SUPPORTING INFORMATION FOR

New Coumarin Dipicolinate Europium Complexes with a Rich Chemical Speciation and Tunable Luminescence

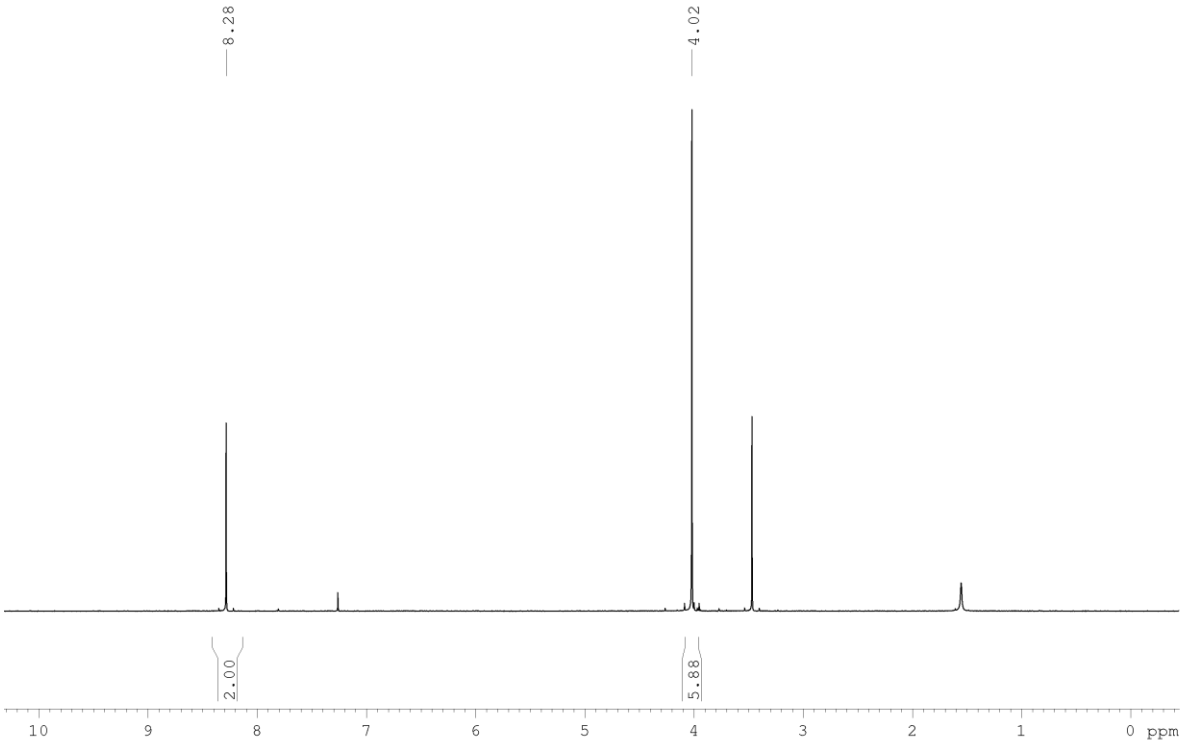


Figure S 1. ^{1}H-NMR spectrum of compound 1.

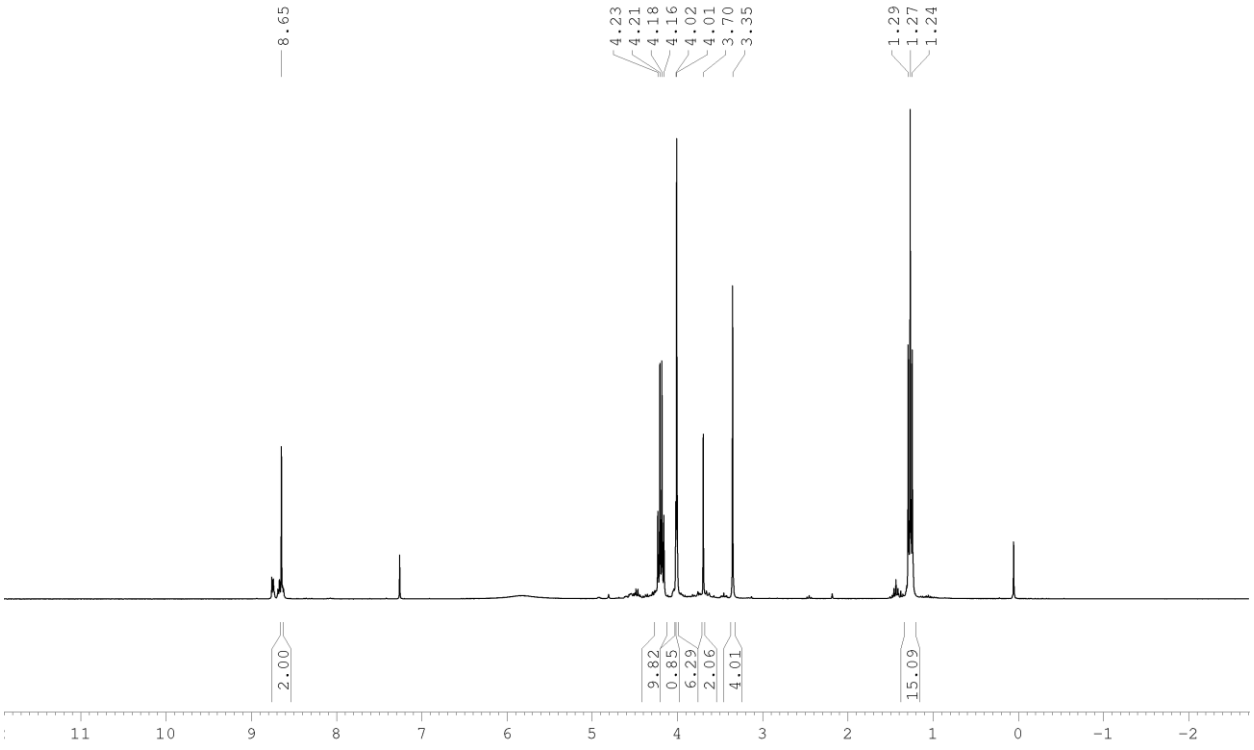


Figure S 2. ^{1}H-NMR spectrum of compound 2.

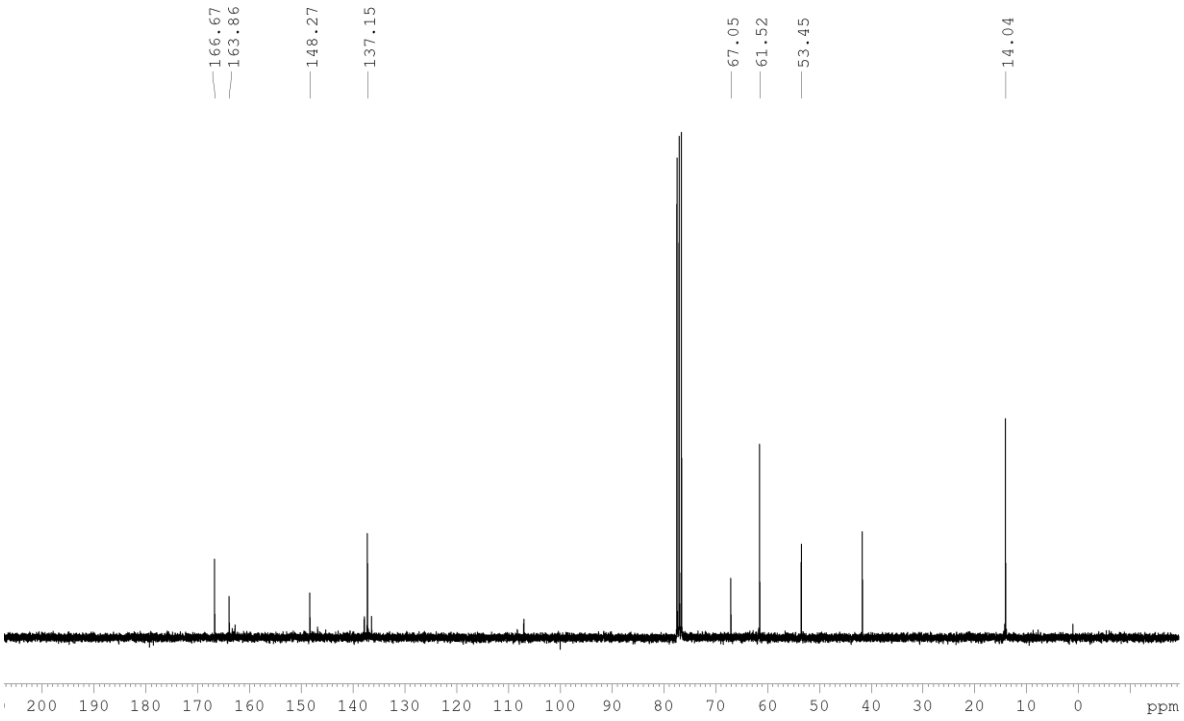


Figure S 3. ^{13}C-NMR spectrum of compound 2.

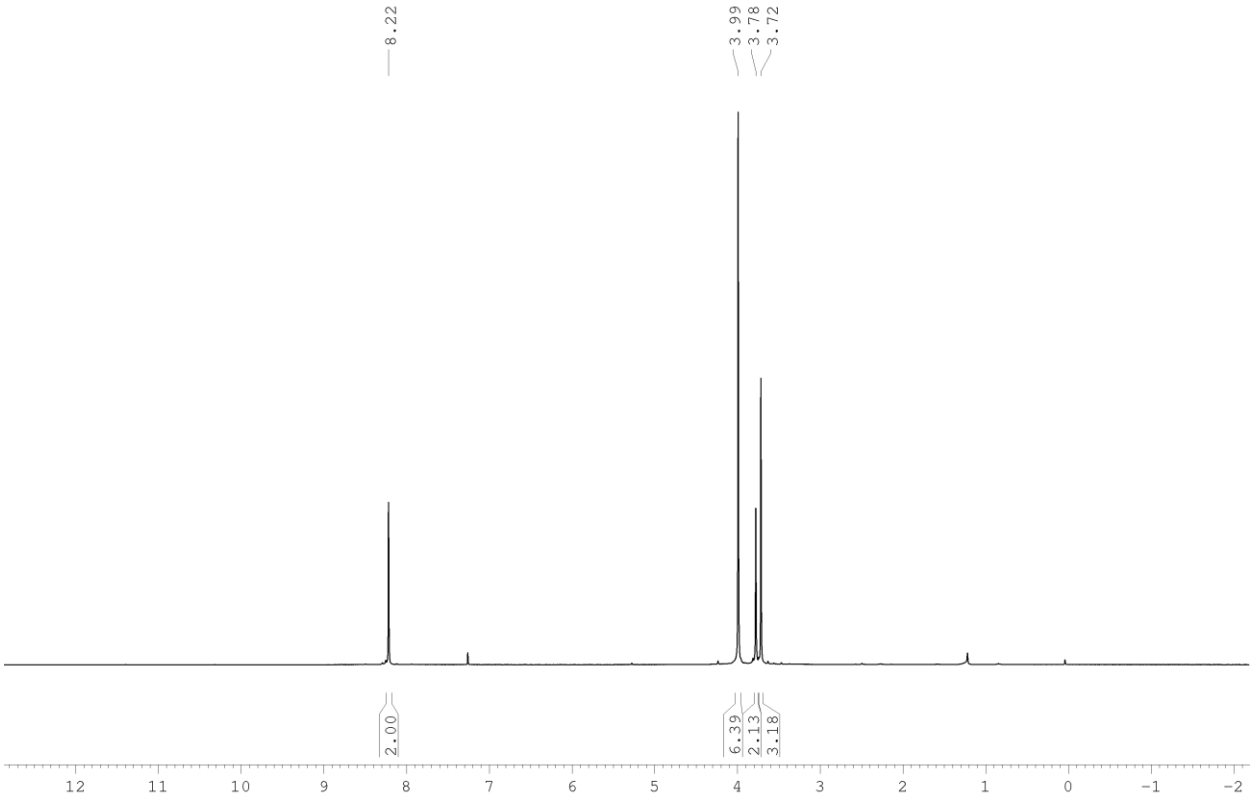


Figure S 4. ^{1}H-NMR spectrum of compound 3.

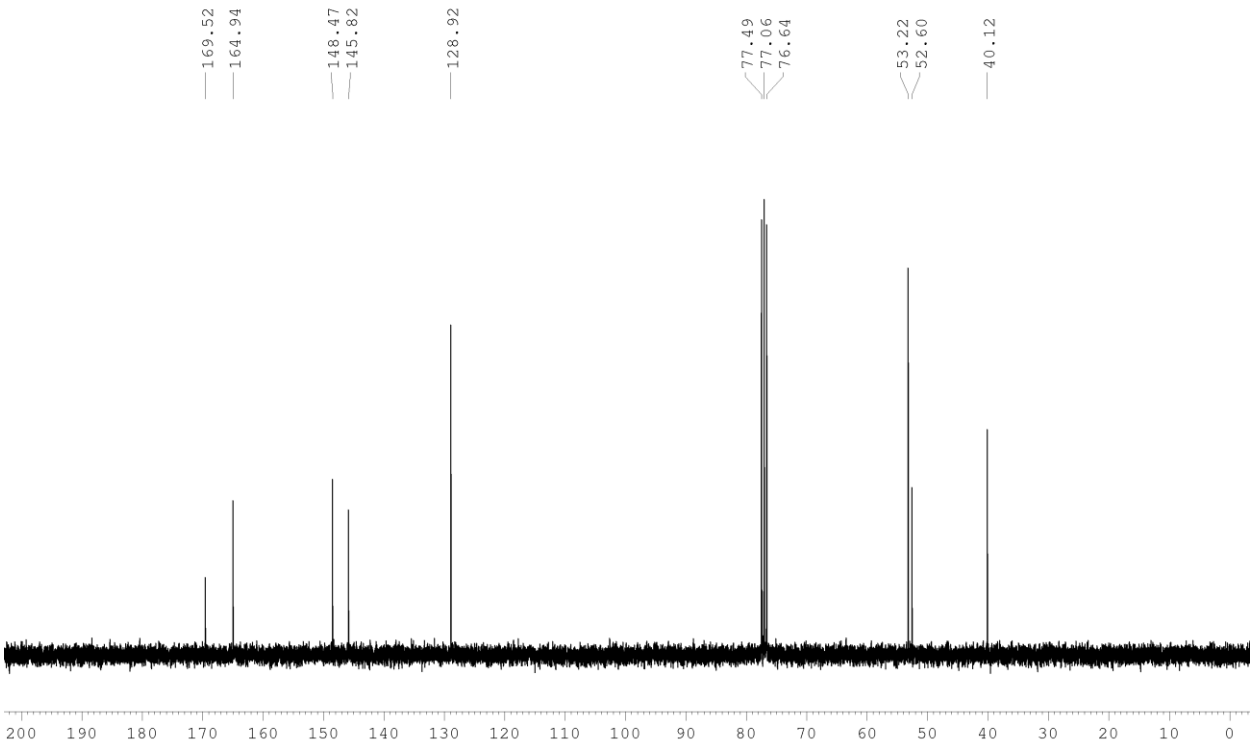


Figure S 5. ^{13}C-NMR spectrum of compound 3.

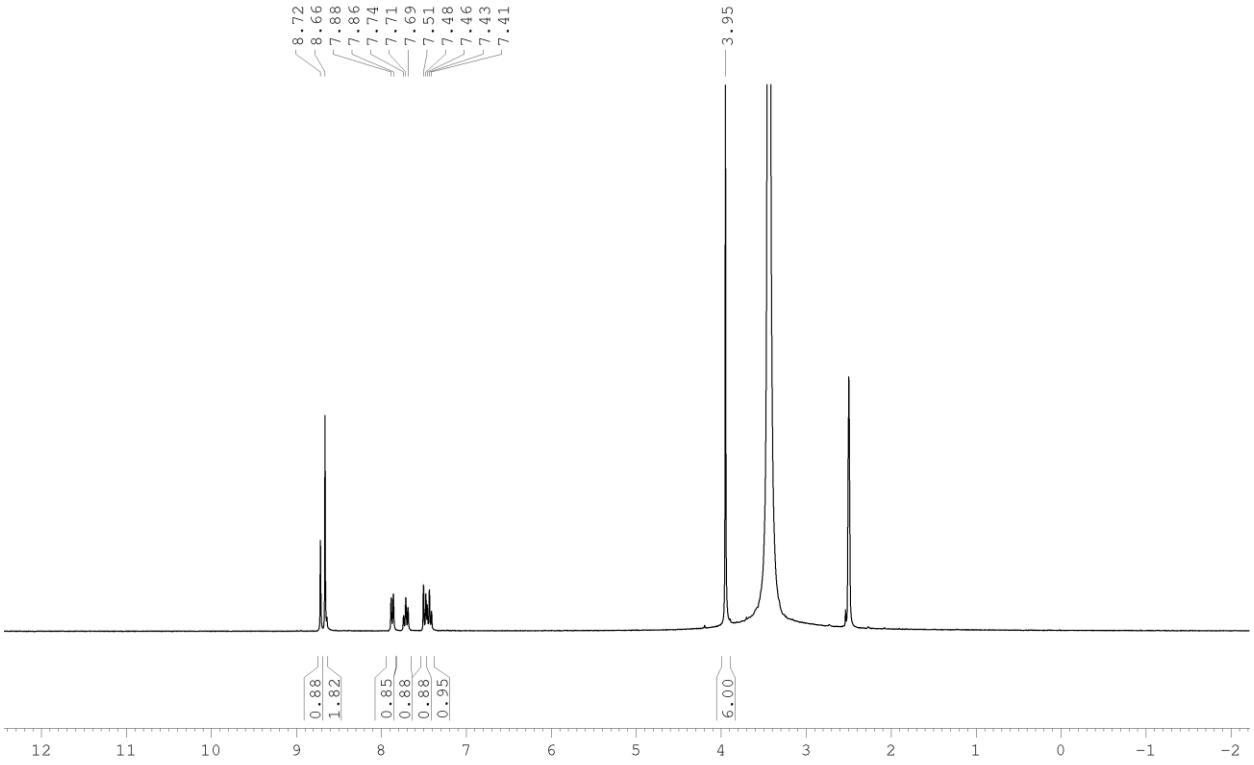


Figure S 6. ^{1}H-NMR spectrum of compound 4.

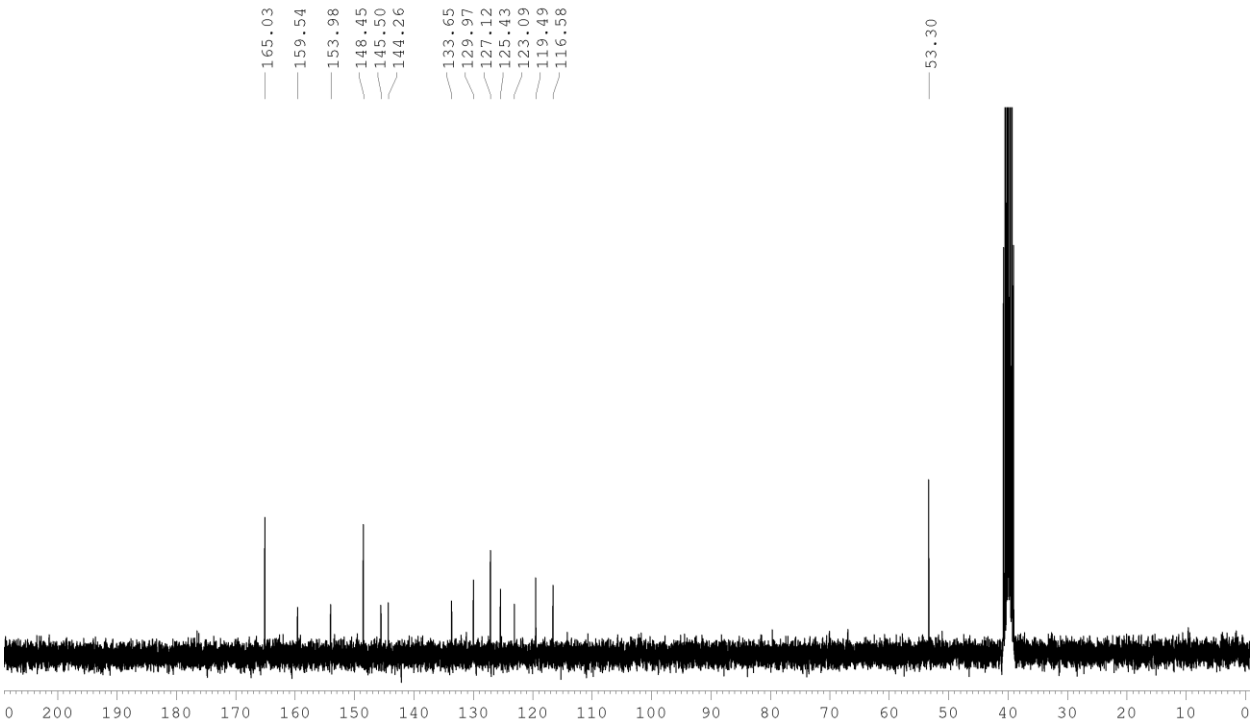


Figure S 7. ^{13}C-NMR spectrum of compound 4.

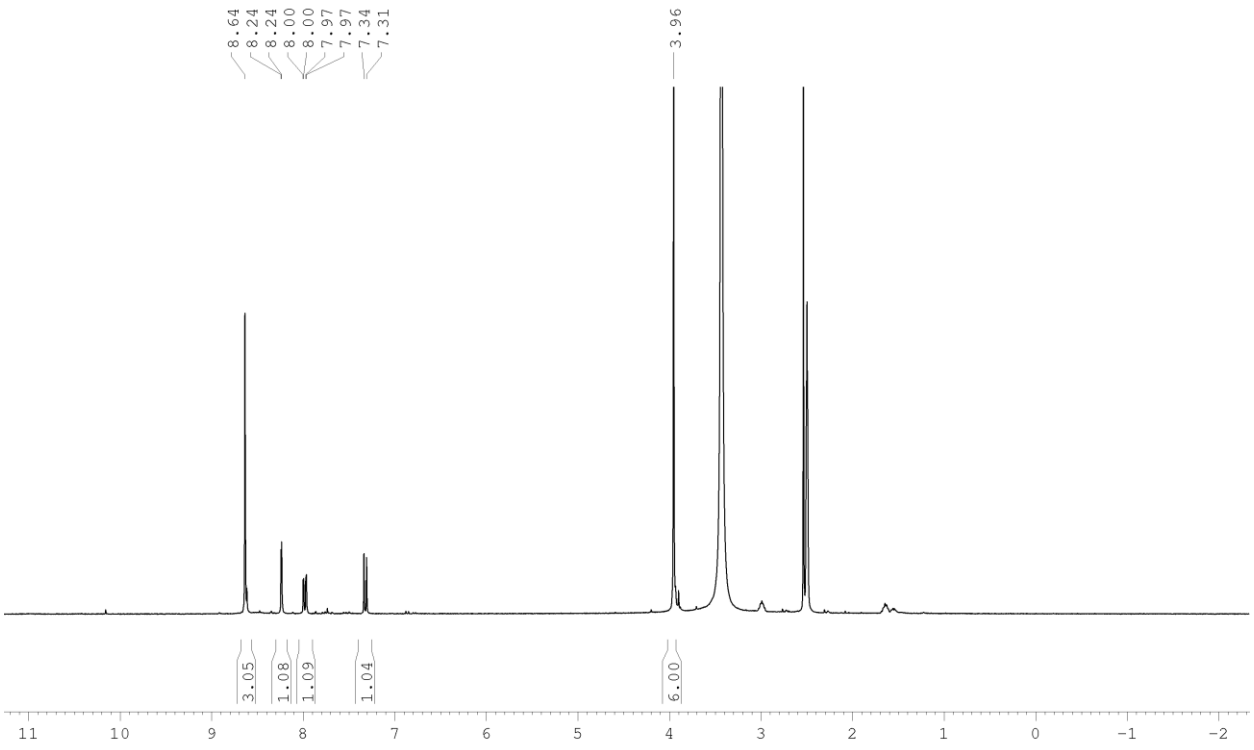


Figure S 8. ^{1}H-NMR spectrum of compound 5.

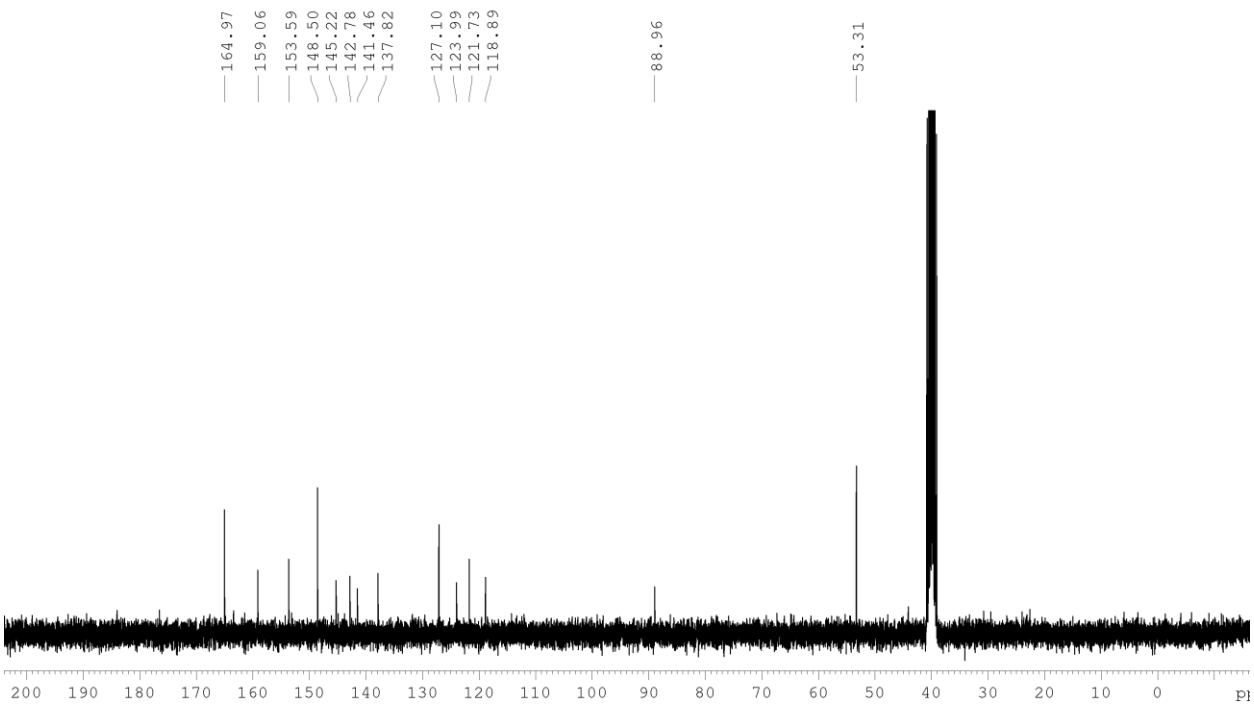


Figure S 9. ^{13}C-NMR spectrum of compound 5.

