Supporting Information
for

Water-Soluble Sulfonate Schiff-Base Ligands as Fluorescent Detectors for Metal Ions in Drinking Water and Biological Systems

Meredith J. Reimann[†,‡] Duncan R. Salmon,[†,§] Jacqueline T. Horton, Eric C. Gier and Latisha R. Jefferies*

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Figure S2: Absorbance spectrum of L_{1-4} in different solvents.

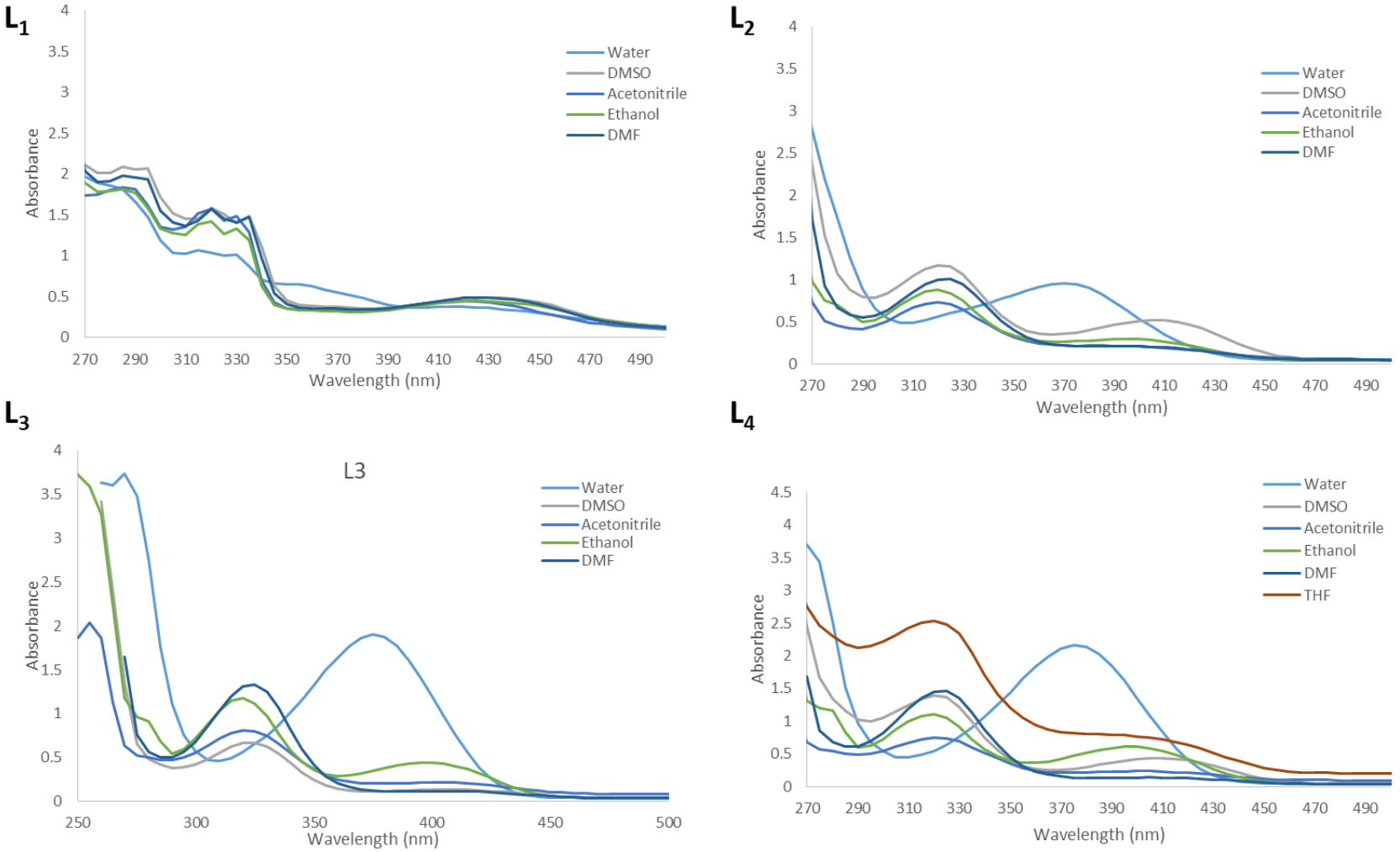
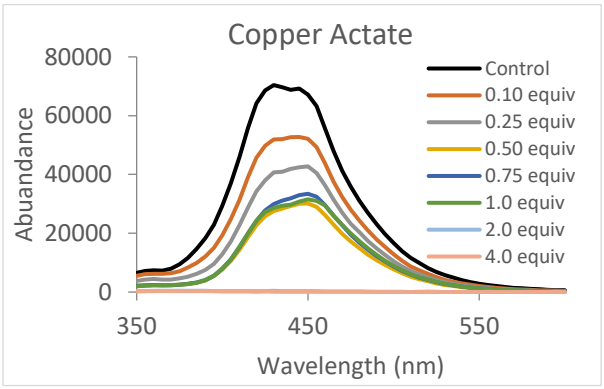
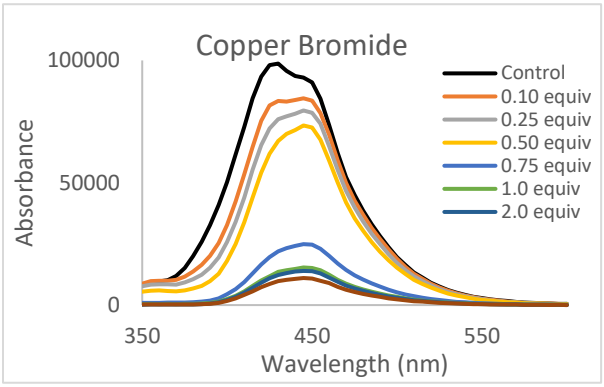
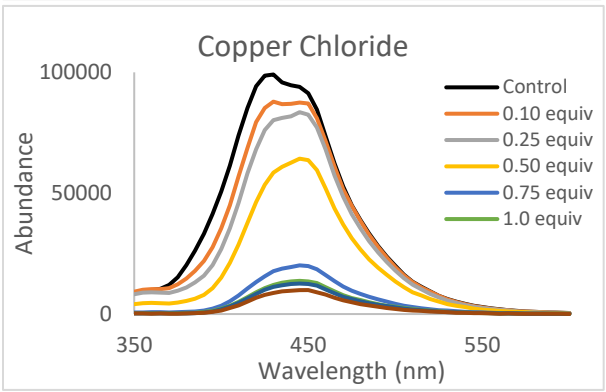


