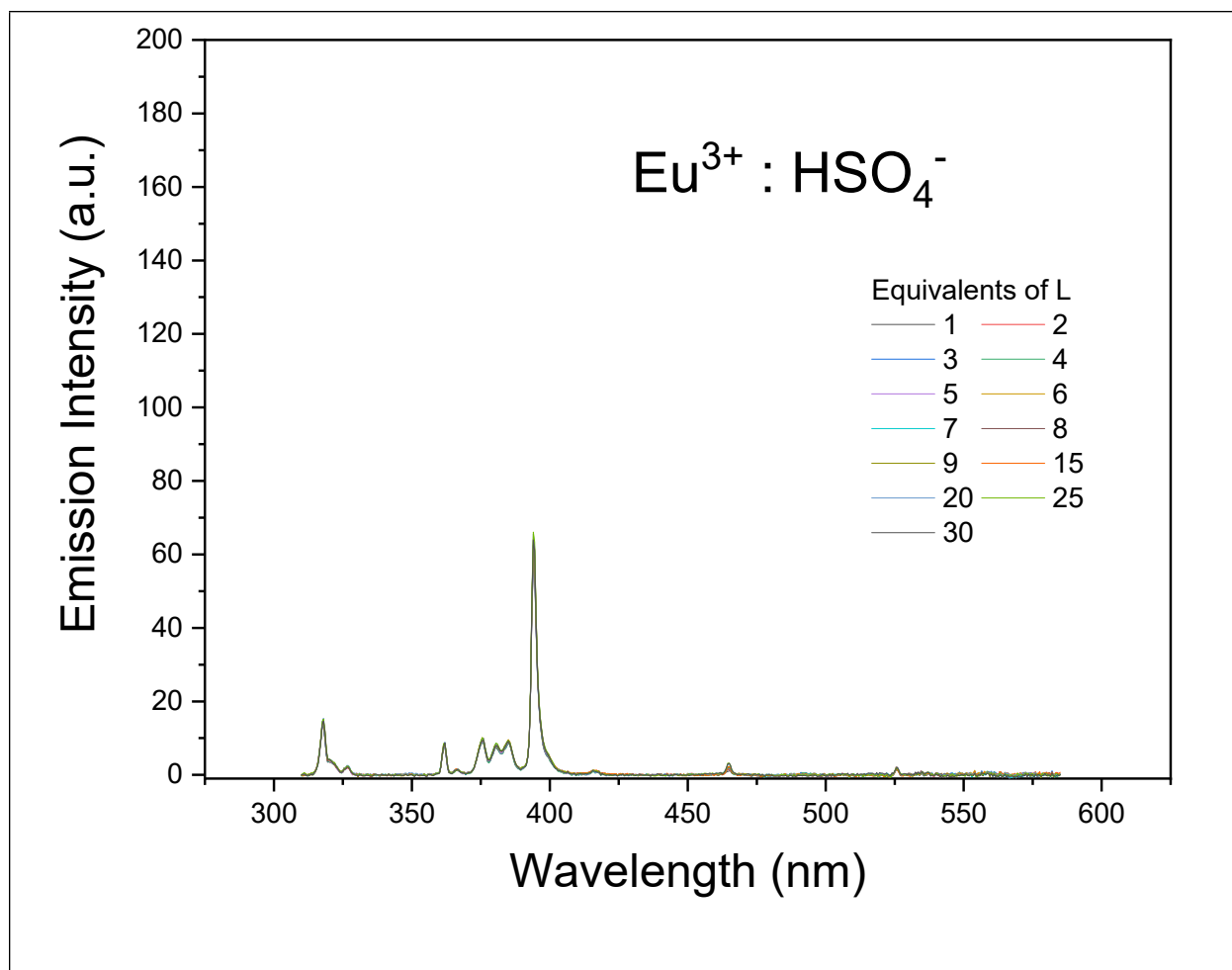


Figure S26. Excitation spectrum of Eu^{3+} in KCl-MES buffer with various equivalents of HSO_4^- .

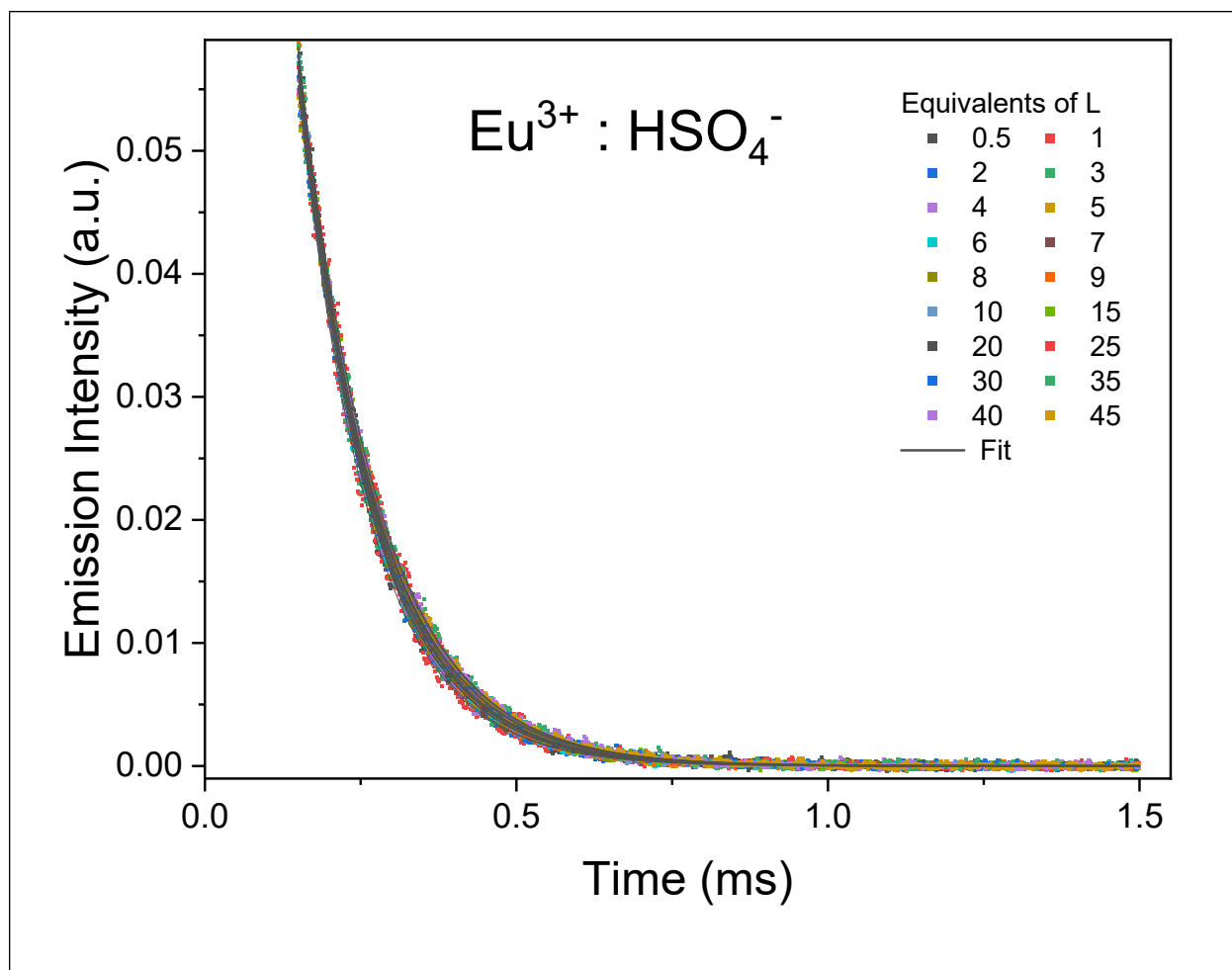


Figure S27. Time-resolved emission decay trace of Eu^{3+} in KCl-MES buffer with various equivalents of HSO_4^- . The decay traces has been fit with a mono-exponential decay function.”

Table S4. Fitting parameters for emission decay traces of $\text{Eu}^{3+} : \text{HSO}_4^-$.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
0.5	4.16742E-5	1.52875E-5	0.22135	9.20721E-4	112.58962	0.26137
1	-3.02104E-5	1.58451E-5	0.20649	9.23353E-4	113.97595	0.28716
2	-6.61678E-6	1.52992E-5	0.20176	8.2033E-4	117.5884	0.27599
3	5.18042E-5	1.38527E-5	0.19557	7.2757E-4	118.51125	0.25606
4	-6.08107E-6	1.5141E-5	0.20584	8.18002E-4	117.25395	0.26839
5	8.01727E-6	1.36623E-5	0.20398	7.08904E-4	119.05862	0.24117
6	1.81114E-6	1.4894E-5	0.19907	7.6506E-4	119.51556	0.26851
7	-2.84748E-5	1.46396E-5	0.19997	7.17759E-4	121.65964	0.25883
8	9.10263E-6	1.5079E-5	0.19651	7.47143E-4	121.16951	0.27221
9	-6.49833E-5	1.49409E-5	0.19647	7.18089E-4	122.59304	0.26716
10	-1.04418E-5	1.74335E-5	0.19576	8.63282E-4	121.1975	0.31586
15	-4.26008E-5	1.45869E-5	0.19171	6.69984E-4	124.75691	0.26352
20	-1.31277E-6	1.75074E-5	0.19032	8.0432E-4	124.74516	0.3186
25	-4.13821E-5	1.61947E-5	0.18553	6.82322E-4	129.02613	0.29437
30	5.71128E-5	1.53287E-5	0.17998	6.78137E-4	126.58759	0.29154
35	-1.63635E-5	1.52164E-5	0.18578	6.46478E-4	128.60447	0.27691
40	-3.06379E-5	1.47278E-5	0.17816	6.10907E-4	129.81998	0.27746
45	-4.36307E-6	1.51367E-5	0.1769	6.42917E-4	128.61815	0.28927

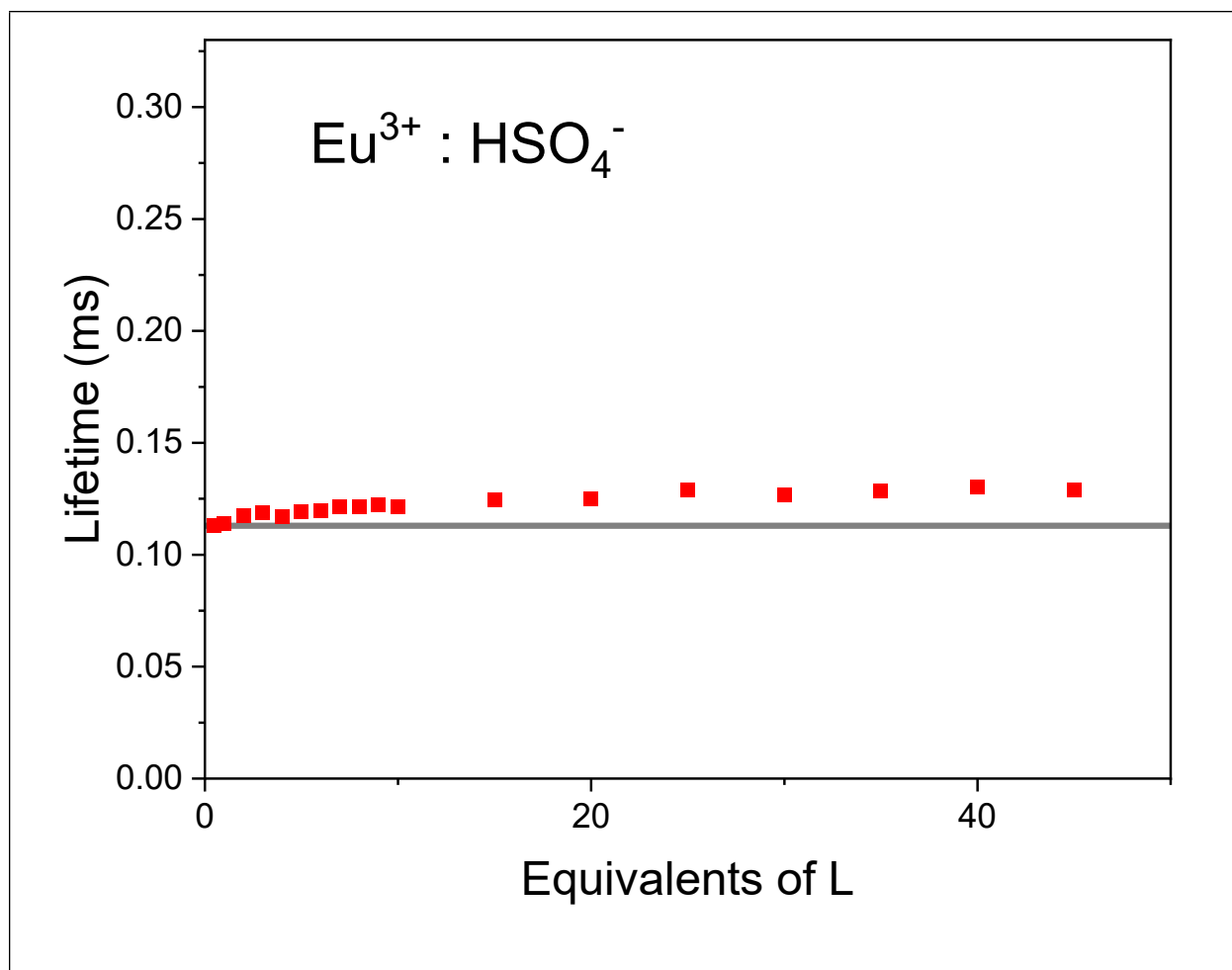


Figure S28. Excited state lifetime of Eu^{3+} in KCl-MES buffer as a function of equivalents of HSO_4^- . The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu^{3+} in water.

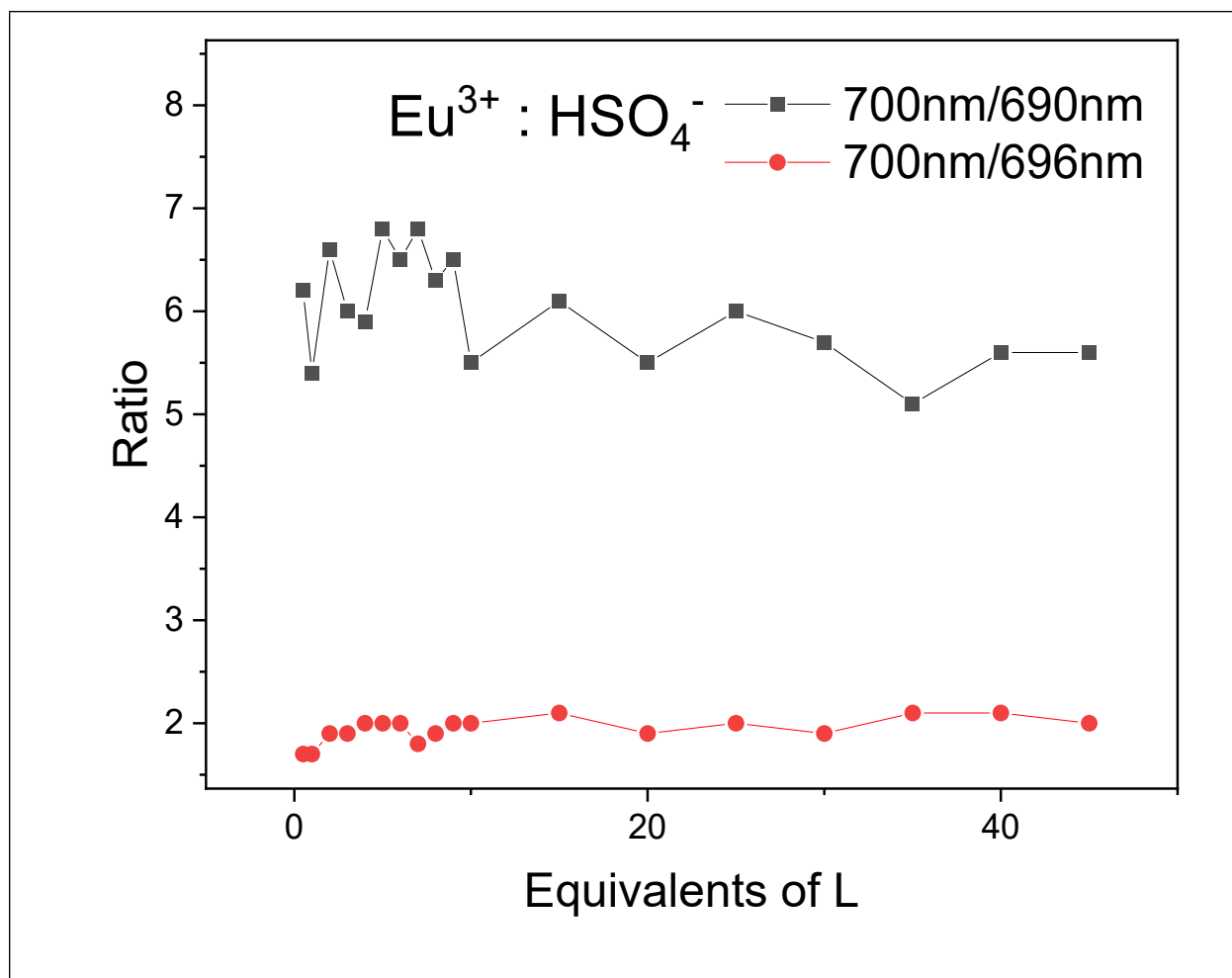


Figure S29. Ratios of emission intensity of Eu³⁺ in KCl-MES buffer as a function of equivalents of HSO₄⁻. The ratios give an indication of the changes in LF-splitting (see main text).

$\text{Eu}^{3+} : \text{SO}_4^{2-}$

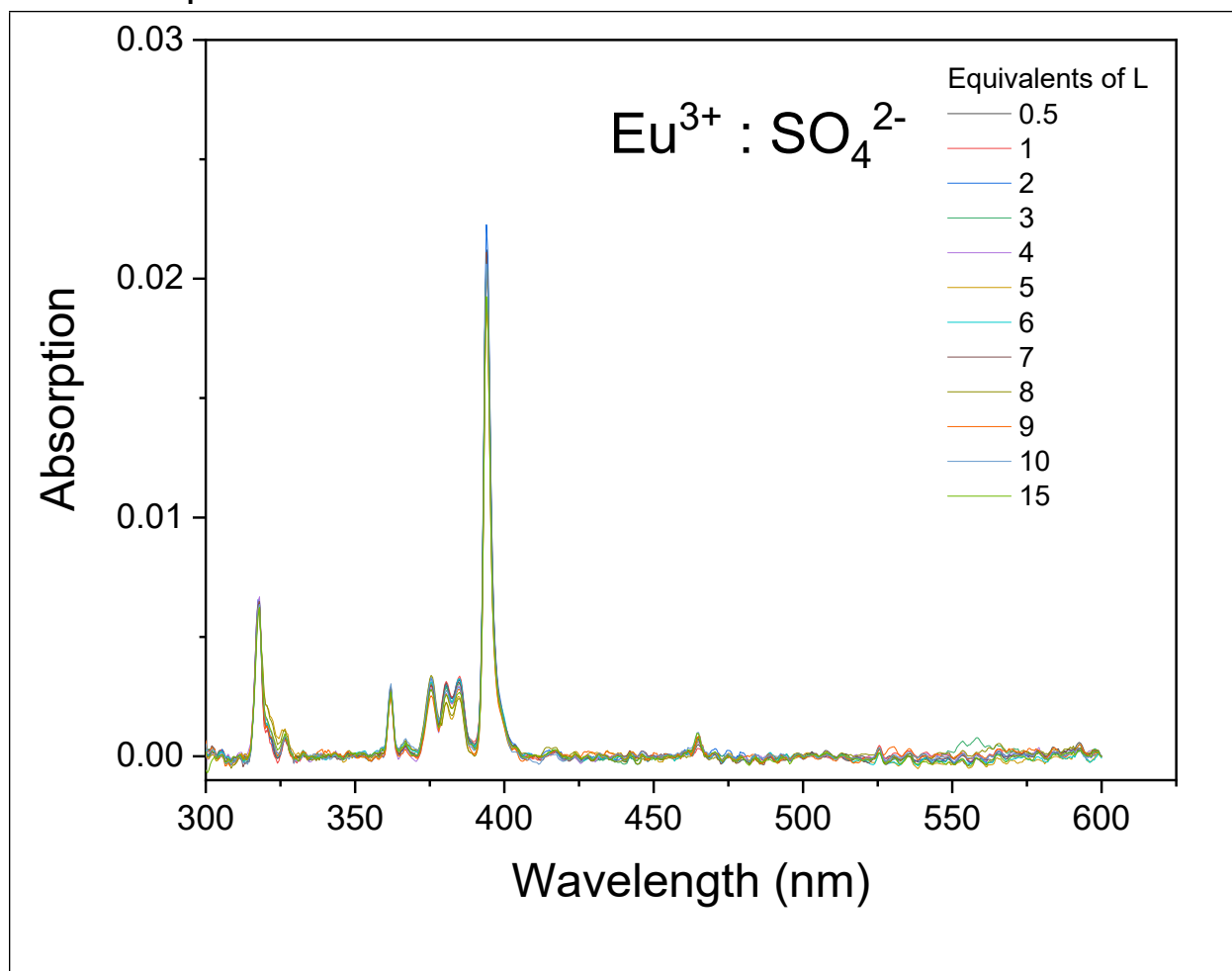


Figure S30. Absorption of Eu^{3+} in KCl-MES buffer with various equivalents of SO_4^{2-} .