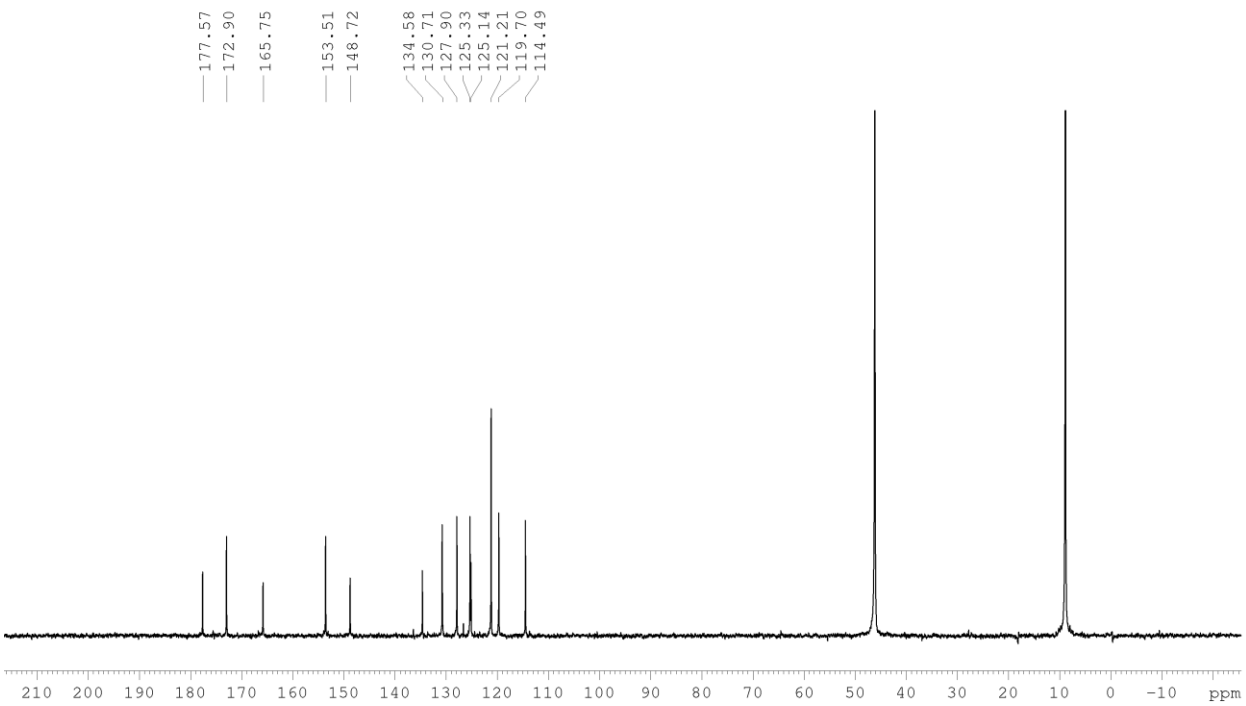


Figure S 10. ^{13}C-NMR spectrum of the triethylammonium salt of HL_1.

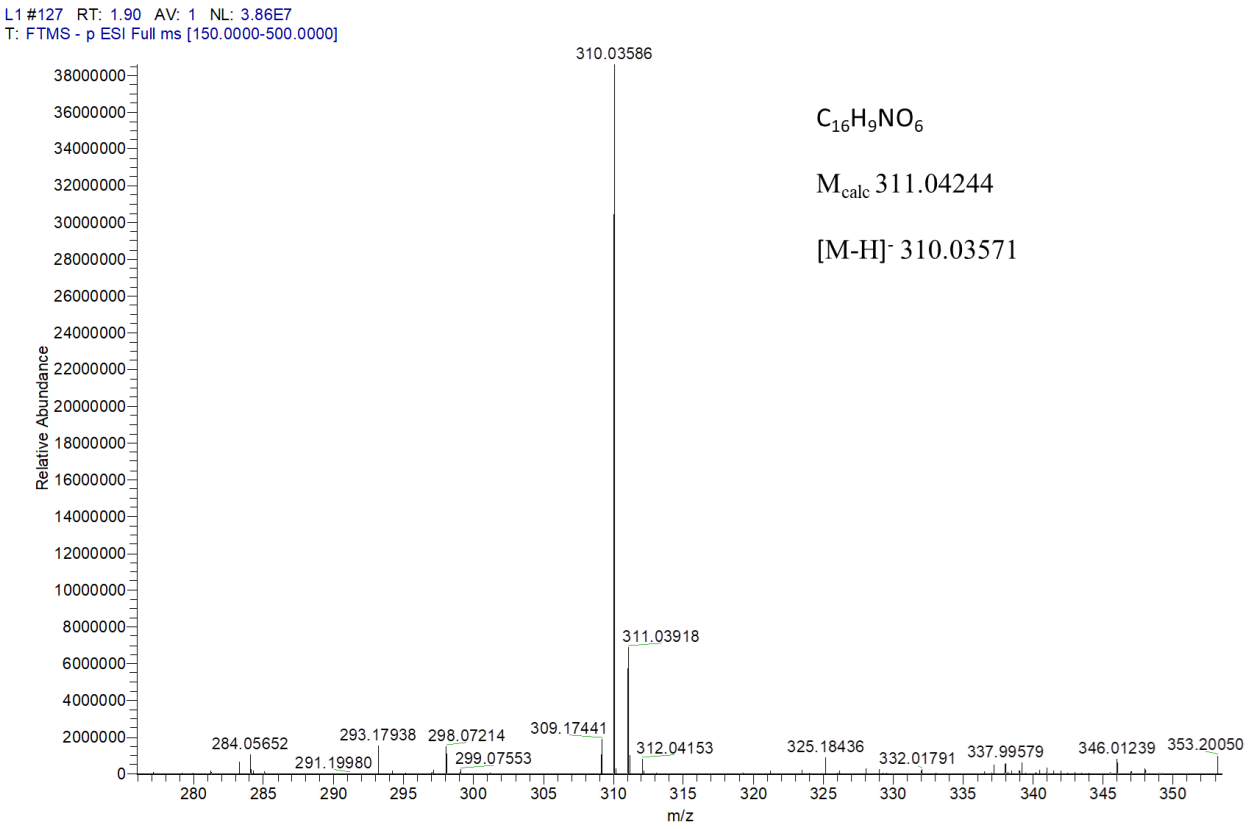


Figure S 11. HMRS spectrum of compound HL_1.

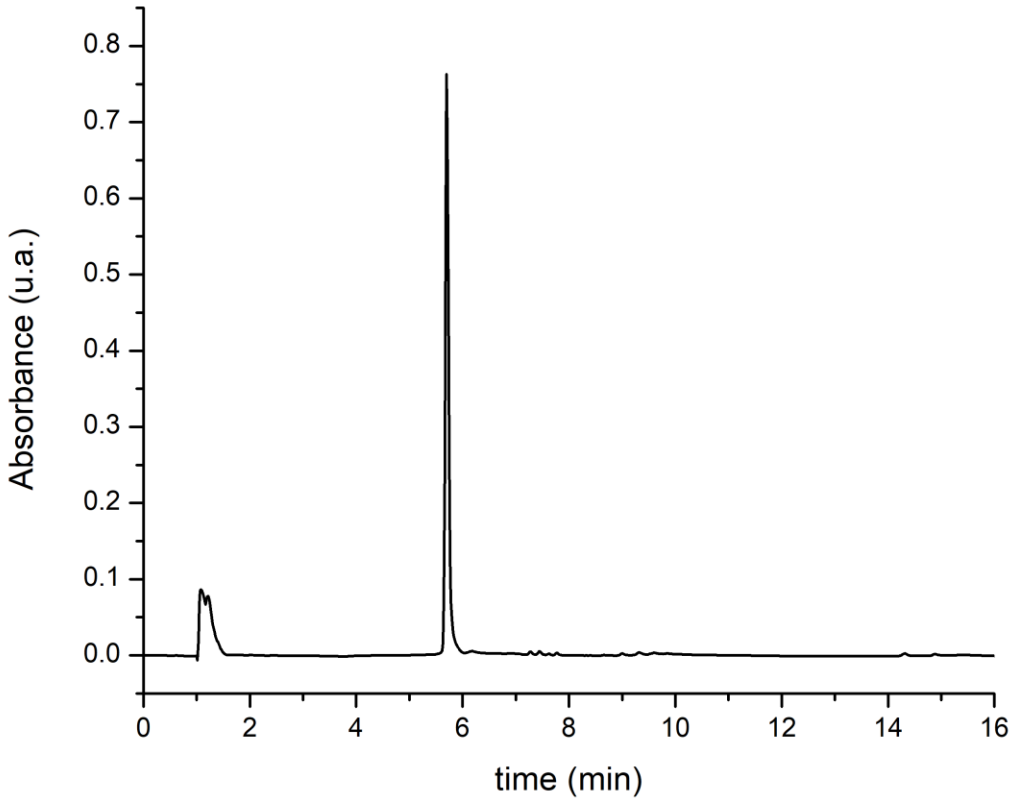


Figure S 12. HPLC chromatogram of the triethylammonium salt of HL_1.

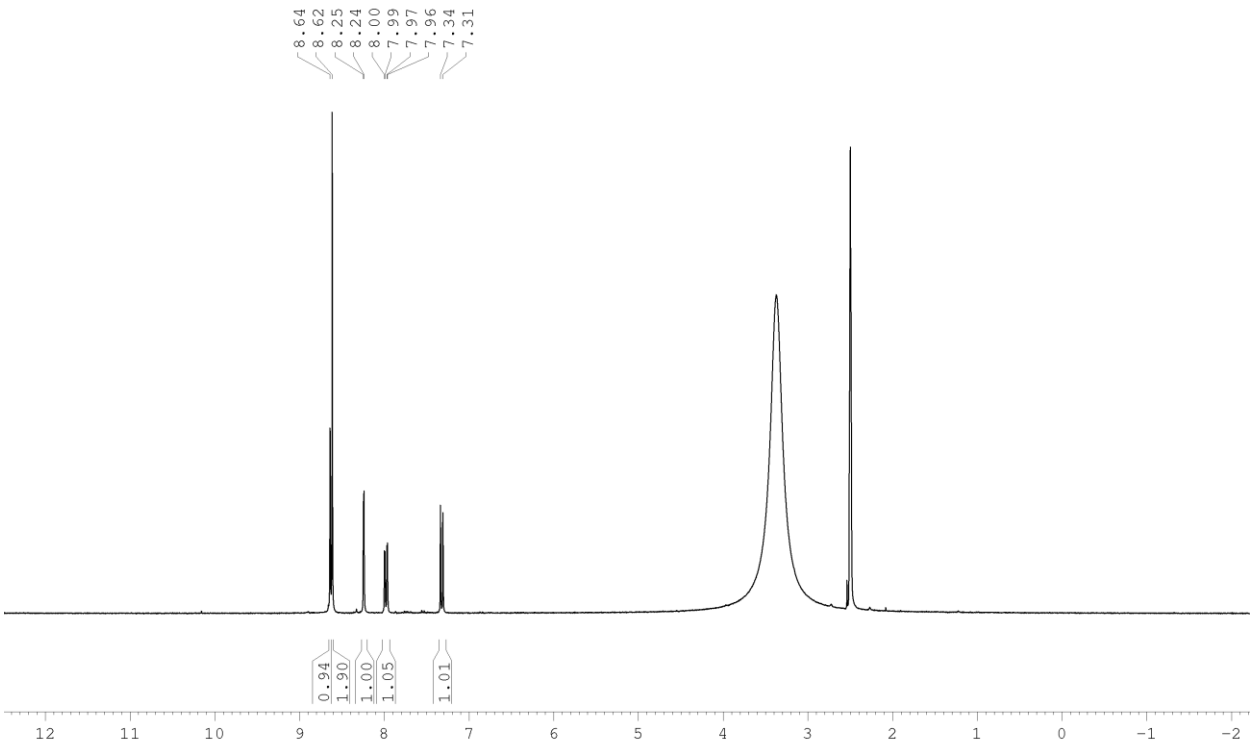


Figure S 13. ^{1}H-NMR spectrum of compound HL_2.

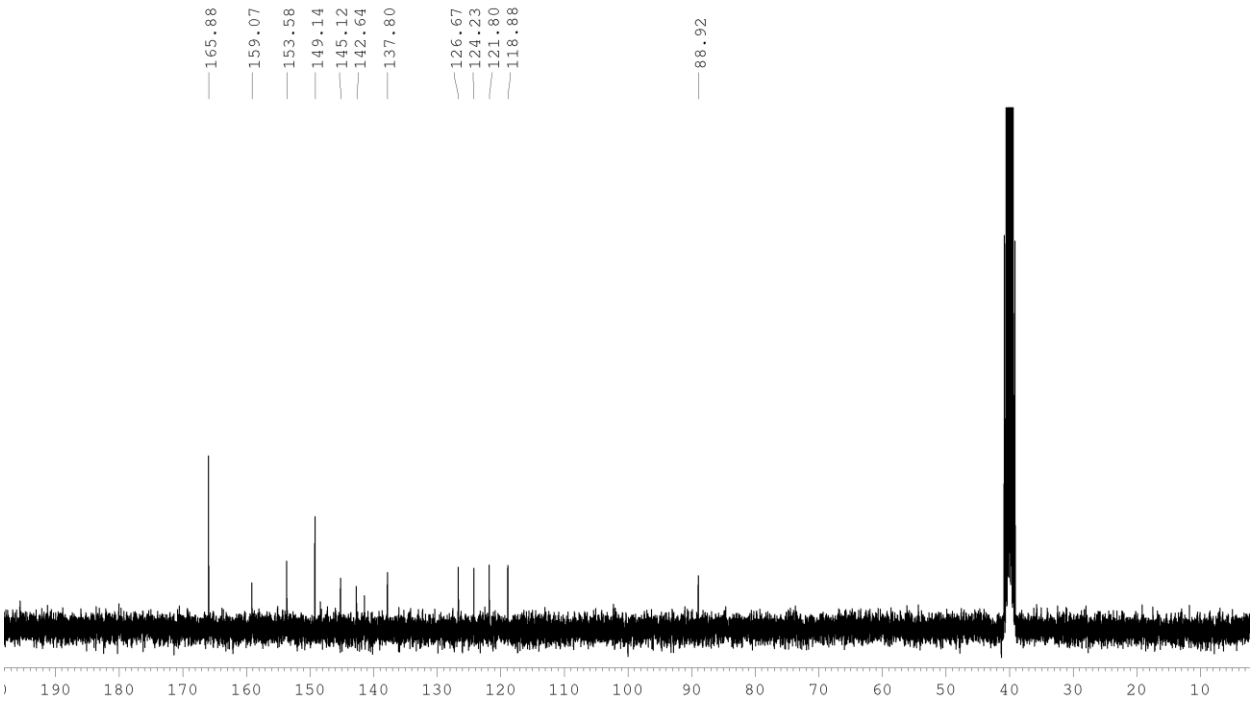


Figure S 14. ^{13}C-NMR spectrum of compound HL_2.

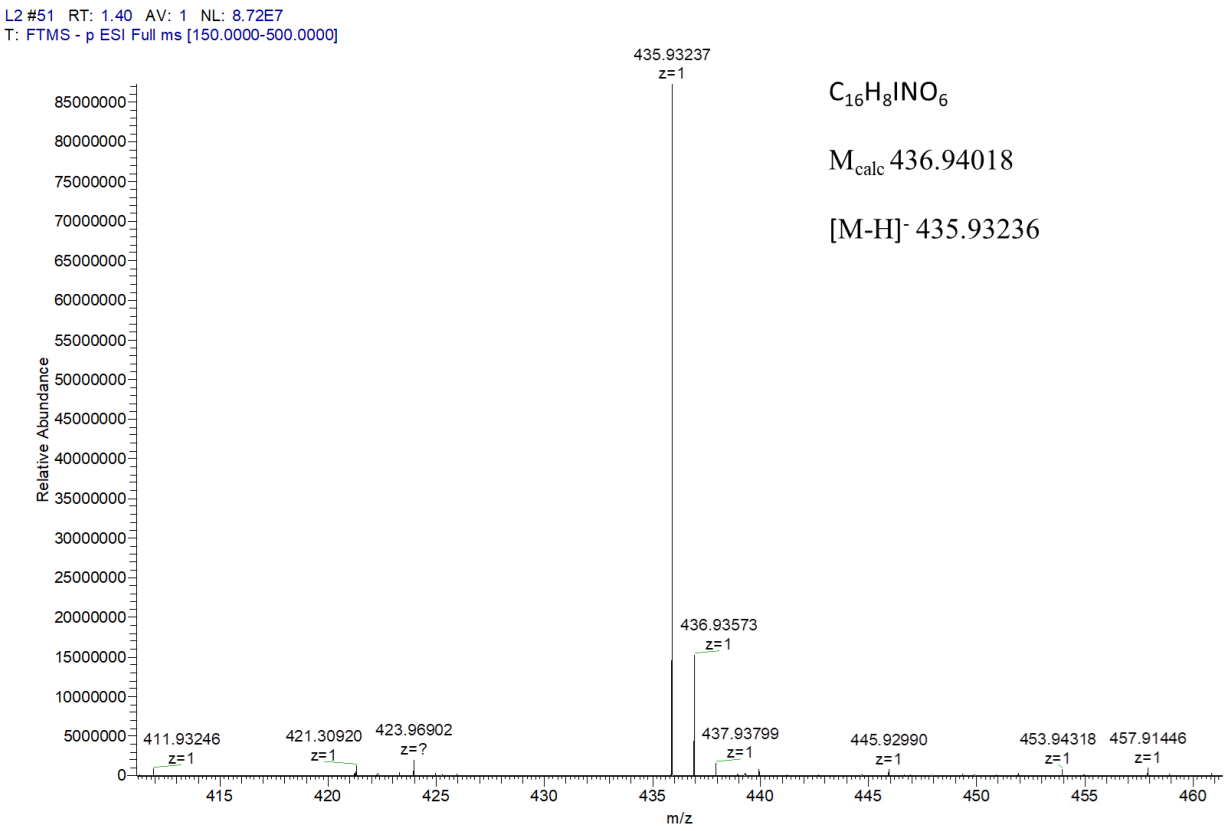


Figure S 15. HMRS spectrum of compound HL_2.

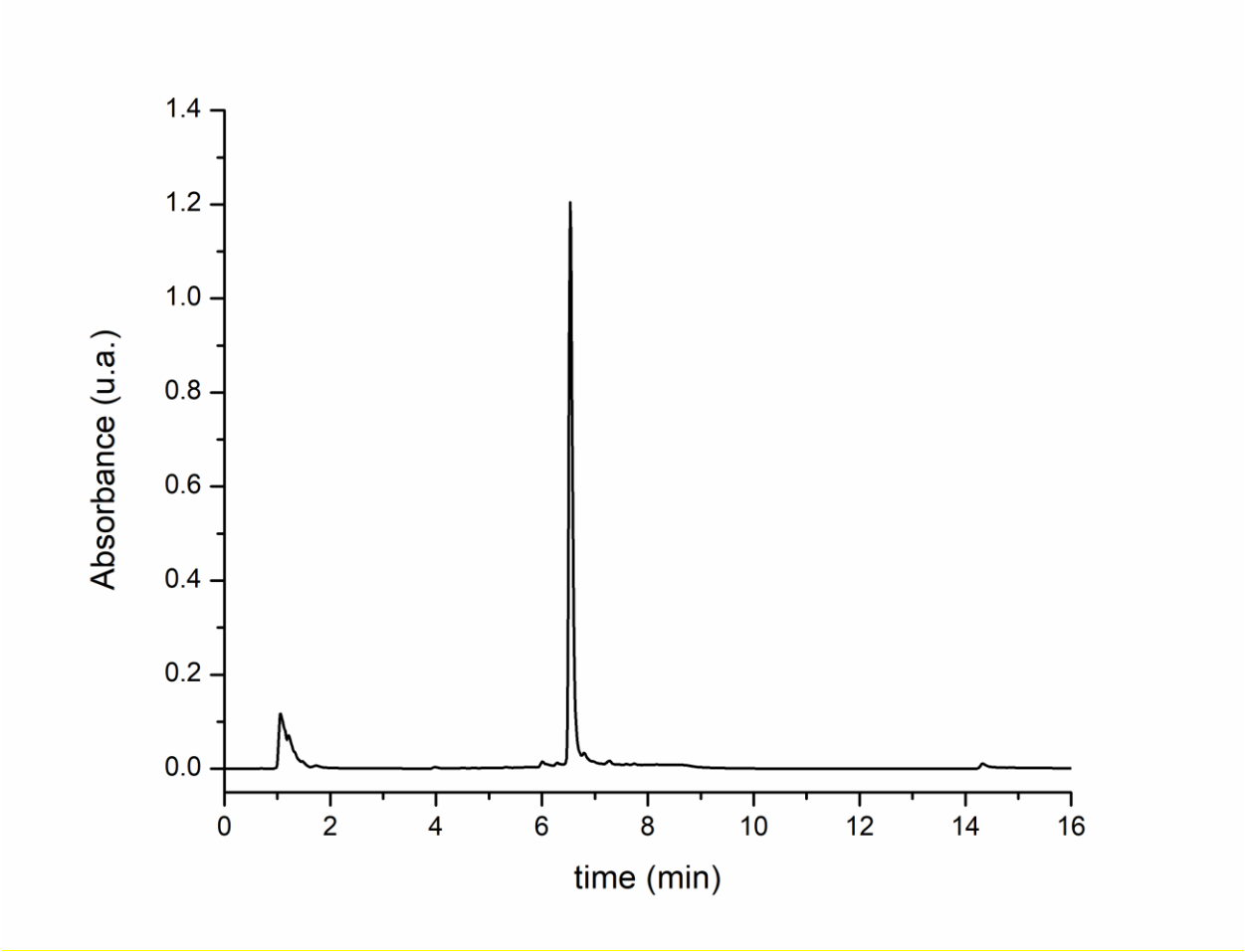


Figure S 16. HPLC chromatogram of the triethylammonium salt of HL_2.

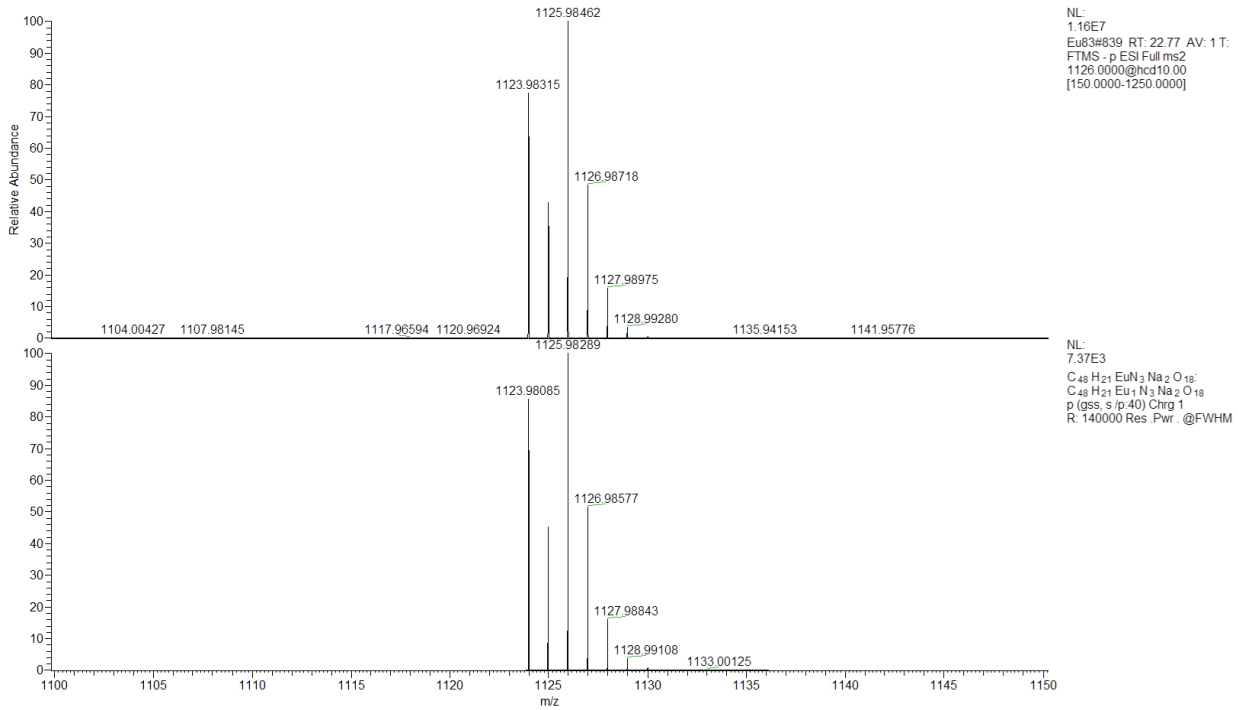


Figure S 17. HRMS spectrum of $Na_3[Eu(L_1)_3]$ complex (above) with the relative calculated one (below).