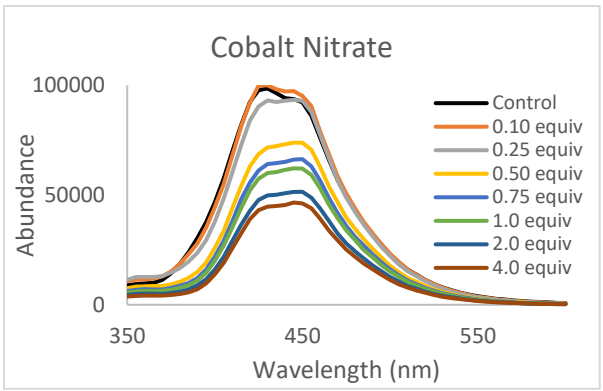
Figure S2: Fluorescence quenching spectra of L_1 (10 µM) and L_{2-4} (1 mM) in deionized water upon addition of varying amounts of metal ions.

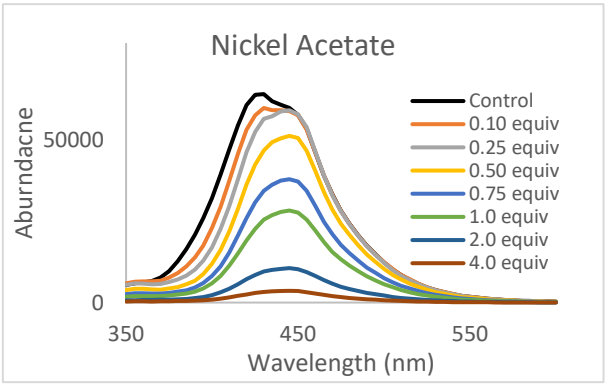
Quenching Spectrum for L_1

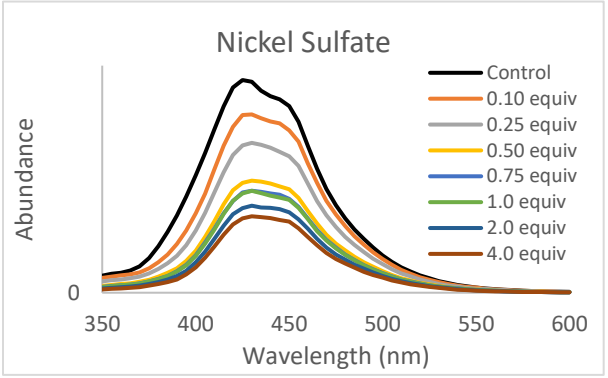


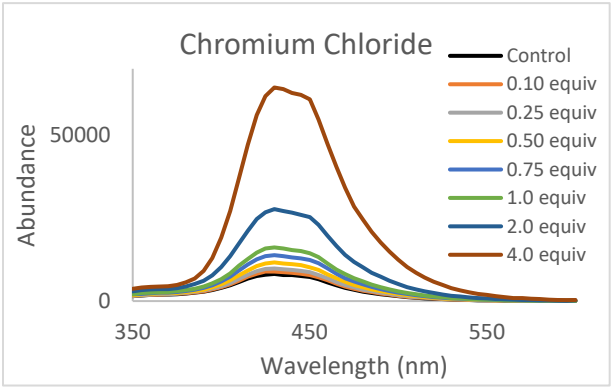


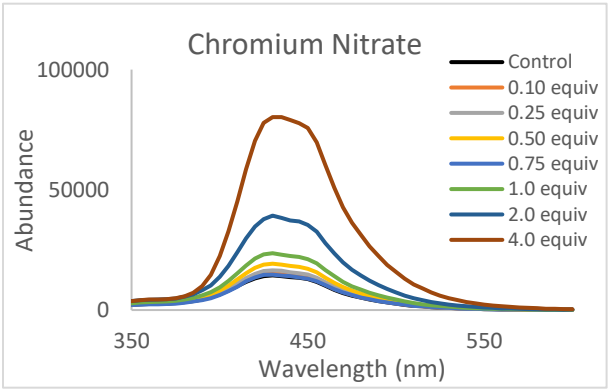


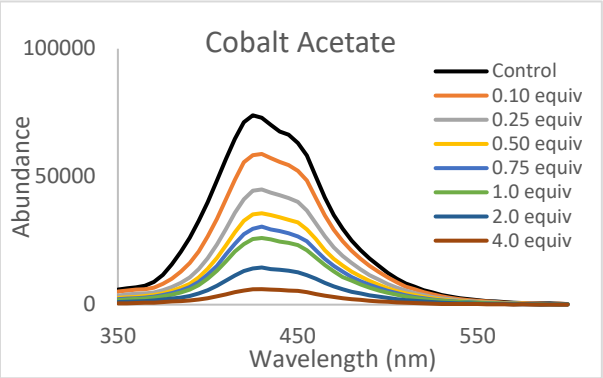


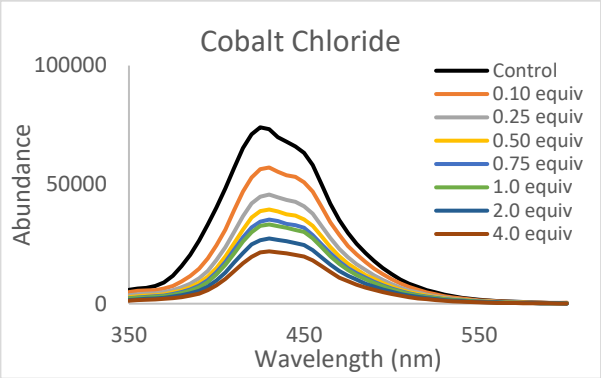









Cobalt Acetate
100000
50000
0
Abundance
350
450
550
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Cobalt Chloride
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Abundance
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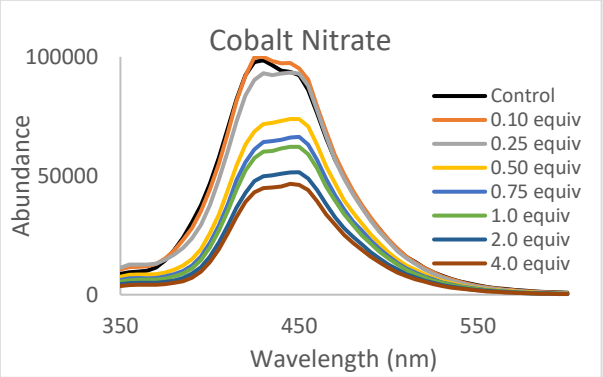
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv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Abundance
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450
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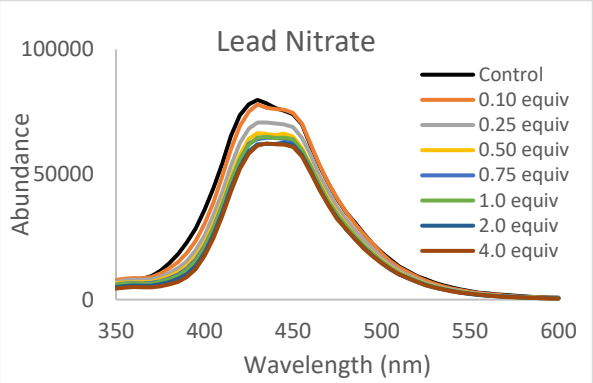
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Lead Nitrate
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Abundance
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Wavelength (nm)