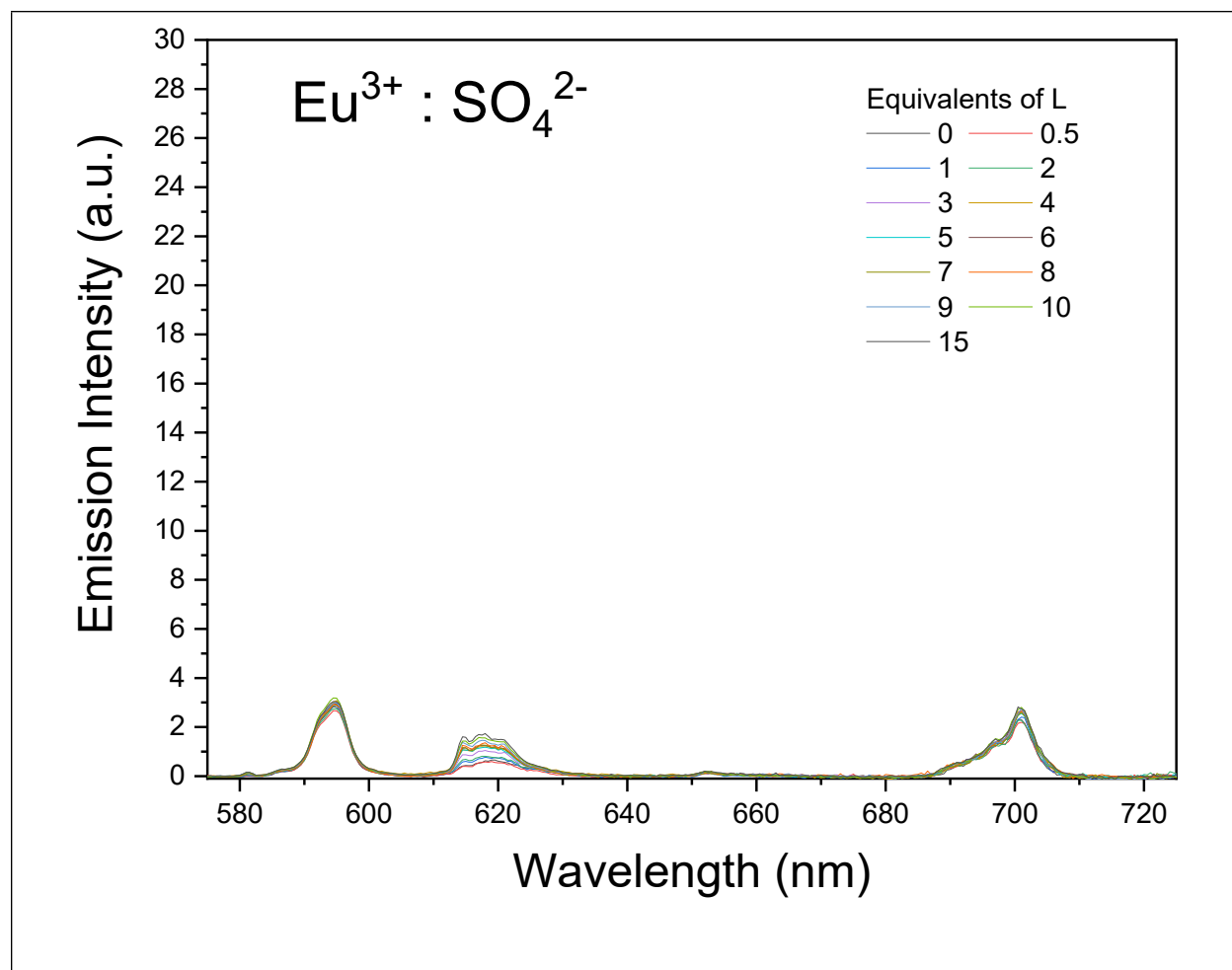


Figure S31. Emission spectrum of Eu^{3+} in KCl-MES buffer with various equivalents of SO_4^{2-} .

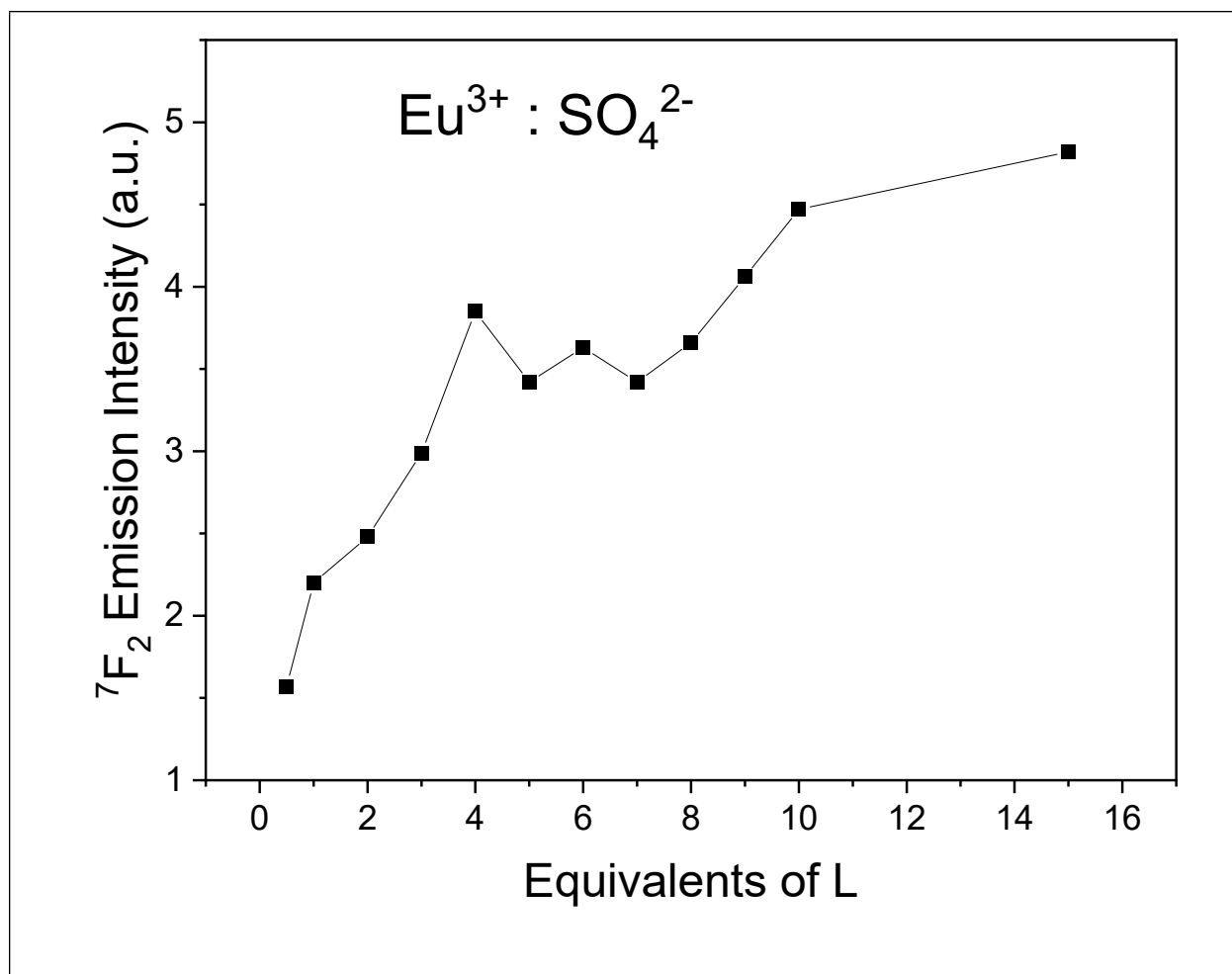


Figure S32. Emission intensity of the ${}^5D_0 \rightarrow {}^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of SO_4^{2-} . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

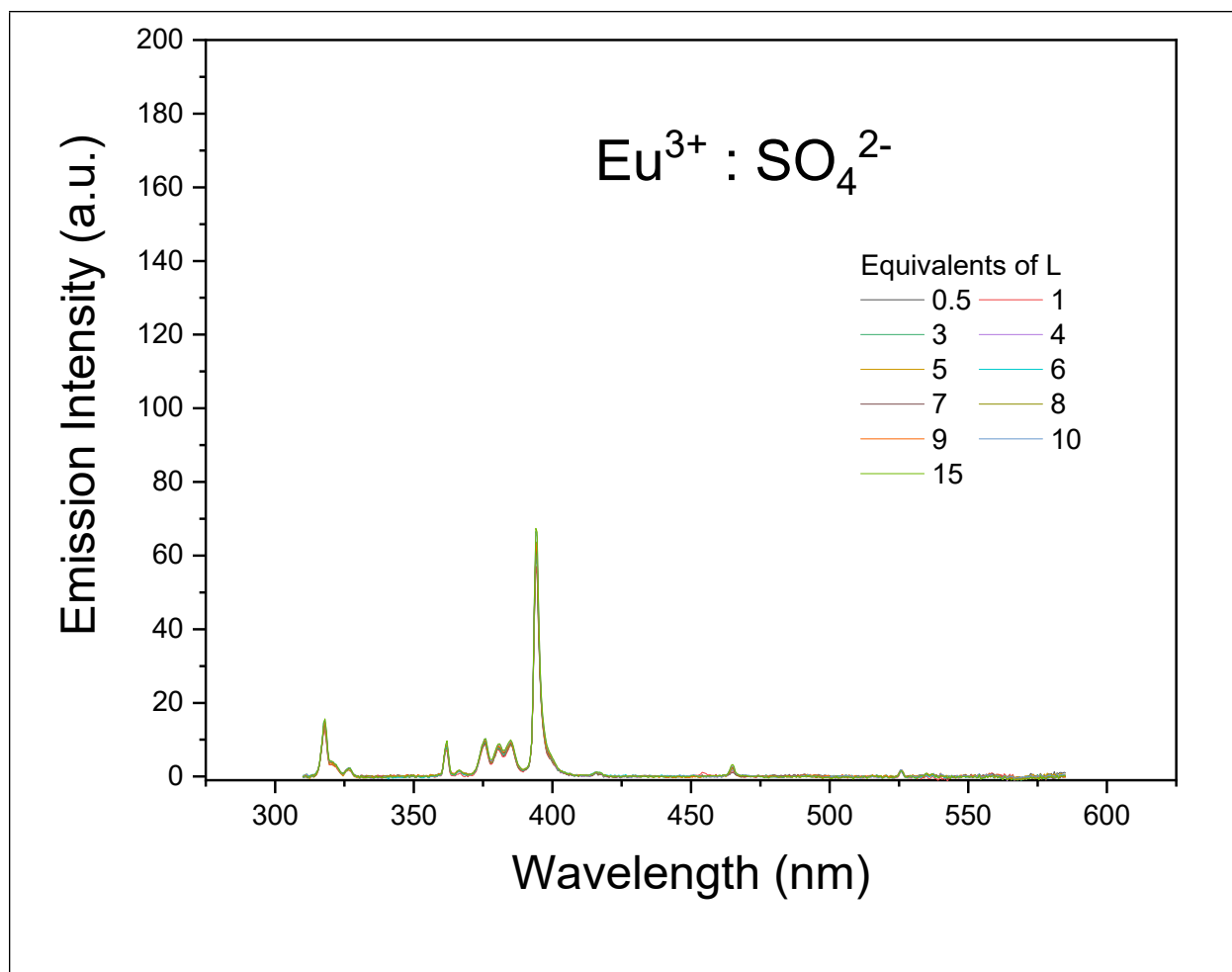


Figure S33. Excitation spectrum of Eu^{3+} in KCl-MES buffer with various equivalents of SO_4^{2-} .

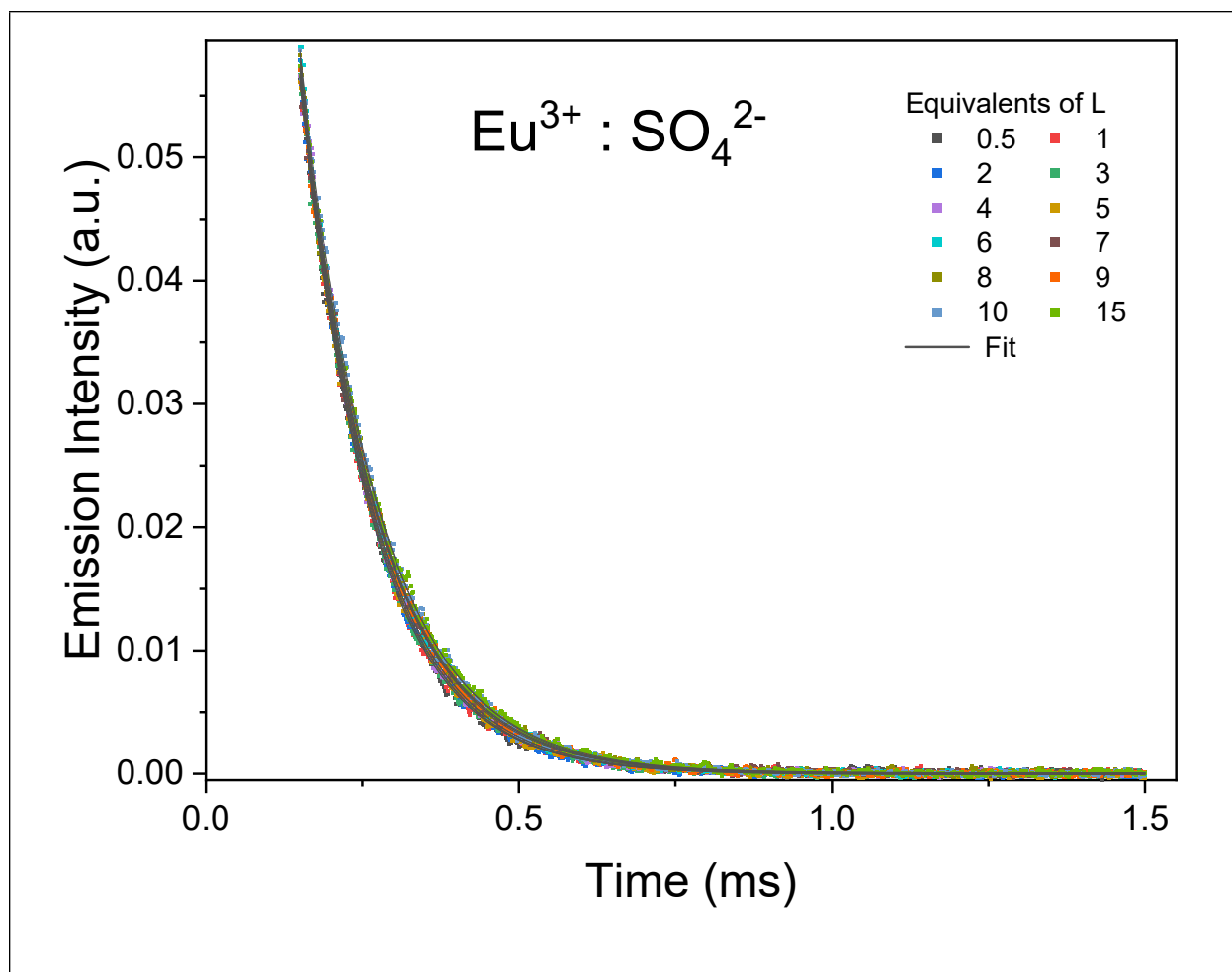


Figure S34. Time-resolved emission decay trace of Eu^{3+} in KCl-MES buffer with various equivalents of SO_4^{2-} . The decay traces has been fit with a mono-exponential decay function.

Table S5. Fitting parameters for emission decay traces of $\text{Eu}^{3+} : \text{SO}_4^{2-}$.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
0.5	3.36803E-5	1.39663E-5	0.20606	7.87431E-4	115.38945	0.25084
1	3.71315E-5	1.15749E-5	0.20894	6.59601E-4	114.92998	0.20575
2	-6.00762E-5	1.52234E-5	0.20491	8.19835E-4	117.39491	0.27079
3	-1.8281E-5	1.44471E-5	0.20394	7.86875E-4	116.89578	0.25917
4	4.73685E-5	1.75695E-5	0.20707	9.40844E-4	117.64589	0.30869
5	-7.76755E-5	1.53236E-5	0.19725	7.77901E-4	120.05309	0.27775
6	5.96644E-5	1.44662E-5	0.20304	7.29269E-4	120.37266	0.25415
7	4.39874E-5	1.49441E-5	0.18759	6.9711E-4	124.0117	0.27724
8	7.23188E-5	1.6183E-5	0.19153	7.54448E-4	124.04044	0.29399
9	-3.73924E-5	1.50823E-5	0.18883	6.96525E-4	124.49403	0.27709
10	-2.55921E-5	1.53821E-5	0.19275	6.87136E-4	126.11003	0.274
15	2.64762E-5	1.43277E-5	0.18561	6.20871E-4	127.61344	0.26257

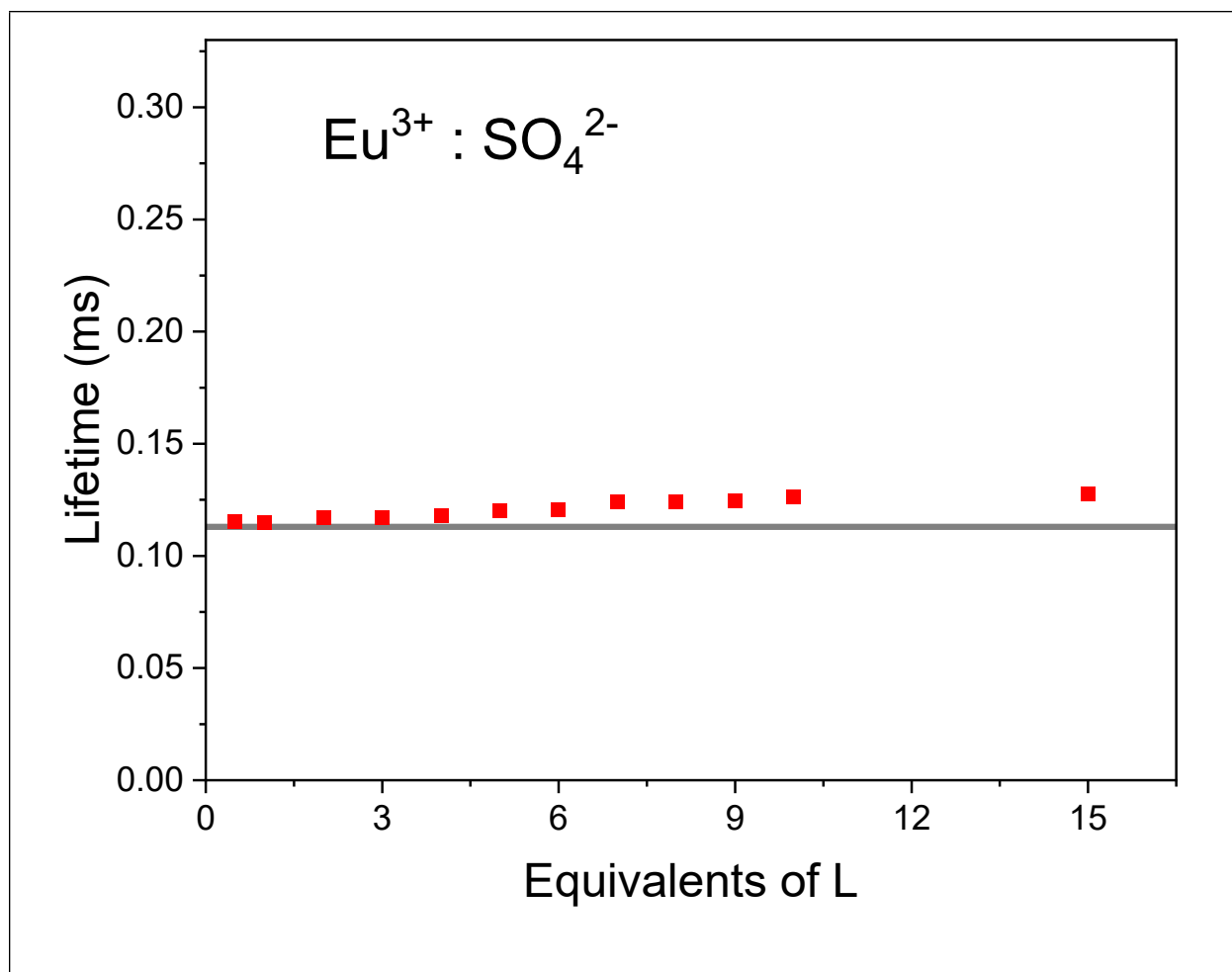


Figure S35. Excited state lifetime of Eu^{3+} in KCl-MES buffer as a function of equivalents of SO_4^{2-} . The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu^{3+} in water.

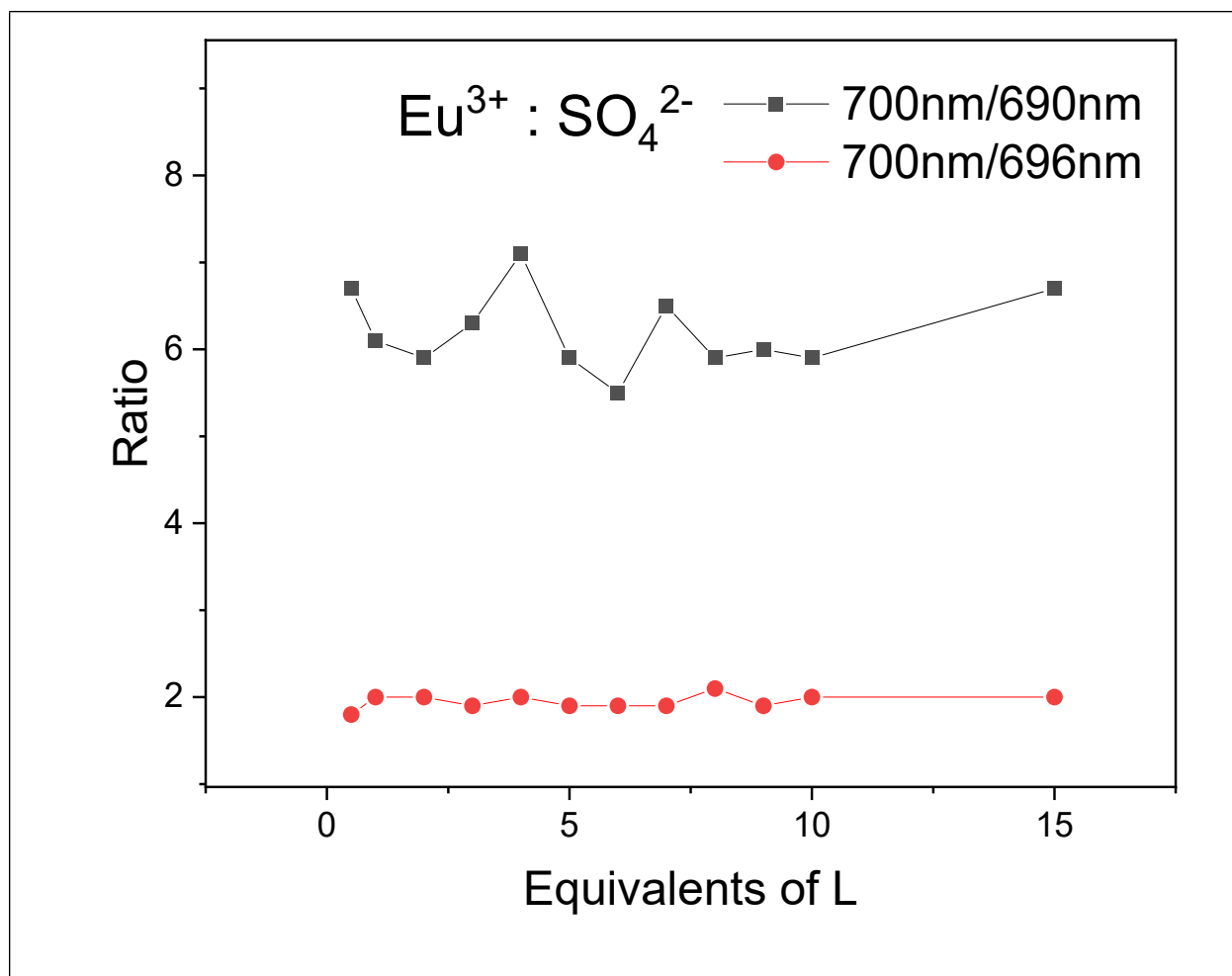


Figure S36. Ratios of emission intensity of Eu^{3+} in KCl-MES buffer as a function of equivalents of SO_4^{2-} . The ratios give an indication of the changes in LF-splitting (see main text).