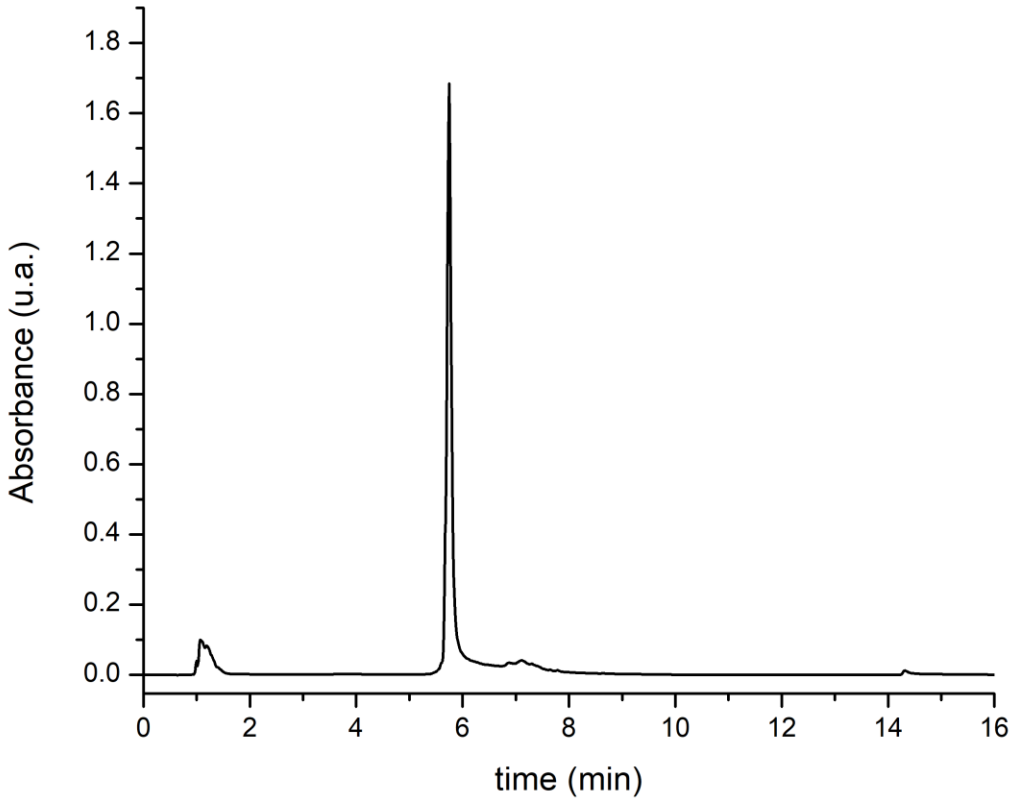


Figure S 18. HPLC chromatogram of $Na_3[Eu(L_1)_3]$ complex.

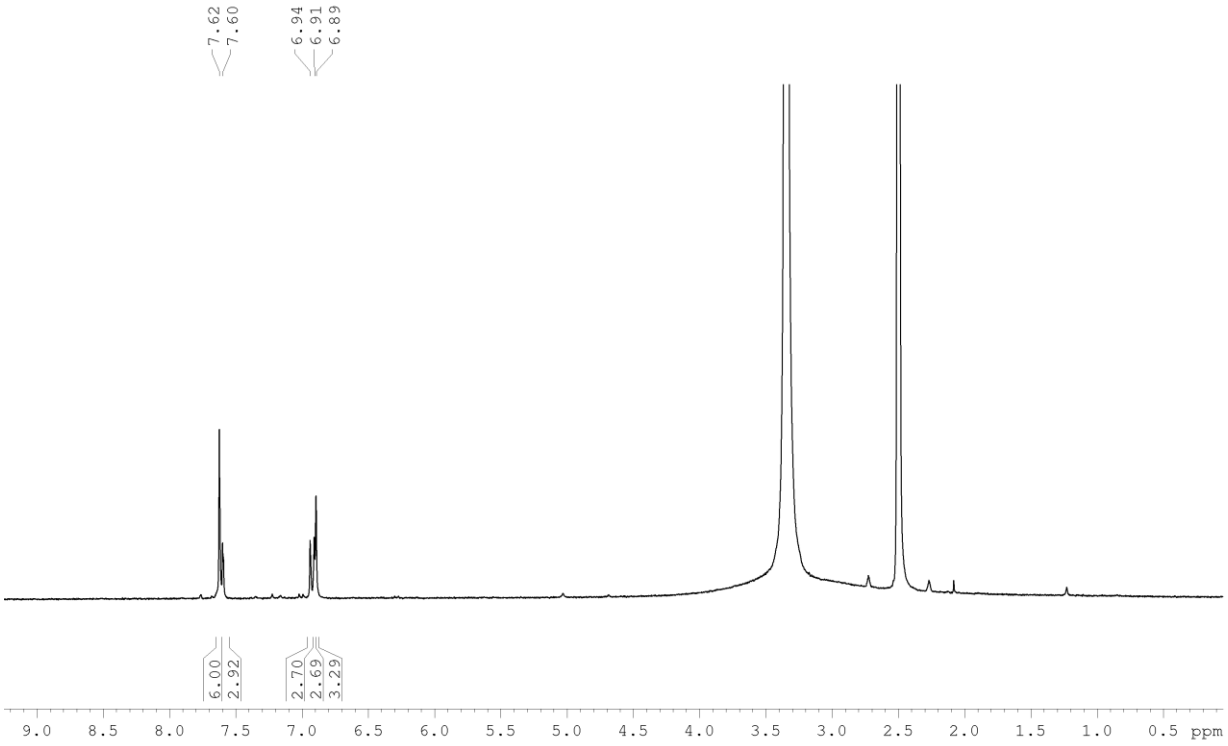


Figure S 19. ^{1}H-NMR spectrum of $Na_3[Eu(L2)_3]$ complex.

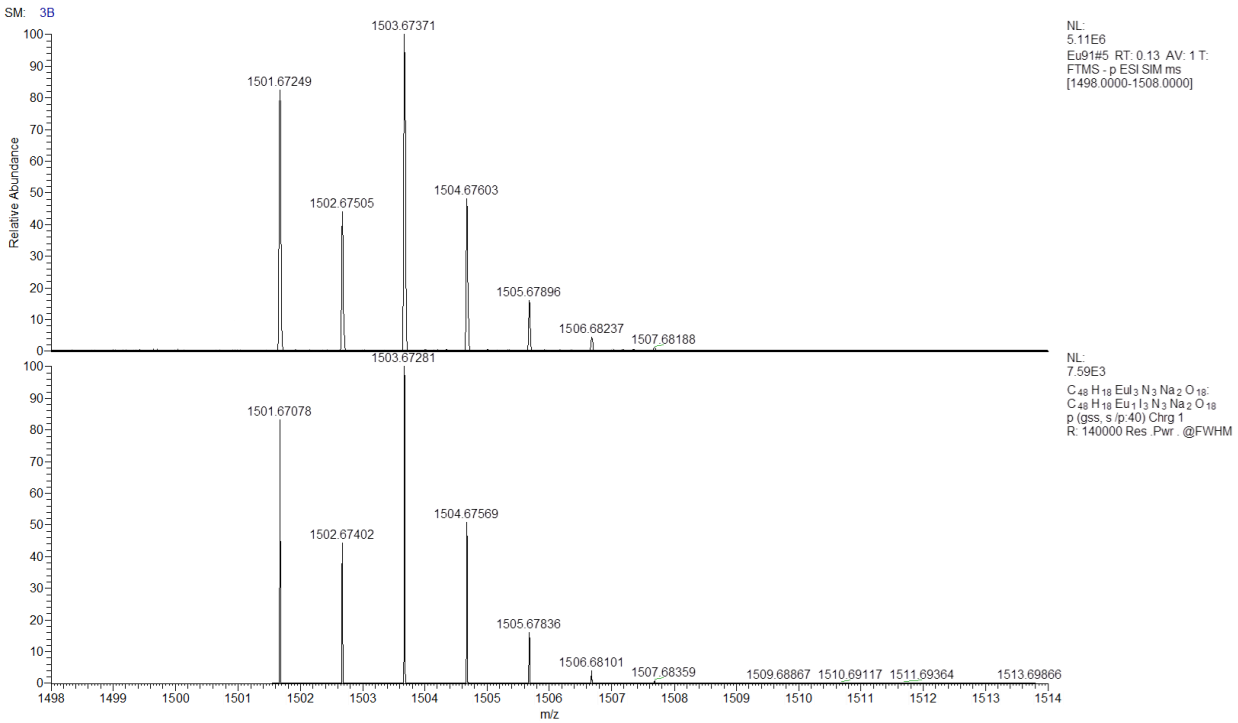


Figure S 20. HRMS spectrum of $Na_3[Eu(L_2)_3]$ complex (above) with the relative calculated one (below).

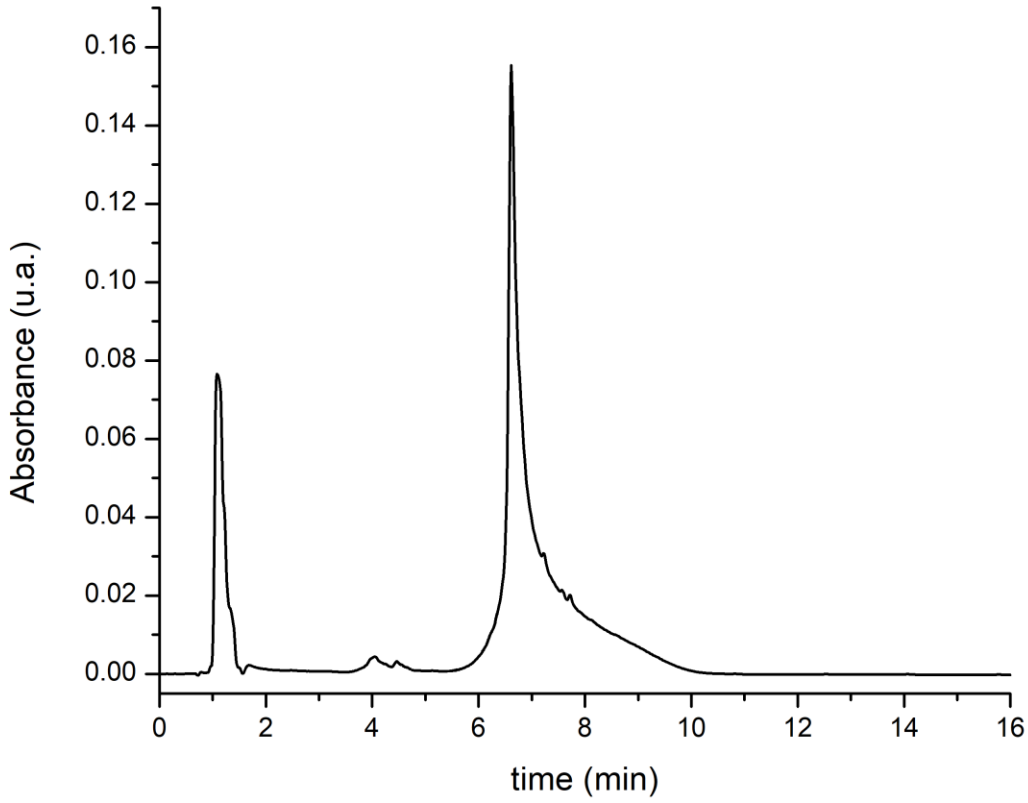


Figure S 21. HPLC chromatogram of $Na_3[Eu(L_2)_3]$ complex.

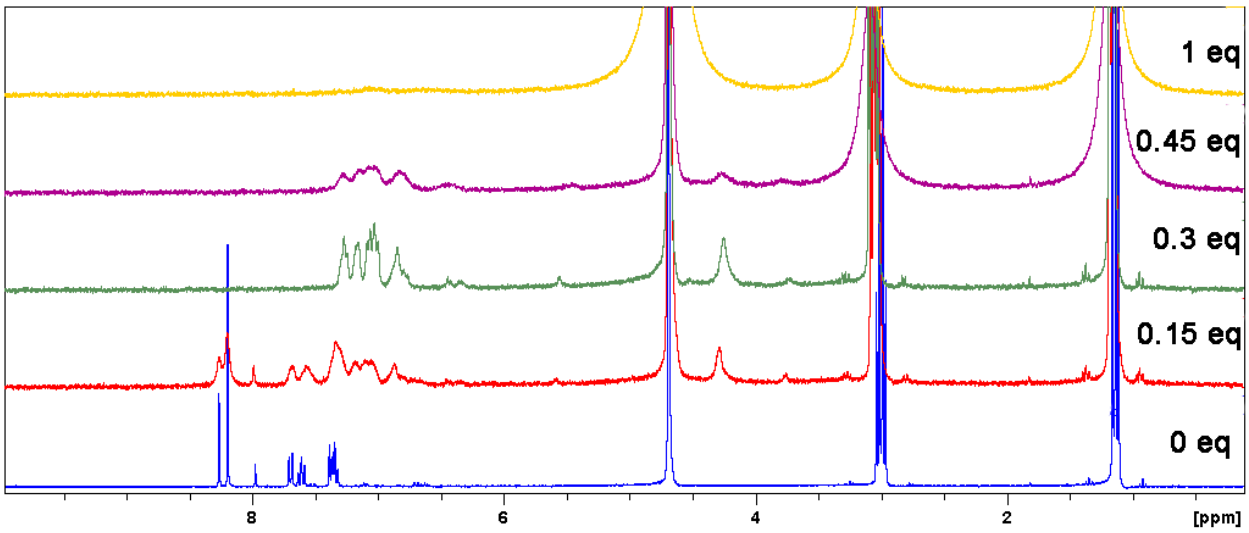


Figure S 22. ^{1}H-NMR titration (400 MHz, D_2O) of L_1 (triethylammonium salt) with Eu^{3+} (chloride hexahydrate salt).

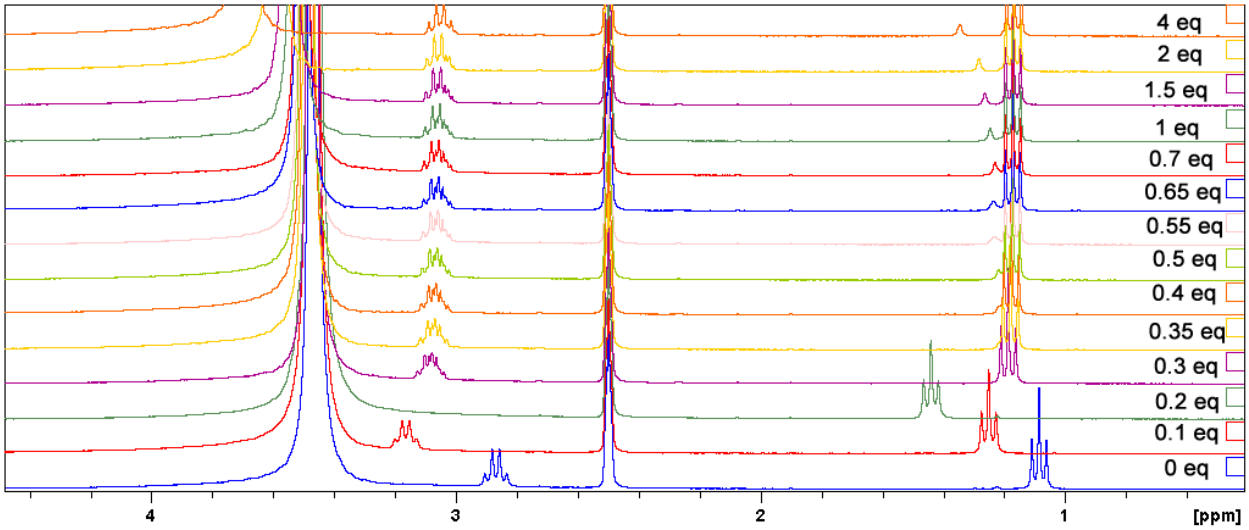


Figure S 23. ^{1}H-NMR titration (400 MHz, DMSOd) of L_1 (triethylammonium salt) with Eu^{3+} (chloride hexahydrate salt), particular of the counterion dynamic.

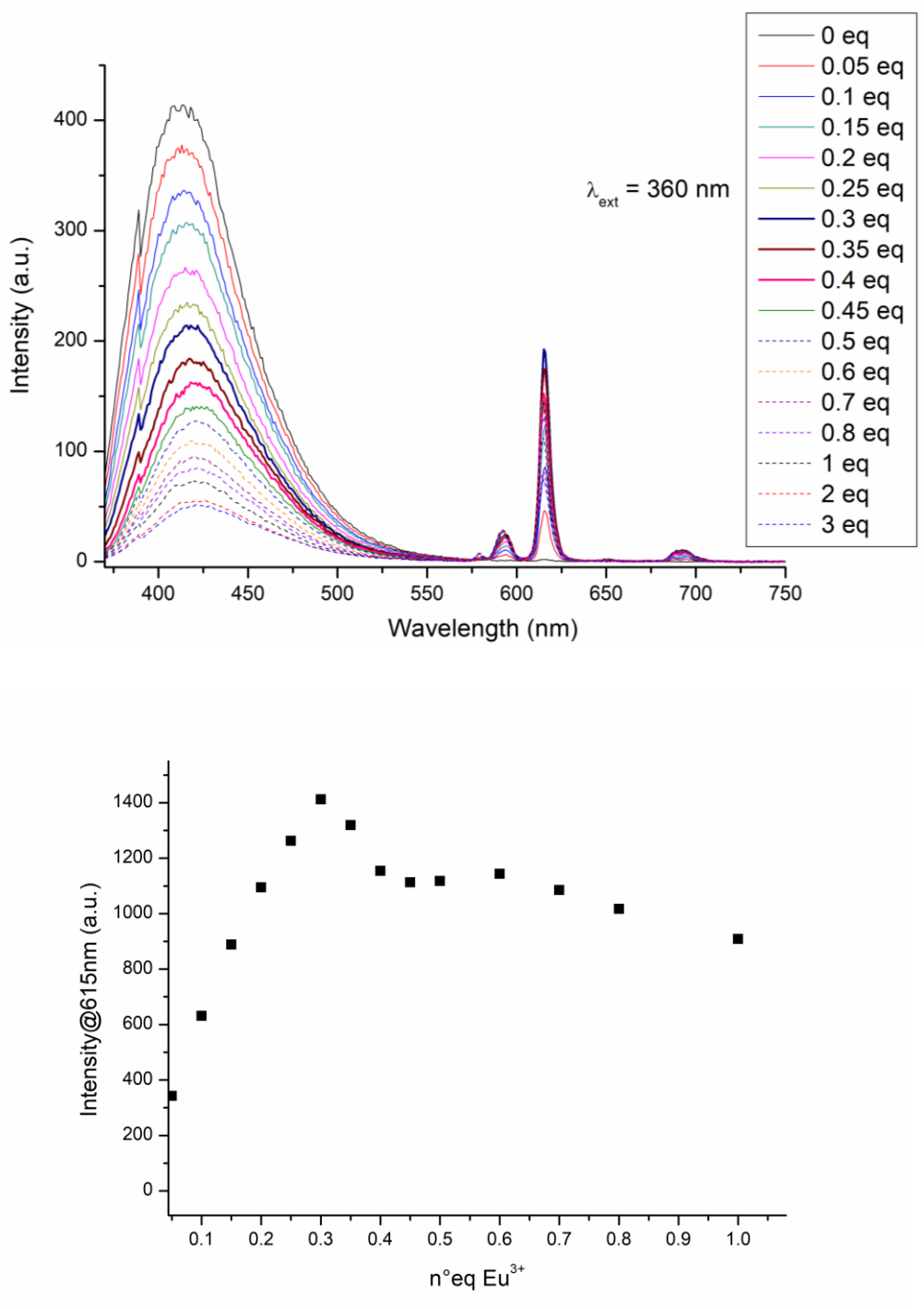
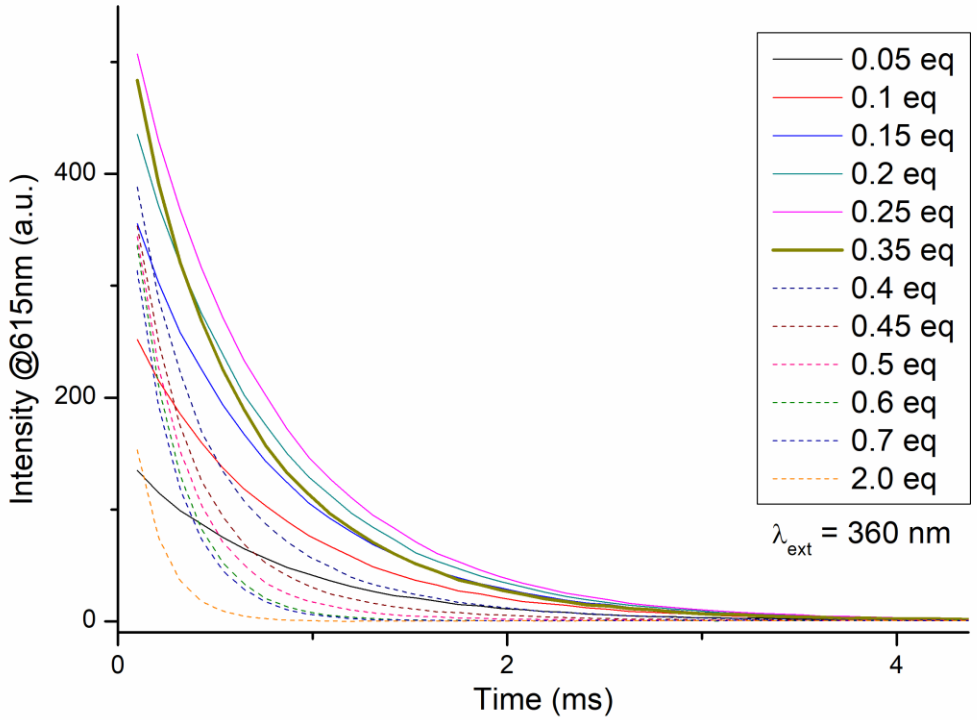


Figure S 24. Fluorescence titration spectra of L_1^{2-} in Tris HCl with Eu^{3+} (above) and titration curve monitoring the fluorescence at 615 nm (below).


Intensity @615nm (a.u.)
400
200
0
0
2
4
Time (ms)
0.05 eq
0.1 eq
0.15 eq
0.2 eq
0.25 eq
0.35 eq
0.4 eq
0.45 eq
0.5 eq
0.6 eq
0.7 eq
2.0 eq
λext = 360 nm

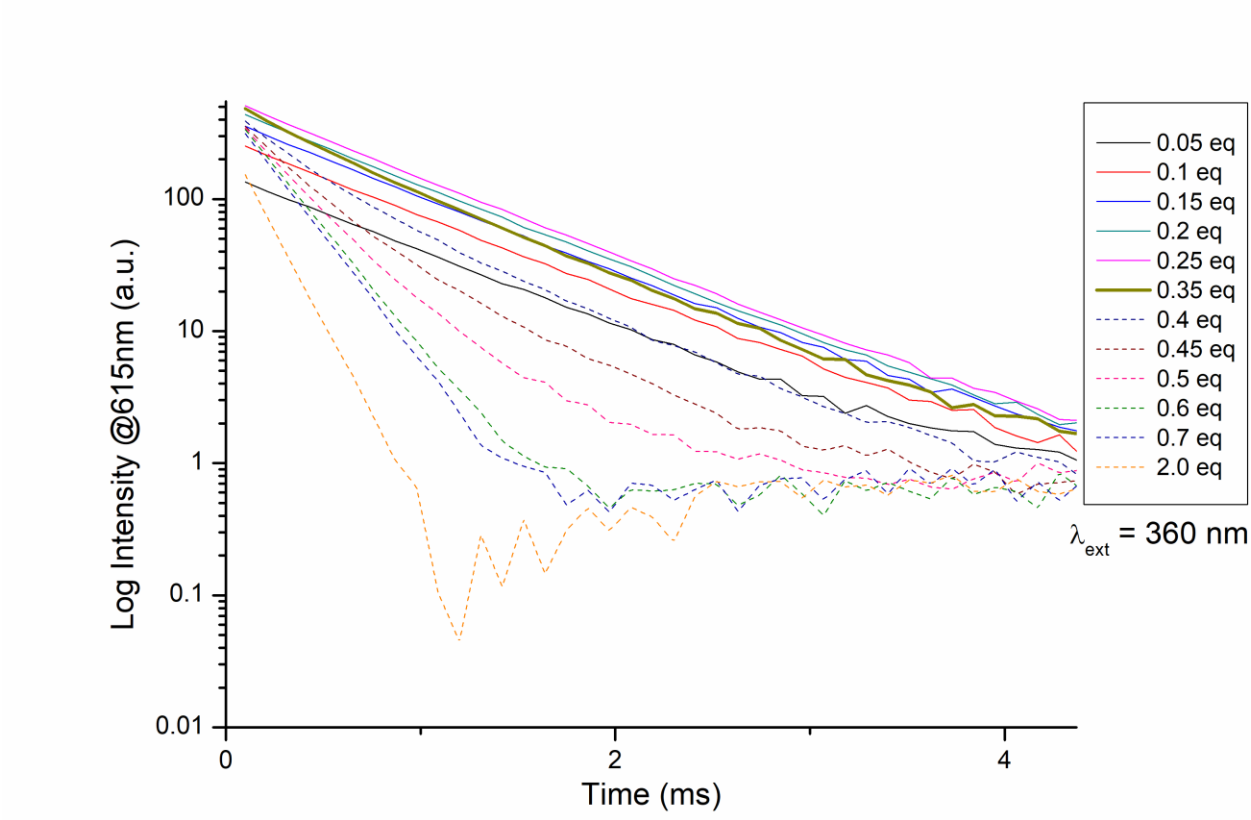
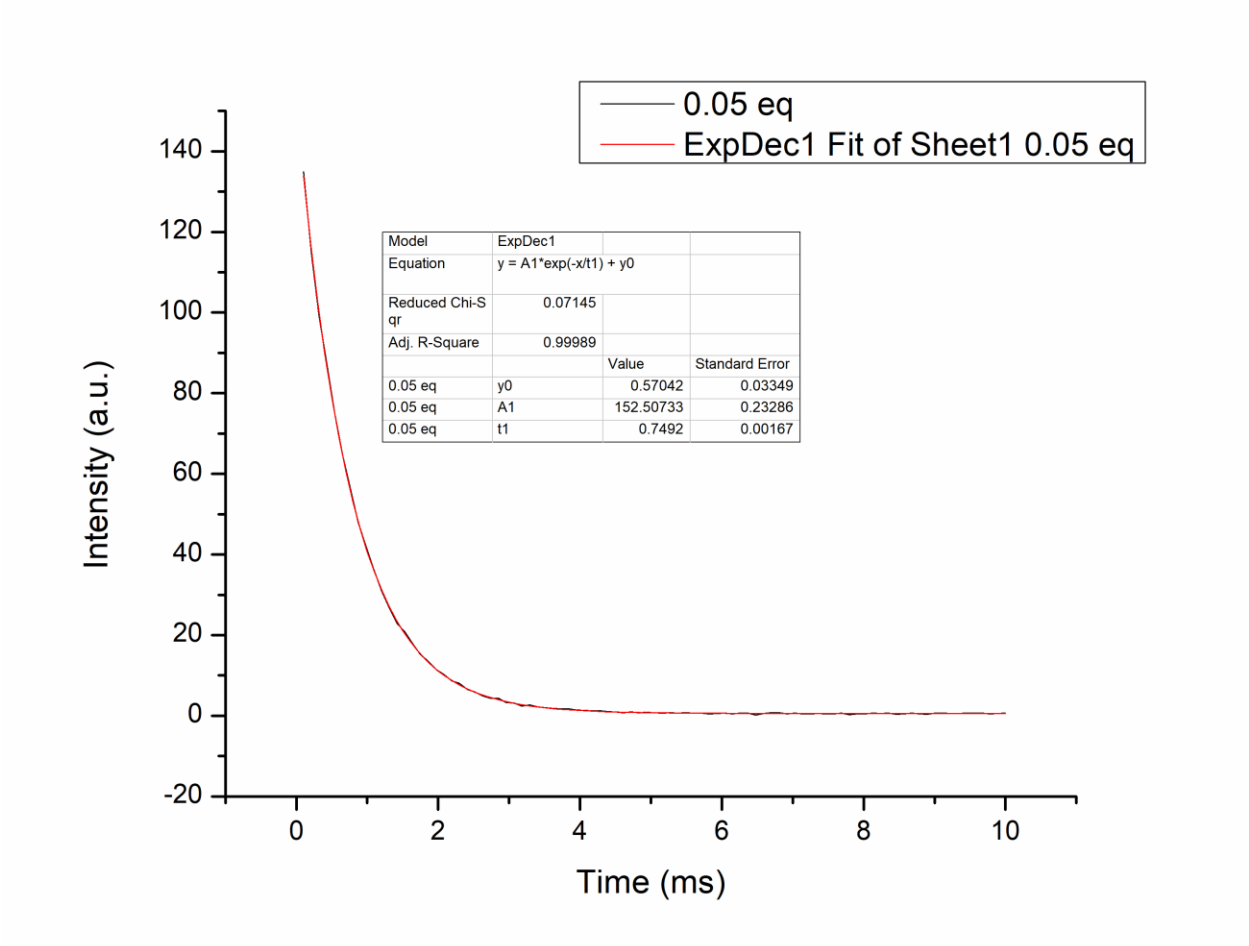


Figure S 25. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm.