Control
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0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
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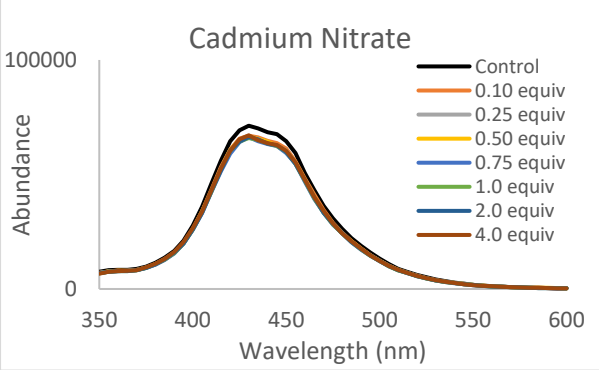
Cadmium Nitrate
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Abundance
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400
450
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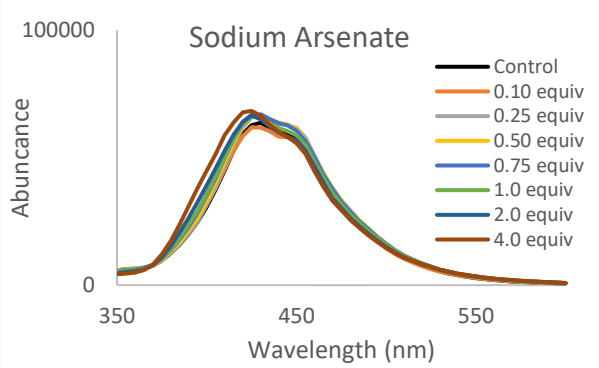
550
600
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv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Abuncance
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Wavelength (nm)
Control
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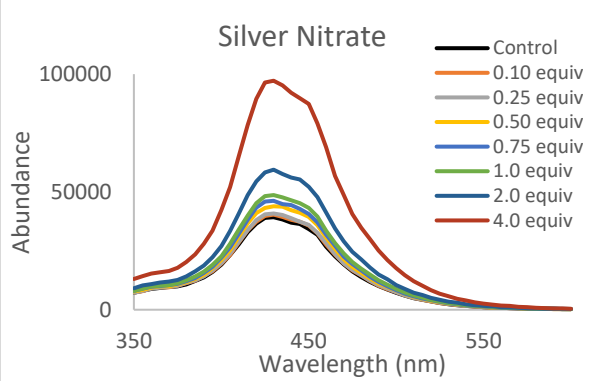
1.0 equiv
2.0 equiv
4.0 equiv


Silver Nitrate
100000
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Abundance
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450
550
Wavelength (nm)
Control
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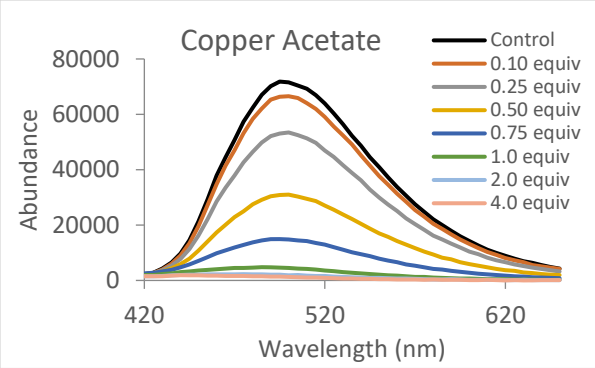
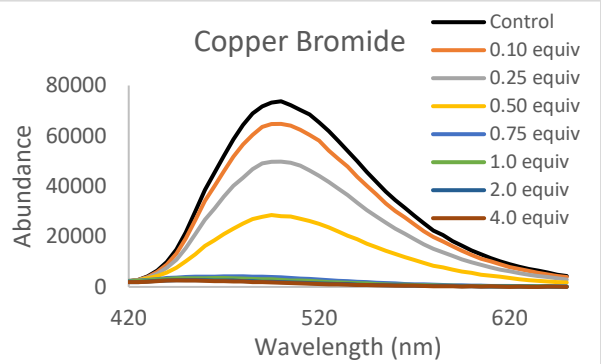
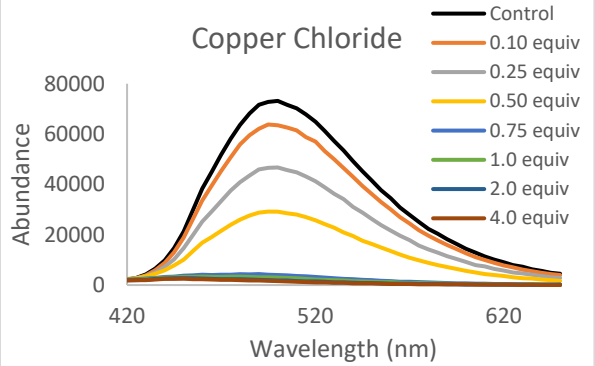
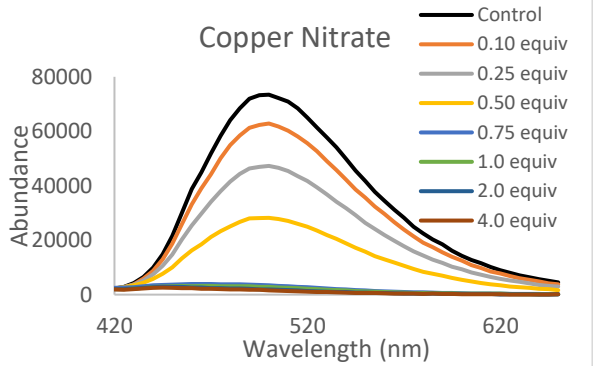
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv

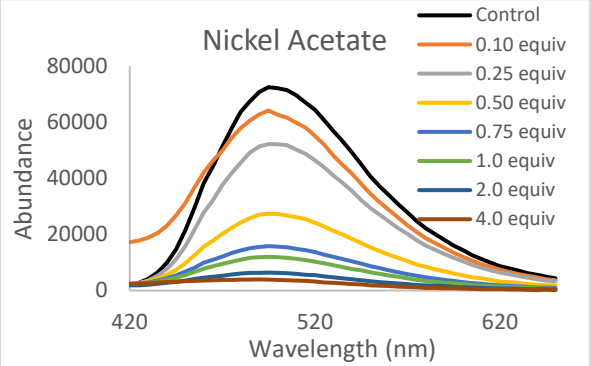
Quenching Spectrum for L_2

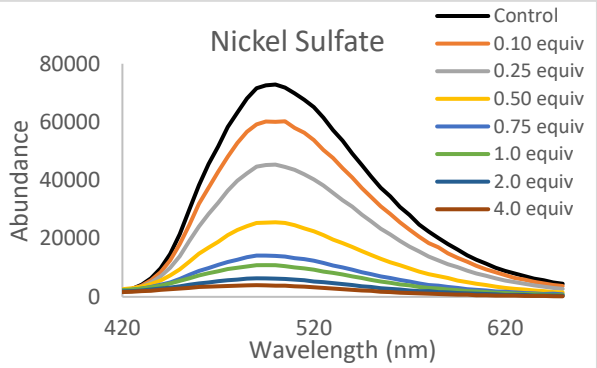


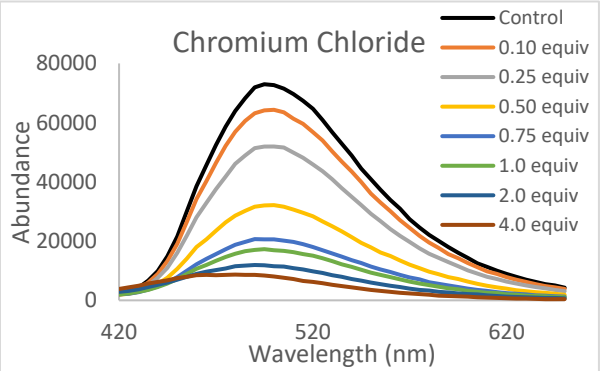


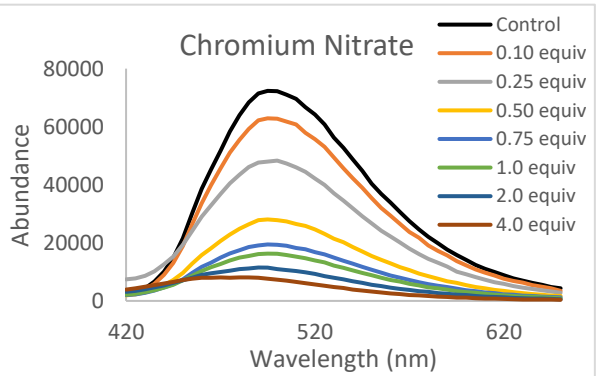


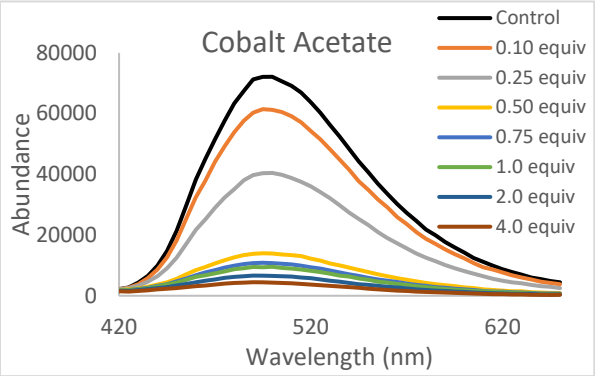








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60000
40000
20000
0
420
520
620
Wavelength (nm)
Control
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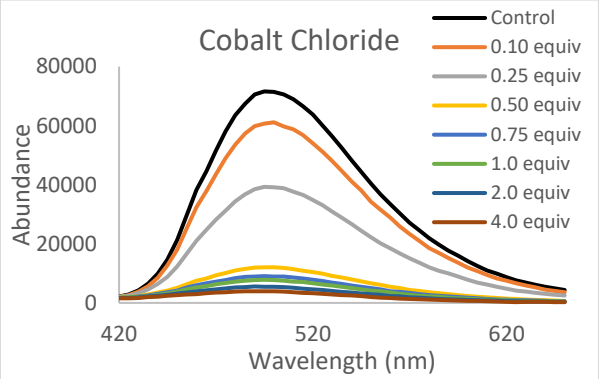
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Cobalt Chloride
Abundance
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60000
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20000
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Wavelength (nm)
Control
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0.25 equiv
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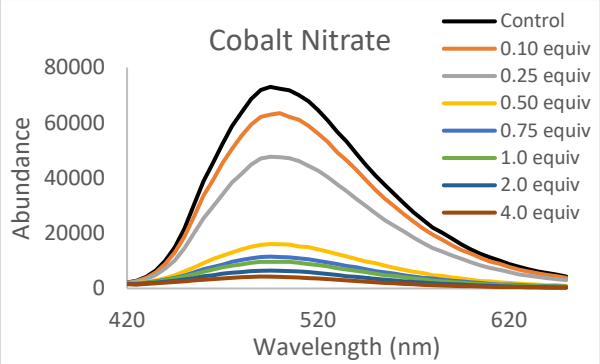
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Cobalt Nitrate
Abundance
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40000
20000
0
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Wavelength (nm)
Control
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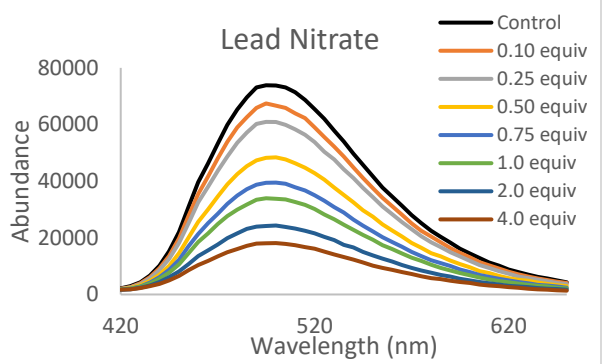