$\text{Eu}^{3+} : \text{Cl}^-$

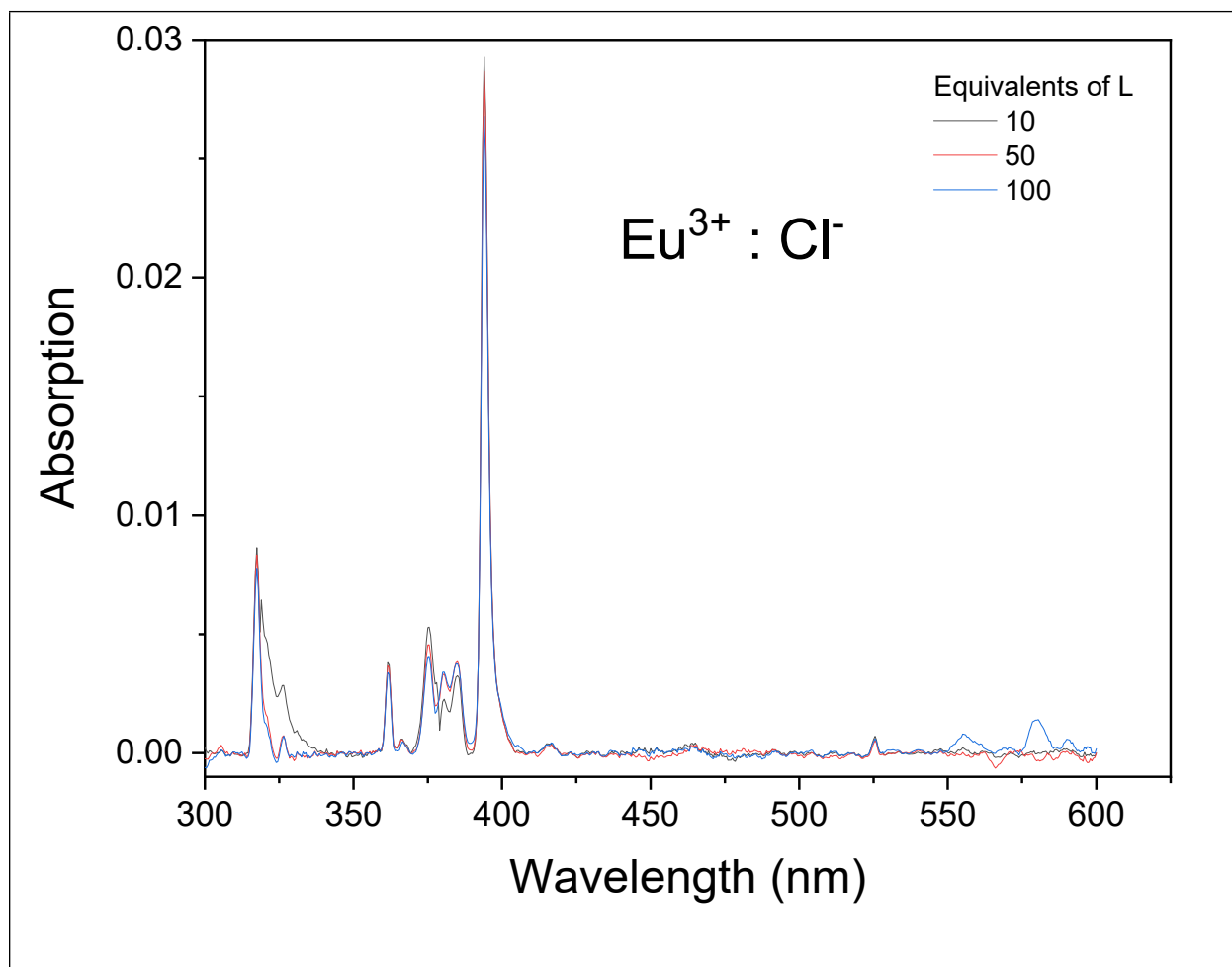


Figure S37. Absorption of Eu^{3+} in KCl-MES buffer with various equivalents of Cl^- .

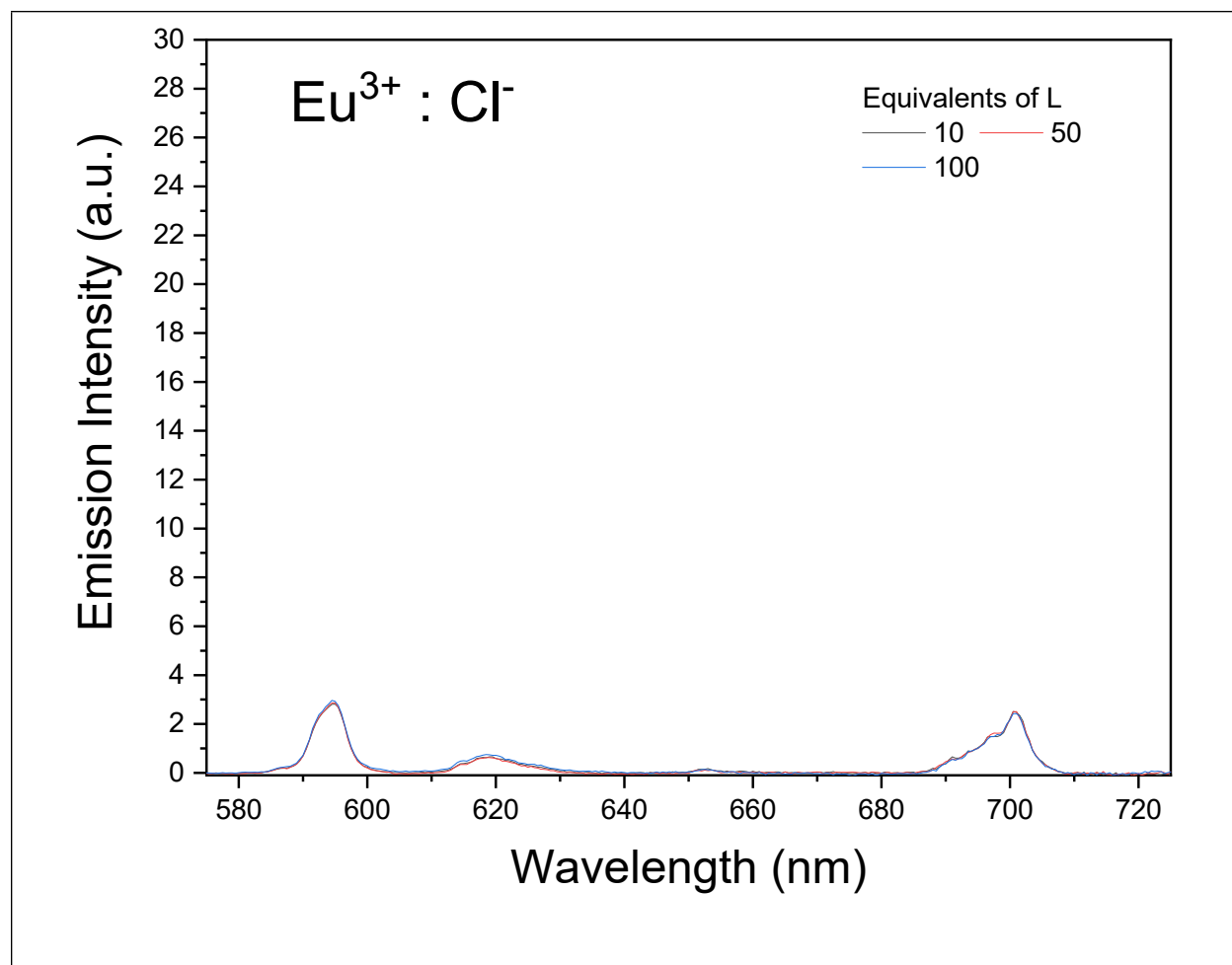


Figure S38. Emission spectrum of Eu^{3+} in KCl-MES buffer with various equivalents of Cl^- .

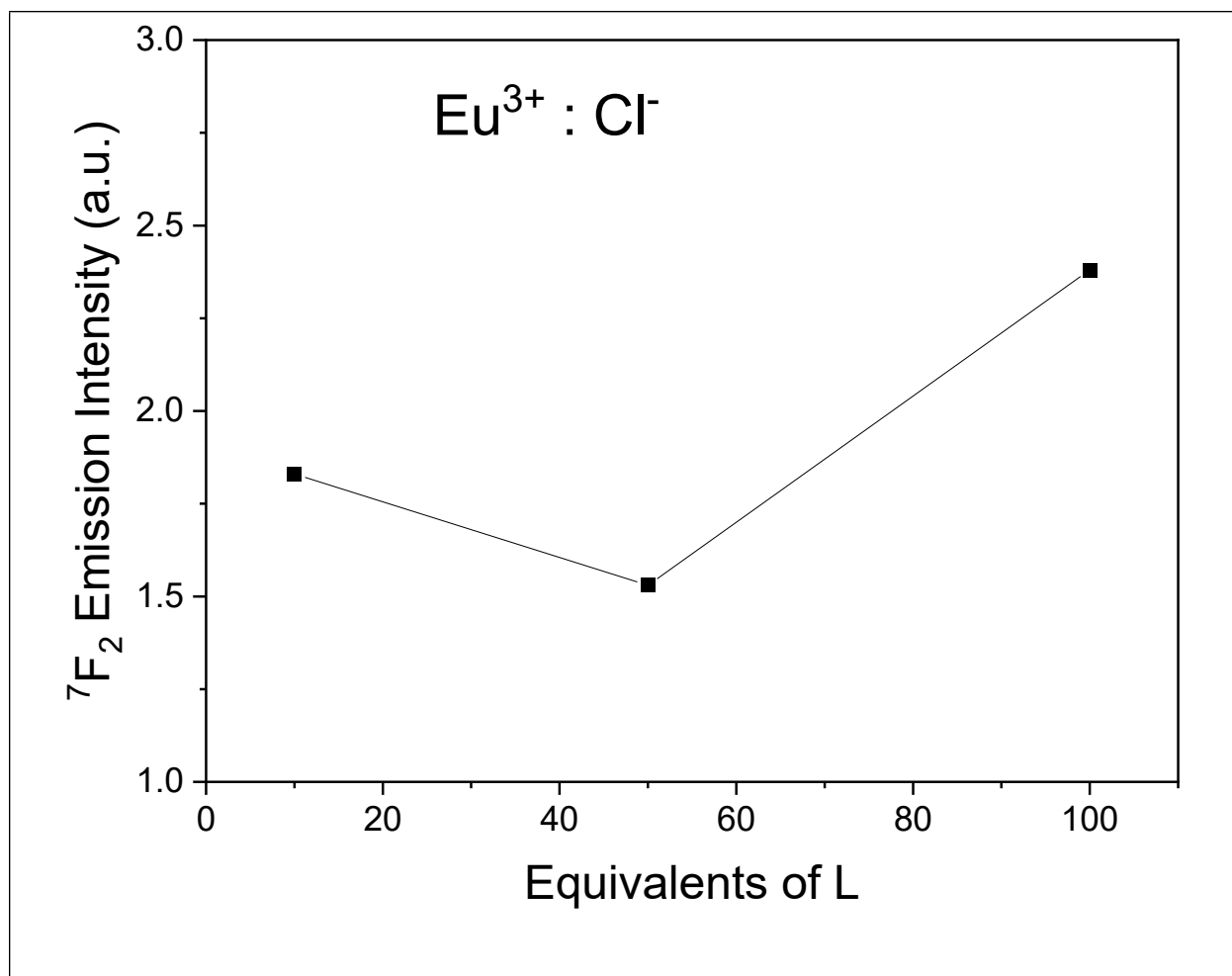


Figure S39. Emission intensity of the $^5D_0 \rightarrow ^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of AcO^- . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

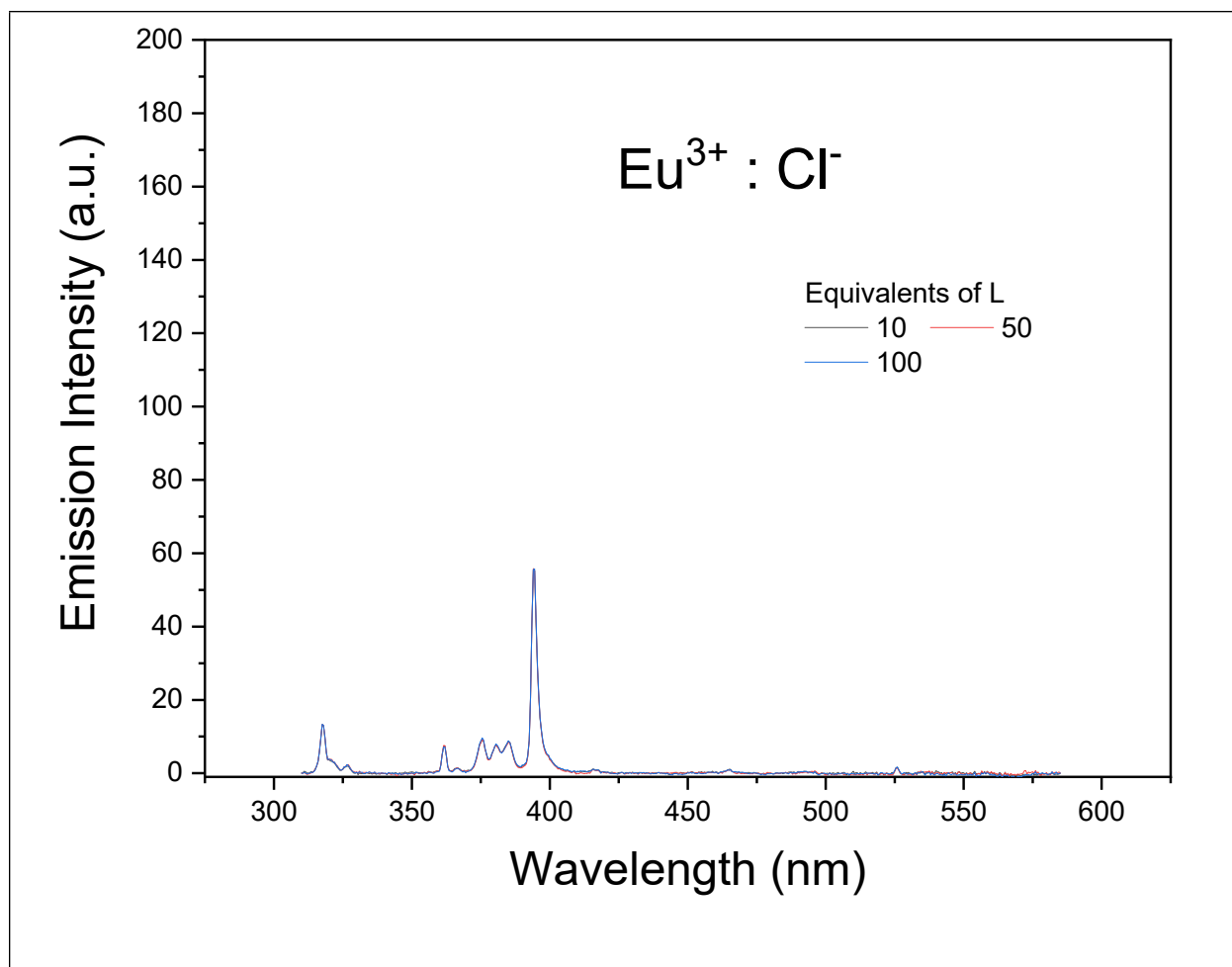


Figure S40. Excitation spectrum of Eu³⁺ in KCl-MES buffer with various equivalents of Cl⁻.

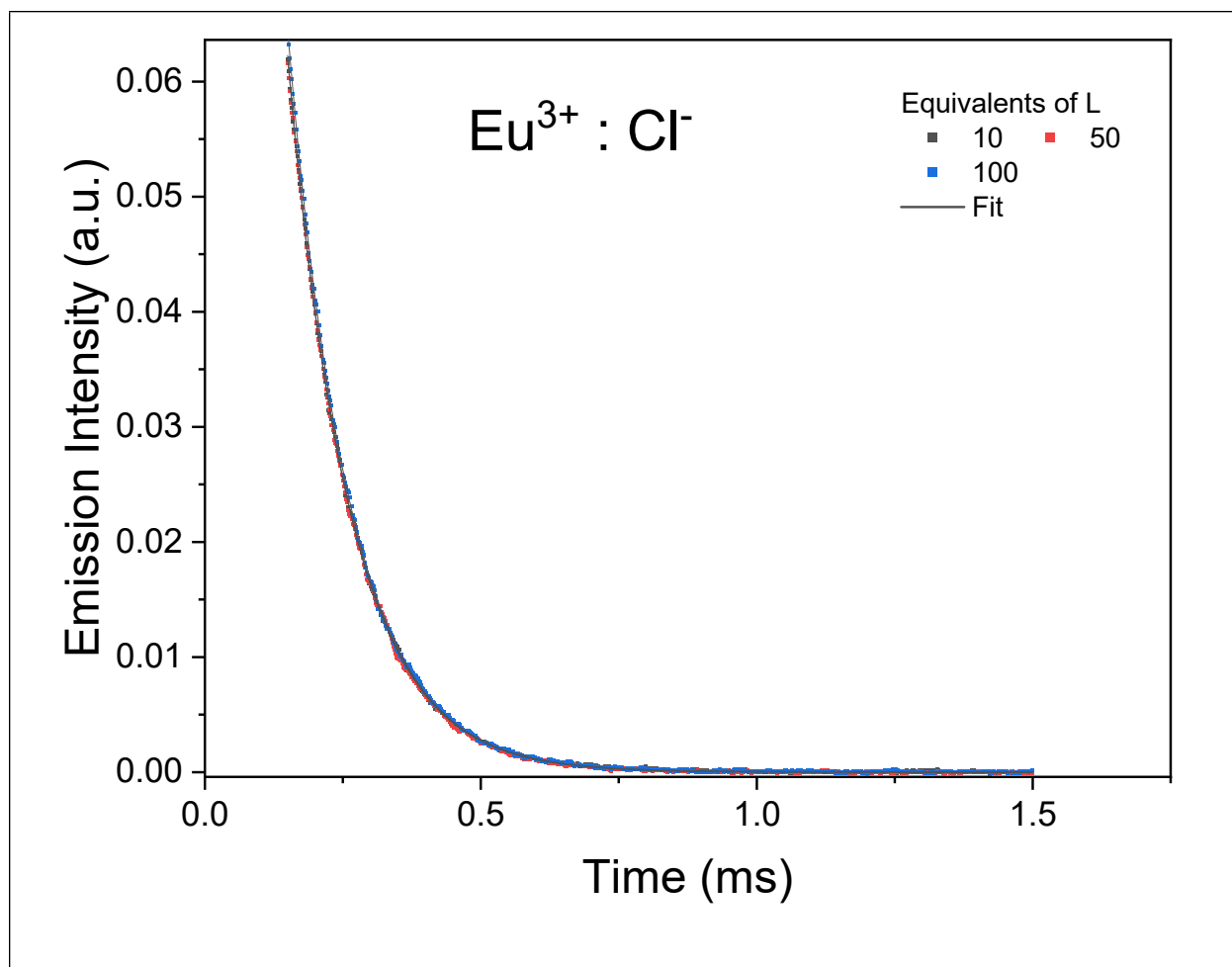


Figure S41. Time-resolved emission decay trace of Eu³⁺ in KCl-MES buffer with various equivalents of Cl⁻. The decay traces has been fit with a mono-exponential decay function.

Table S6. Fitting parameters for emission decay traces of $\text{Eu}^{3+} : \text{Cl}^-$.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
10	1.82153E-5	7.0639E-6	0.23636	4.27105E-4	112.42685	0.11325
50	-3.51845E-5	6.81515E-6	0.23658	4.148E-4	112.15225	0.10941
100	3.7568E-5	6.77181E-6	0.24812	4.21087E-4	111.26971	0.10442

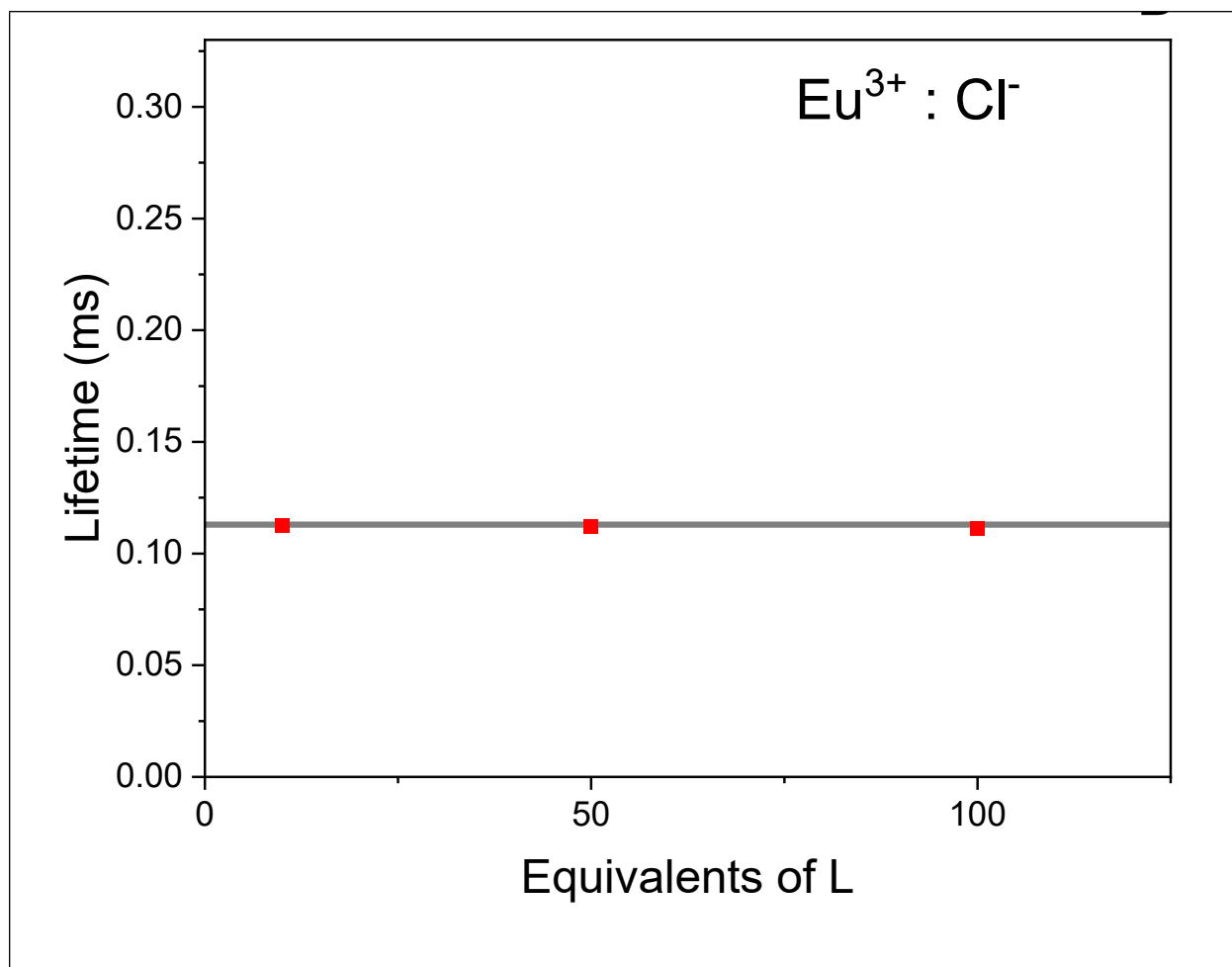


Figure S42. Excited state lifetime of Eu³⁺ in KCl-MES buffer as a function of equivalents of Cl⁻. The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu³⁺ in water.