0.05 eq
ExpDec1 Fit of Sheet1 0.05 eq
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 0.07145
Adj. R-Square 0.99989
Value Standard Error
0.05 eq y0 0.57042 0.03349
0.05 eq A1 152.50733 0.23286
0.05 eq t1 0.7492 0.00167
Intensity (a.u.)
Time (ms)
140
120
100
80
60
40
20
0
-20
0
2
4
6
8
10

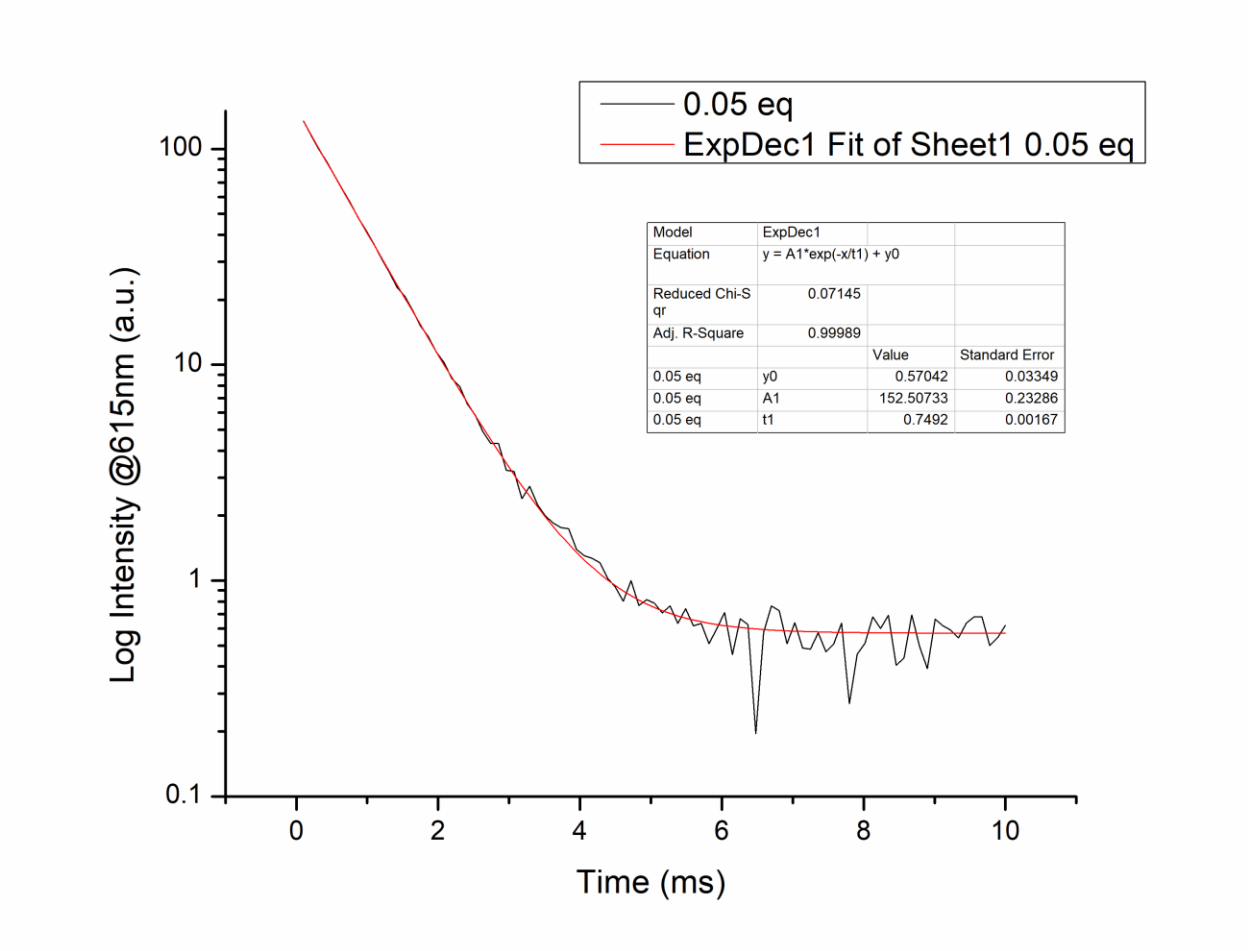
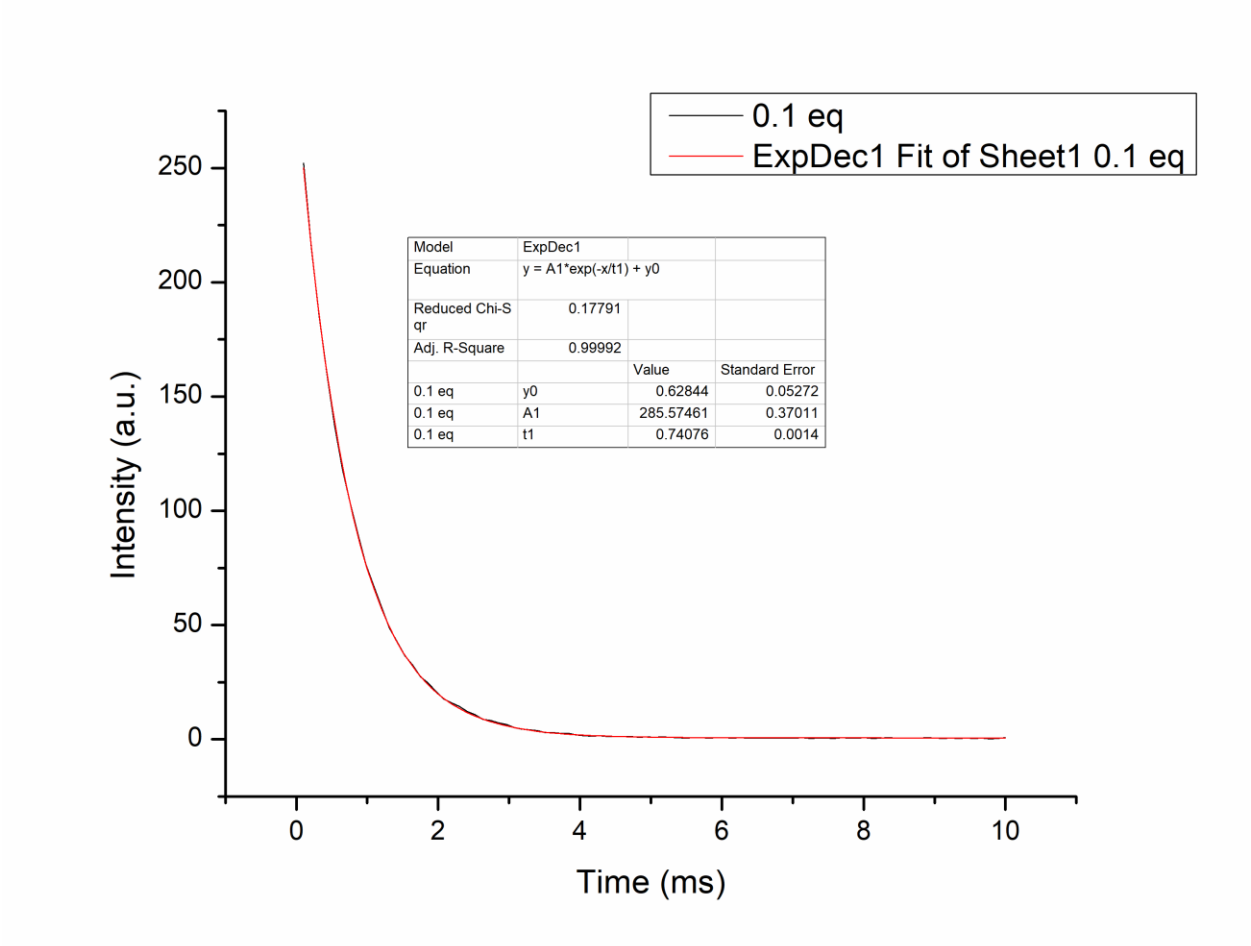


Figure S 26. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.05 eq


0.1 eq
ExpDec1 Fit of Sheet1 0.1 eq
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 0.17791
Adj. R-Square 0.99992
Value Standard Error
0.1 eq y0 0.62844 0.05272
0.1 eq A1 285.57461 0.37011
0.1 eq t1 0.74076 0.0014
Intensity (a.u.)
250
200
150
100
50
0
0
2
4
6
8
10
Time (ms)

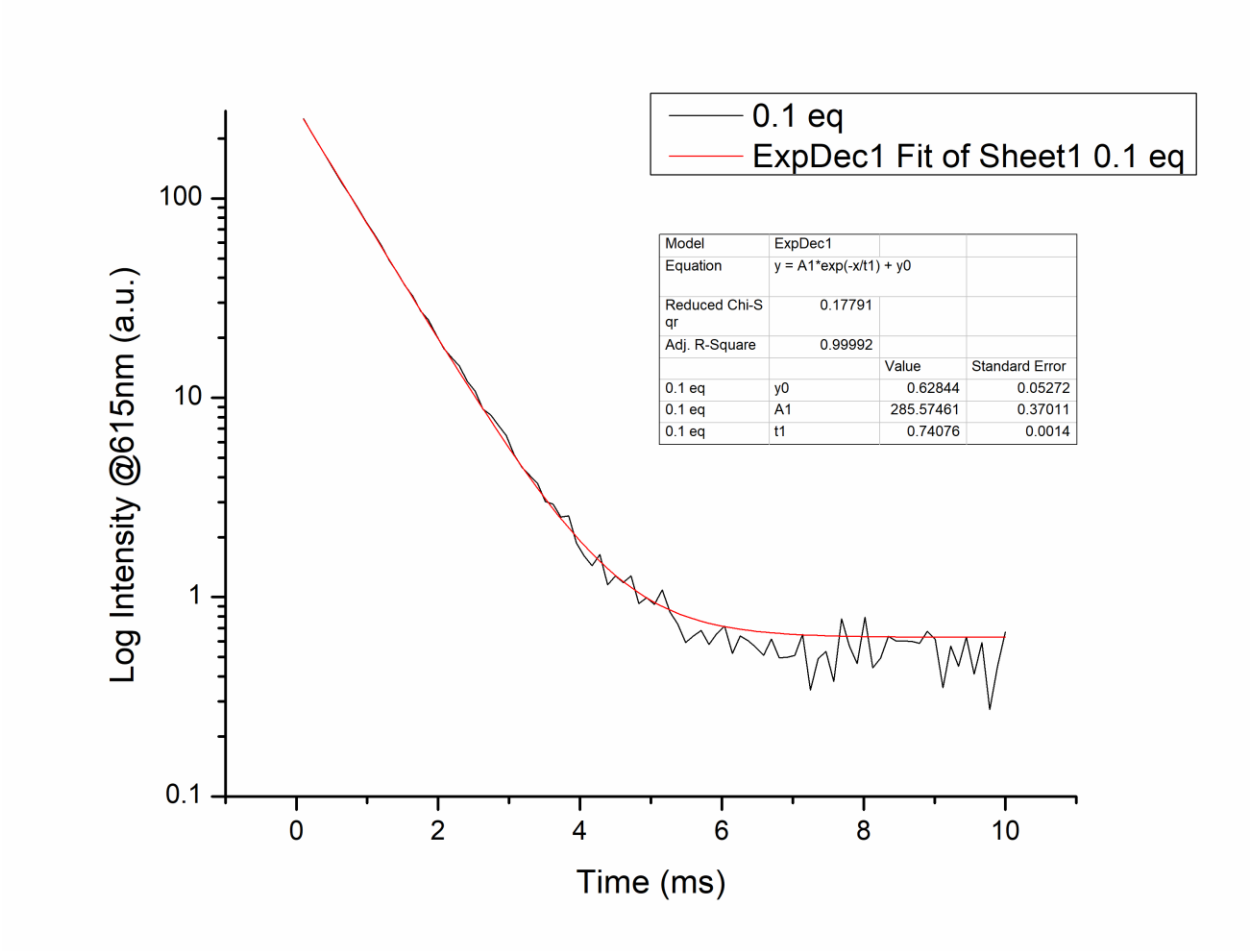
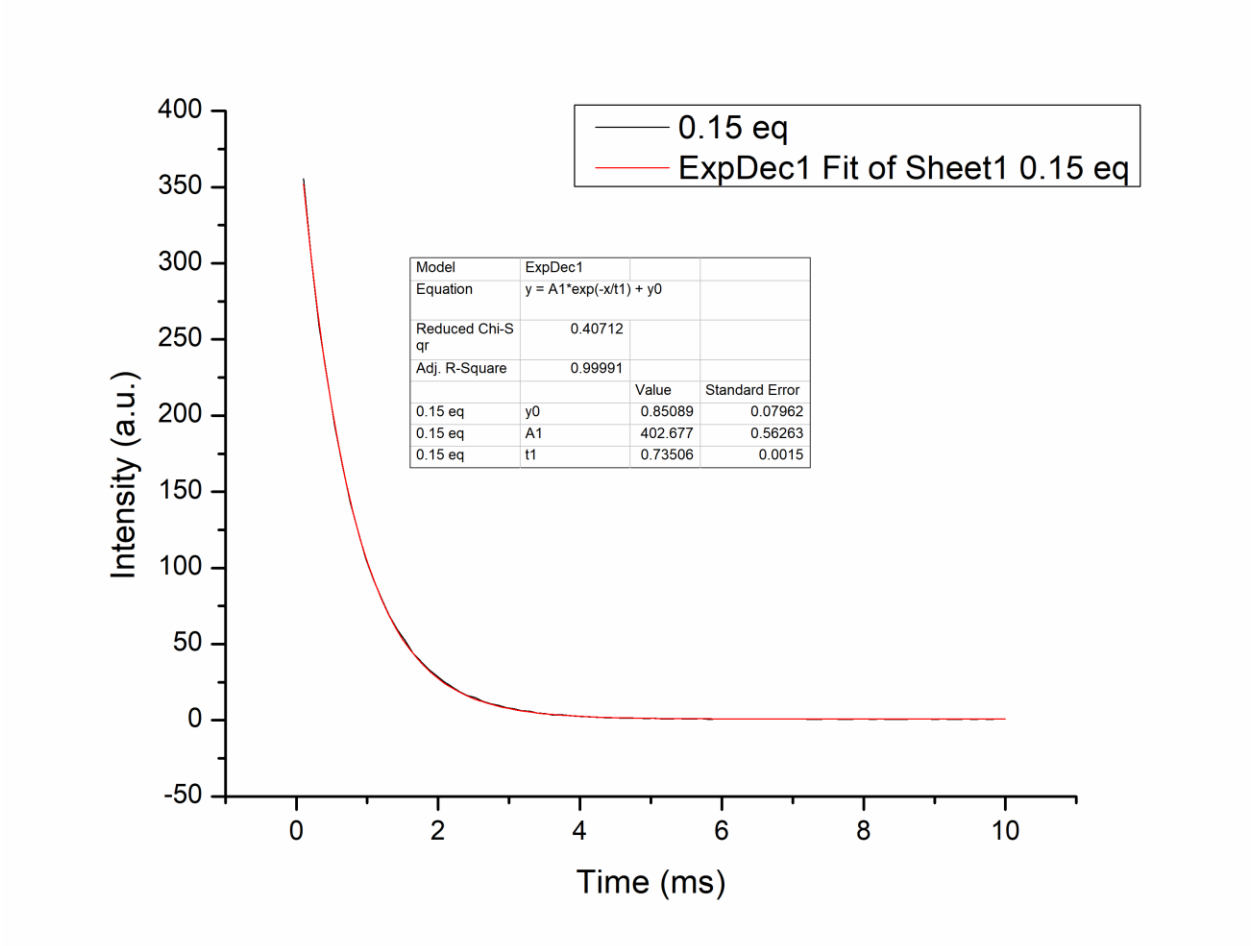


Figure S 27. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.1 eq


0.15 eq
ExpDec1 Fit of Sheet1 0.15 eq
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 0.40712
Adj. R-Square 0.99991
Value Standard Error
0.15 eq y0 0.85089 0.07962
0.15 eq A1 402.677 0.56263
0.15 eq t1 0.73506 0.0015
Intensity (a.u.)
Time (ms)
400
350
300
250
200
150
100
50
0
-50
0
2
4
6
8
10

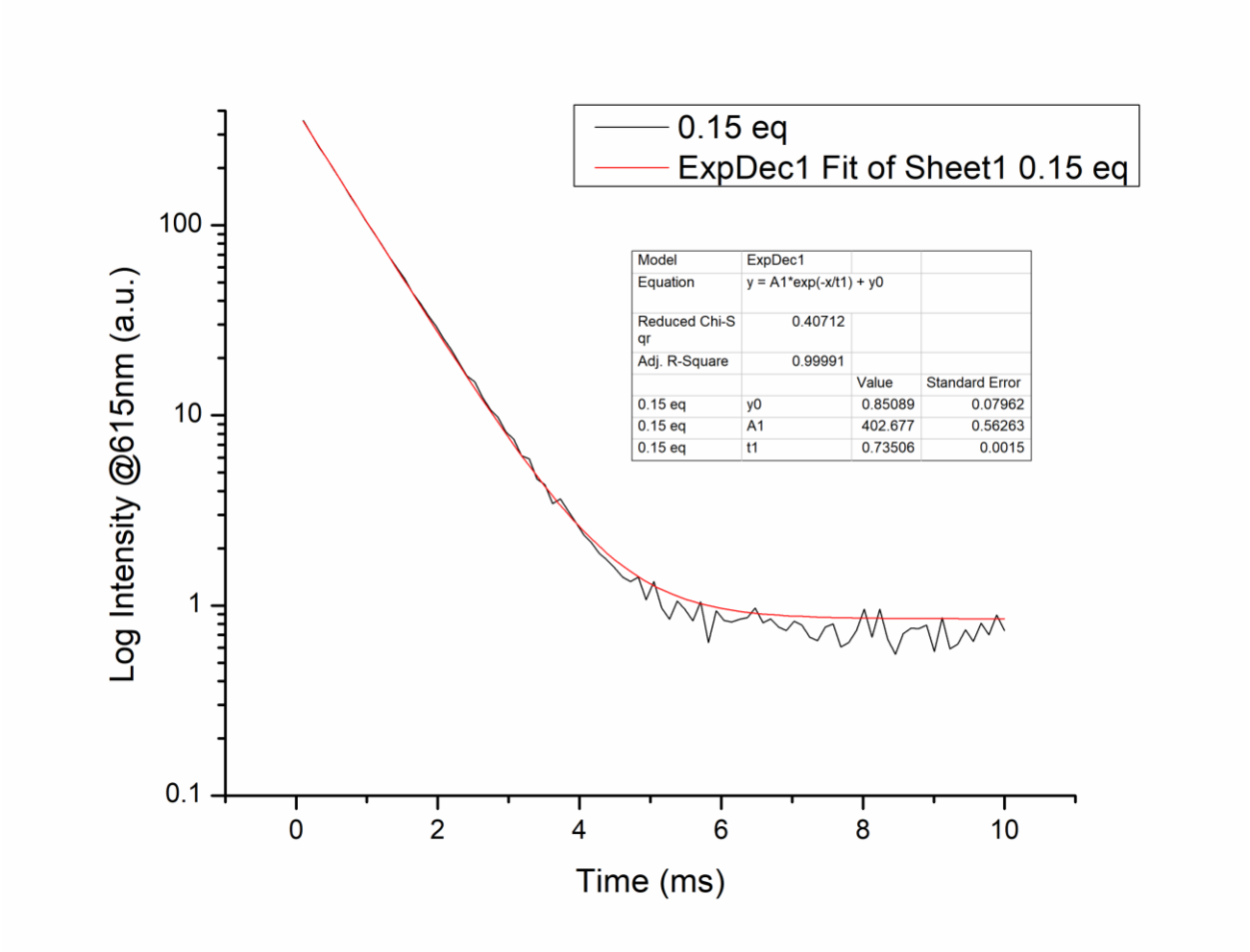
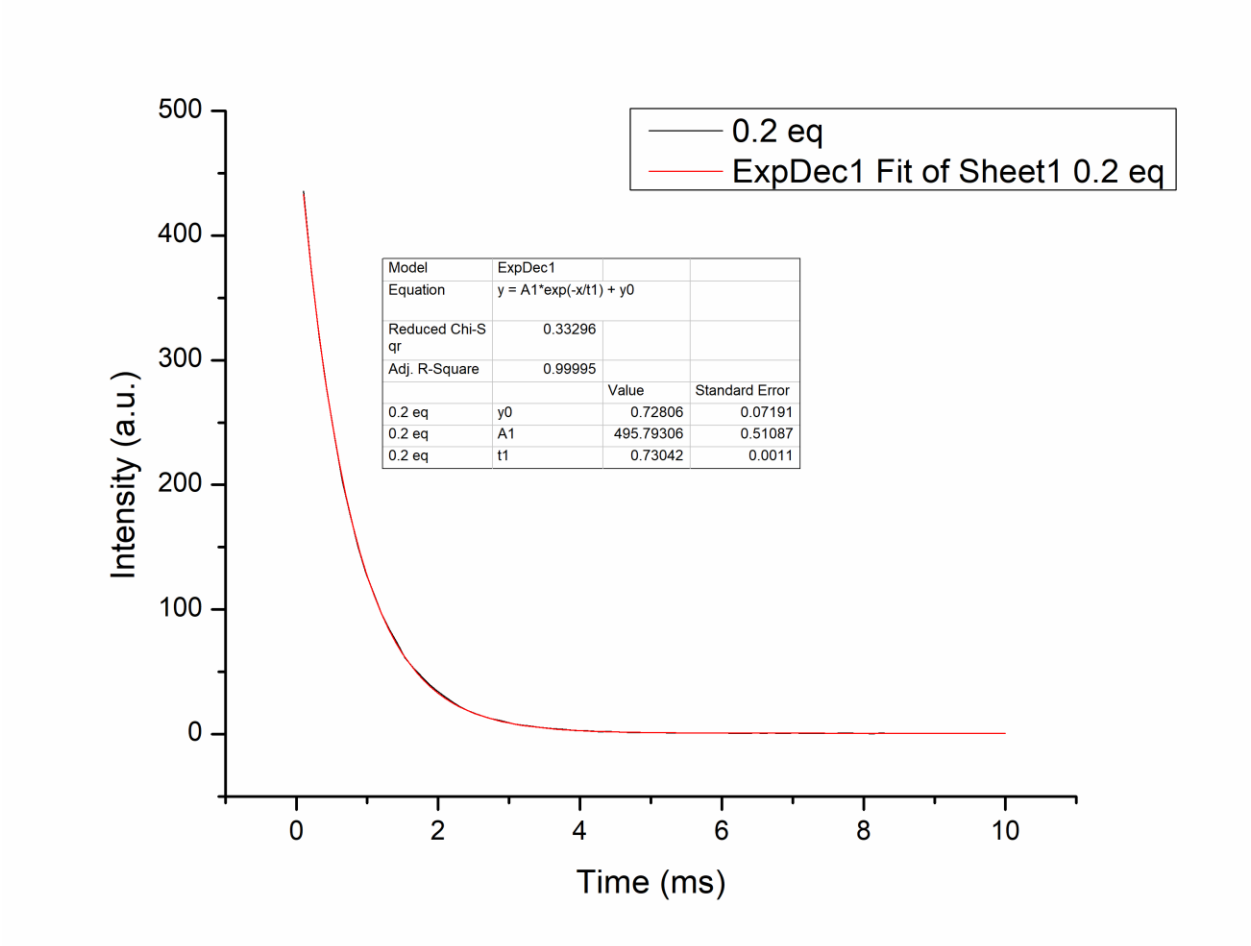


Figure S 28. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.15 eq



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	0.33296		
Adj. R-Square	0.99995		
		Value	Standard Error
0.2 eq	y0	0.72806	0.07191
0.2 eq	A1	495.79306	0.51087
0.2 eq	t1	0.73042	0.0011