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Lead Nitrate
Abundance
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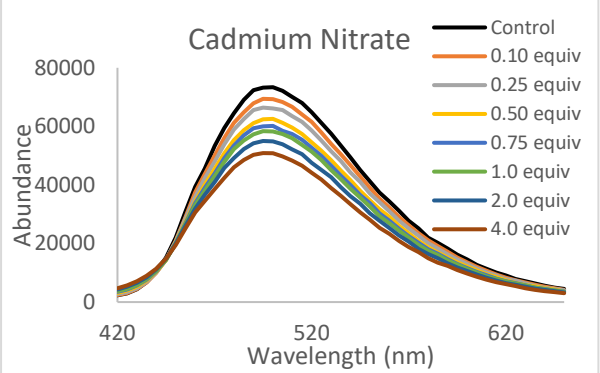
60000
40000
20000
0
420
520
620
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Cadmium Nitrate
Abundance
80000
60000
40000
20000
0
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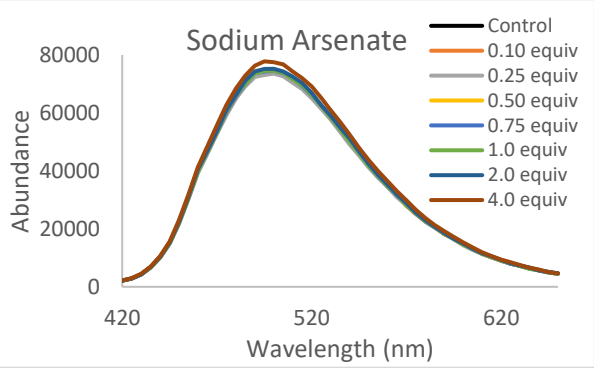
520
620
Wavelength (nm)
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Sodium Arsenate
Abundance
80000
60000
40000
20000
0
420
520
620
Wavelength (nm)
Control
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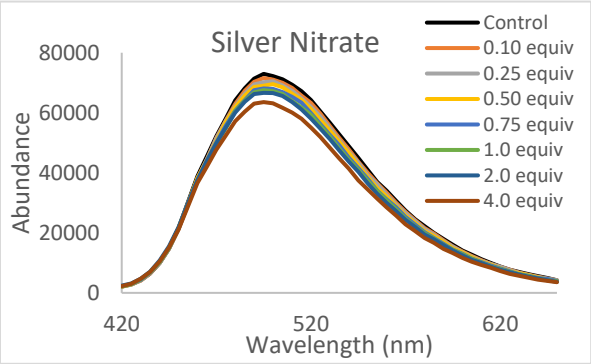
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv


Silver Nitrate
Abundance
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40000
20000
0
420
520
620
Wavelength (nm)
Control
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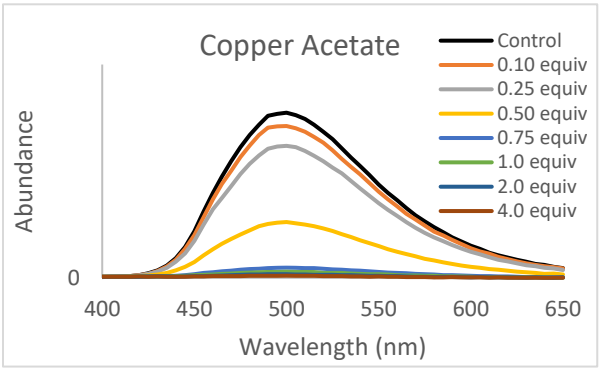
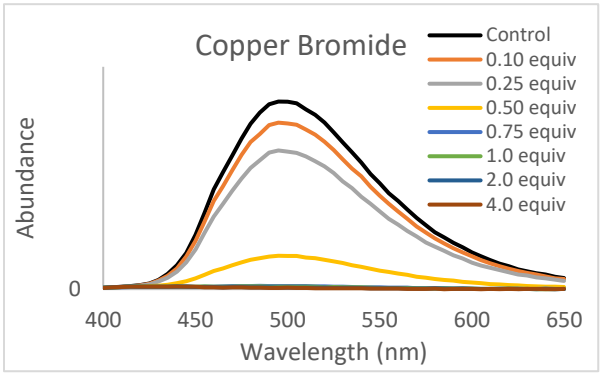
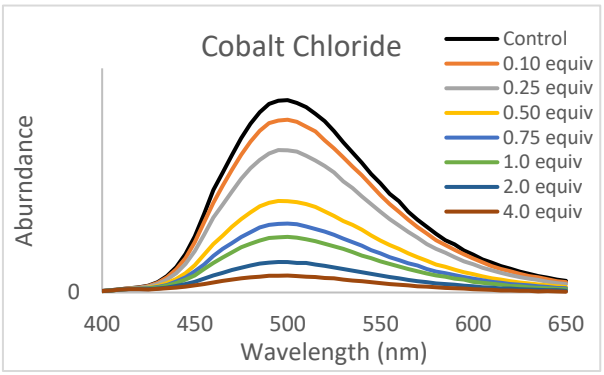
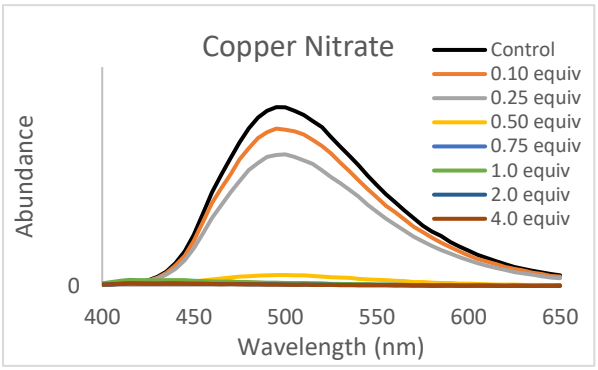
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv

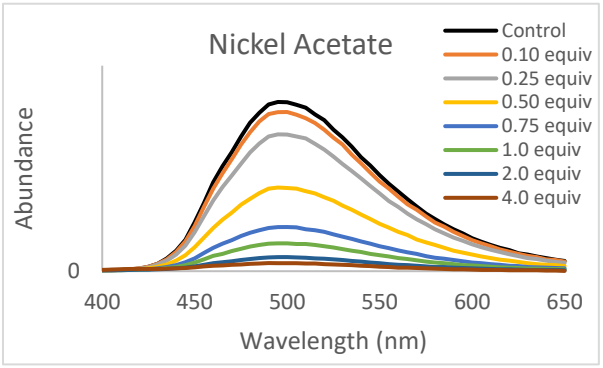
Quenching Spectrum for L_3

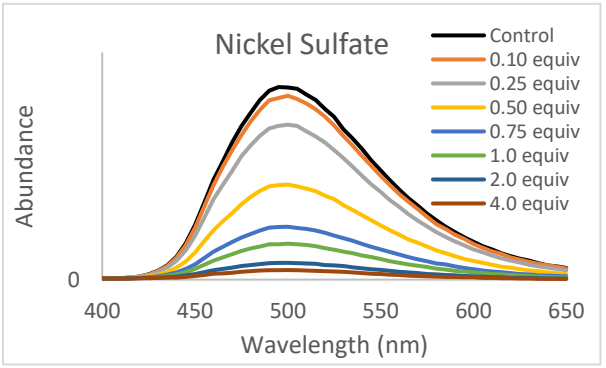


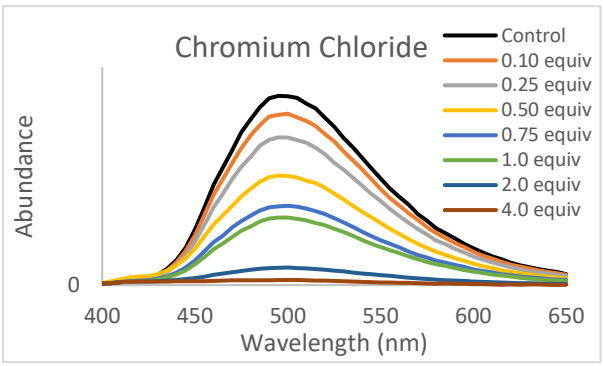


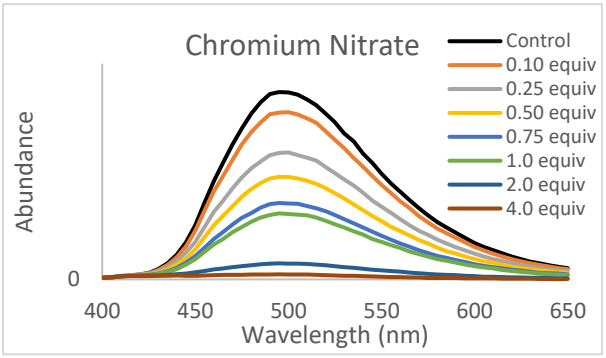


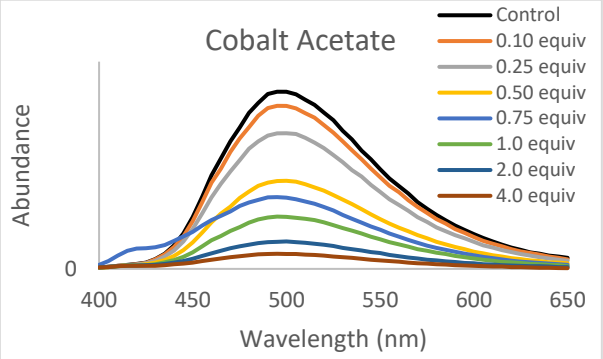








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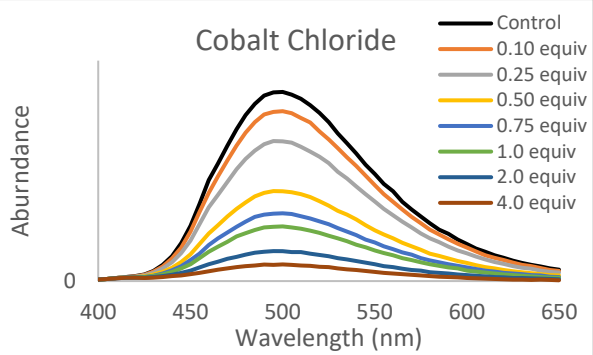
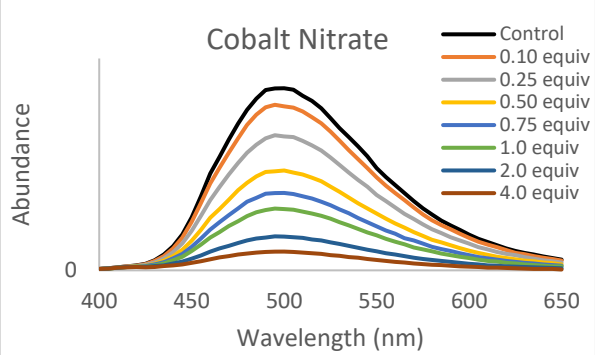
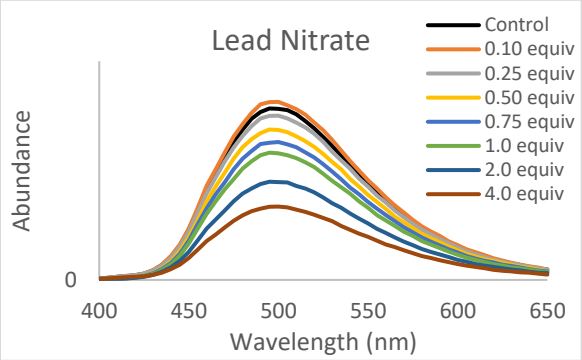
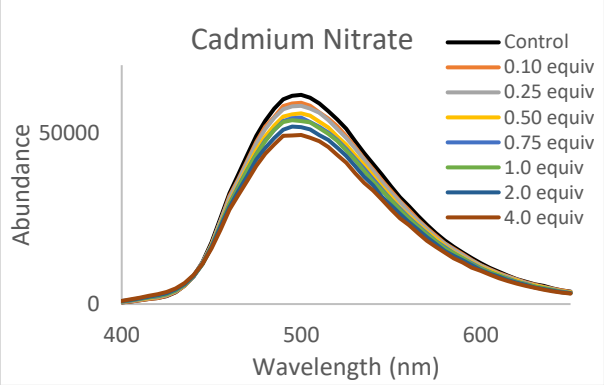
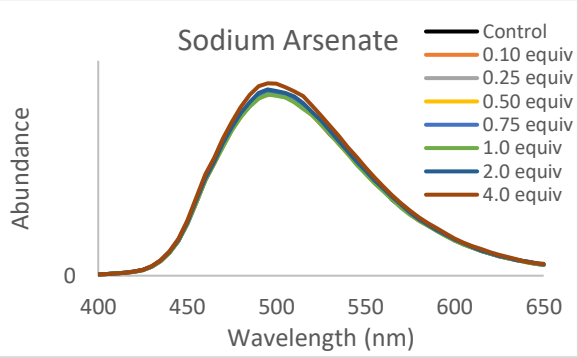
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
0
400
450
500
550
600
650
Wavelength (nm)