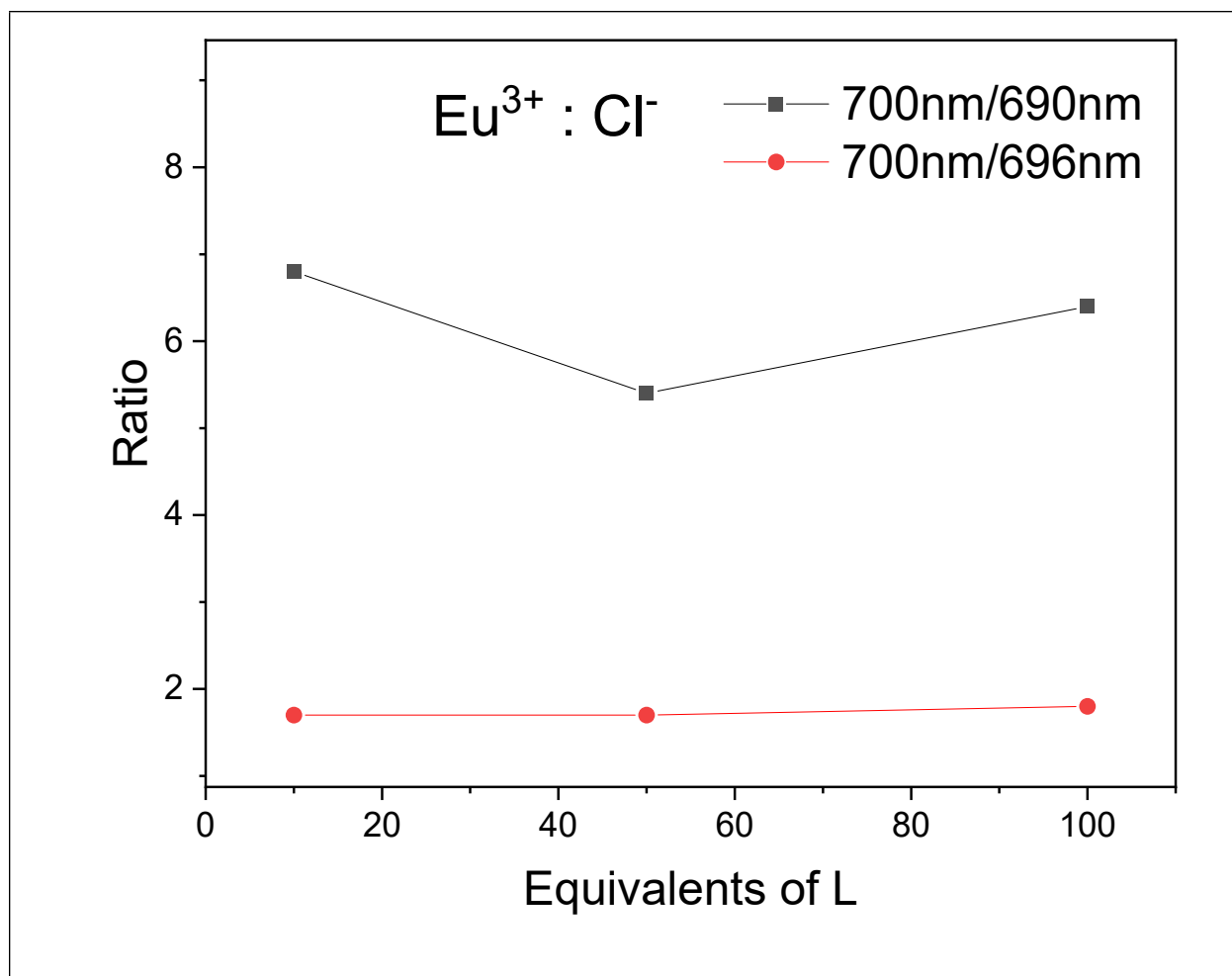


Figure S43. Ratios of emission intensity of Eu^{3+} in KCl-MES buffer as a function of equivalents of Cl^- . The ratios give an indication of the changes in LF-splitting (see main text).

$\text{Eu}^{3+} : \text{ClO}_4^-$

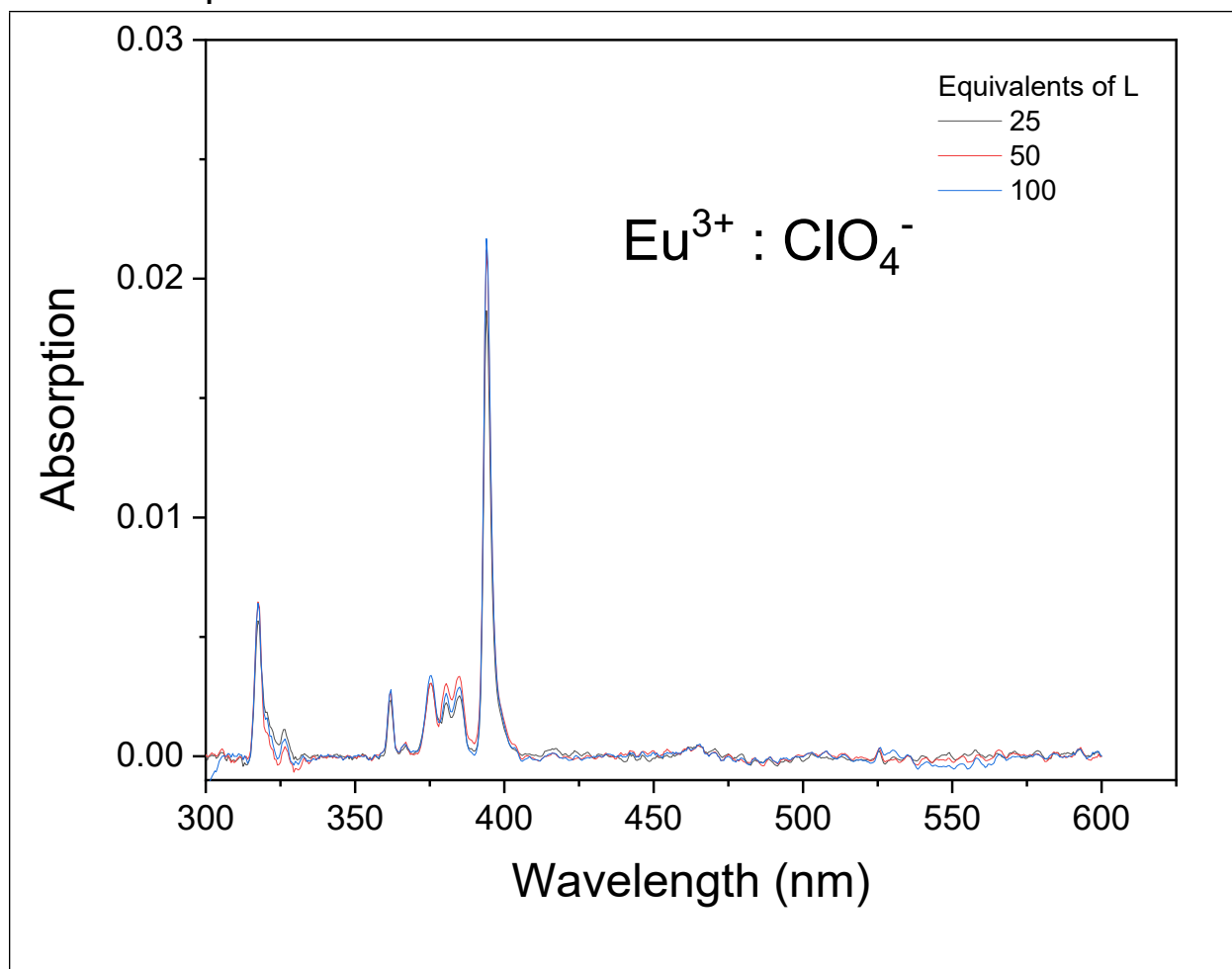


Figure S44. Absorption of Eu^{3+} in NaCl-MES buffer with various equivalents of ClO_4^- .

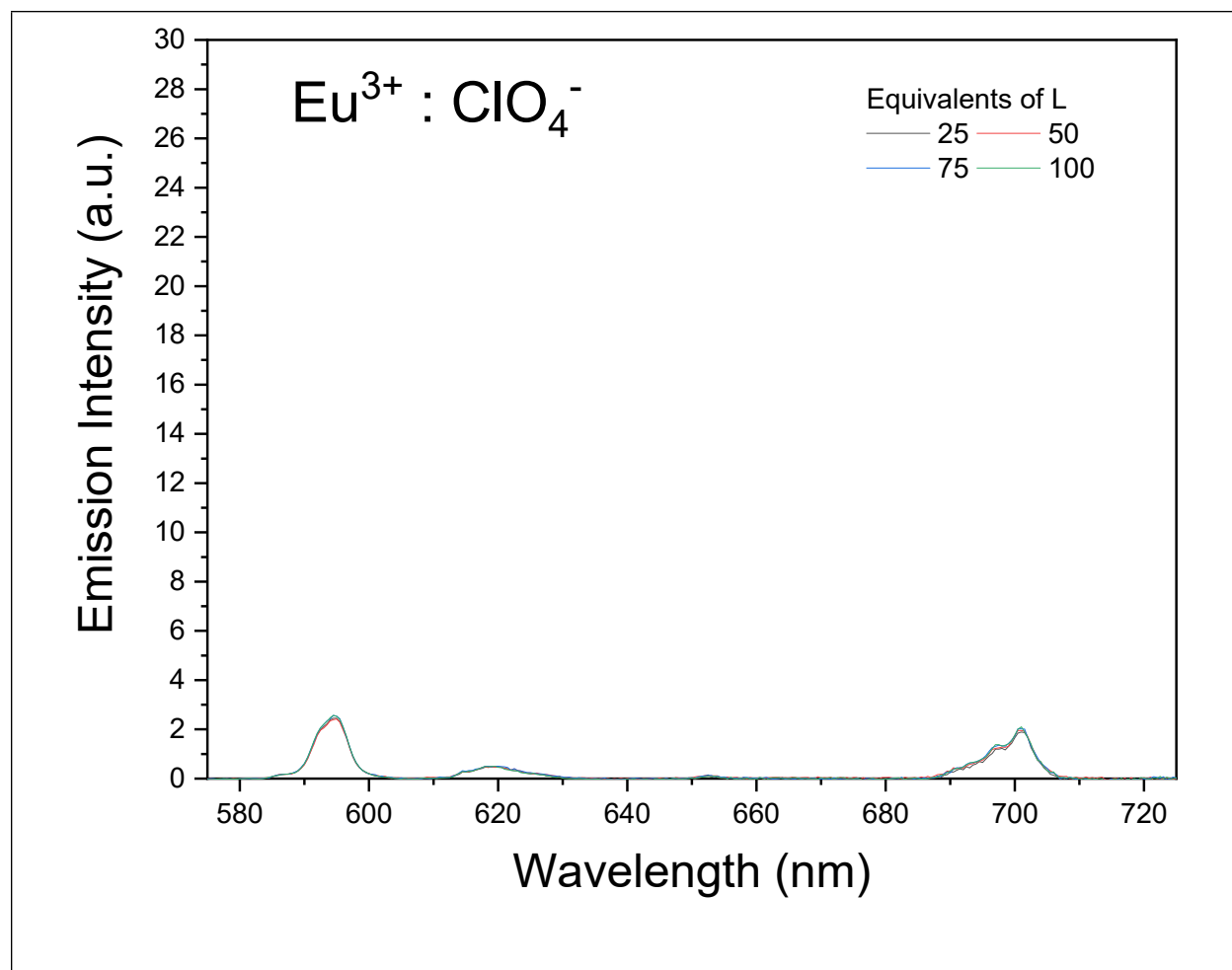


Figure S45. Emission spectrum of Eu^{3+} in NaCl-MES buffer with various equivalents of ClO_4^- .

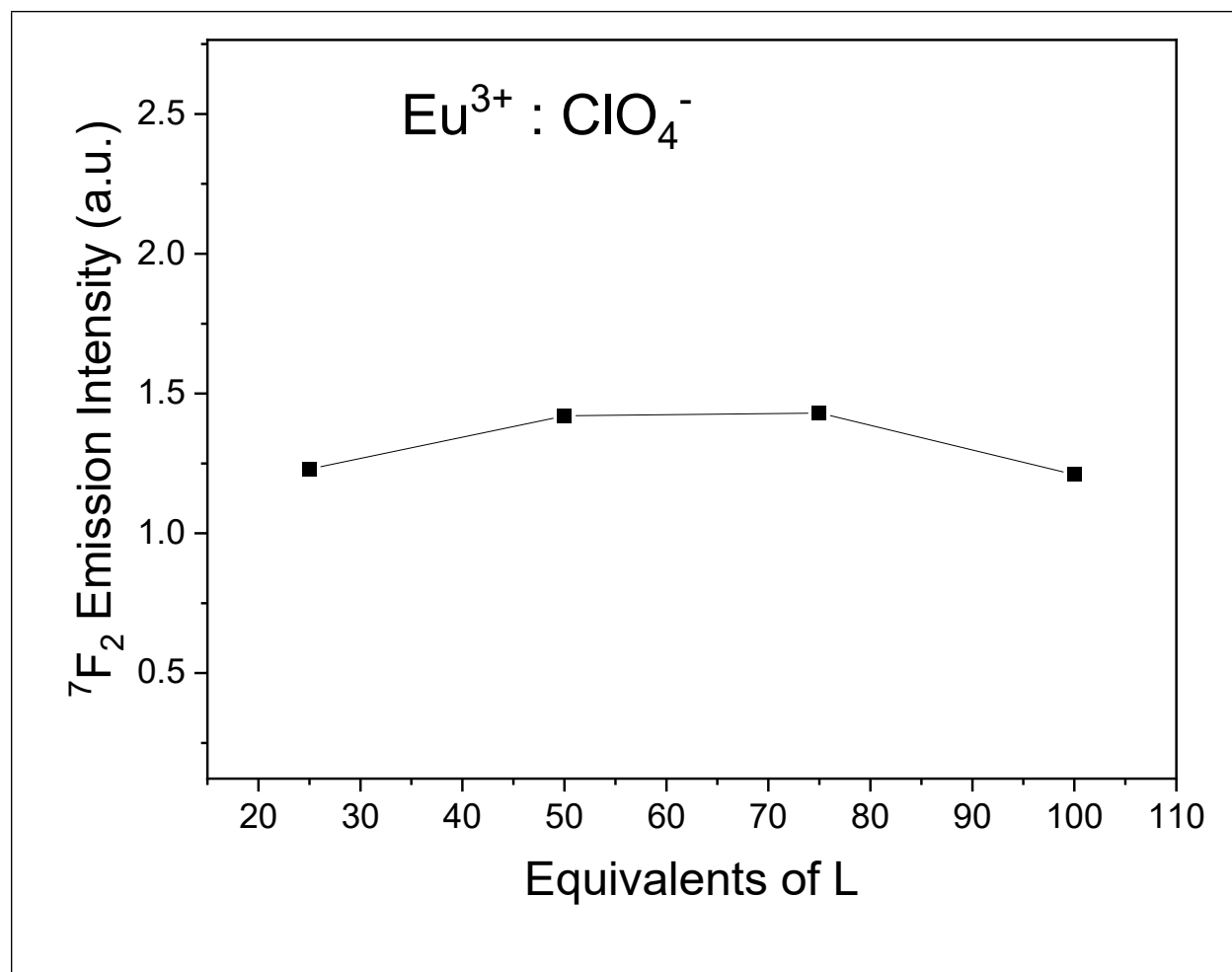


Figure S46. Emission intensity of the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ emission band of Eu^{3+} in NaCl-MES buffer as a function of equivalents of ClO_4^- . The emission intensity was taken as the integration over the full ${}^7\text{F}_2$ band (606-637 nm).

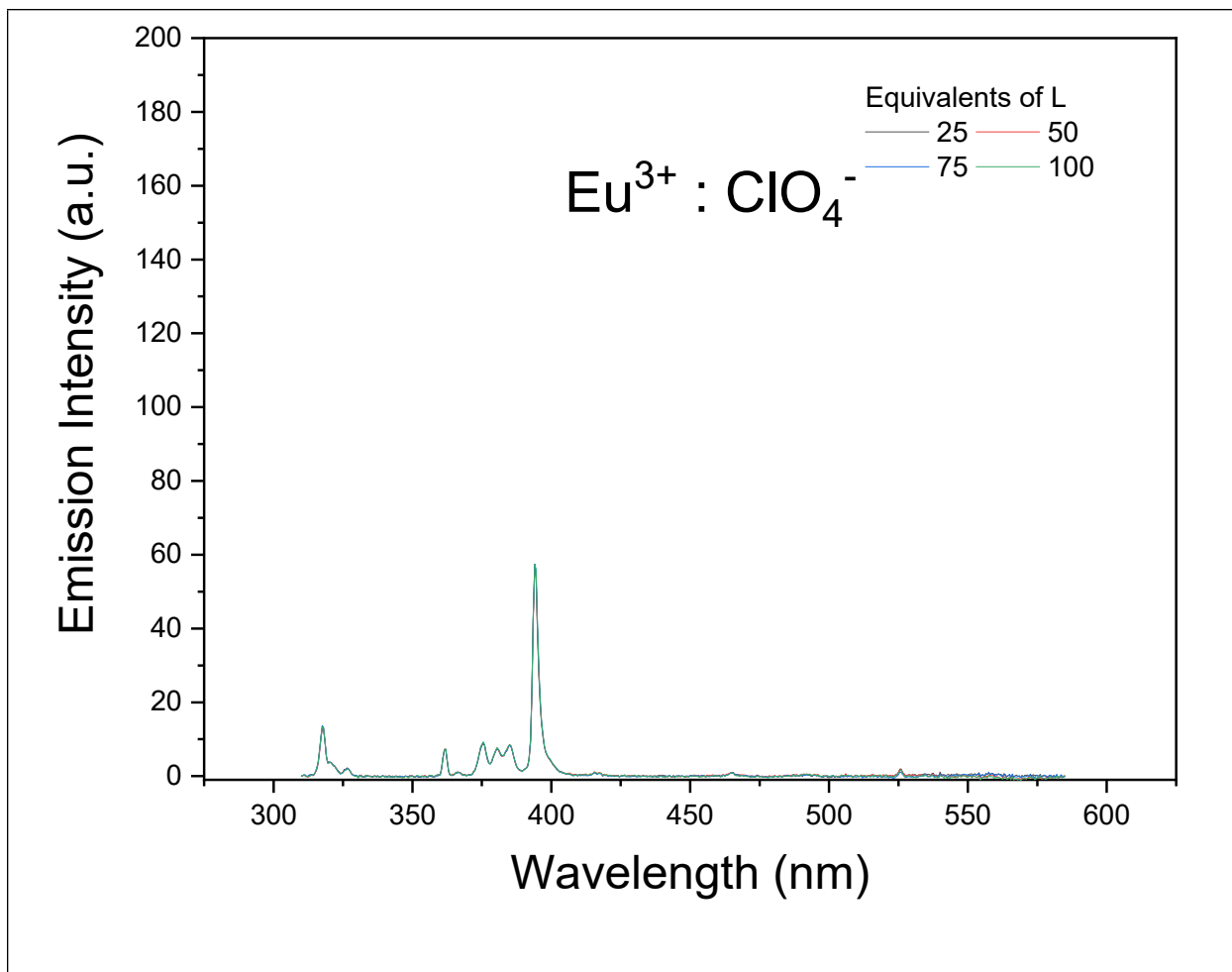


Figure S47. Excitation spectrum of Eu^{3+} in NaCl-MES buffer with various equivalents of ClO_4^- .

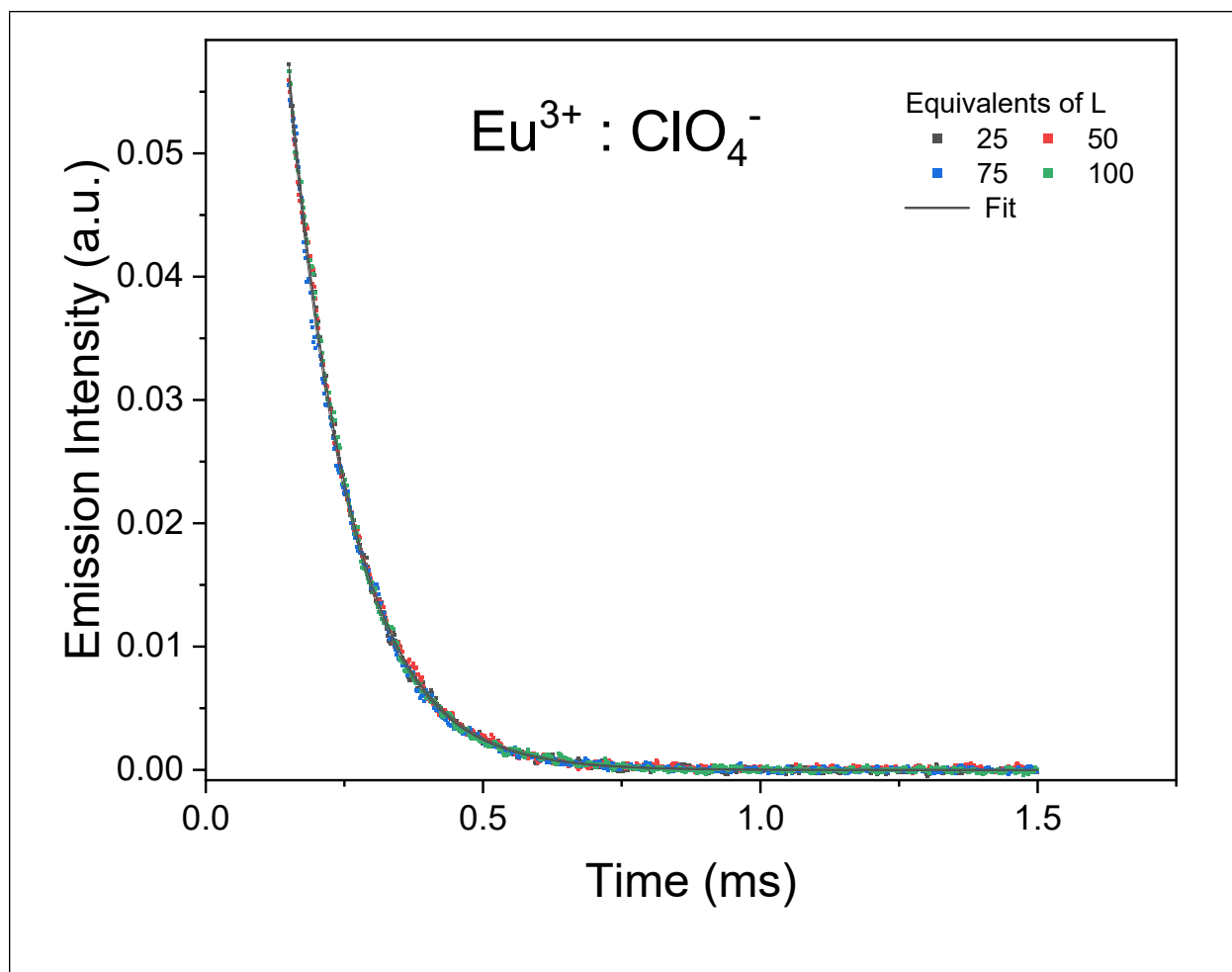


Figure S48. Time-resolved emission decay trace of Eu^{3+} in NaCl-MES buffer with various equivalents of ClO_4^- . The decay traces has been fit with a mono-exponential decay function.