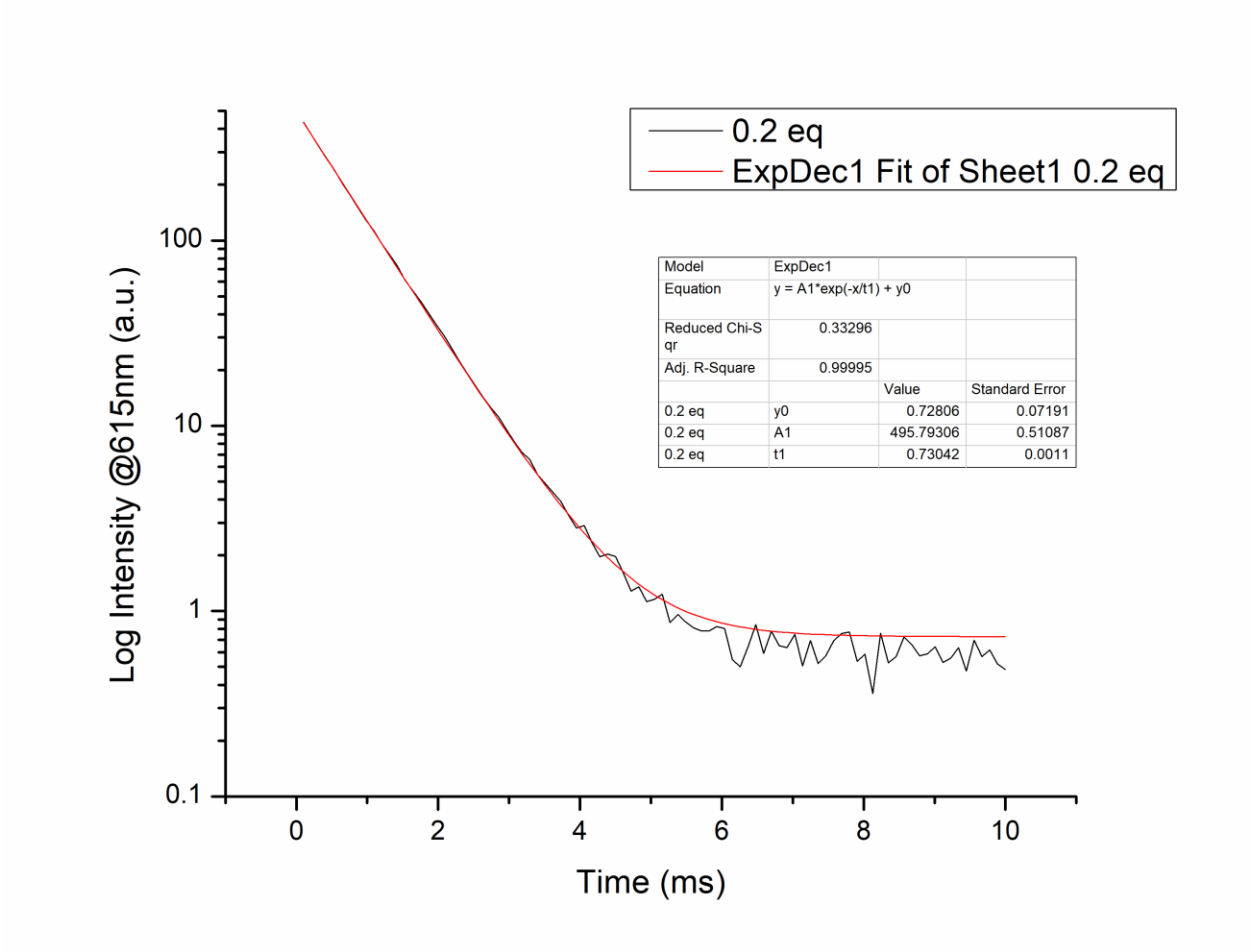
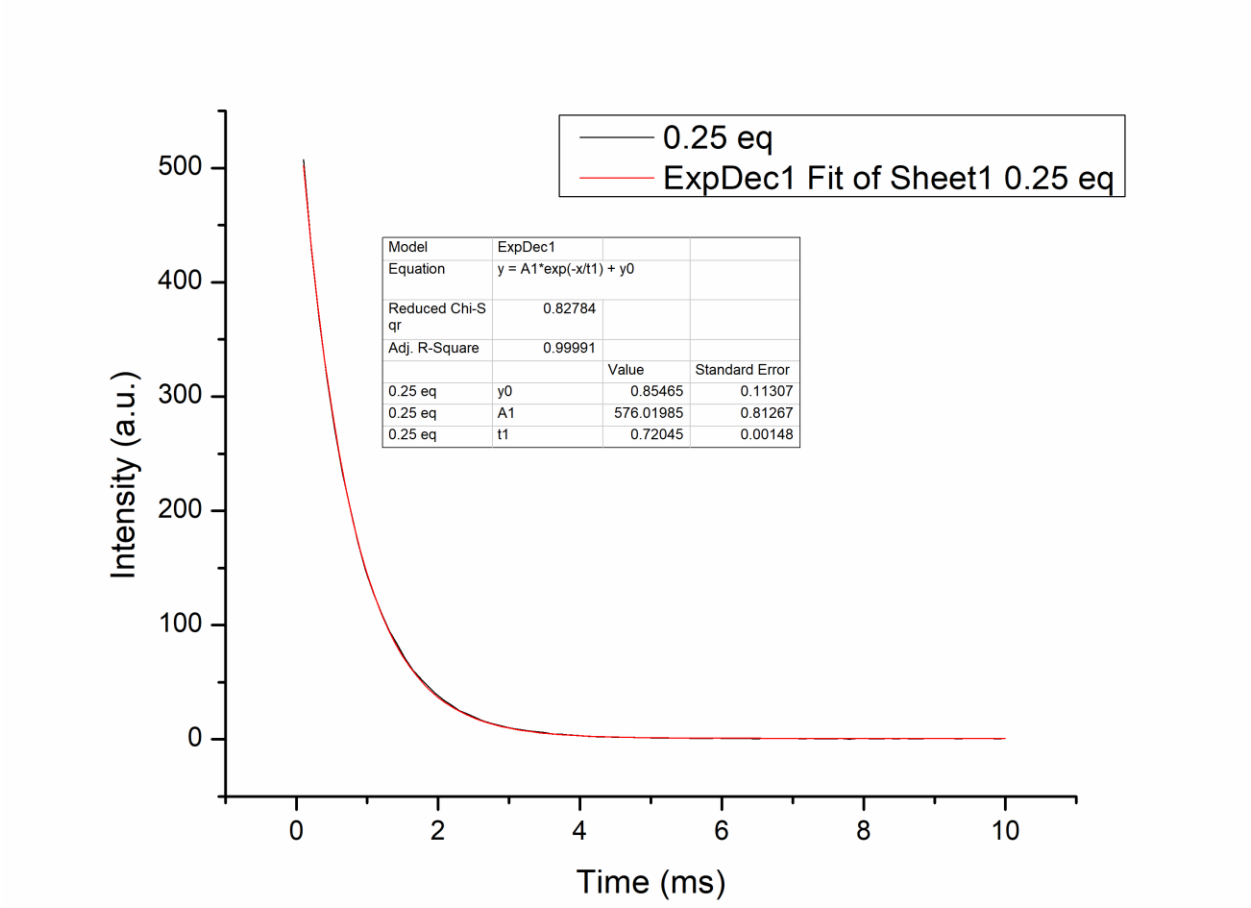


Figure S 29. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.2 eq


0.25 eq
ExpDec1 Fit of Sheet1 0.25 eq
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 0.82784
Adj. R-Square 0.99991
Value Standard Error
0.25 eq y0 0.85465 0.11307
0.25 eq A1 576.01985 0.81267
0.25 eq t1 0.72045 0.00148
Intensity (a.u.)
Time (ms)
0
100
200
300
400
500
0
2
4
6
8
10

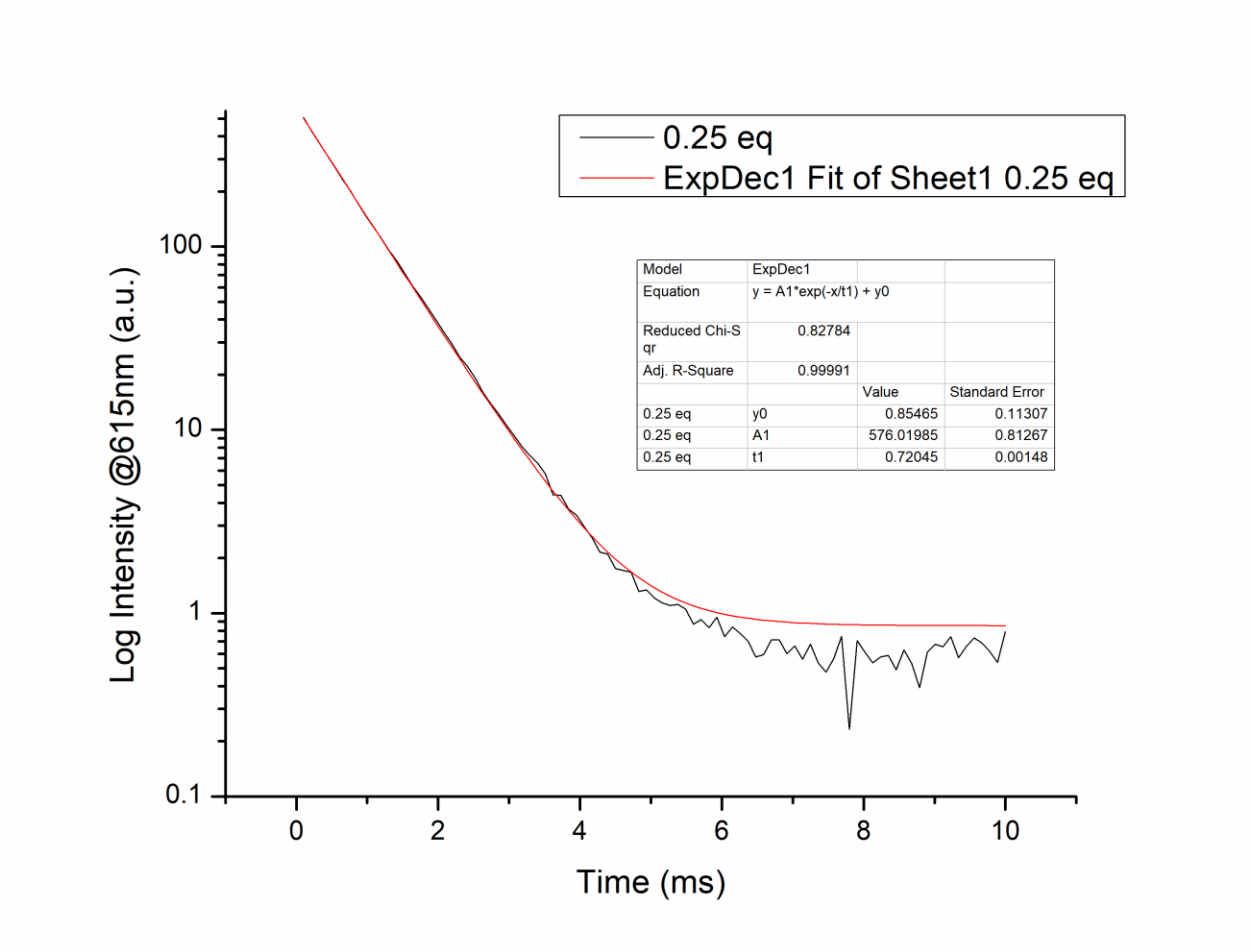
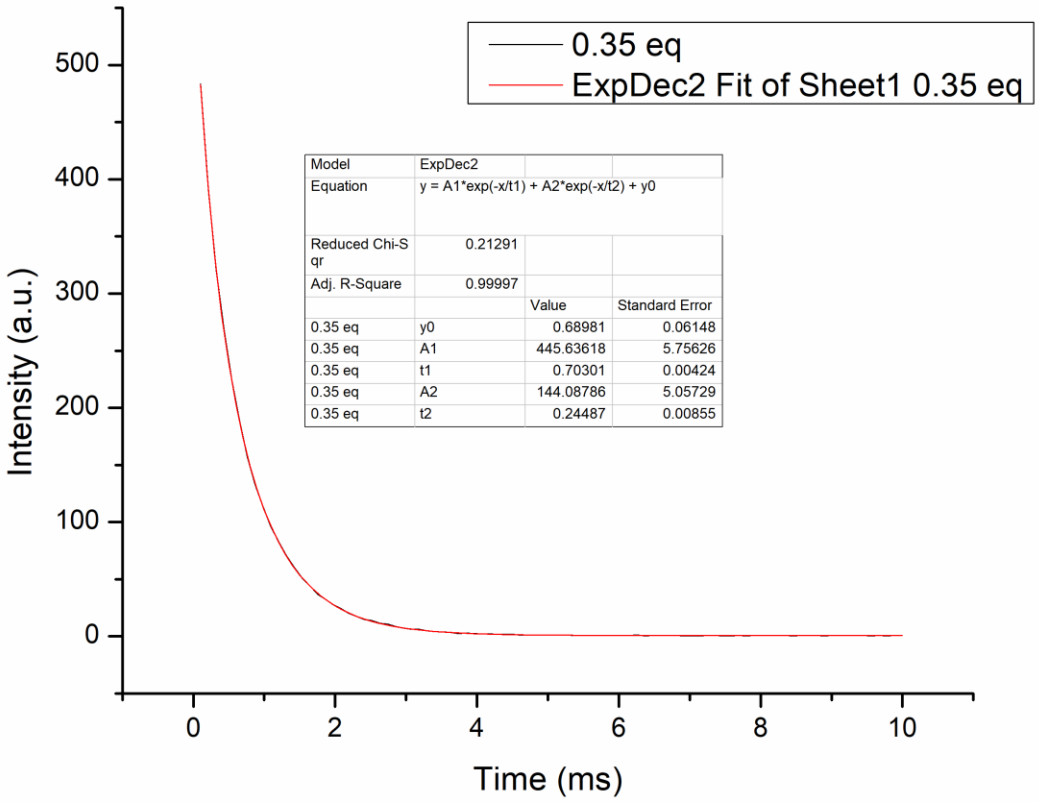


Figure S 30. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.25 eq



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	0.21291		
Adj. R-Square	0.99997		
		Value	Standard Error
0.35 eq	y0	0.68981	0.06148
0.35 eq	A1	445.63618	5.75626
0.35 eq	t1	0.70301	0.00424
0.35 eq	A2	144.08786	5.05729
0.35 eq	t2	0.24487	0.00855

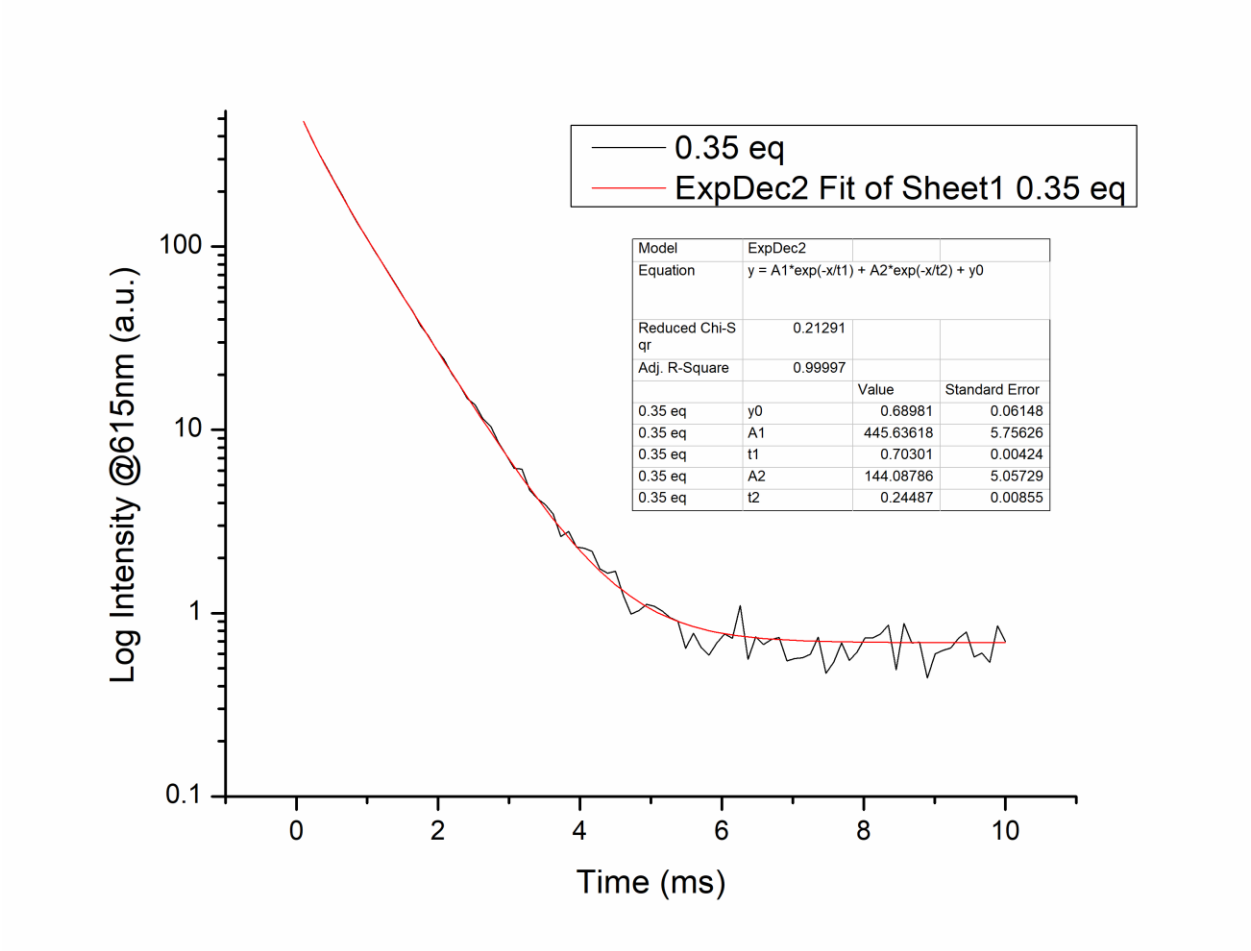
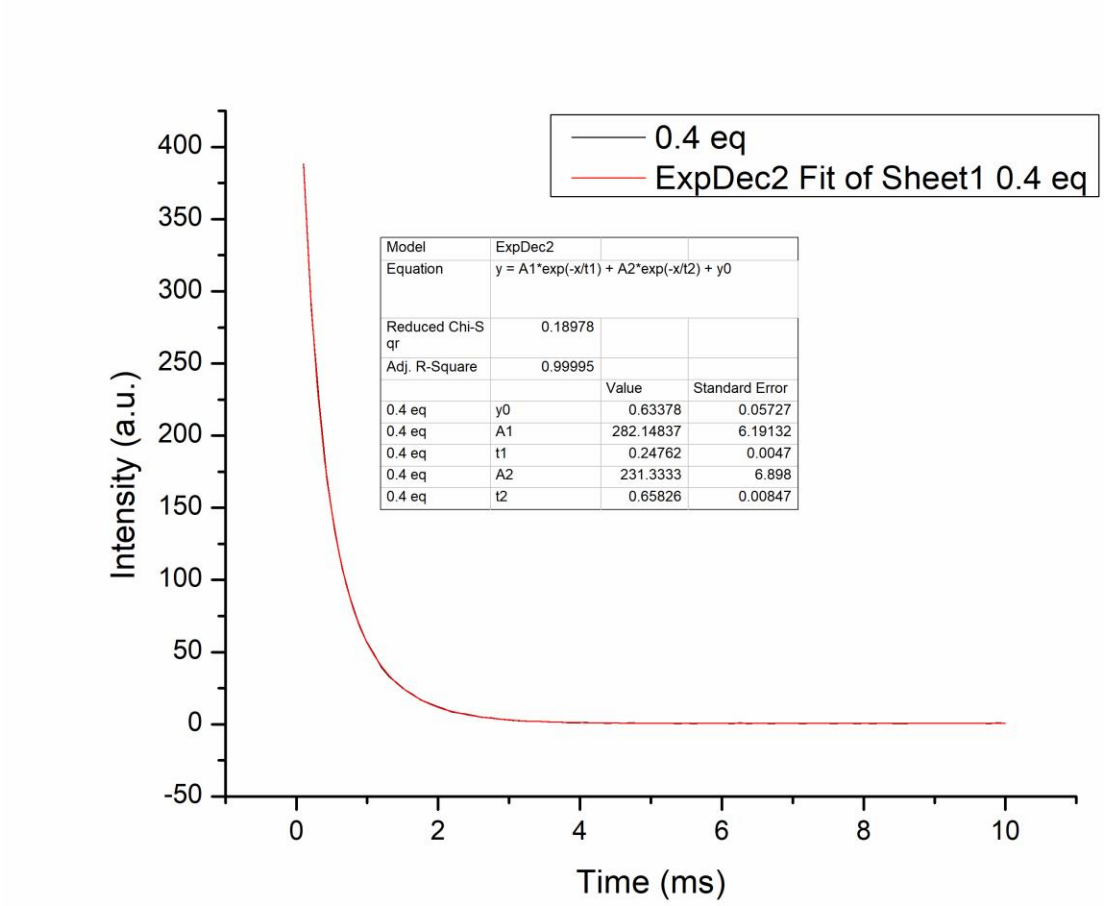


Figure S 31. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.35 eq



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	0.18978		
Adj. R-Square	0.99995		
		Value	Standard Error
0.4 eq	y0	0.63378	0.05727
0.4 eq	A1	282.14837	6.19132
0.4 eq	t1	0.24762	0.0047
0.4 eq	A2	231.3333	6.898
0.4 eq	t2	0.65826	0.00847

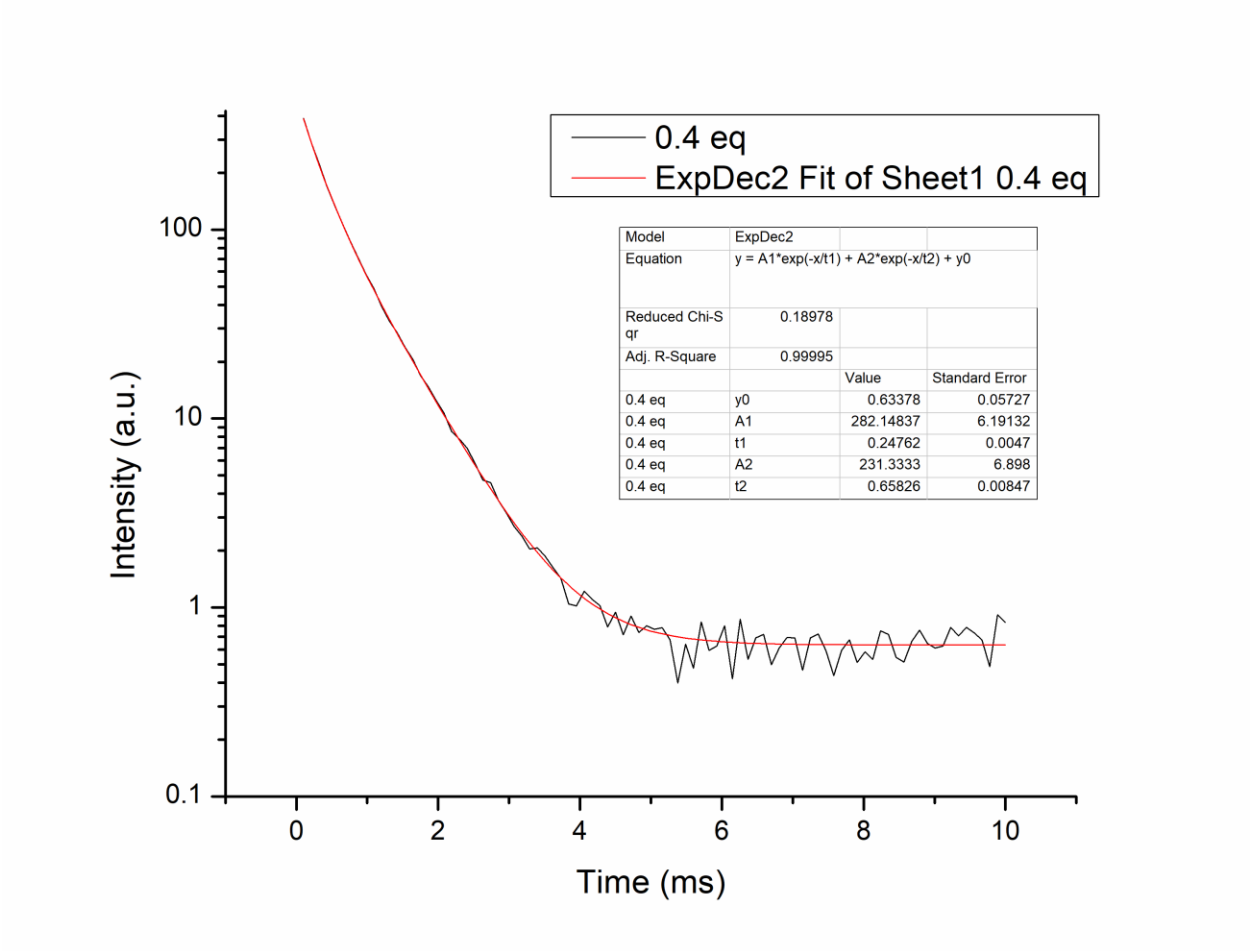
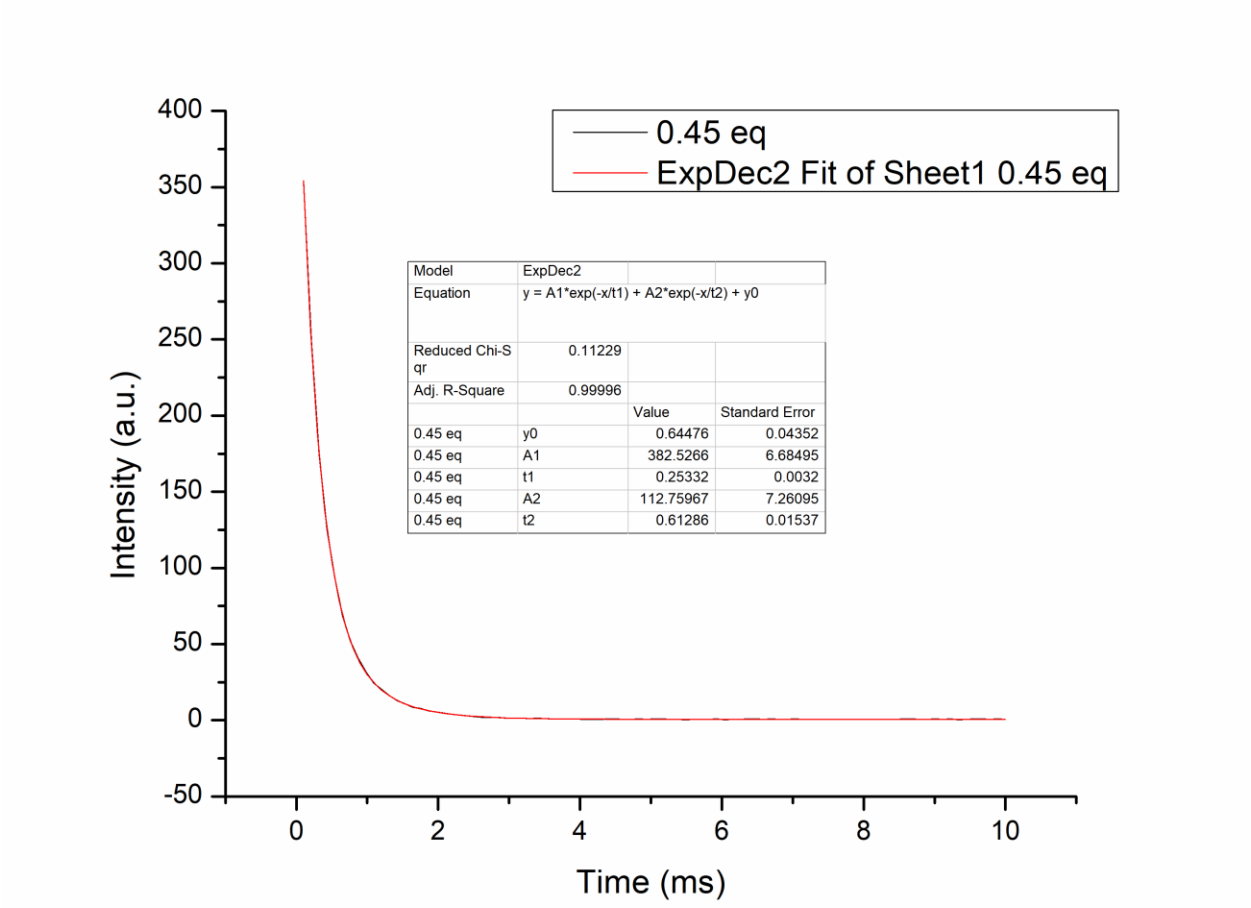