Cobalt Chloride
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Aburndance
0
400
450
500
550
600
650
Wavelength (nm)


Cobalt Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
0
400
450
500
550
600
650
Wavelength (nm)


Lead Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
0
400
450
500
550
600
650
Wavelength (nm)


Cadmium Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
50000
0
400
500
600
Wavelength (nm)


Sodium Arsenate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
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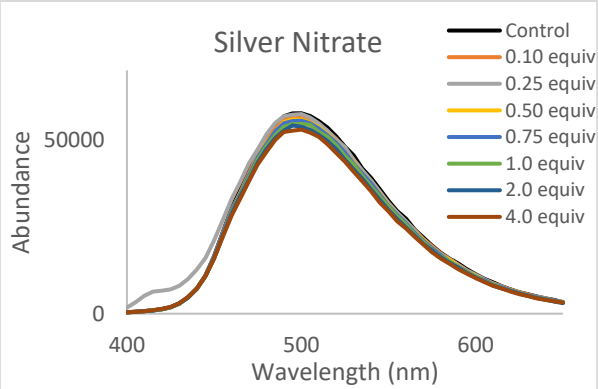
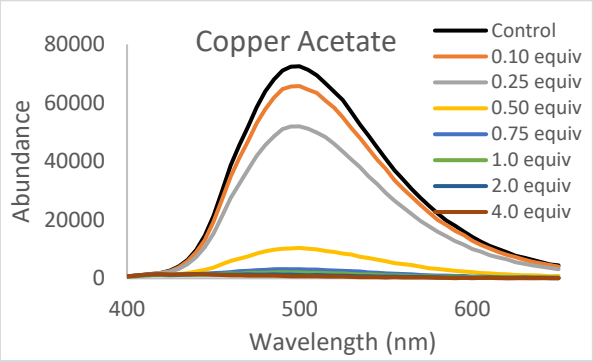
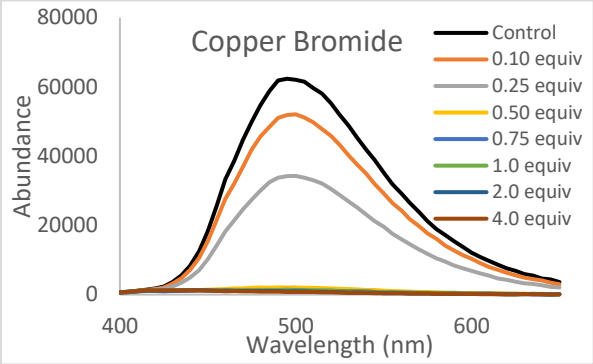
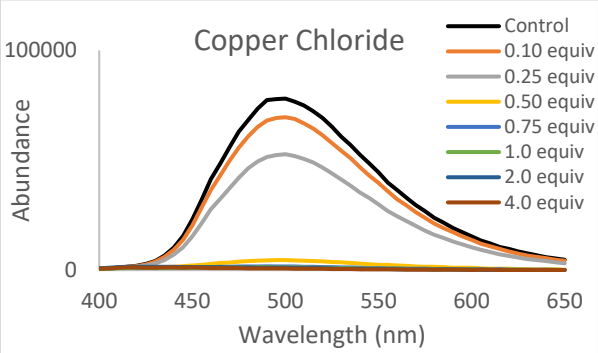
650
Wavelength (nm)

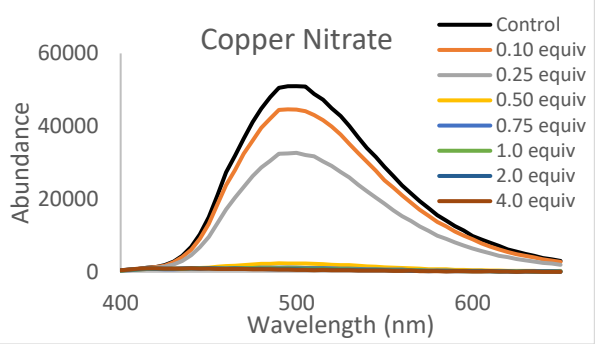

Silver Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
50000
0
400
500
600
Wavelength (nm)