Table S7. Fitting parameters for emission decay traces of $\text{Eu}^{3+} : \text{ClO}_4^-$.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
25	-5.48427E-5	1.42481E-5	0.21585	8.60649E-4	112.46709	0.25006
50	4.16029E-5	1.58827E-5	0.21096	9.3661E-4	113.47337	0.28288
75	-1.26346E-5	1.80902E-5	0.21269	0.00112	111.56605	0.32462
100	-4.2986E-5	1.43669E-5	0.21928	8.83699E-4	111.71682	0.24975

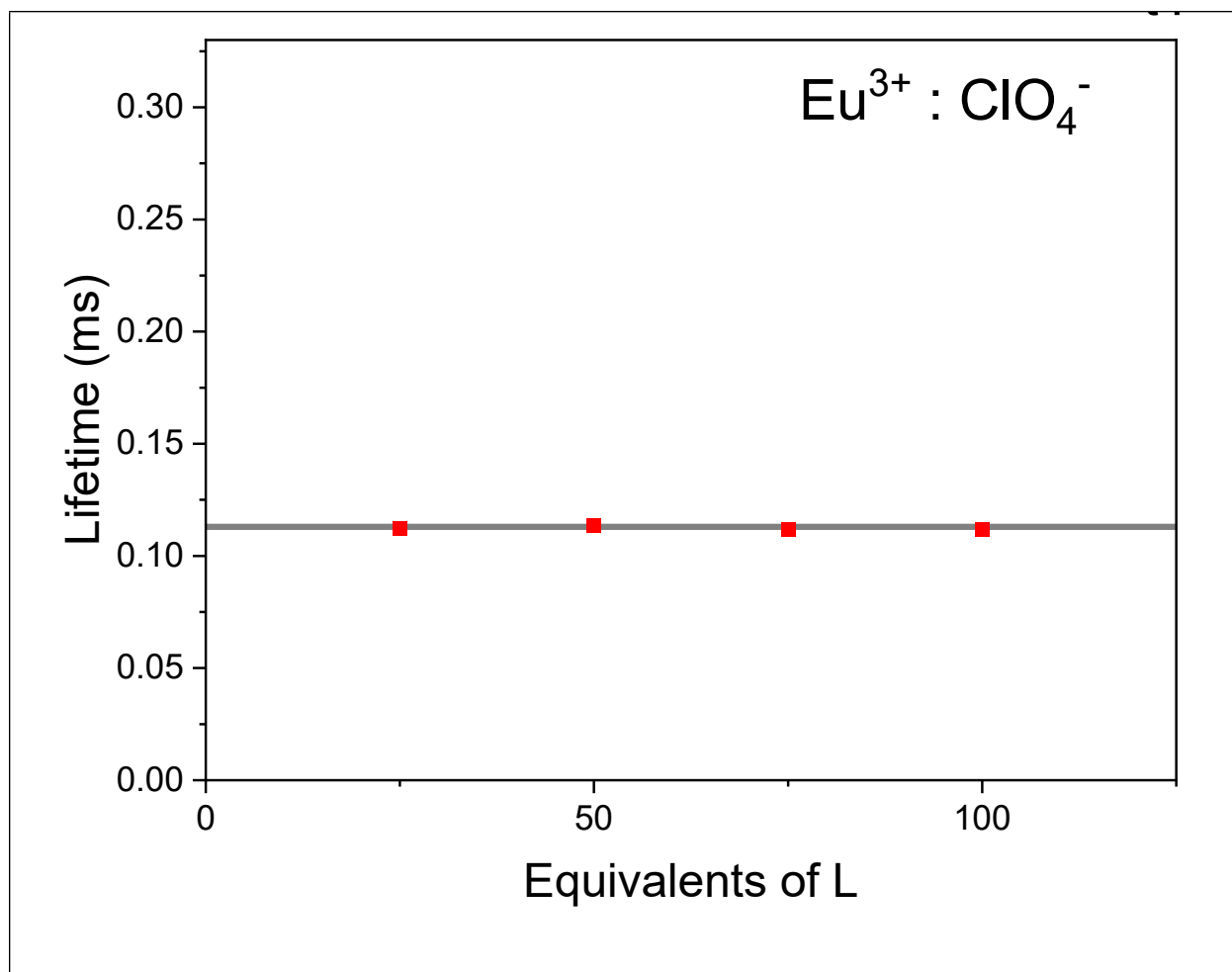


Figure S49. Excited state lifetime of Eu³⁺ in NaCl-MES buffer as a function of equivalents of ClO₄⁻. The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu³⁺ in water.

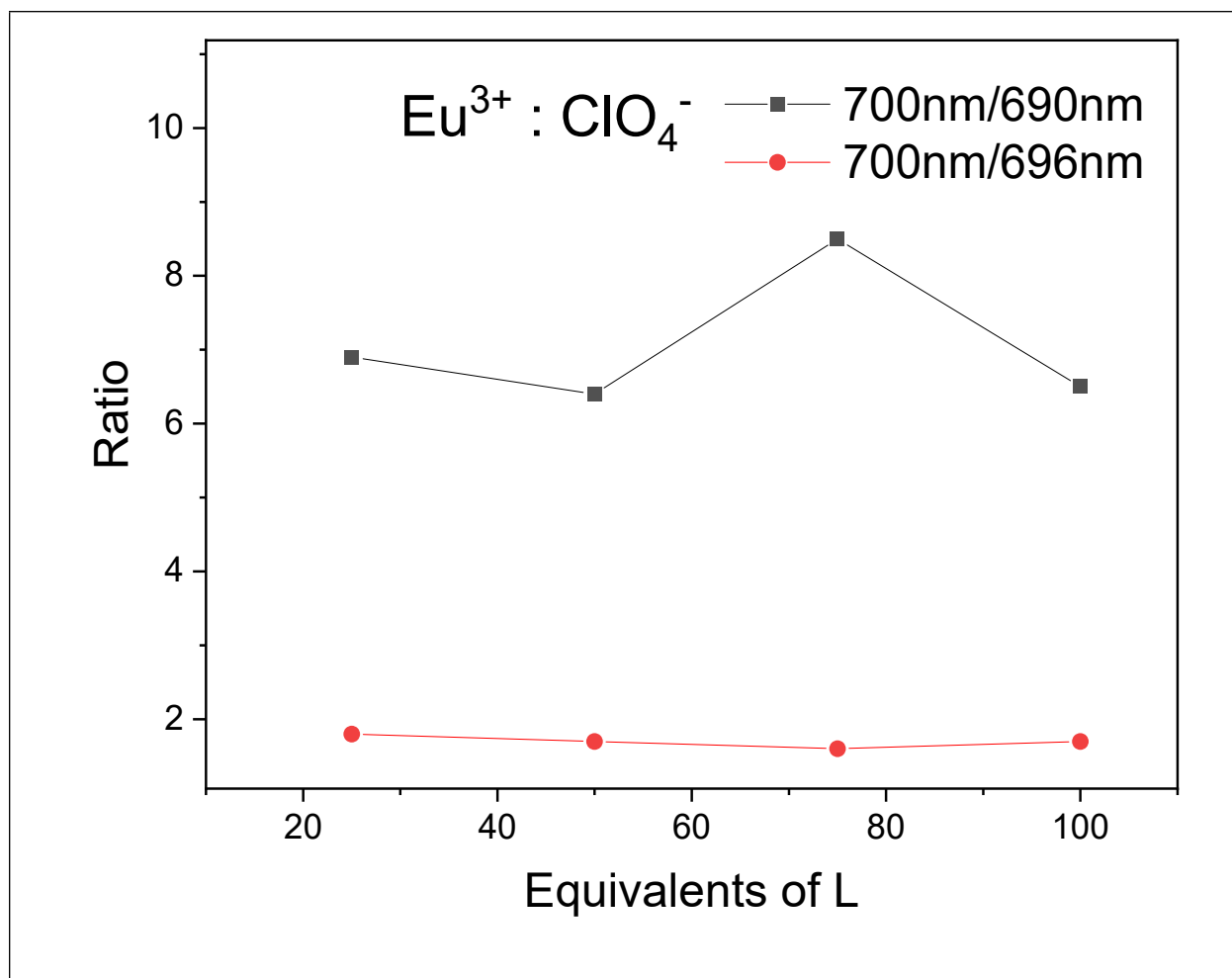
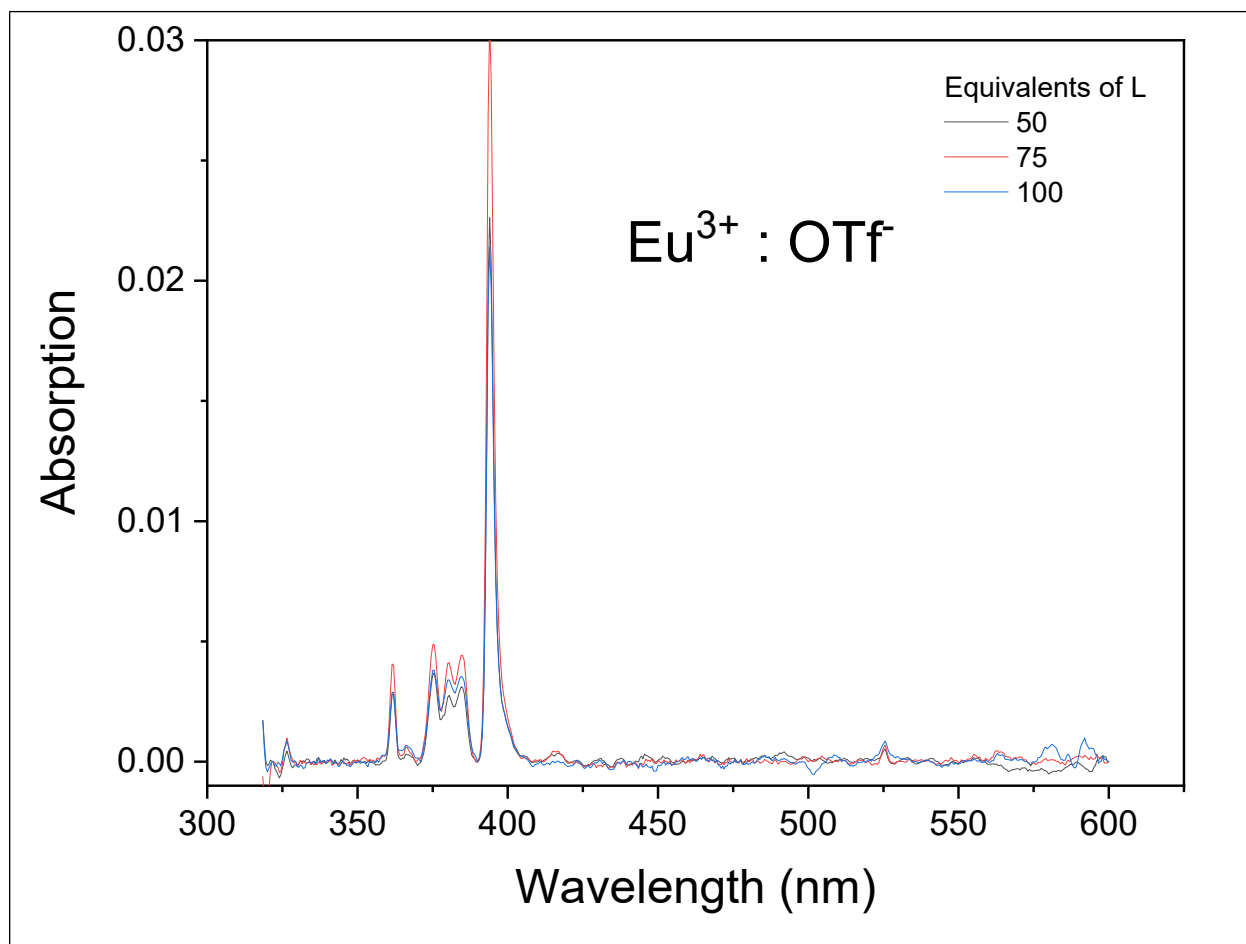


Figure S50. Ratios of emission intensity of Eu^{3+} in NaCl-MES buffer as a function of equivalents of ClO_4^- . The ratios give an indication of the changes in LF-splitting (see main text).

Eu³⁺ : OTf



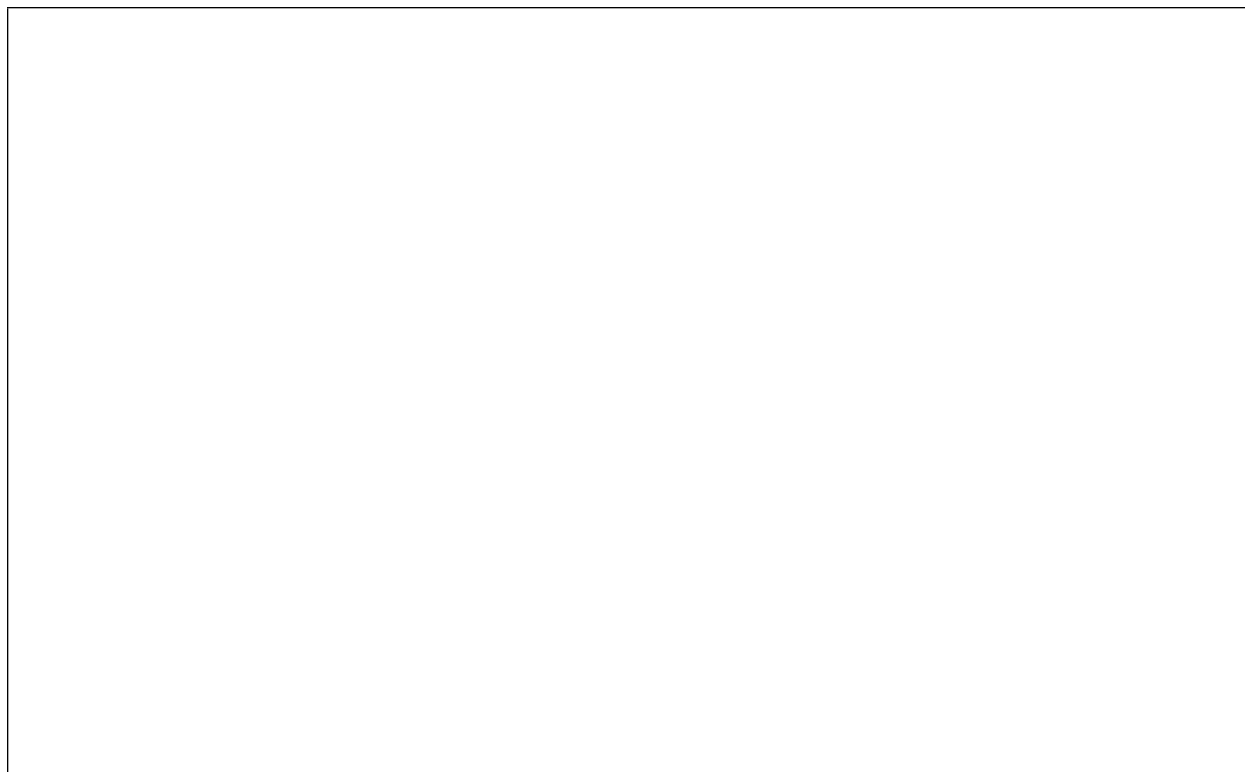


Figure S51. Absorption of Eu^{3+} in KCl-MES buffer with various equivalents of OTf.

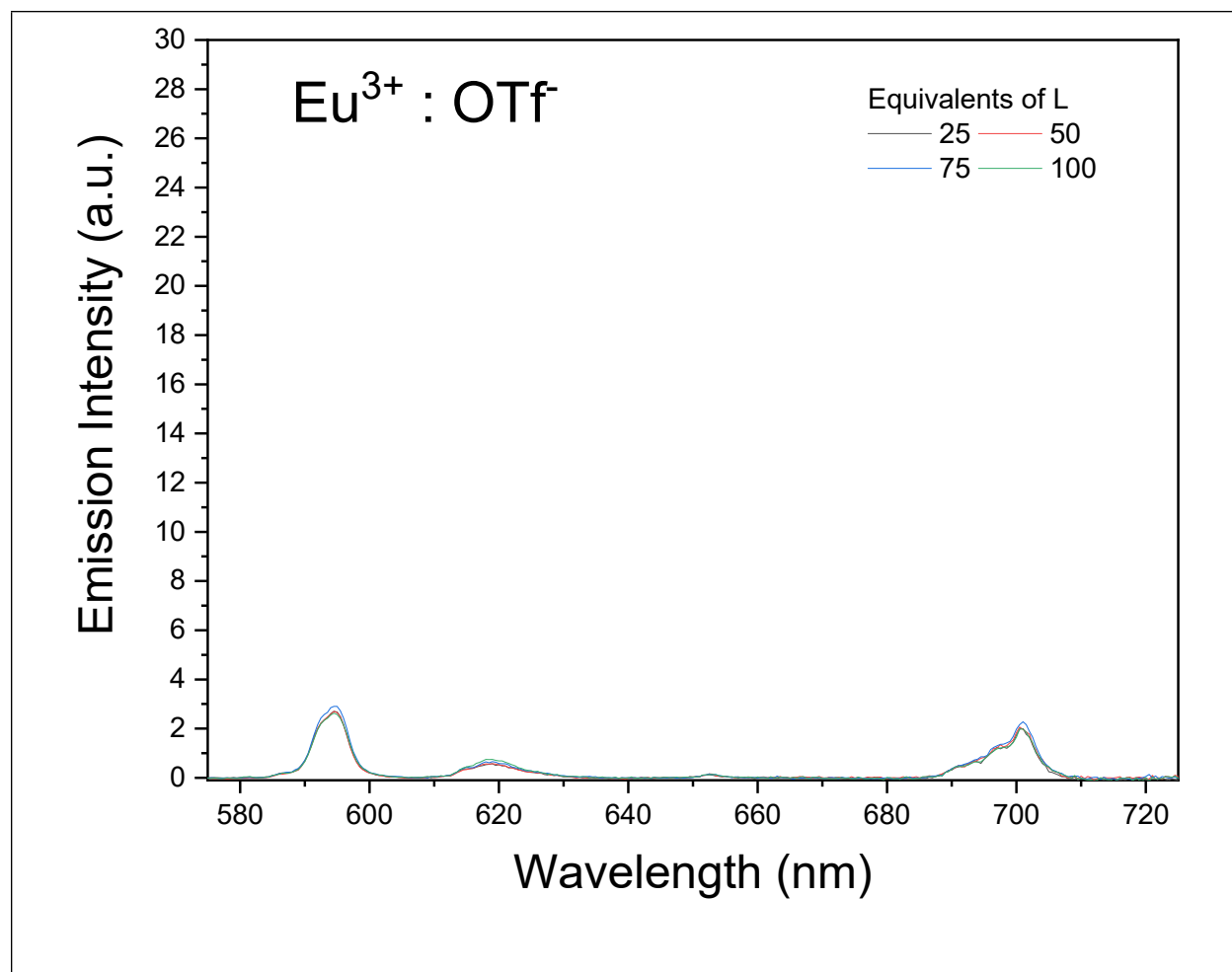


Figure S52. Emission spectrum of Eu³⁺ in KCl-MES buffer with various equivalents of OTf.

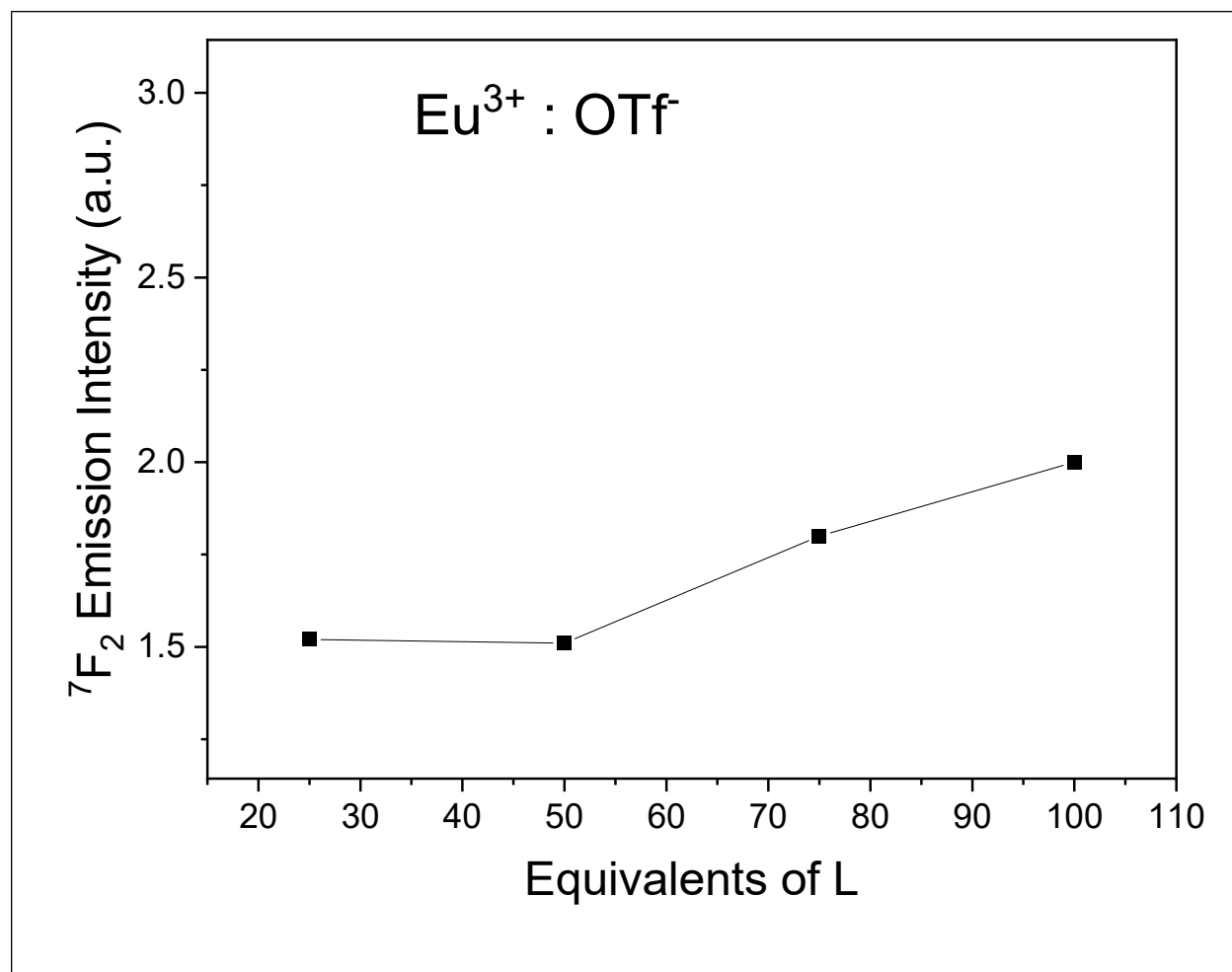


Figure S53. Emission intensity of the $^5D_0 \rightarrow ^7F_2$ emission band of Eu^{3+} in KCl-MES buffer as a function of equivalents of AcO^- . The emission intensity was taken as the integration over the full 7F_2 band (606-637 nm).