Figure S 32. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.4 eq



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	0.11229		
Adj. R-Square	0.99996		
		Value	Standard Error
0.45 eq	y0	0.64476	0.04352
0.45 eq	A1	382.5266	6.68495
0.45 eq	t1	0.25332	0.0032
0.45 eq	A2	112.75967	7.26095
0.45 eq	t2	0.61286	0.01537

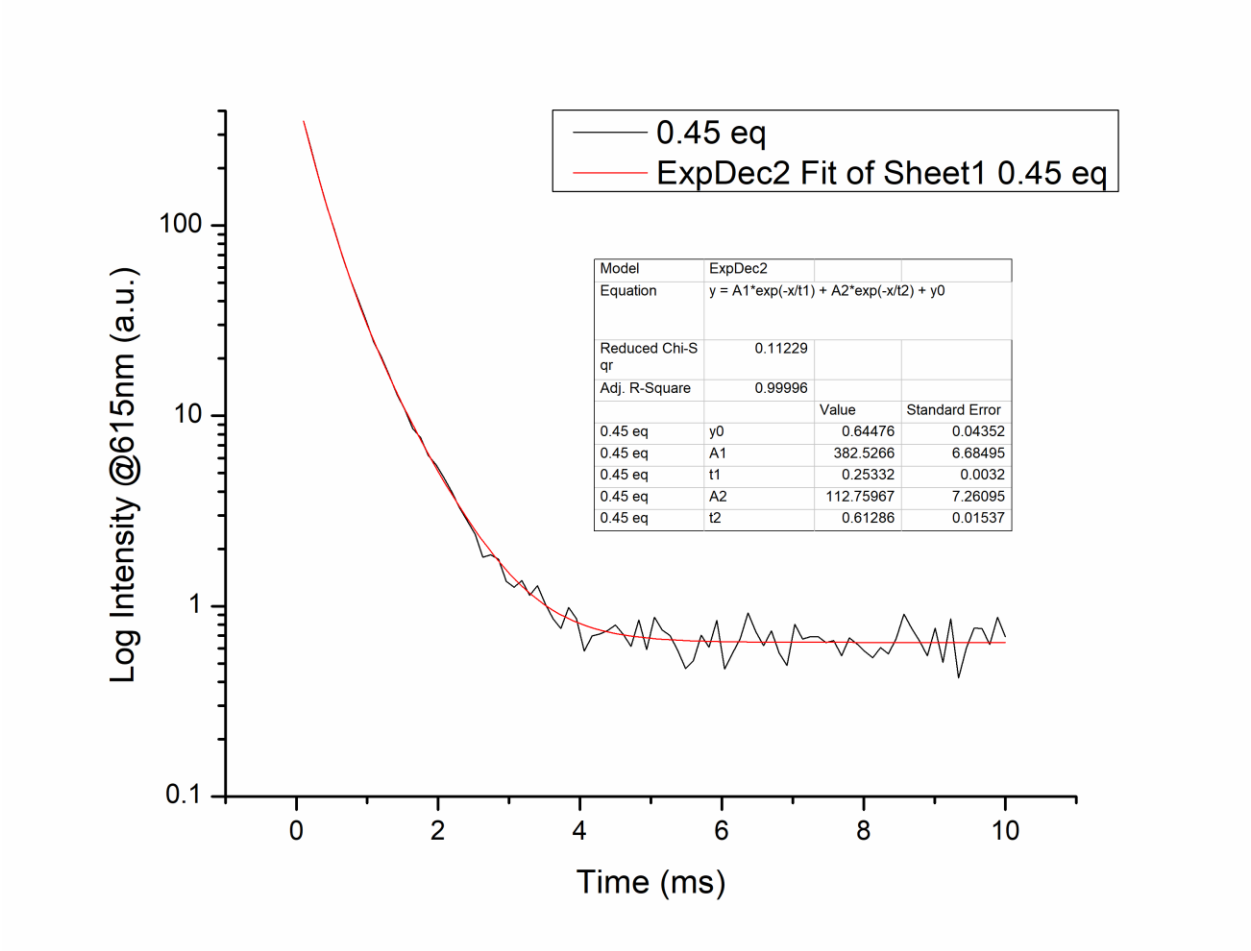
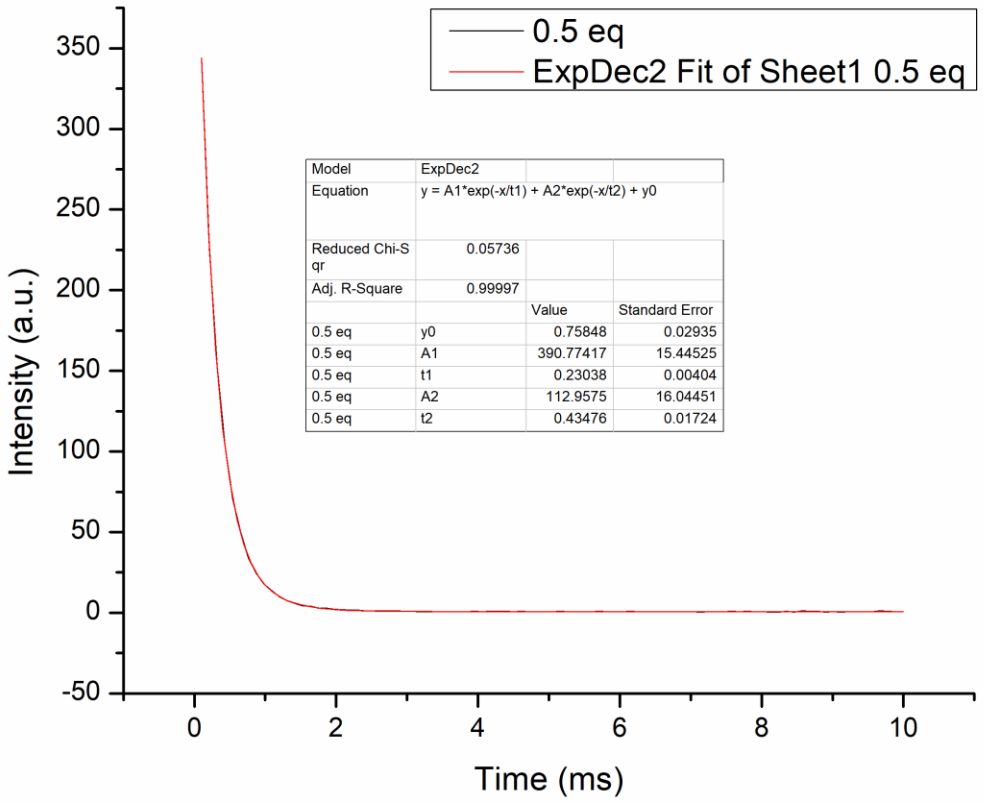


Figure S 33. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.45 eq



Model	ExpDec2		
Equation	y = A1*exp(-x/t1) + A2*exp(-x/t2) + y0		
Reduced Chi-Sqr	0.05736		
Adj. R-Square	0.99997		
		Value	Standard Error
0.5 eq	y0	0.75848	0.02935
0.5 eq	A1	390.77417	15.44525
0.5 eq	t1	0.23038	0.00404
0.5 eq	A2	112.9575	16.04451
0.5 eq	t2	0.43476	0.01724

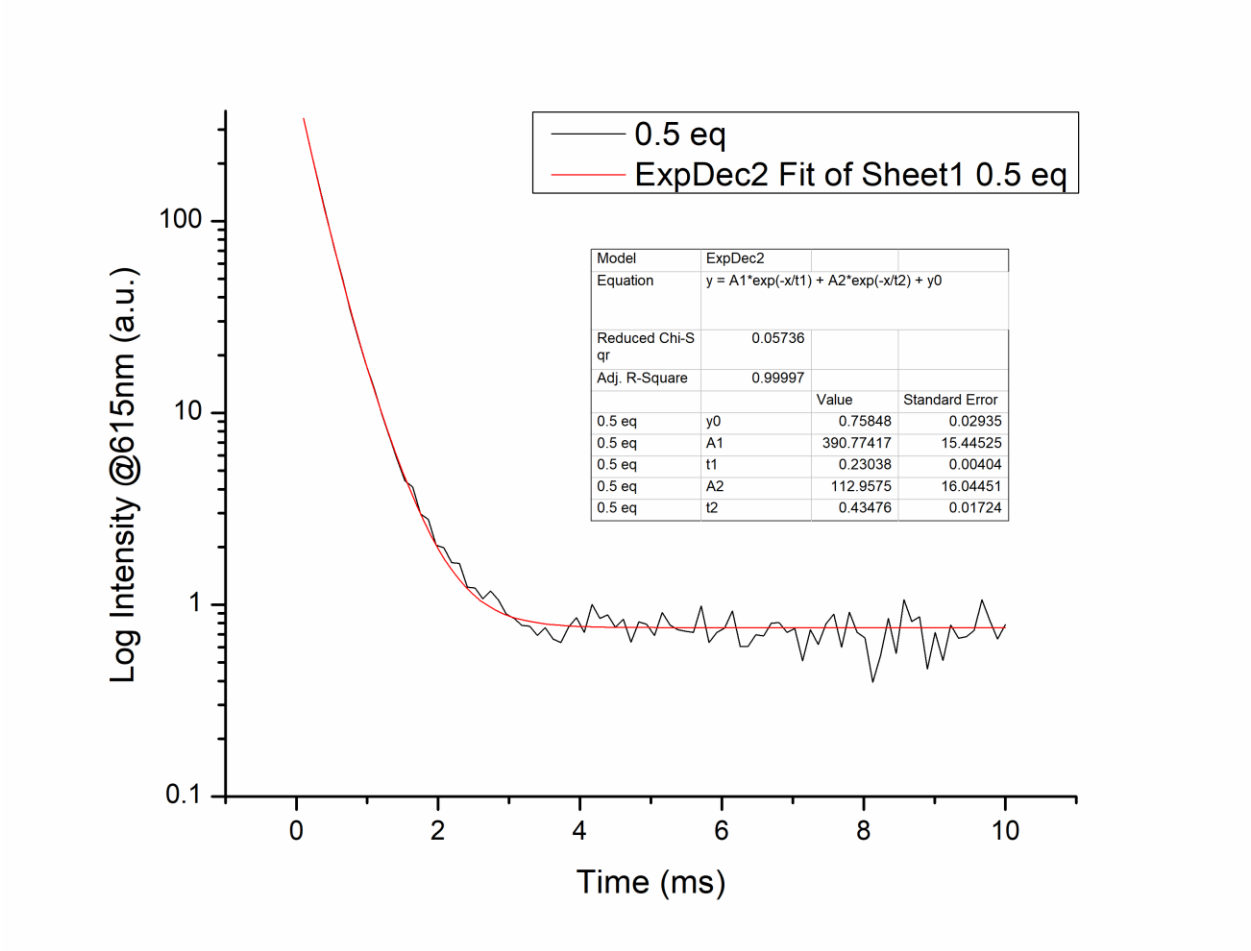
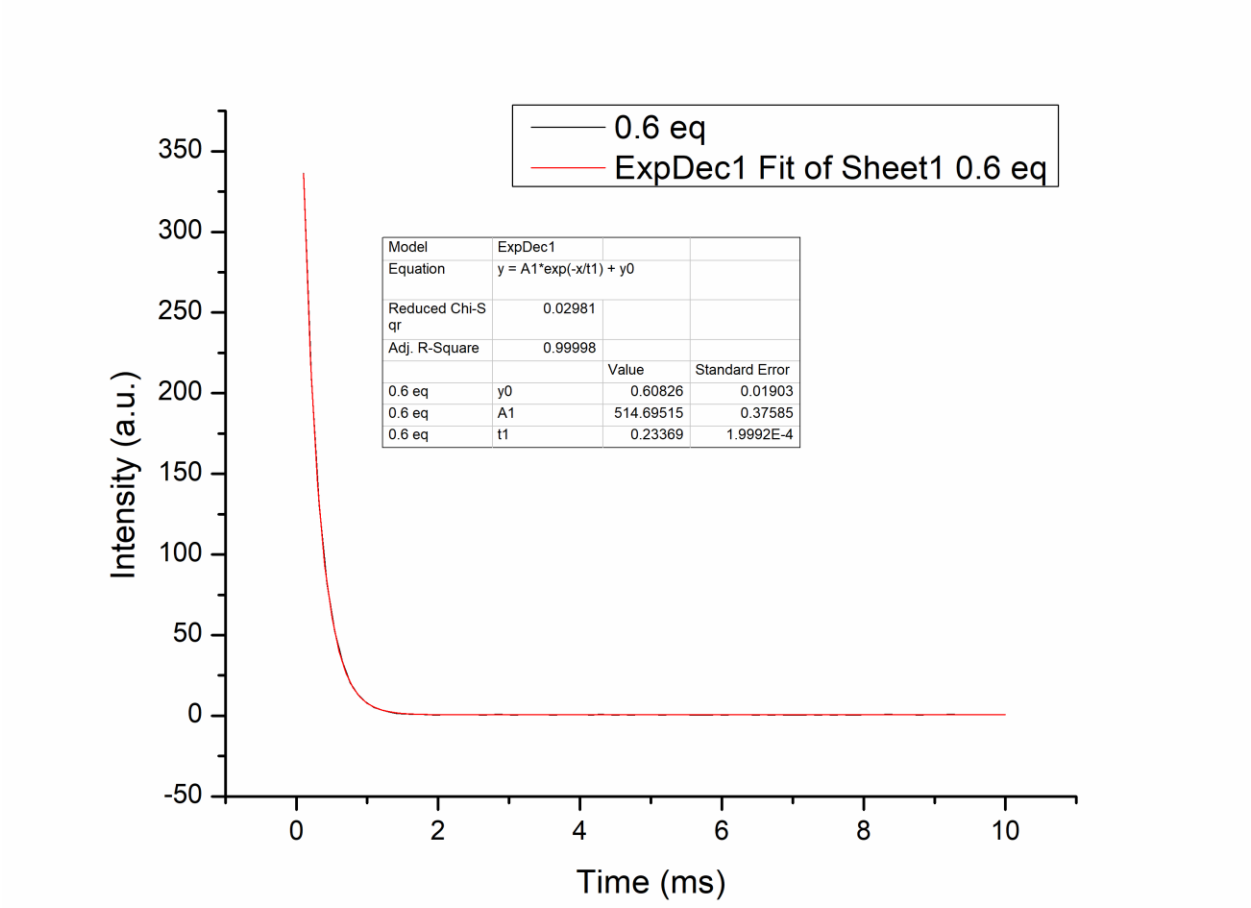


Figure S 34. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.5 eq


0.6 eq
ExpDec1 Fit of Sheet1 0.6 eq
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 0.02981
Adj. R-Square 0.99998
Value Standard Error
0.6 eq y0 0.60826 0.01903
0.6 eq A1 514.69515 0.37585
0.6 eq t1 0.23369 1.9992E-4
Intensity (a.u.)
Time (ms)
350
300
250
200
150
100
50
0
-50
0
2
4
6
8
10

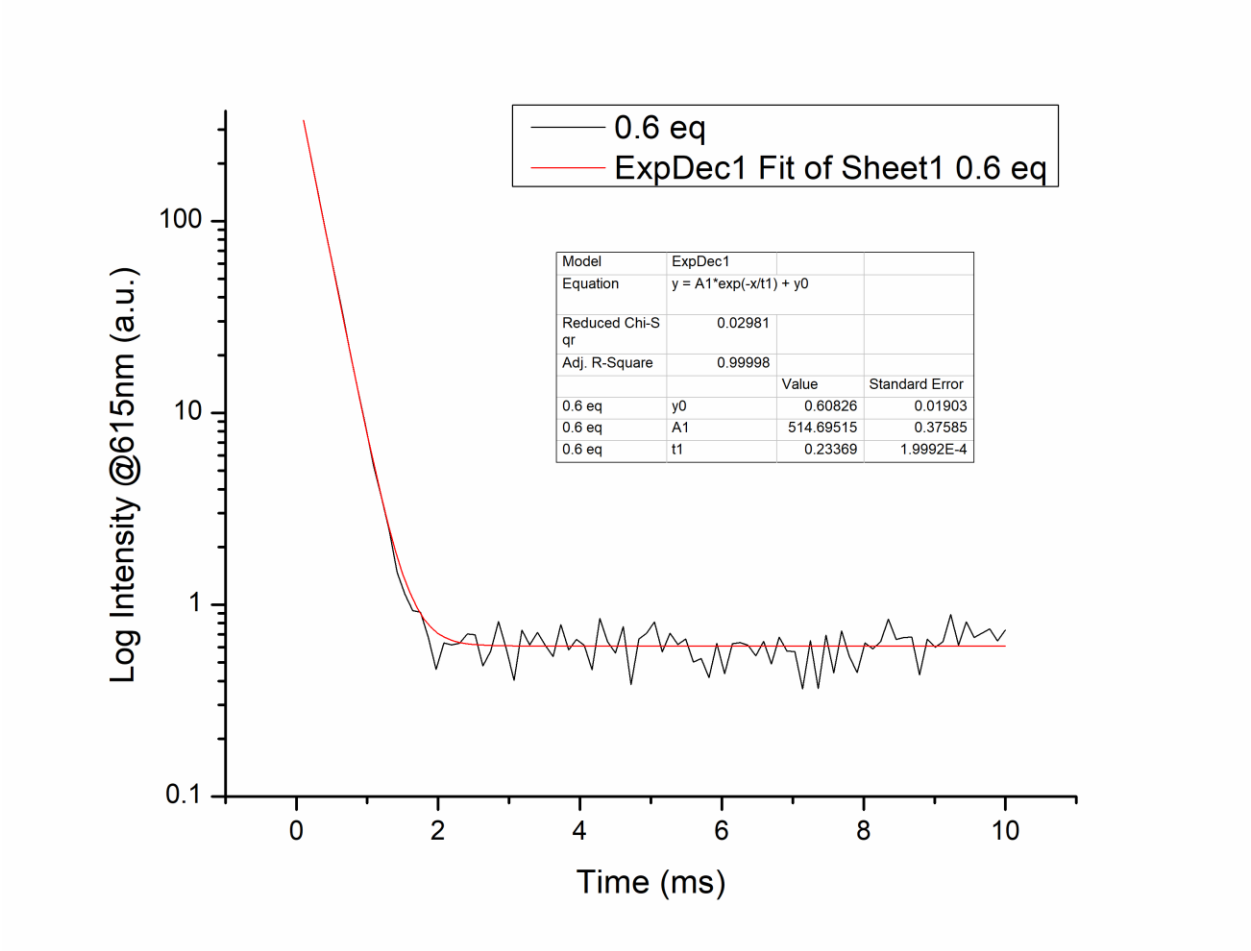
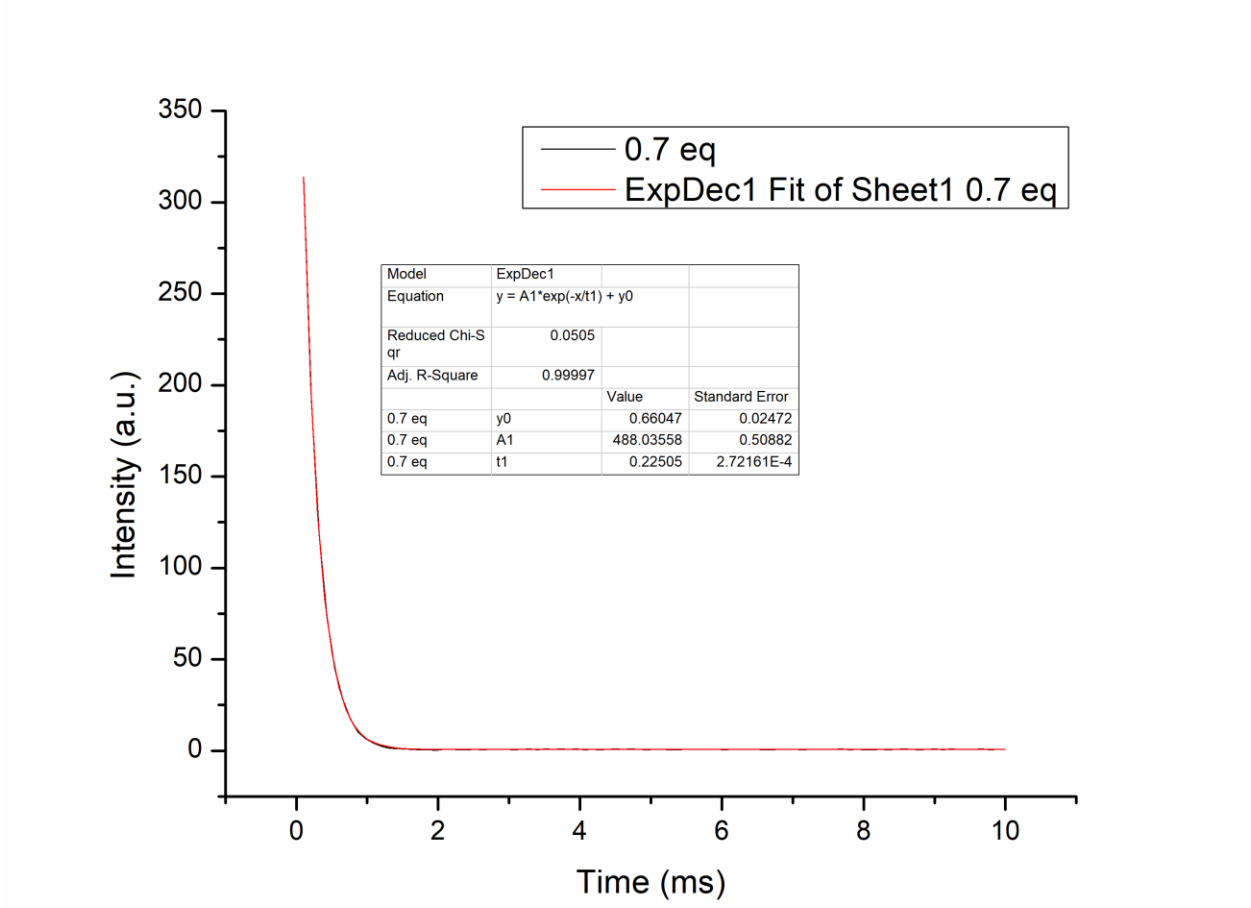


Figure S 35. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.6 eq



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	0.0505		
Adj. R-Square	0.99997		
		Value	Standard Error
0.7 eq	y0	0.66047	0.02472
0.7 eq	A1	488.03558	0.50882
0.7 eq	t1	0.22505	2.72161E-4

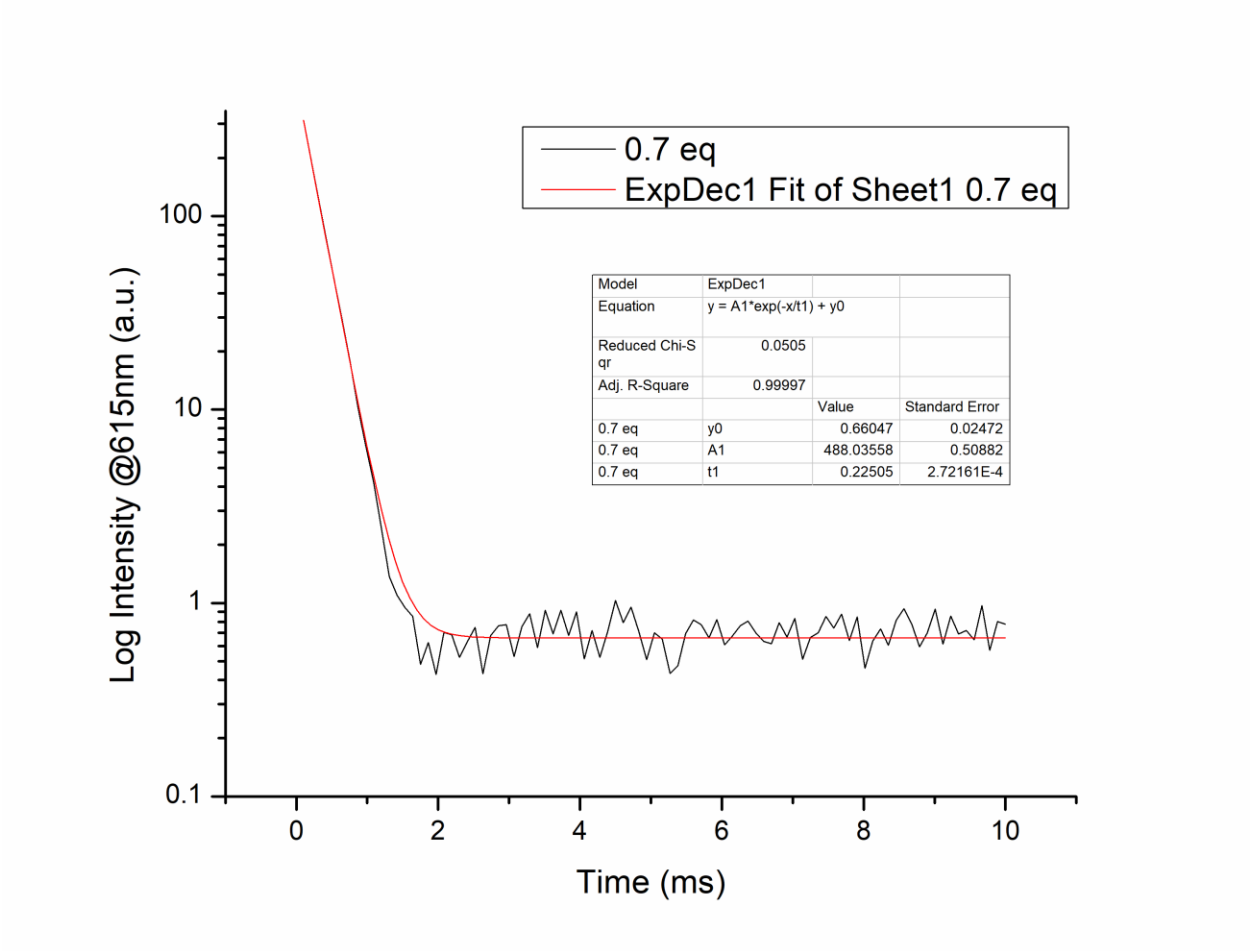
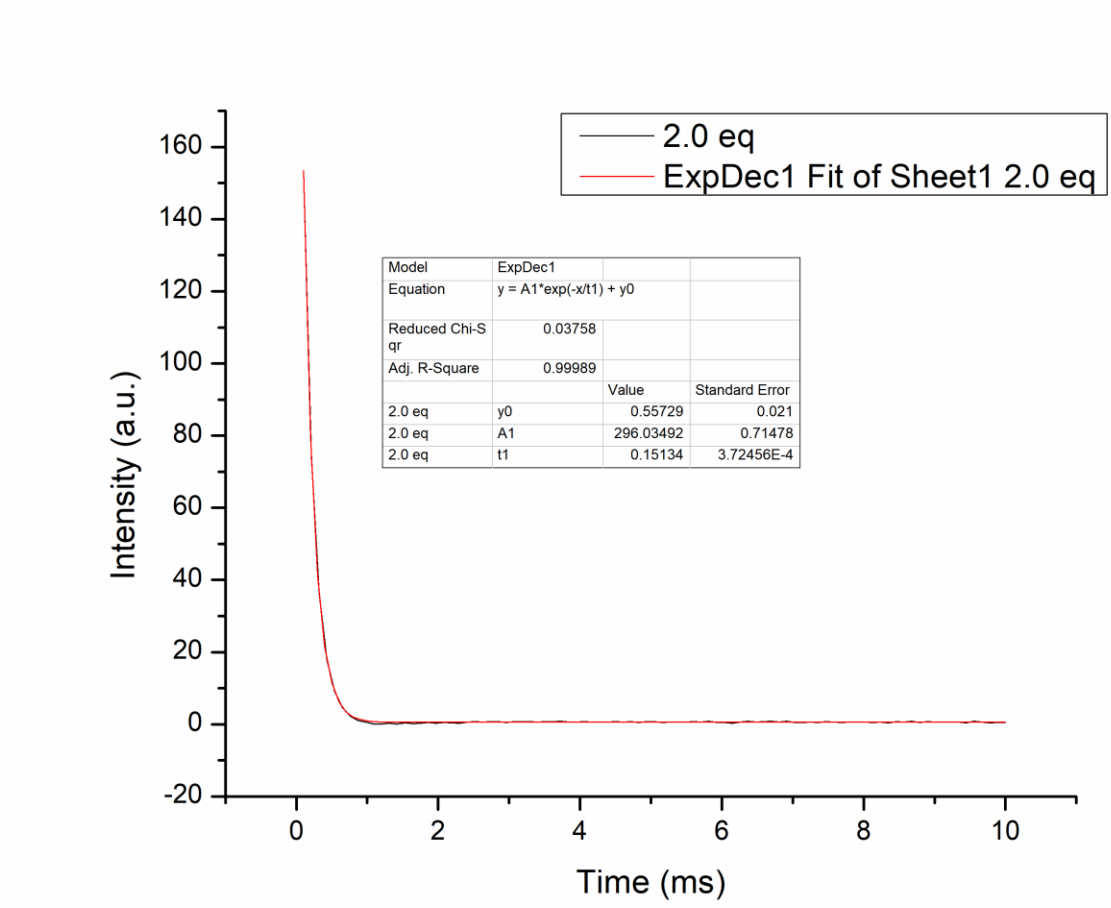


Figure S 36. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 0.7 eq



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	0.03758		
Adj. R-Square	0.99989		
		Value	Standard Error
2.0 eq	y0	0.55729	0.021
2.0 eq	A1	296.03492	0.71478
2.0 eq	t1	0.15134	3.72456E-4

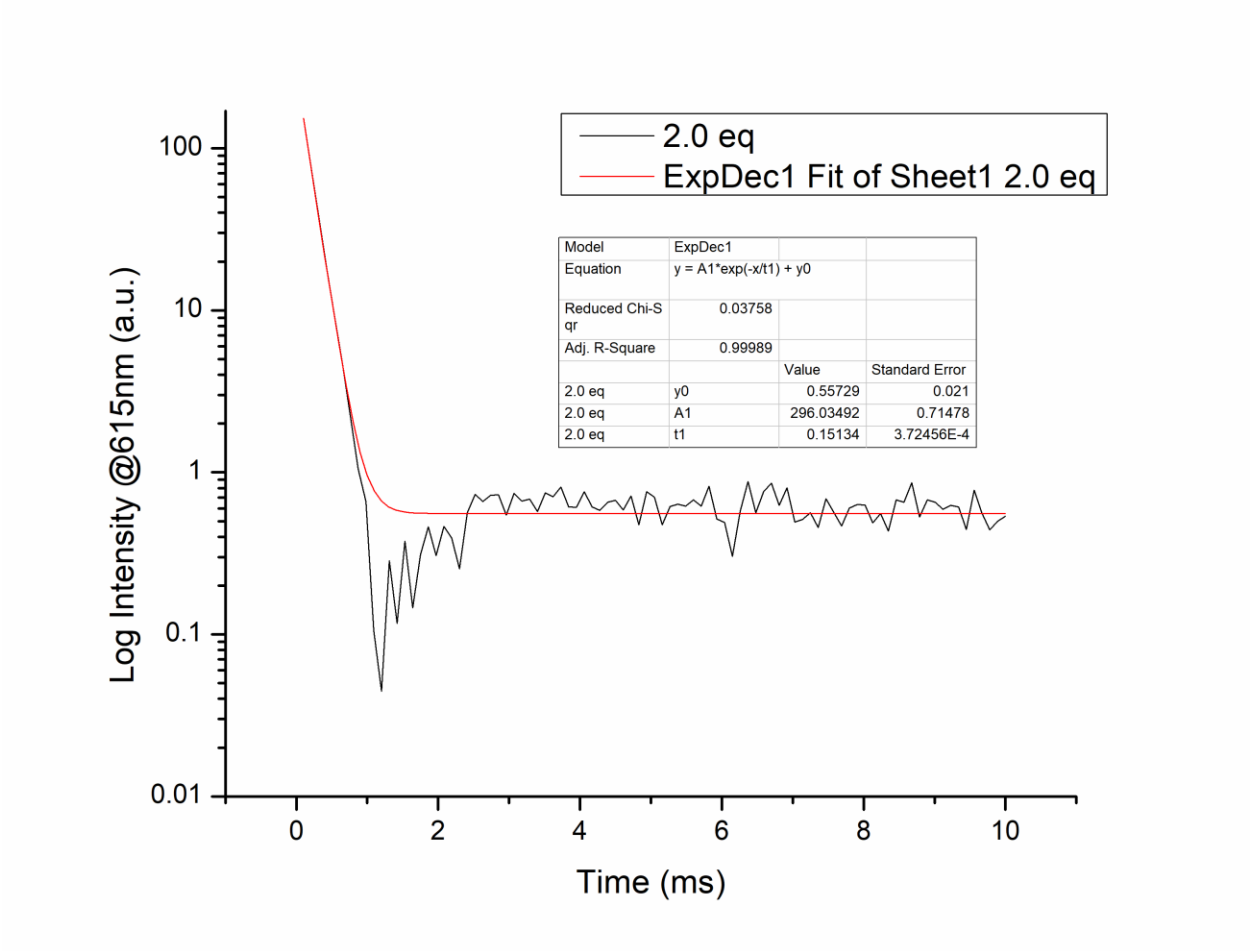


Figure S 37. Fluorescence decay fitting of L_1^{2-} in Tris HCl with increasing amounts of Eu^{3+} monitoring at 615 nm and exciting at 360 nm: 2 eq

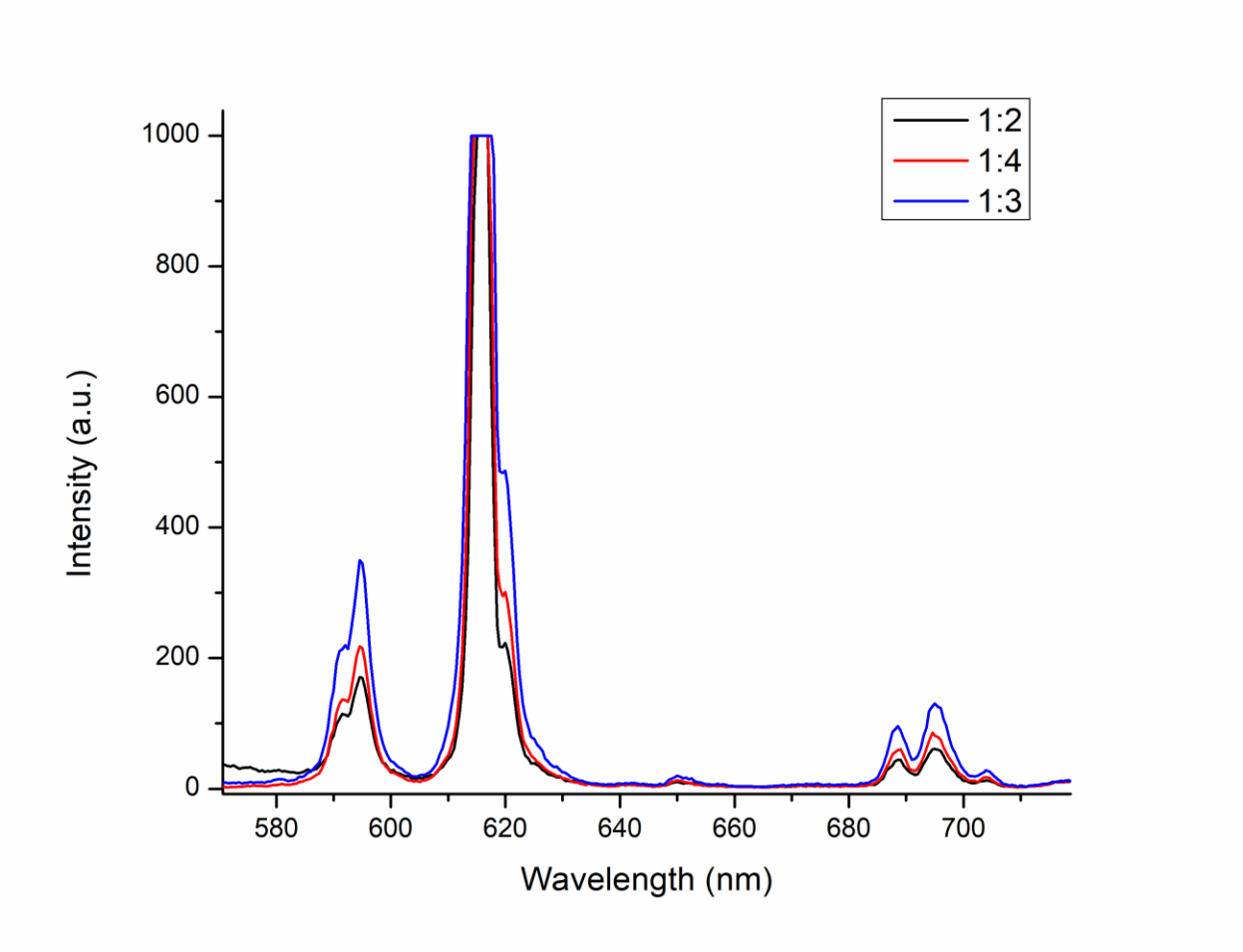
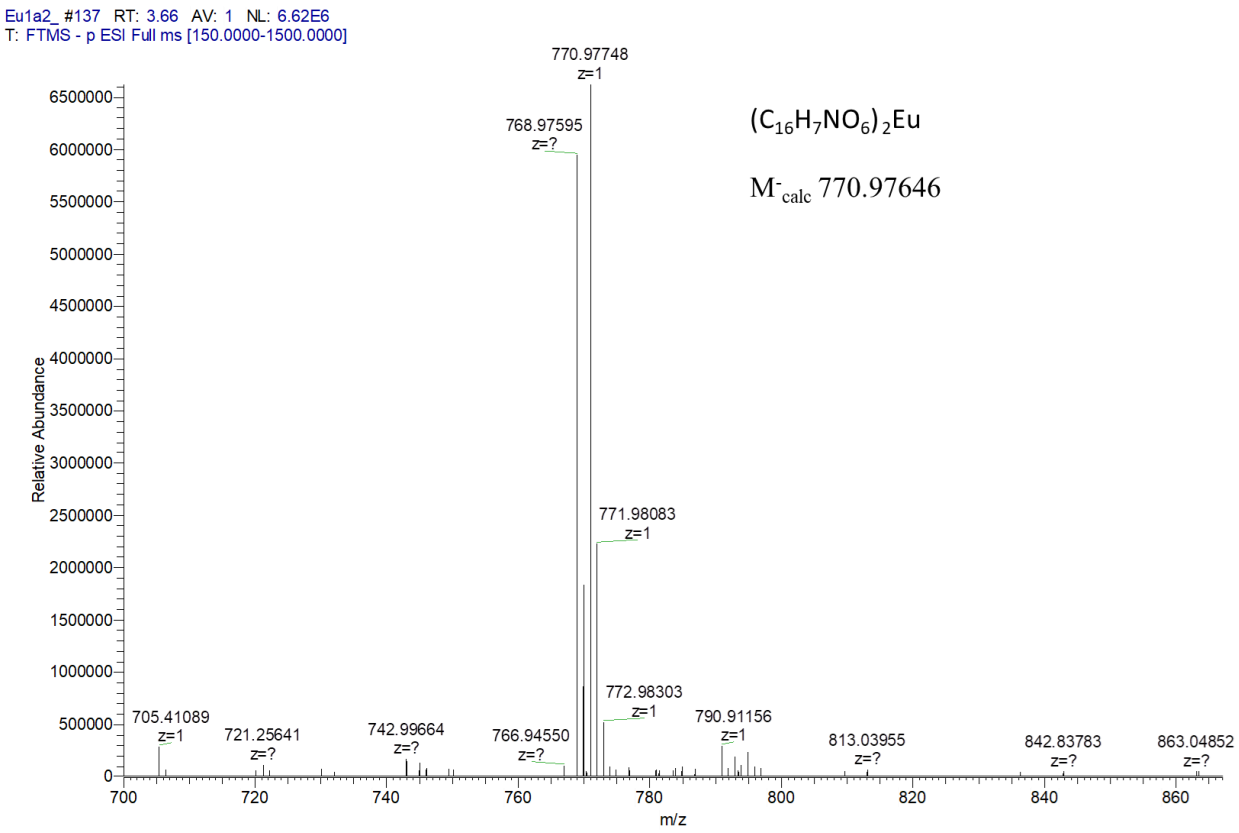


Figure S 38. Fluorescence spectra comparison (excitation at 360 nm) in DMSO between Eu^{3+}/L_2^{2-} in 1:2 (black), 1:3 (blue) and 1:4 (red) molar ratios.


Eu1a2_ #137 RT: 3.66 AV: 1 NL: 6.62E6
T: FTMS - p ESI Full ms [150.0000-1500.0000]
770.97748
z=1
768.97595
z=?
771.98083
z=1
772.98303
z=1
705.41089
z=1
721.25641
z=?
742.99664
z=?
766.94550
z=?
790.91156
z=1
813.03955
z=?
842.83783
z=?
863.04852
z=?
Relative Abundance
m/z
$(C_{16}H_7NO_6)_2Eu$
M^-_{calc} 770.97646

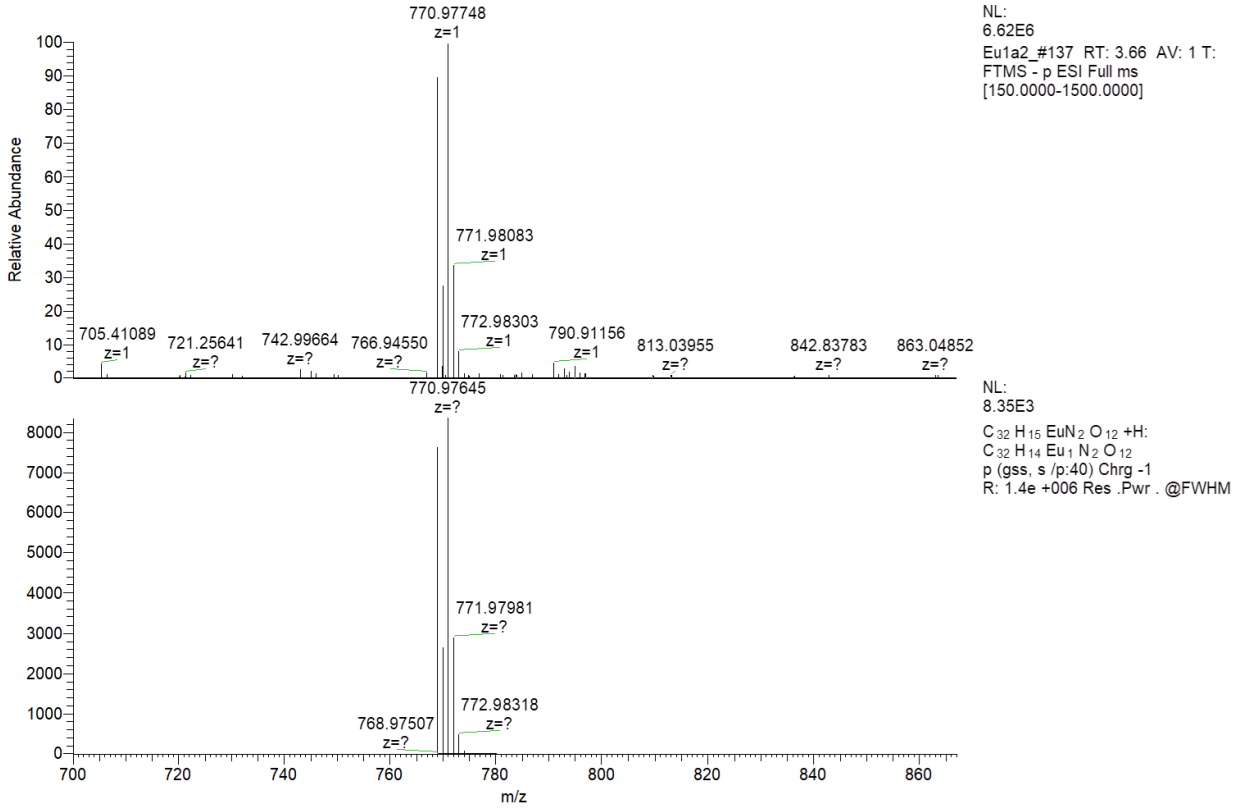


Figure S 39. HRMS spectra of DMSO mixture Eu^{3+}:L_1^{2-} in 1:2 molar ratio.

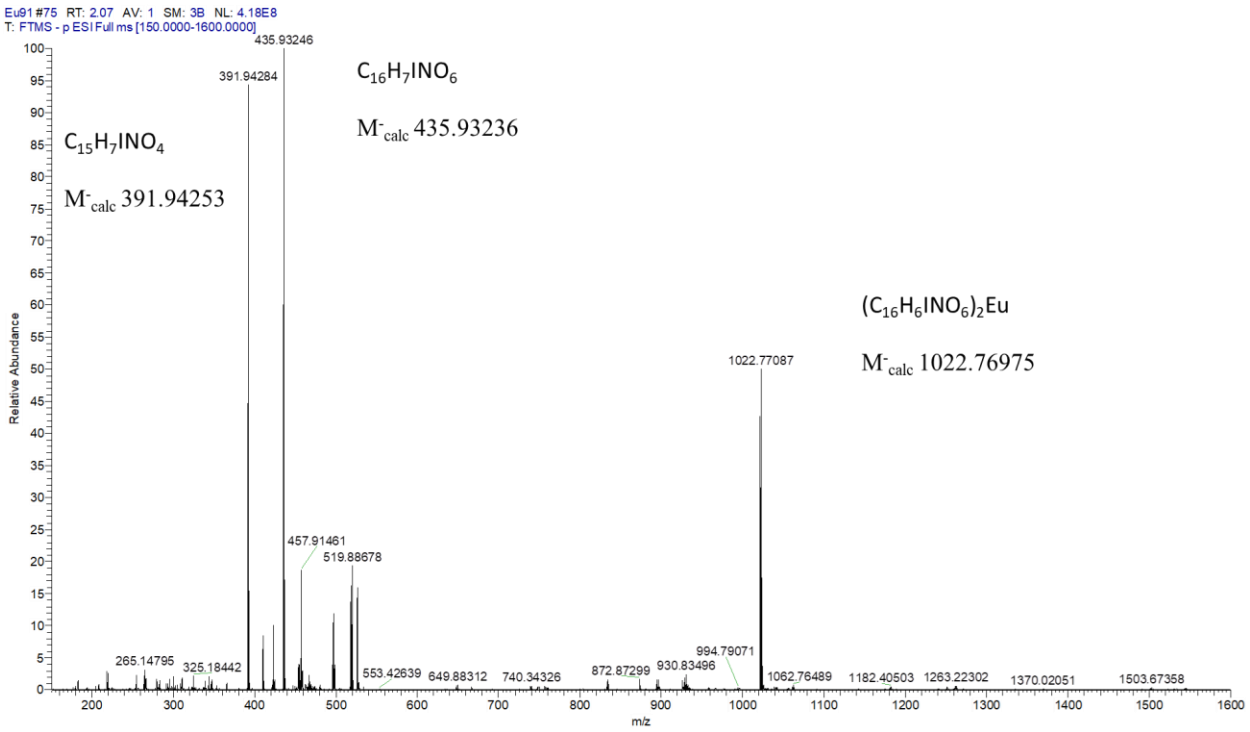


Figure S 40. HMRS spectrum of DMSO mixture Eu^{3+}:L_2^{2-} in 1:2 molar ratio.

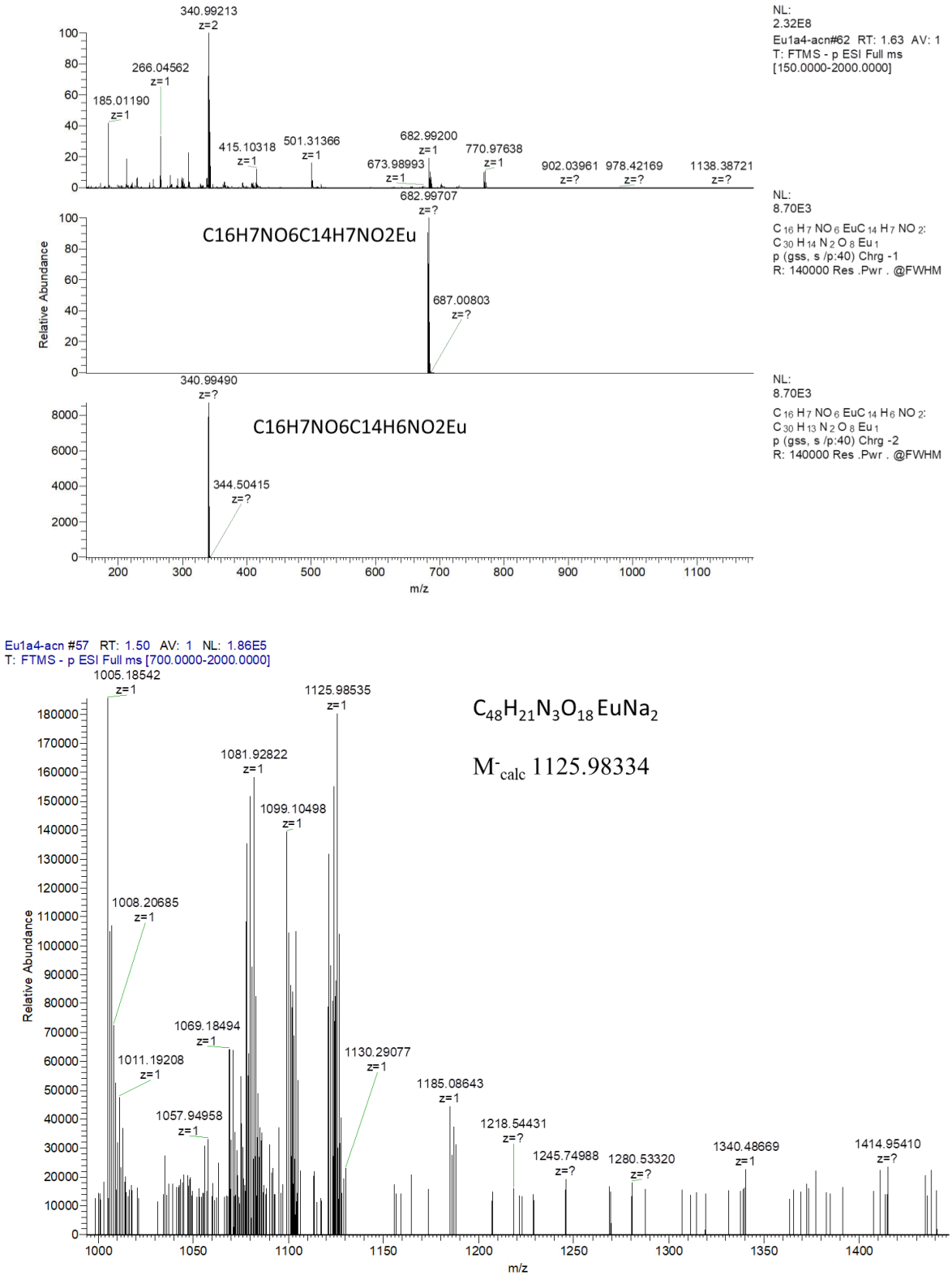
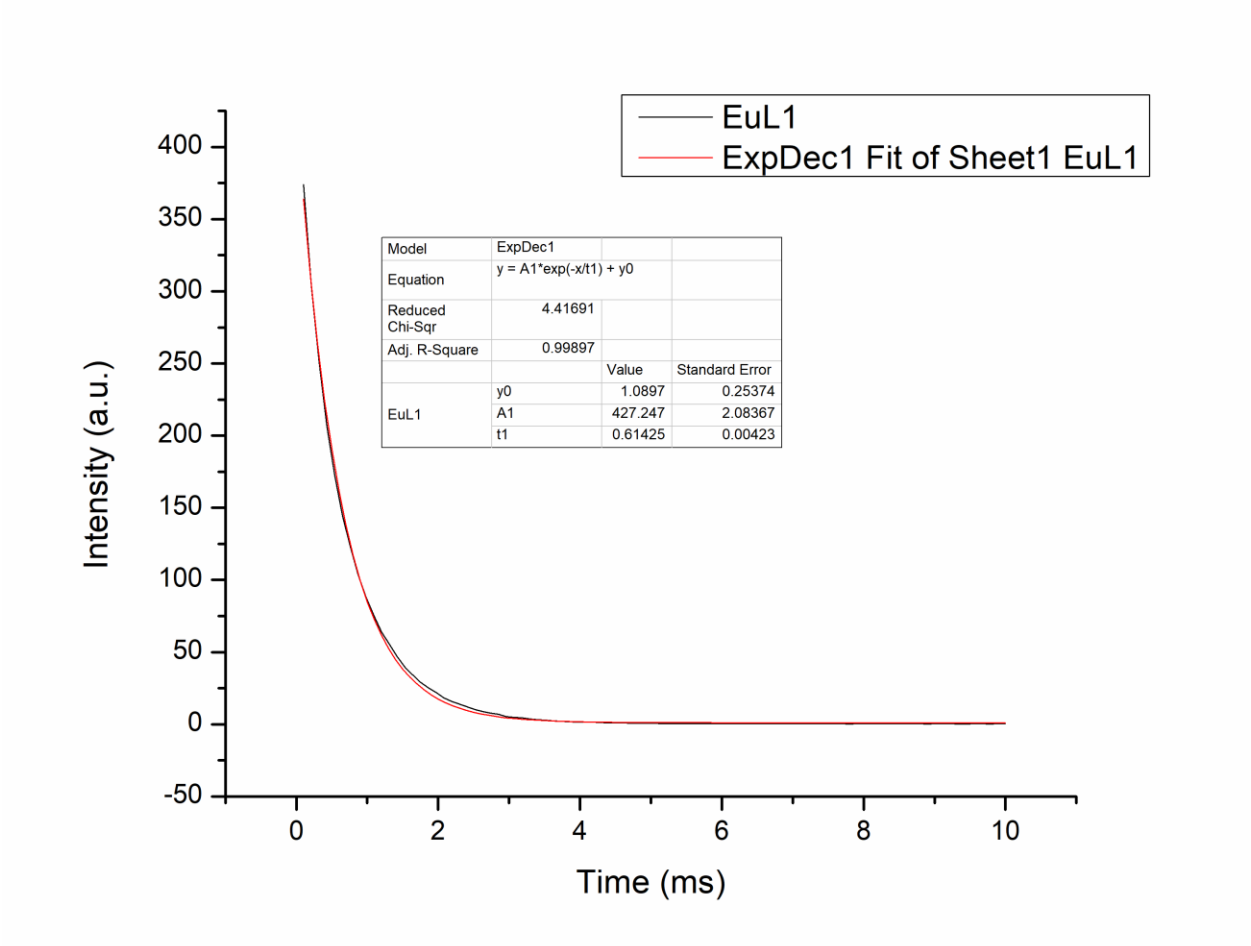


Figure S 41. HMRS spectrum of DMSO mixture Eu^{3+}:L_1^{2-} in 1:4 molar ratio.