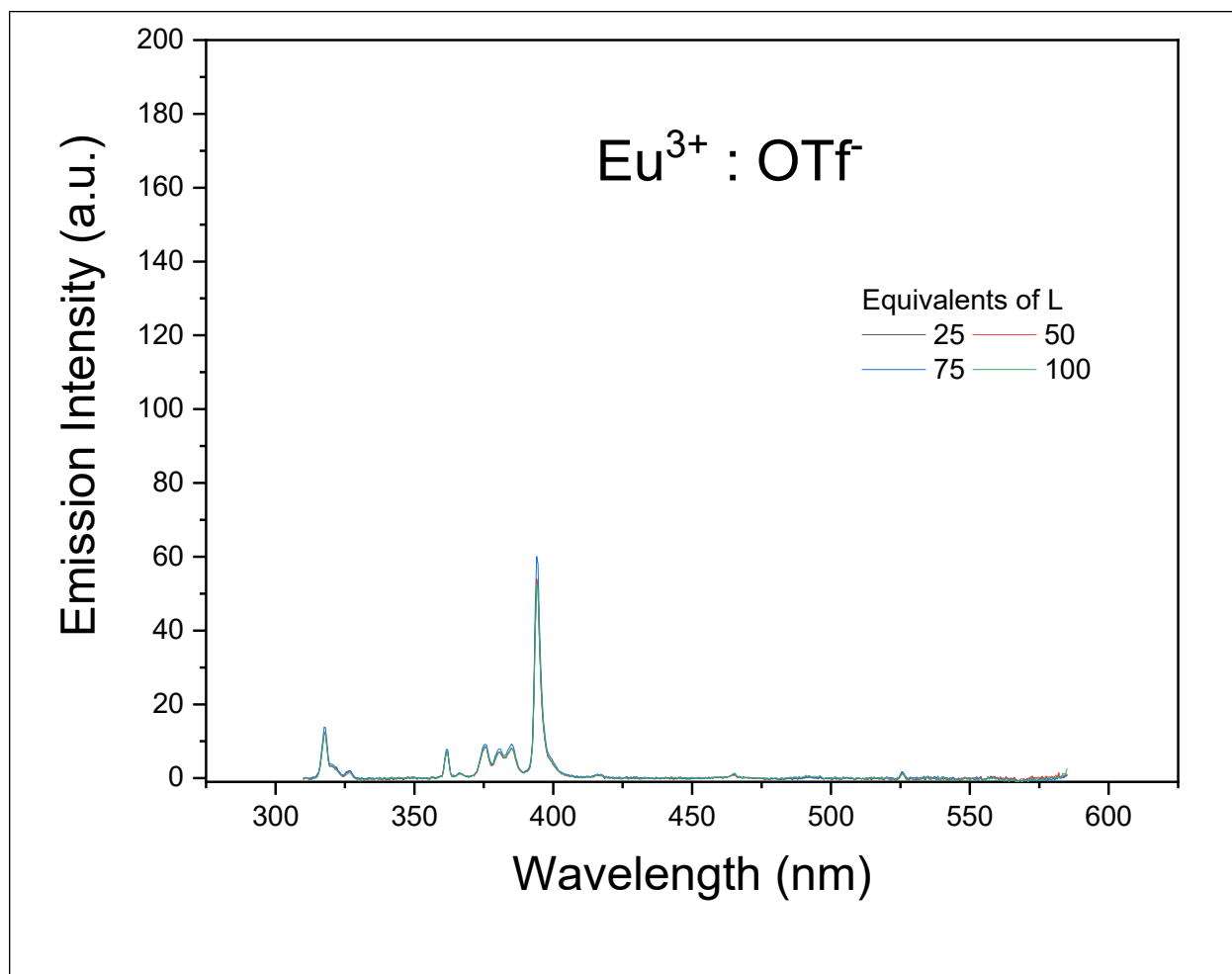


Figure S54. Excitation spectrum of Eu³⁺ in KCl-MES buffer with various equivalents of OTf⁻.

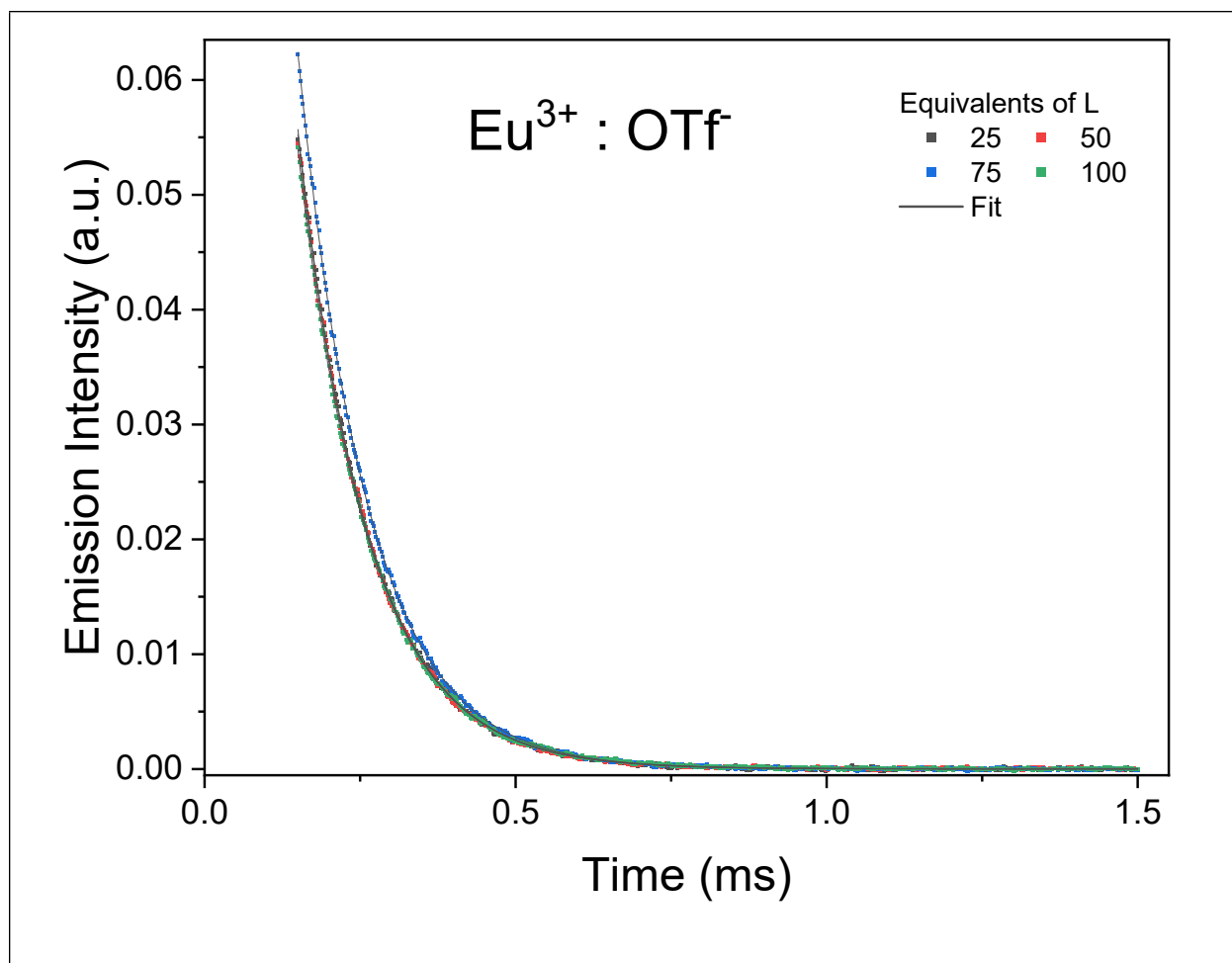


Figure S55. Time-resolved emission decay trace of Eu³⁺ in KCl-MES buffer with various equivalents of OTf. The decay traces has been fit with a mono-exponential decay function.

Table S8. Fitting parameters for emission decay traces of Eu^{3+} : OTf.

Trace	$y = A1 \cdot \exp(-x/t1) + y0$					
	y0	y0 (Error)	A1	A1 (Error)	t1	t1 (error)
25	-5.6932E-6	7.83155E-6	0.20997	4.66699E-4	113.03249	0.14064
50	9.87622E-6	7.43641E-6	0.20946	4.48494E-4	112.53194	0.13442
75	-6.89192E-6	6.68021E-6	0.23658	4.02555E-4	112.56624	0.10688
100	3.31164E-5	6.18182E-6	0.20149	3.61763E-4	113.79683	0.11498

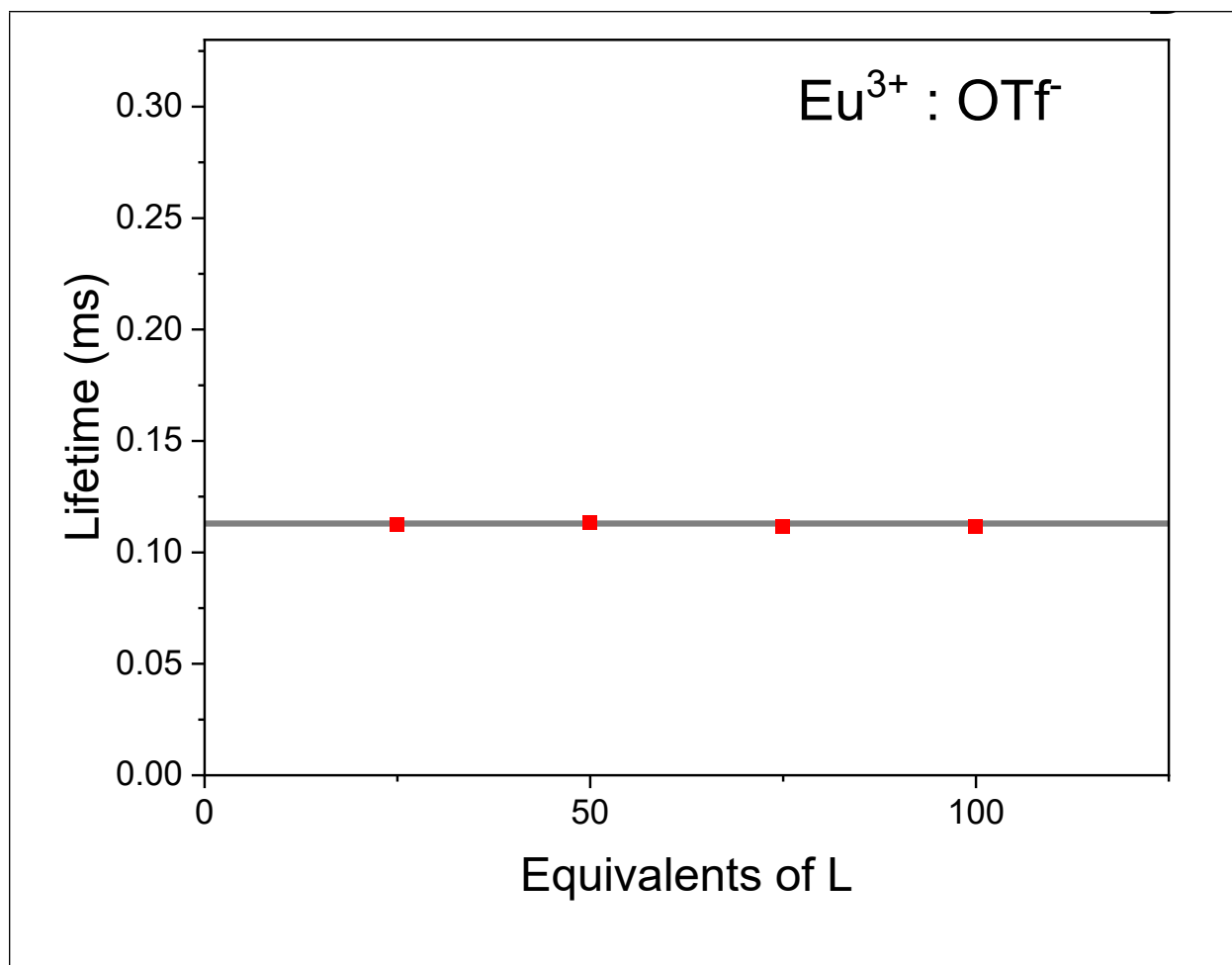


Figure S56. Excited state lifetime of Eu³⁺ in KCl-MES buffer as a function of equivalents of OTf. The lifetimes has been determined from a mono-exponential decay function. The grey bar indicates the excited state lifetime of Eu³⁺ in water.

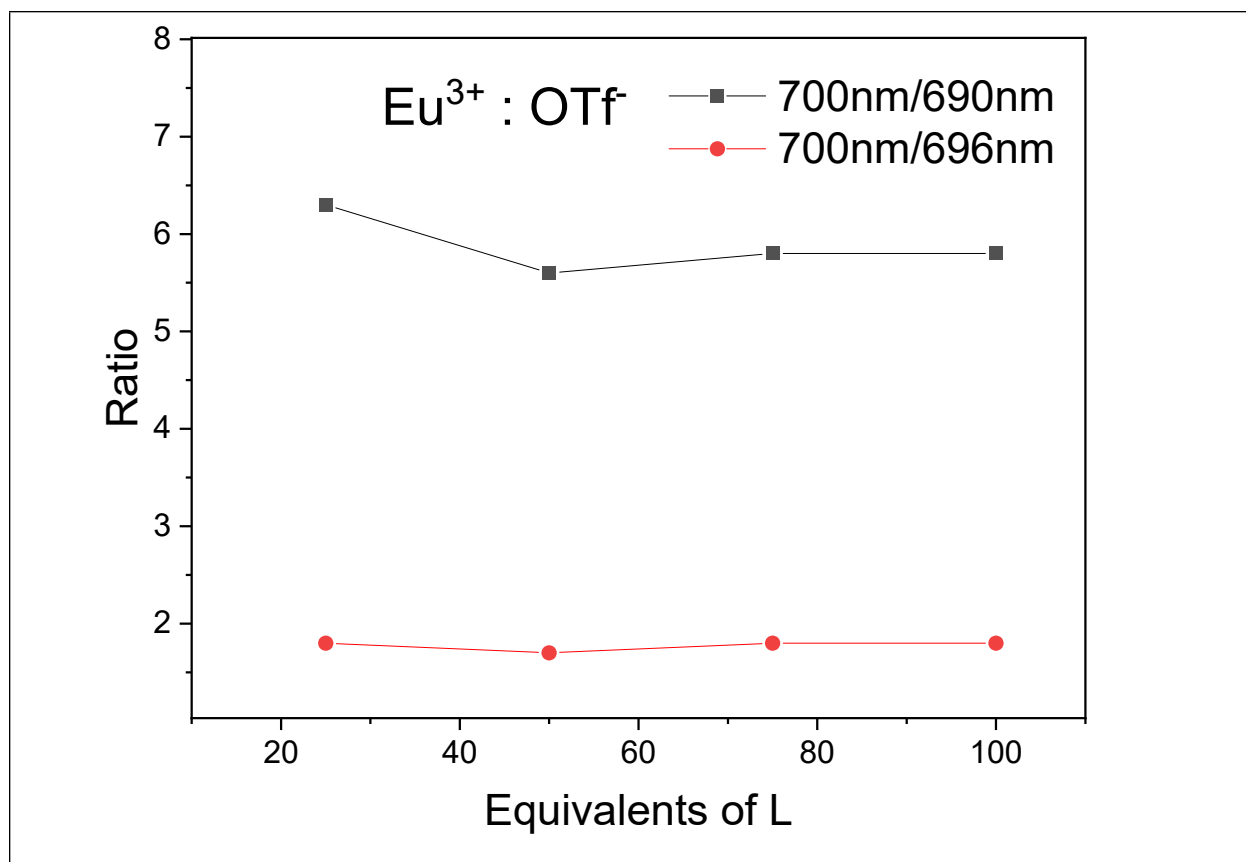


Figure S57. Ratios of emission intensity of Eu^{3+} in KCl-MES buffer as a function of equivalents of OTf. The ratios give an indication of the changes in LF-splitting (see main text).

System Screening

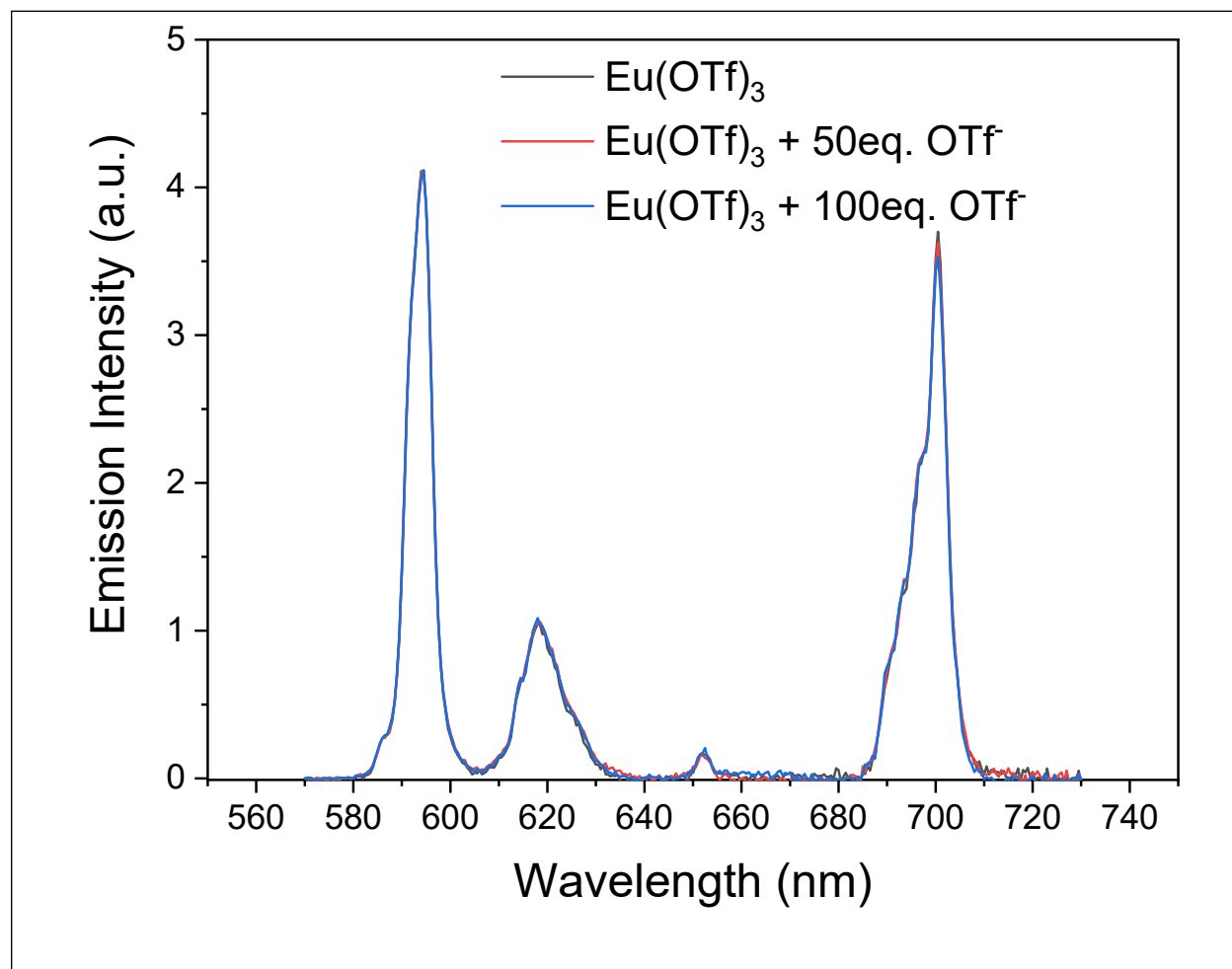


Figure S58. Emission spectrum of Eu(OTf)₃ in H₂O with 0, 50 and 100 eq. of OTf.

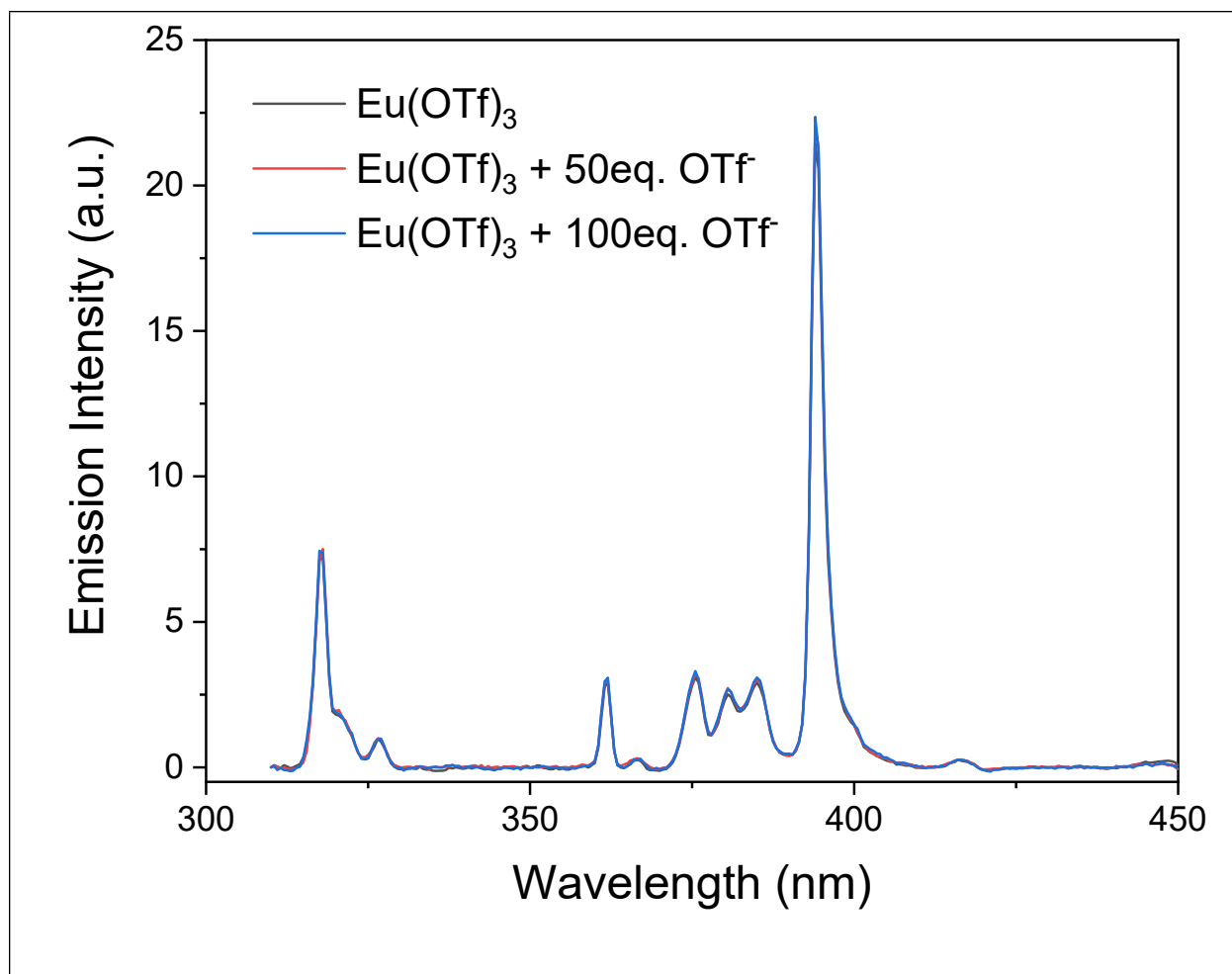


Figure S59. Excitation spectrum of $\text{Eu}(\text{OTf})_3$ in H_2O with 0, 50 and 100 eq. of OTf.