EuL1
ExpDec1 Fit of Sheet1 EuL1
Model ExpDec1
Equation y = A1*exp(-x/t1) + y0
Reduced Chi-Sqr 4.41691
Adj. R-Square 0.99897
Value Standard Error
EuL1 y0 1.0897 0.25374
A1 427.247 2.08367
t1 0.61425 0.00423
Intensity (a.u.)
Time (ms)
400
350
300
250
200
150
100
50
0
-50
0
2
4
6
8
10

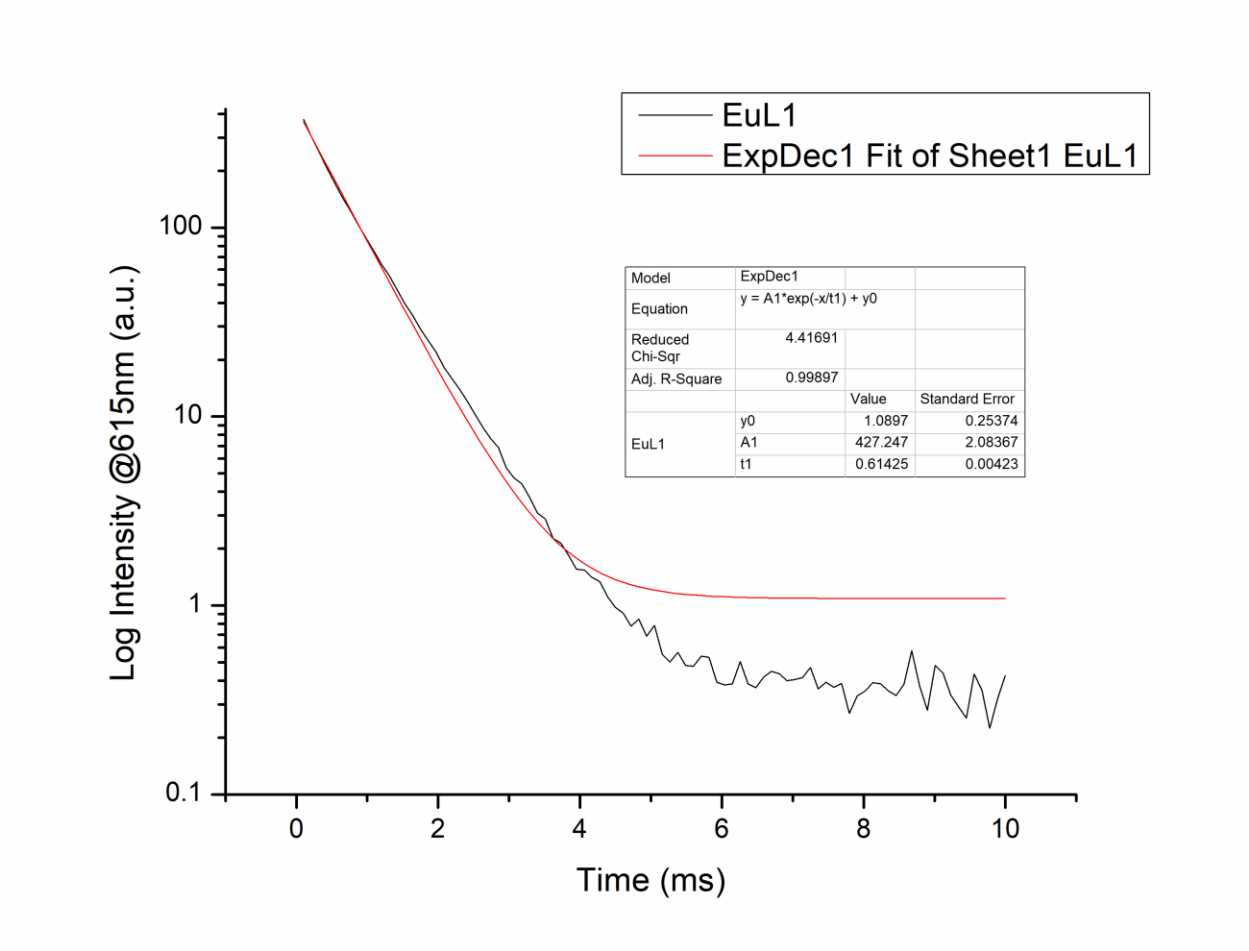
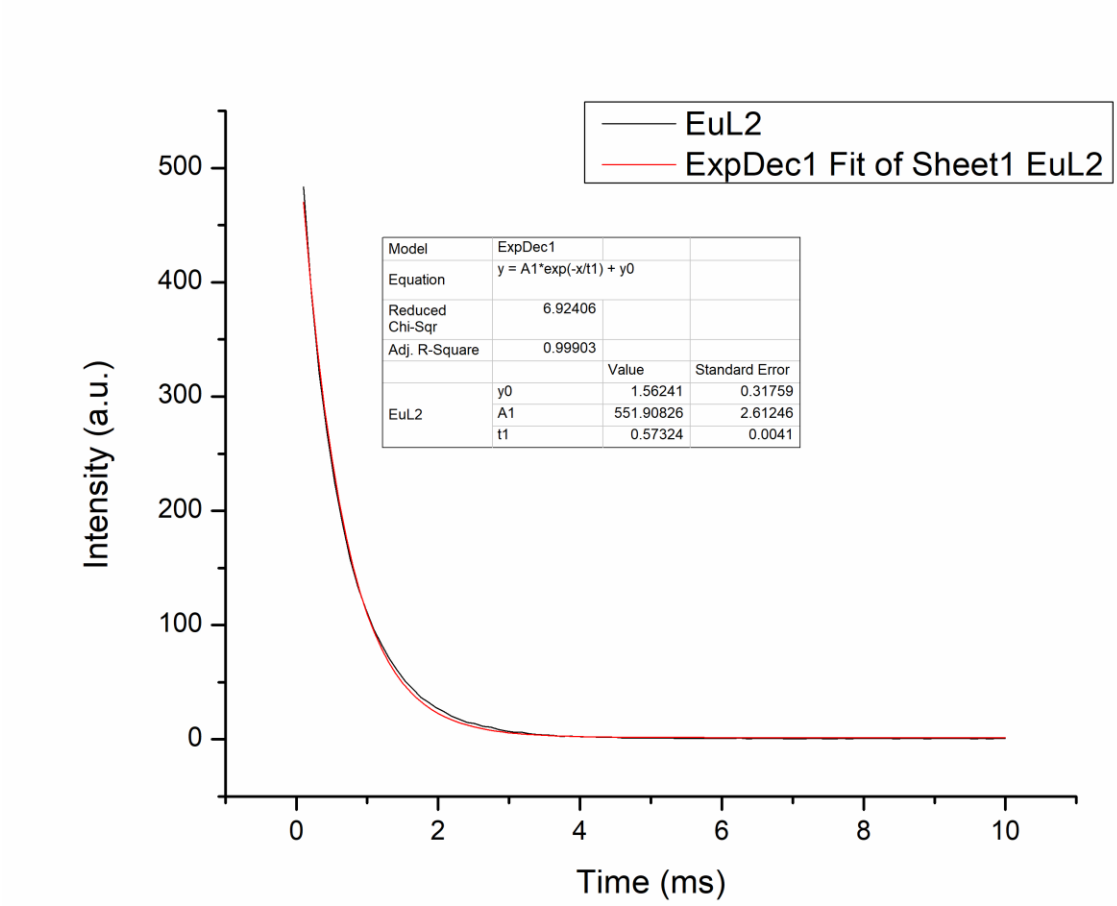


Figure S 42. Fluorescence decay fitting of isolated $Na_3[Eu(L_1)_3]$ in water, monitoring at 615 nm and exciting at 360 nm.



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	6.92406		
Adj. R-Square	0.99903		
		Value	Standard Error
EuL2	y0	1.56241	0.31759
	A1	551.90826	2.61246
	t1	0.57324	0.0041

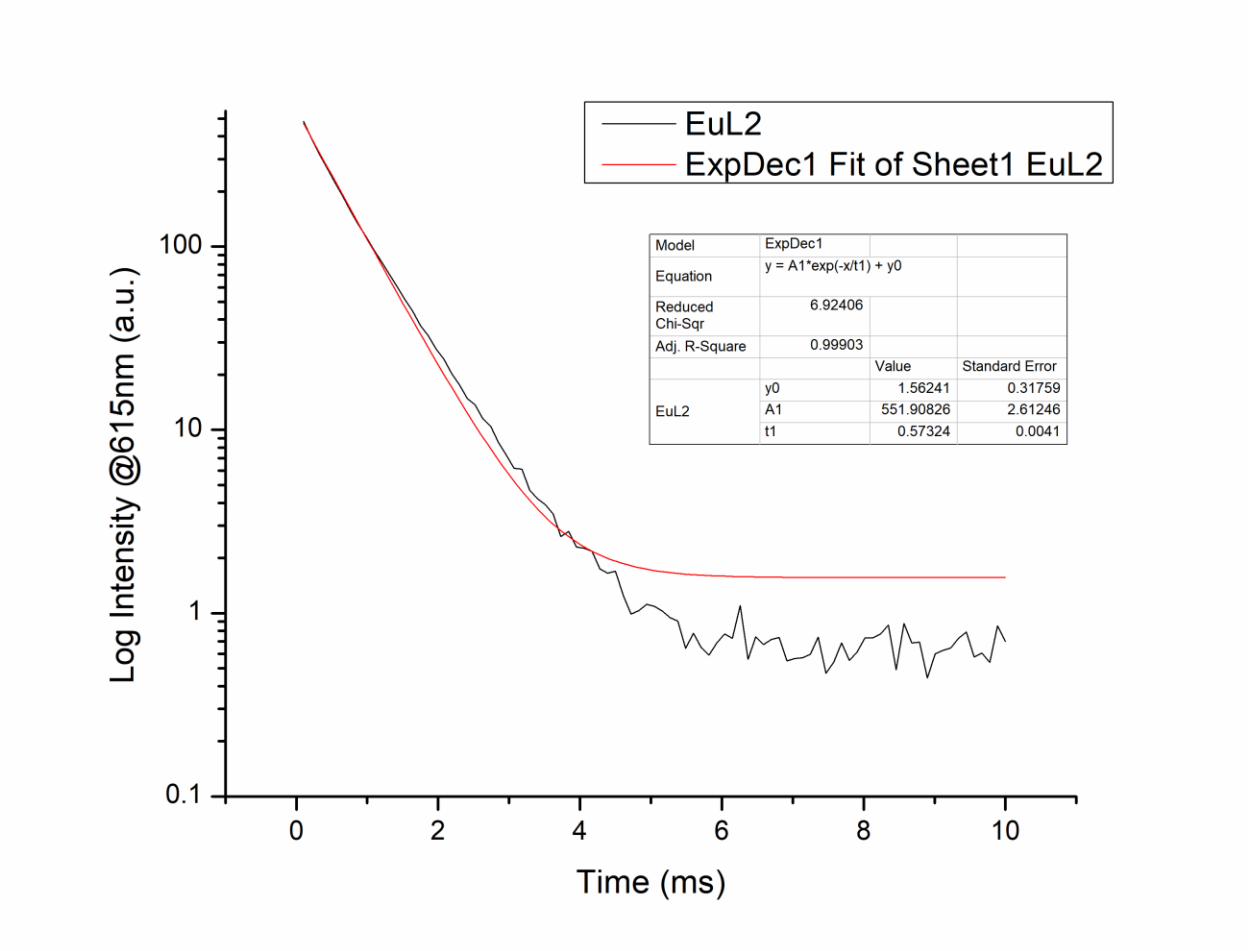


Figure S 43. Fluorescence decay fitting of isolated $Na_3[Eu(L_2)_3]$ in water, monitoring at 615 nm and exciting at 360 nm.

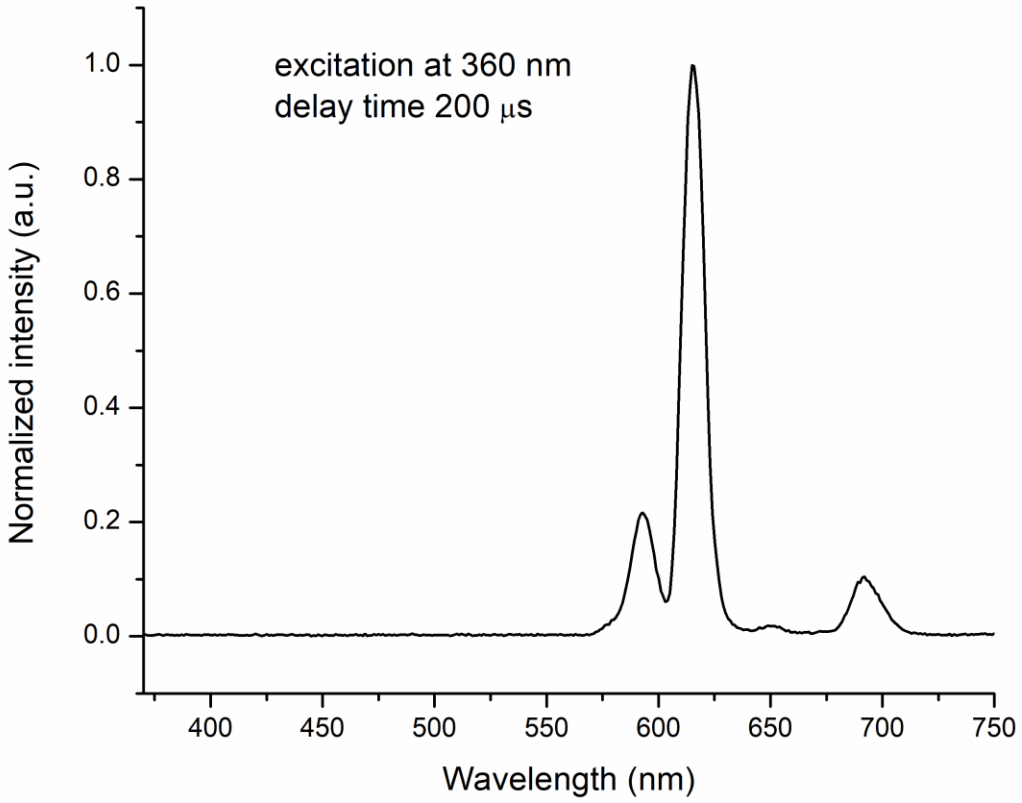
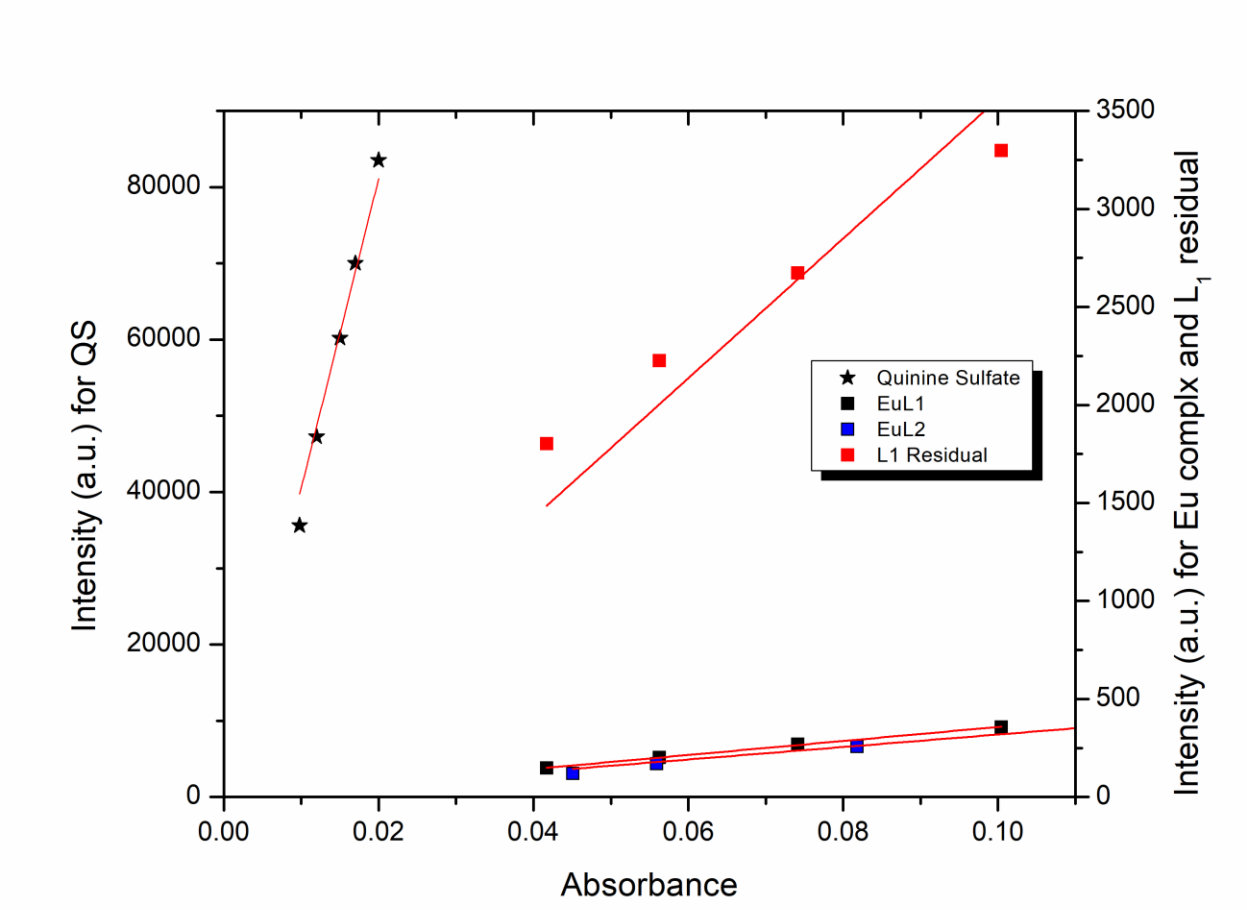
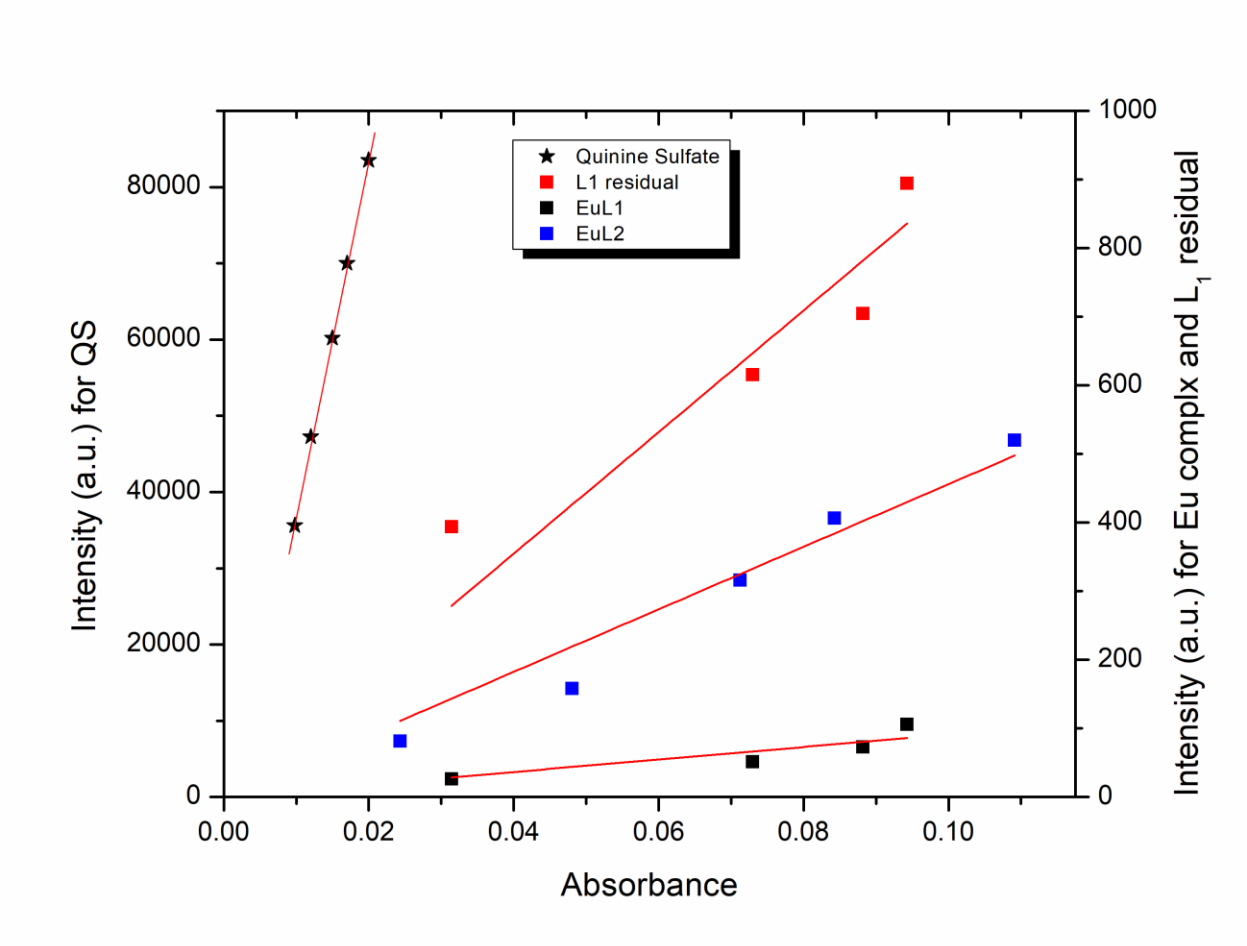


Figure S 44. Phosphorescence spectrum of $Na_3[Eu(L_1)_3]$ complex in water with 200μs of delay time.



	A	B	C	D
1	Equation	y = a + b*x		
2	Weight	No Weighting		
3	Residual Sum of Squares	25.31818	858.61091	228267.4124
4	Pearson's r	0.99995	0.9983	0.99564
5	Adj. R-Square	0.99987	0.99547	0.98839
6			Value	Standard Error
7	EuL1	Intercept	0	--
8		Slope	3573.43801	20.29393
9	EuL2	Intercept	0	--
10		Slope	3188.71511	107.44075
11	L1 Residual	Intercept	0	--
12		Slope	35618.79804	1926.95606

Figure S 45. Quantum yields plot of isolated tris complexes in water solution (above) and fitting details (below).



	A	B	C	D
1	Equation	y = a + b*x		
2	Weight	No Weighting		
3	Residual Sum of Squares	23754.20021	682.19915	5694.37765
4	Pearson's r	0.99349	0.98258	0.99497
5	Adj. R-Square	0.98269	0.95394	0.98744
6			Value	Standard Error
7	L1 residual	Intercept	0	--
8		Slope	8865.68405	587.03511
9	EuL1	Intercept	0	--
10		Slope	910.95335	99.48313
11	EuL2	Intercept	0	--
12		Slope	4560.45093	229.68249

Figure S 46. Quantum yields plot of isolated tris complexes in DMSO solution (above) and fitting details (below).

	A	B	C	D
1	Equation	y = a + b*x		
2	Weight	No Weighting		
3	Residual Sum of Squares	2.62986E7		
4	Pearson's r	0.99931		
5	Adj. R-Square	0.99827		
6			Value	Standard Error
7	Quinine Sulfate	Intercept	0	--
8		Slope	4.05511E6	75478.94658

Figure S 47. Fitting details of quinine sulfate in 0.5 M H_2SO_4.