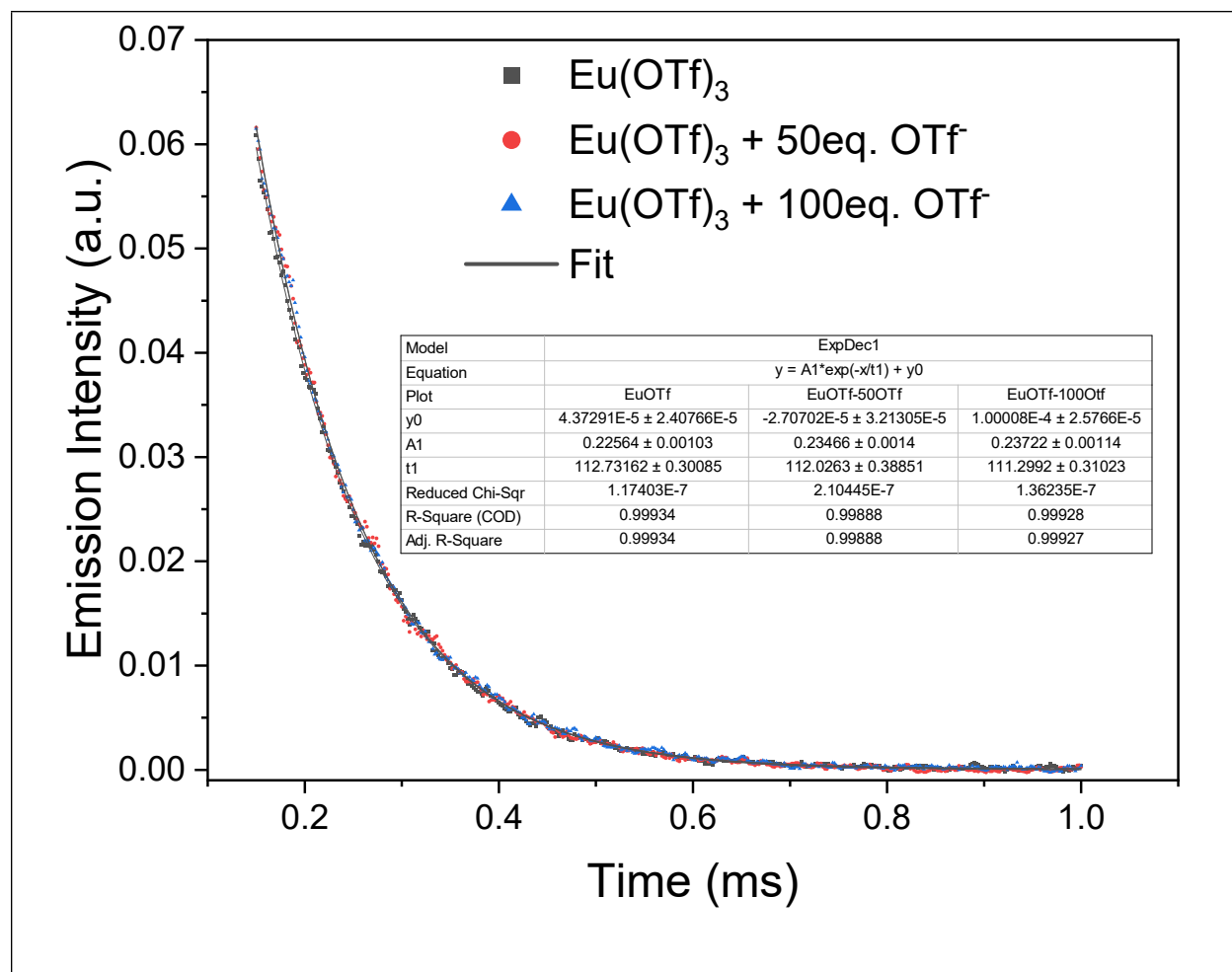


Figure S60. Time-resolved emission decay traces of $\text{Eu}(\text{OTf})_3$ in H_2O with 0, 50 and 100 eq. of OTf. The data was fit with a mono-exponential decay function

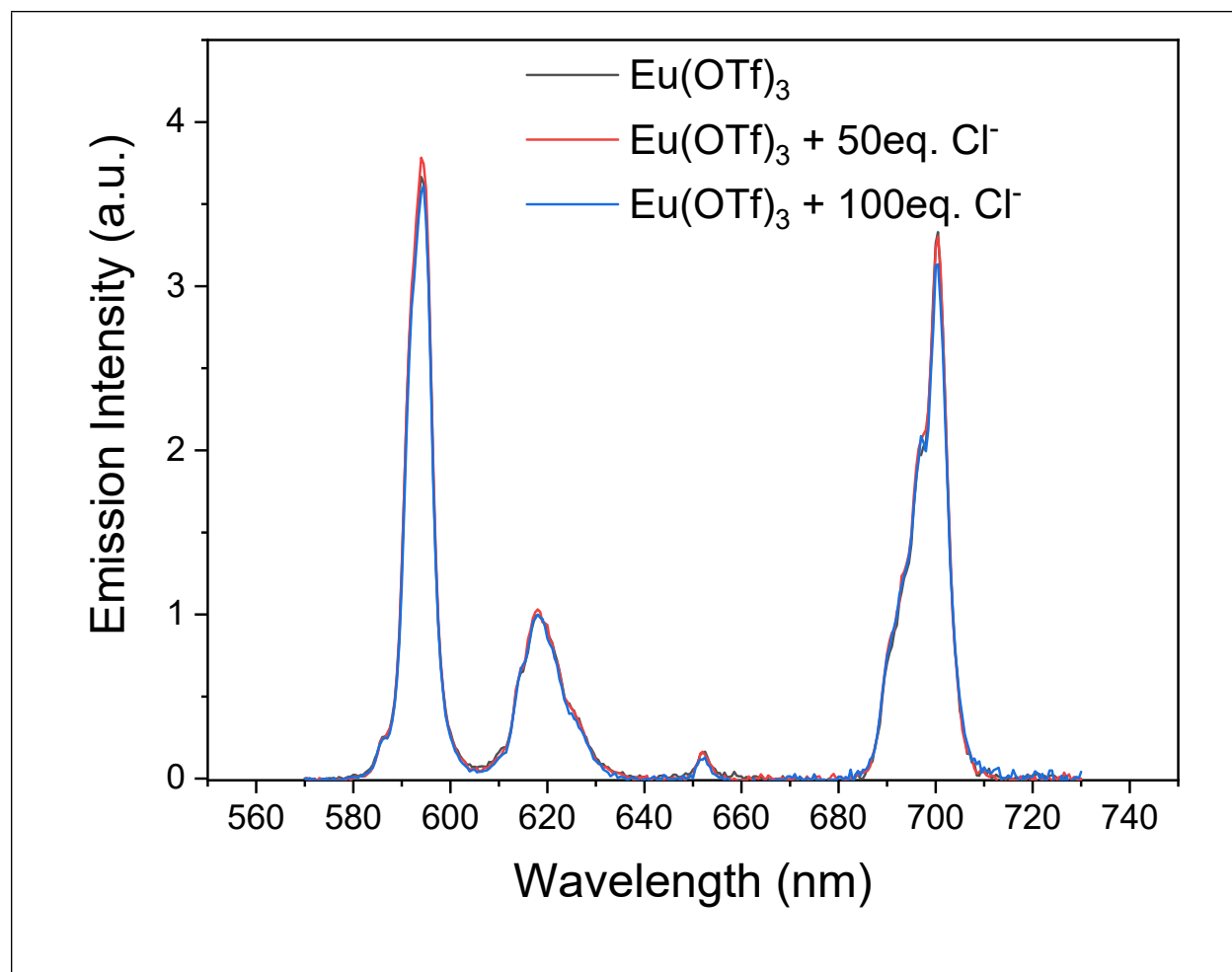


Figure S61. Emission spectrum of $\text{Eu}(\text{OTf})_3$ in H_2O with 0, 50 and 100 eq. of Cl^- .

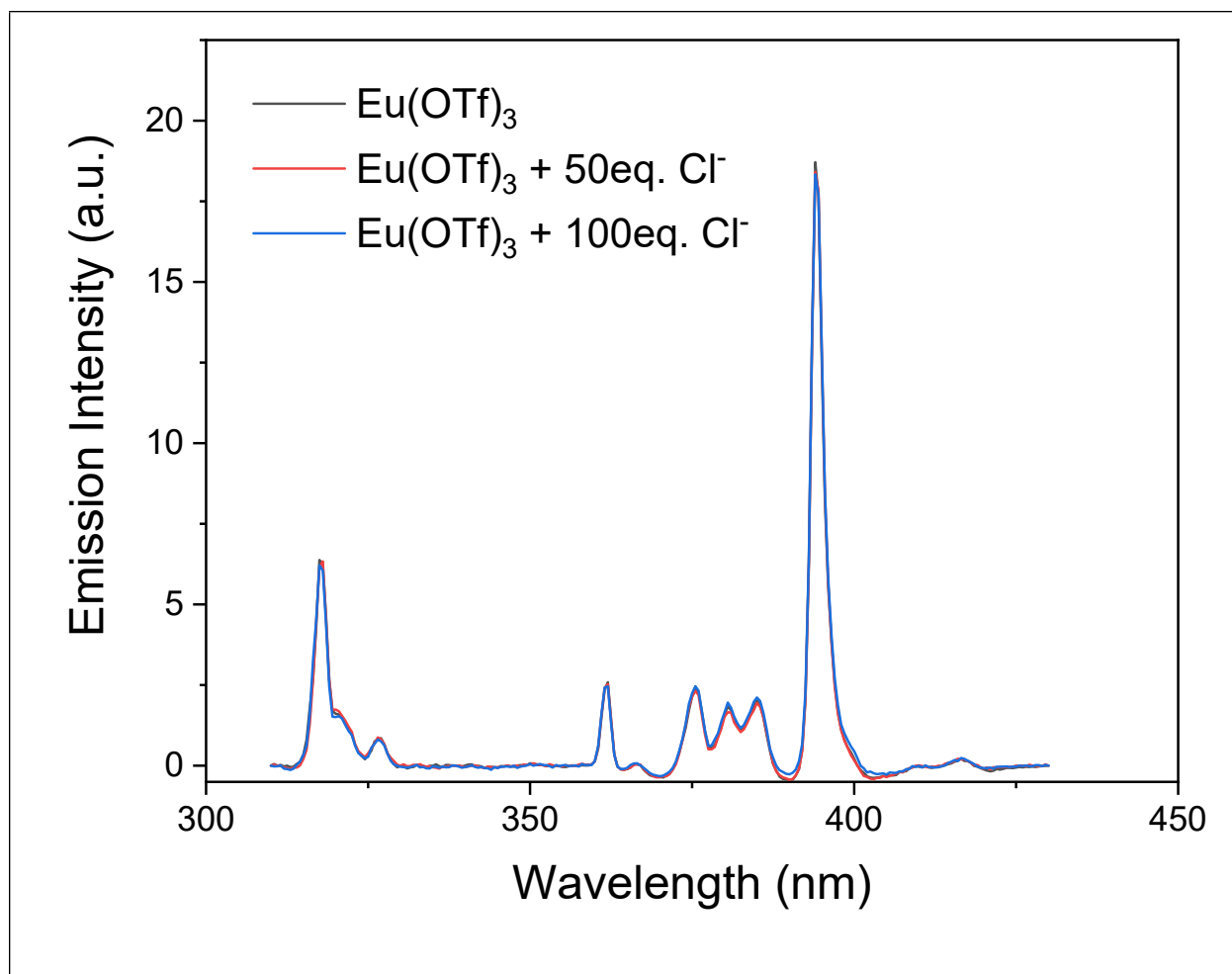


Figure S62. Excitation spectrum of $\text{Eu}(\text{OTf})_3$ in H_2O with 0, 50 and 100 eq. of Cl^- .

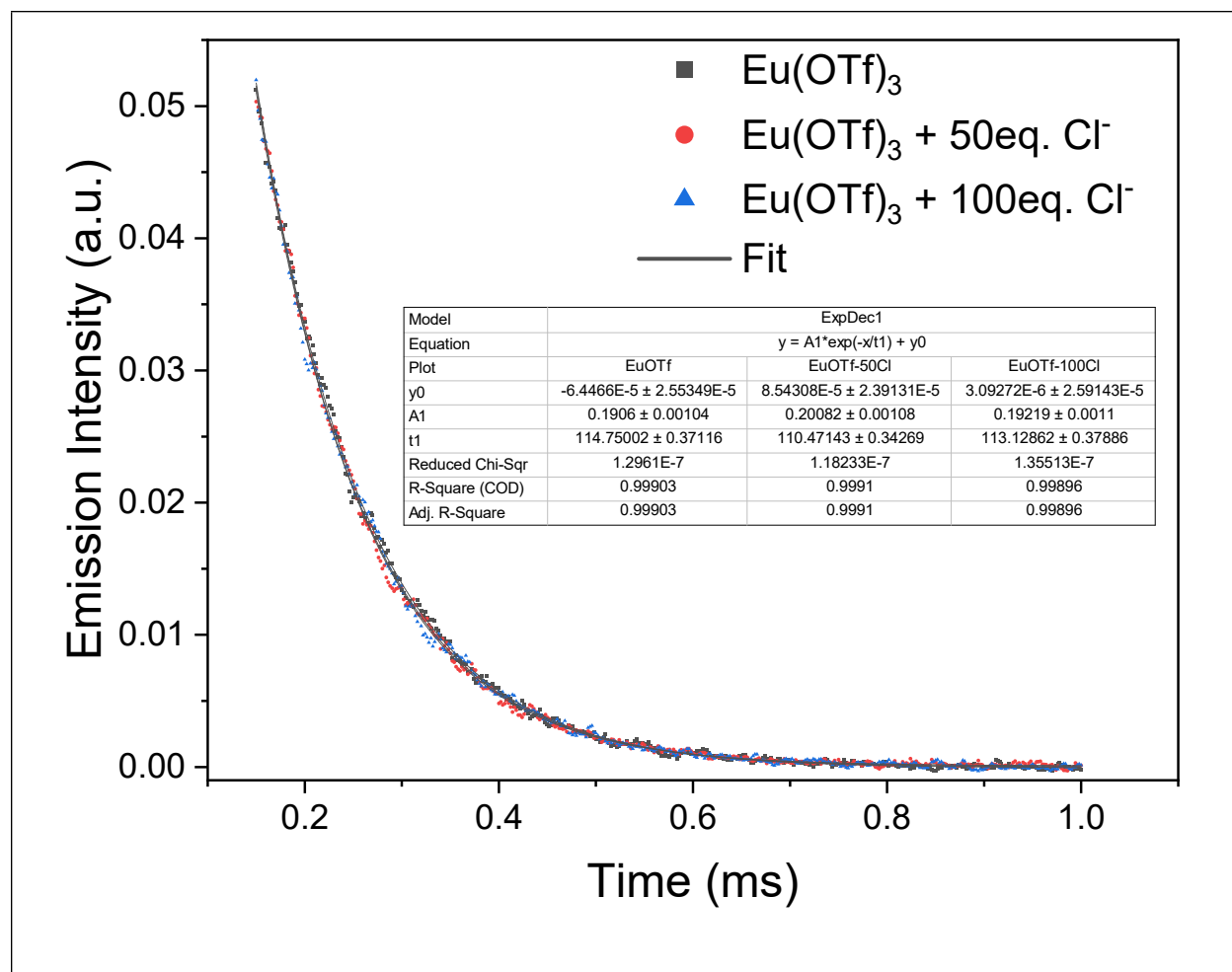


Figure S63. Time-resolved emission decay traces of $\text{Eu}(\text{OTf})_3$ in H_2O with 0, 50 and 100 eq. of Cl^- . The data was fit with a mono-exponential decay function

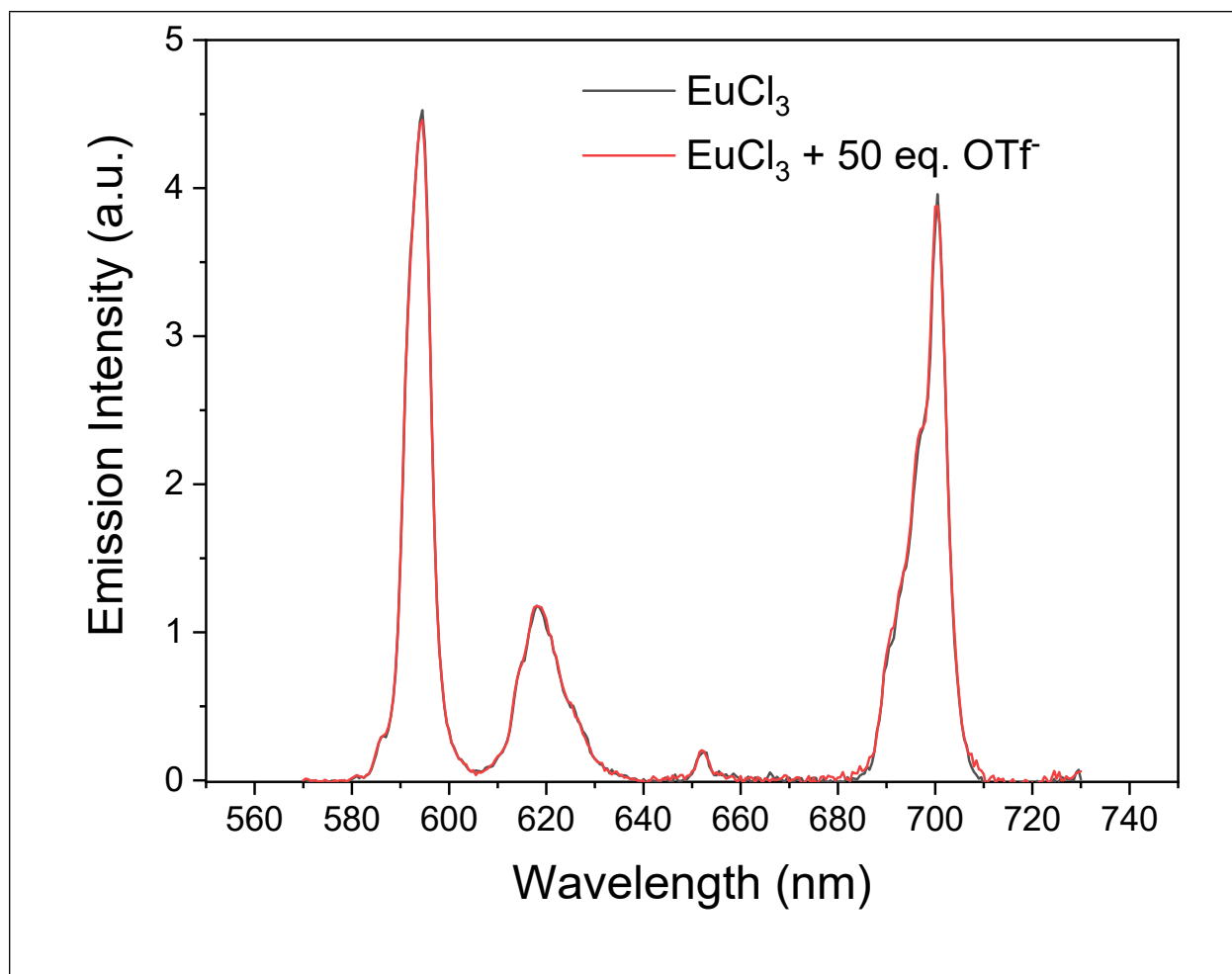


Figure S64. Emission spectrum of $\text{Eu}(\text{Cl})_3$ in H_2O with 0 and 100 eq. of OTf.

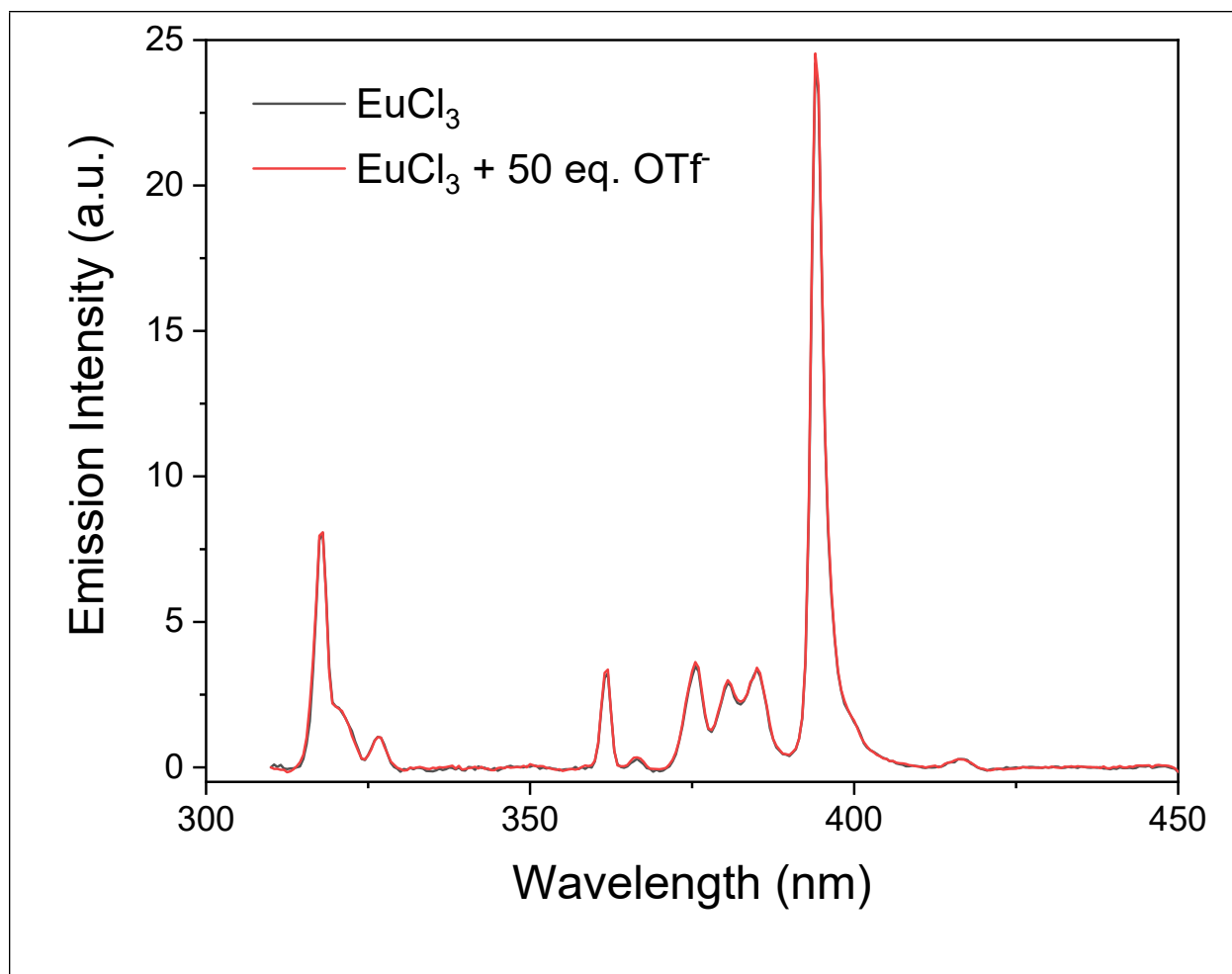


Figure S65. Excitation spectrum of $\text{Eu}(\text{Cl})_3$ in H_2O with 0 and 100 eq. of OTf.

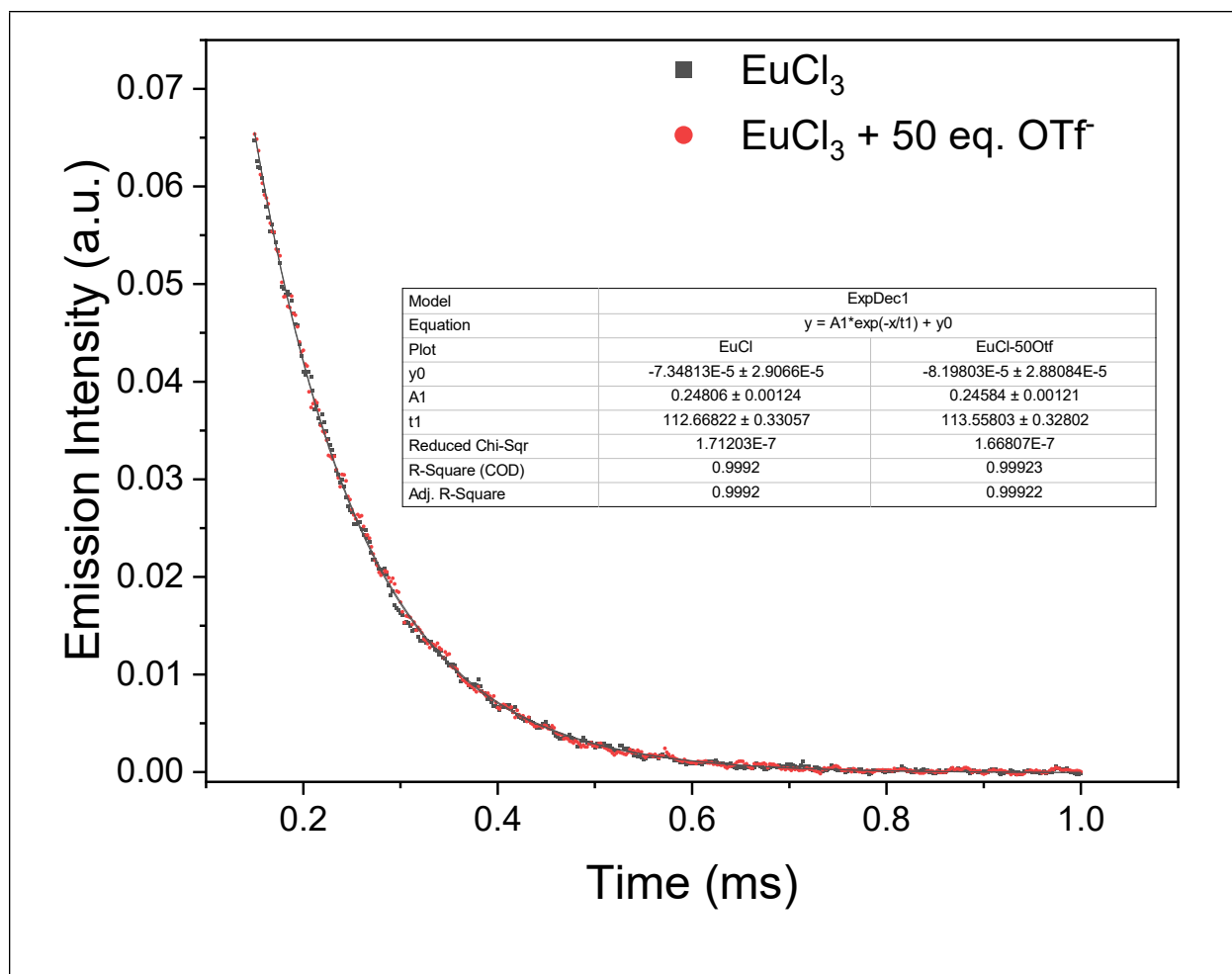


Figure S66. Time-resolved emission decay traces of $\text{Eu}(\text{Cl})_3$ in H_2O with 0 and 50 eq. of OTf. The data was fit with a mono-exponential decay function

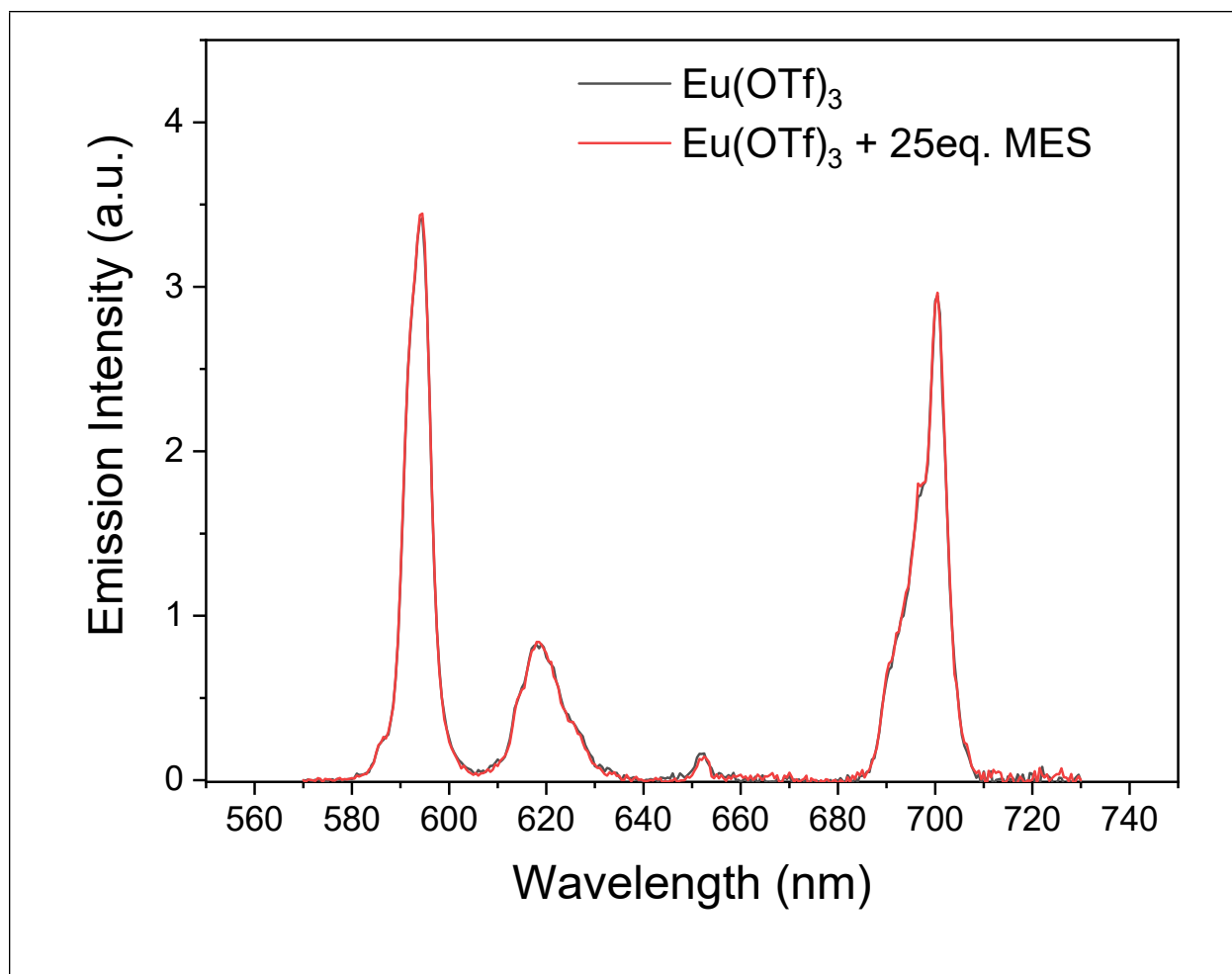


Figure S67. Emission spectrum of $\text{Eu}(\text{OTf})_3$ in H_2O with 0 and 25 eq. of MES.

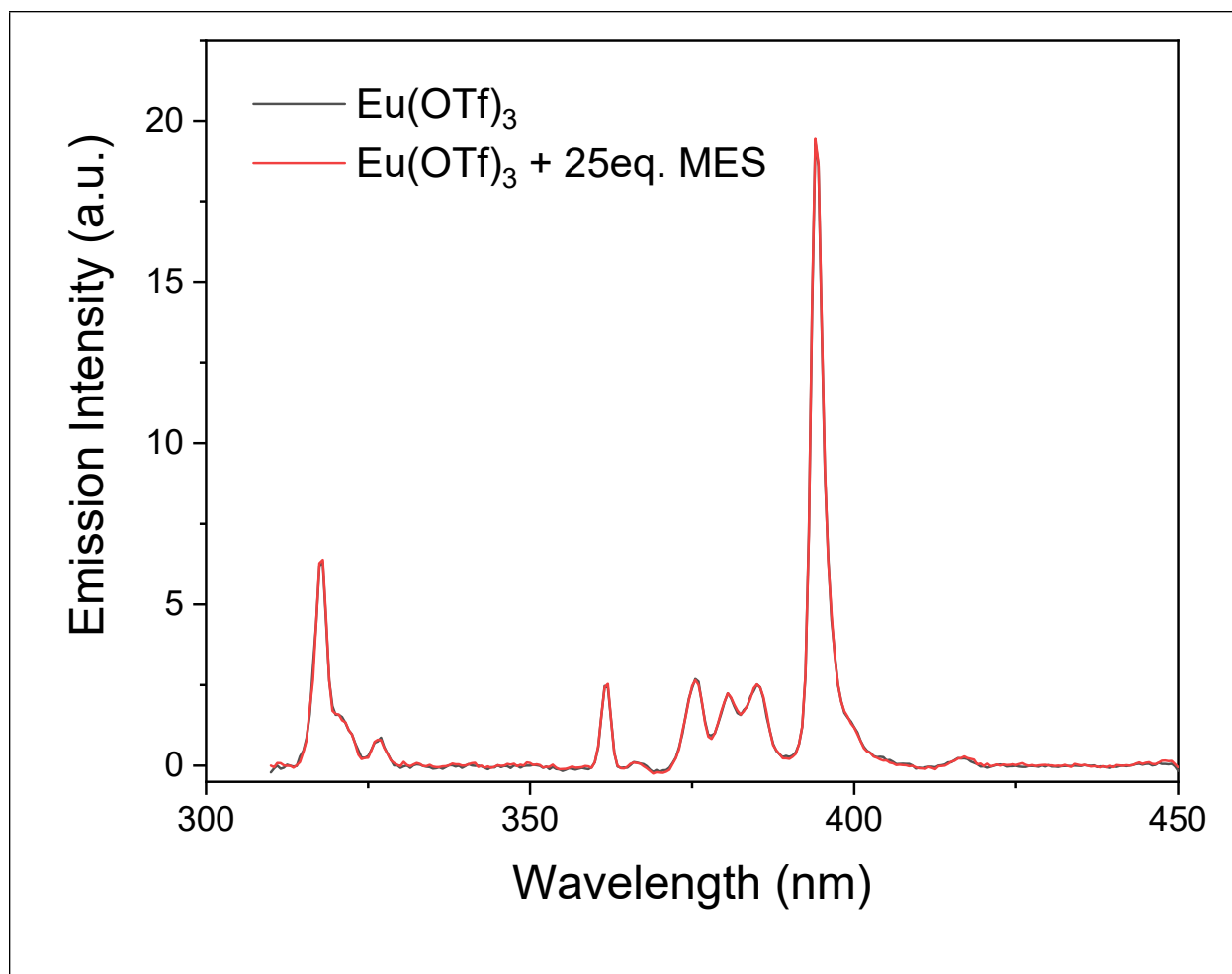


Figure S68. Excitation spectrum of $\text{Eu}(\text{OTf})_3$ in H_2O with 0 and 25 eq. of MES.

pH and Conductivity

Table S9. pH and conductivity of Eu^{3+} in NaCl-MES buffer (EDTA, ClO_4^-) or KCl-MES buffer (AcO^- , NO_3^- , HSO_4^- , SO_4^- , Cl^- , OTf) with the ligands studied. Samples were prepared by adding 3.000 mL of Eu^{3+} Stock, the noted amount of Ligand Stock and adding water up to 4.000 mL. The final samples all contain 0.001 M $\text{Eu}(\text{CF}_3\text{SO}_3)_3$, 1M NaCl/KCl and 0.02M MES as well as the noted concentration of ligand.

	Equivalent s	$\text{Eu}(\text{CF}_3\text{SO}_3)_3$ (M)	L Sample (M)	Eu^{3+} Stock ^a (mL)	L Stock (mL)	Water (mL)	L Stock ^b (M)	pH	Conductivity	Ionic Strength ^c $\times 10^6$
Eu^{3+} (a)	-	0.01	-	3.000	-	1.000	-	5.47	108.5	1.74
EDTA	0.05	0.01	0.0005	3.000	0.017	0.983	0.12	5.35	90.5	1.45
	0.1	0.01	0.001	3.000	0.033	0.967	0.12	5.25	95.4	1.53
	0.2	0.01	0.002	3.000	0.067	0.933	0.12	5.07	92.5	1.48
	0.3	0.01	0.003	3.000	0.100	0.900	0.12	4.77	93	1.49
	0.4	0.01	0.004	3.000	0.133	0.867	0.12	3.89	92.4	1.48
	0.5	0.01	0.005	3.000	0.167	0.833	0.12	2.99	96.9	1.55
	0.6	0.01	0.006	3.000	0.200	0.800	0.12	2.74	95	1.52
	0.7	0.01	0.007	3.000	0.233	0.767	0.12	2.58	89.8	1.44
	0.8	0.01	0.008	3.000	0.267	0.733	0.12	2.4	91.2	1.46
	0.9	0.01	0.009	3.000	0.300	0.700	0.12	2.35	92.2	1.48
	1	0.01	0.01	3.000	0.333	0.667	0.12	2.44	92.1	1.47
	1.5	0.01	0.015	3.000	0.500	0.500	0.12	5.2	93.7	1.50
	2	0.01	0.02	3.000	0.667	0.333	0.12	5.56	90.2	1.44
3	0.01	0.03	3.000	1.000	0.000	0.12	6.15	86.8	1.39	
AcO^-	0.2	0.01	0.002	3.000	0.002	0.998	4	5.58	113.6	1.82
	0.4	0.01	0.004	3.000	0.004	0.996	4	5.6	113.9	1.82
	0.6	0.01	0.006	3.000	0.006	0.994	4	5.63	113.3	1.81
	0.8	0.01	0.008	3.000	0.008	0.992	4	5.7	114	1.82
	1	0.01	0.01	3.000	0.010	0.990	4	5.66	111.9	1.79
	2	0.01	0.02	3.000	0.020	0.980	4	5.75	114.7	1.84
	3	0.01	0.03	3.000	0.030	0.970	4	5.81	114.6	1.83
	4	0.01	0.04	3.000	0.040	0.960	4	5.86	114.1	1.83
	5	0.01	0.05	3.000	0.050	0.950	4	5.89	106.7	1.71
	7	0.01	0.07	3.000	0.070	0.930	4	-	120.1	1.92
	10	0.01	0.1	3.000	0.100	0.900	4	5.98	113.6	1.82
	15	0.01	0.15	3.000	0.150	0.850	4	6.17	120.1	1.92

20	0.01	0.2	3.000	0.200	0.800	4	6.2 5	119.4	1.91
25	0.01	0.25	3.000	0.250	0.750	4	6.3	125.2	2.00
33	0.01	0.3	3.000	0.300	0.700	4	6.4 3	127.6	2.04
40	0.01	0.4	3.000	0.400	0.600	4	6.4 9	134.5	2.15
50	0.01	0.5	3.000	0.500	0.500	4	6.5 6	135.4	2.17
60	0.01	0.6	3.000	0.600	0.400	4	6.6 4	139.3	2.23
70	0.01	0.7	3.000	0.700	0.300	4	6.7 3	149.8	2.40
80	0.01	0.8	3.000	0.800	0.200	4	-	153.4	2.45
90	0.01	0.9	3.000	0.900	0.100	4	6.8 4	157.4	2.52
100	0.01	1	3.000	1.000	0.000	4	6.8 8	154.8	2.48
130	0.01	1.3	3.000	0.867	0.133	6	7.0 3	164.9	2.64
150	0.01	1.5	3.000	1.000	0.000	6	7.1 4	173.8	2.78

Table S9. Continued

	Equivalent s	Eu(CF ₃ SO ₃) ₃ (M)	L Sample (M)	Eu ³⁺ Stock ^a (mL)	L Stock (mL)	Water (mL)	L Stock ^b (M)	pH	Conductivity	Ionic Strength ^c x10 ⁶
NO ₃ ⁻	3	0.01	0.03	3.000	0.015	0.985	8	5.5	111.6	1.79
	5	0.01	0.05	3.000	0.025	0.975	8	5.5	110.6	1.77
	7	0.01	0.07	3.000	0.035	0.965	8	5.4 9	112.8	1.80
	8	0.01	0.08	3.000	0.040	0.960	8	5.4 9	112.1	1.79
	10	0.01	0.10	3.000	0.050	0.950	8	5.5 1	118.7	1.90
	25	0.01	0.25	3.000	0.125	0.875	8	5.5	121.9	1.95
	30	0.01	0.30	3.000	0.150	0.850	8	5.5	127.2	2.04
	35	0.01	0.35	3.000	0.175	0.825	8	5.5	122.7	1.96
	40	0.01	0.40	3.000	0.200	0.800	8	5.5 3	130.4	2.09
	50	0.01	0.50	3.000	0.250	0.750	8	5.5 2	136	2.18
	60	0.01	0.60	3.000	0.300	0.700	8	5.5 2	131.4	2.10
	80	0.01	0.80	3.000	0.400	0.600	8	5.5 4	142.1	2.27
	100	0.01	1.00	3.000	0.500	0.500	8	5.5 4	155.2	2.48
	133	0.01	1.33	3.000	0.665	0.335	8	5.5 9	162.7	2.60
	150	0.01	1.50	3.000	0.750	0.250	8	5.5 8	164.2	2.63
	200	0.01	2.00	3.000	1.000	0.000	8	5.6 3	187.5	3.00
HSO ₄ ⁻	0.5	0.01	0.01	3.000	0.010	0.990	2	2.2 2	92	1.47
	1	0.01	0.01	3.000	0.020	0.980	2	1.9 8	136.8	2.19
	2	0.01	0.02	3.000	0.040	0.960	2	1.7 4	123.8	1.98
	3	0.01	0.03	3.000	0.060	0.940	2	1.5	140.5	2.25
	4	0.01	0.04	3.000	0.080	0.920	2	1.4 1	140.4	2.25
	5	0.01	0.05	3.000	0.100	0.900	2	1.1 6	102.9	1.65
	6	0.01	0.06	3.000	0.120	0.880	2	1.2 8	142.7	2.28
	7	0.01	0.07	3.000	0.140	0.860	2	1.2 5	143.8	2.30
	8	0.01	0.08	3.000	0.160	0.840	2	1.2 4	137	2.19
	9	0.01	0.09	3.000	0.180	0.820	2	1.1 6	146.1	2.34
	10	0.01	0.10	3.000	0.200	0.800	2	1.1 5	150.1	2.40
	15	0.01	0.15	3.000	0.300	0.700	2	1.0 6	152.7	2.44
	20	0.01	0.20	3.000	0.400	0.600	2	-	-	-
	25	0.01	0.25	3.000	0.500	0.500	2	-	-	-
	30	0.01	0.30	3.000	0.600	0.400	2	-	-	-
	35	0.01	0.35	3.000	0.700	0.300	2	-	-	-
40	0.01	0.4	3.000	0.800	0.200	2	-	-	-	
45	0.01	0.45	3.000	0.900	0.100	2	-	-	-	
S	0.5	0.01	0.01	3.000	0.010	0.990	2	-	132.4	2.12
	1	0.01	0.01	3.000	0.020	0.980	2	5.2	126	2.02

	2	0.01	0.02	3.000	0.040	0.960	2	4 5.2	133	2.13
	3	0.01	0.03	3.000	0.060	0.940	2	5.2 5	124.9	2.00
	4	0.01	0.04	3.000	0.080	0.920	2	5.3 5	91.3	1.46
	5	0.01	0.05	3.000	0.100	0.900	2	5.3 5	89.6	1.43
	6	0.01	0.06	3.000	0.120	0.880	2	5.2 7	124.8	2.00
	7	0.01	0.07	3.000	0.140	0.860	2	5.2 7	129.4	2.07
	8	0.01	0.08	3.000	0.160	0.840	2	5.2 7	124.7	2.00
	9	0.01	0.09	3.000	0.180	0.820	2	5.3 4	95.3	1.52
	10	0.01	0.10	3.000	0.200	0.800	2	5.2 9	133.7	2.14
O	15	0.01	0.15	3.000	0.300	0.700	2	5.3 7	98.5	1.58
Cl ⁻	10	0.01	0.10	3.000	0.100	0.900	4	5.4 1	130.1	2.08
	50	0.01	0.50	3.000	0.500	0.500	4	5.4	149.4	2.39
	100	0.01	1.00	3.000	1.000	0.000	4	5.4 8	177.2	2.84
ClO ₄ ⁻	25	0.01	0.25	3.000	0.250	0.750	4	5.3 8	107.9	1.73
	50	0.01	0.50	3.000	0.500	0.500	4	5.4 4	130.7	2.09
	75	0.01	0.75	3.000	0.750	0.250	4	5.5 4	141	2.26
	100	0.01	1.00	3.000	1.000	0.000	4	5.6 2	158	2.53

Table S9. Continued

	Equivalent s	Eu(CF ₃ SO ₃) ₃ (M)	L Sample (M)	Eu ³⁺ Stock ^a (mL)	L Stock (mL)	Water (mL)	L Stock ^b (M)	pH	Conductivity	Ionic Strength ^c x10 ⁶
OTf ⁻	25	0.01	0.25	3.000	0.250	0.750	4	5.48	153.8	2.46
	50	0.01	0.50	3.000	0.500	0.500	4	5.62	155.7	2.49
	75	0.01	0.75	3.000	0.750	0.250	4	5.69	-	-
	100	0.01	1.00	3.000	1.000	0.000	4	5.76	155.7	2.49

^aEu³⁺ Stock is 0.0132 M Eu(CF₃SO₃)₃, 0.00132 M NaCl/KCl (see experimental section) and 0.0264 M MES.

^bDetails on Ligand Stock preparation can be found in the experimental section. ^ccalculated using the Russell-prefactor of 1.6x10⁻⁵ from ref¹

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