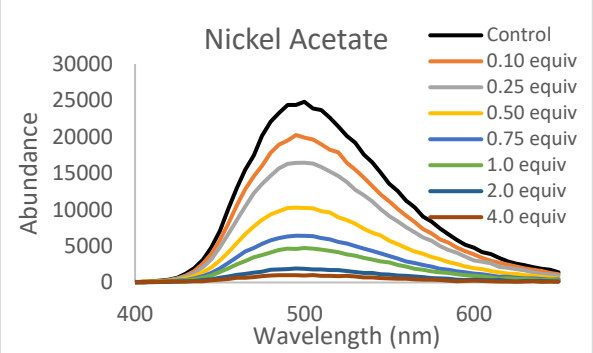
Quenching Spectrum for L_4

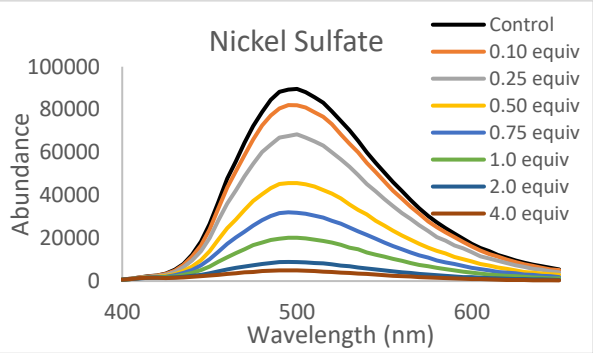


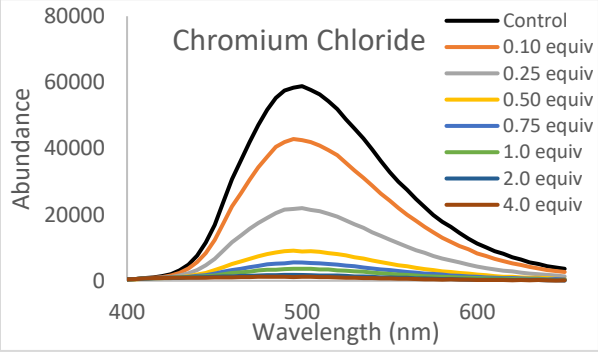


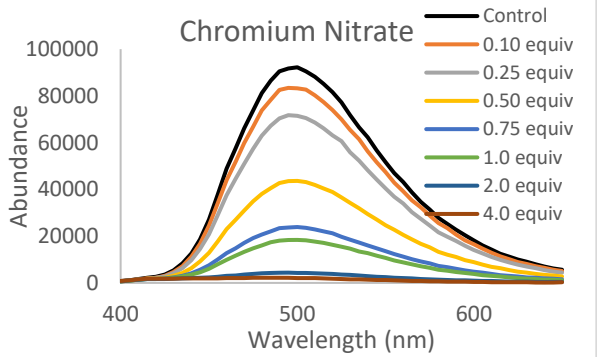


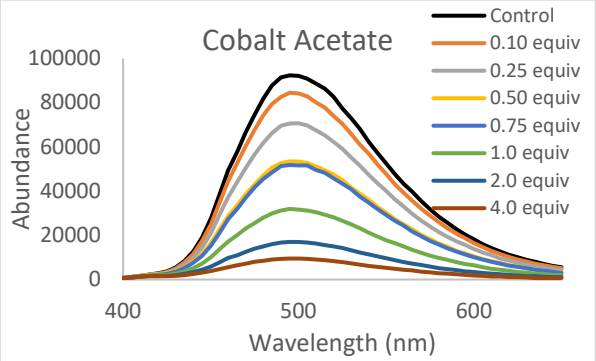


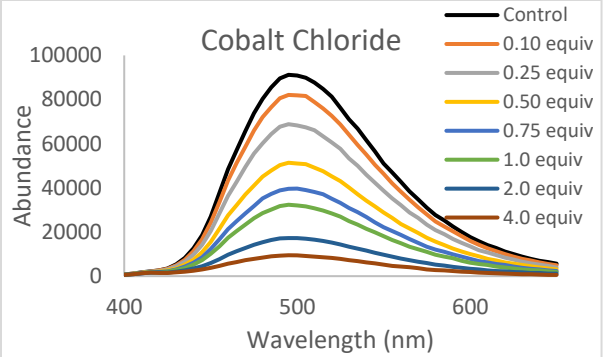


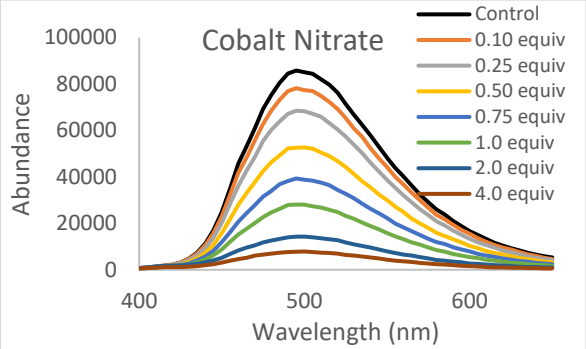


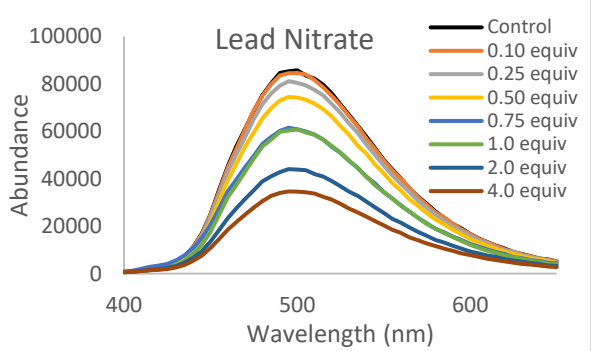


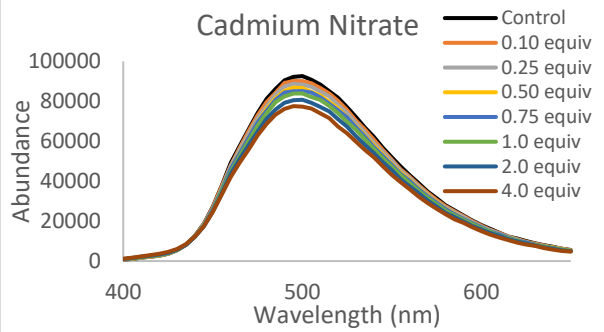


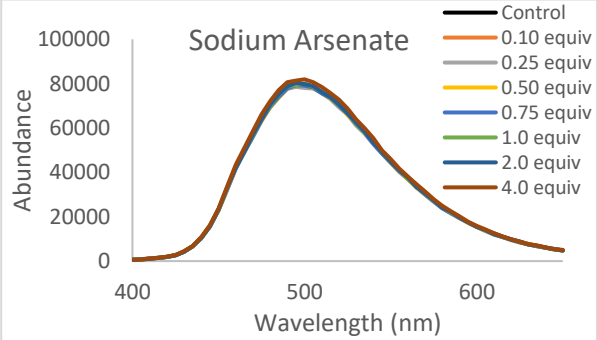

Cobalt Acetate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)


Cobalt Chloride
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)


Cobalt Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)


Lead Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)


Cadmium Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)


Sodium Arsenate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
100000
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)

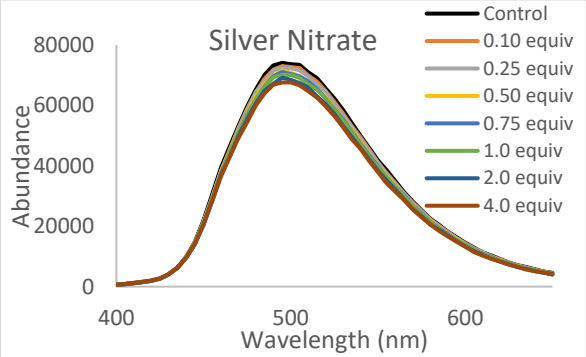

Silver Nitrate
Control
0.10 equiv
0.25 equiv
0.50 equiv
0.75 equiv
1.0 equiv
2.0 equiv
4.0 equiv
Abundance
80000
60000
40000
20000
0
400
500
600
Wavelength (nm)

Figure S3: Fluorescence quenching graphs of L_1 (10 µM) and $L_{2\text{-}4}$ (1 mM) in deionized water upon addition of 1.0 equiv. of varying counterions.

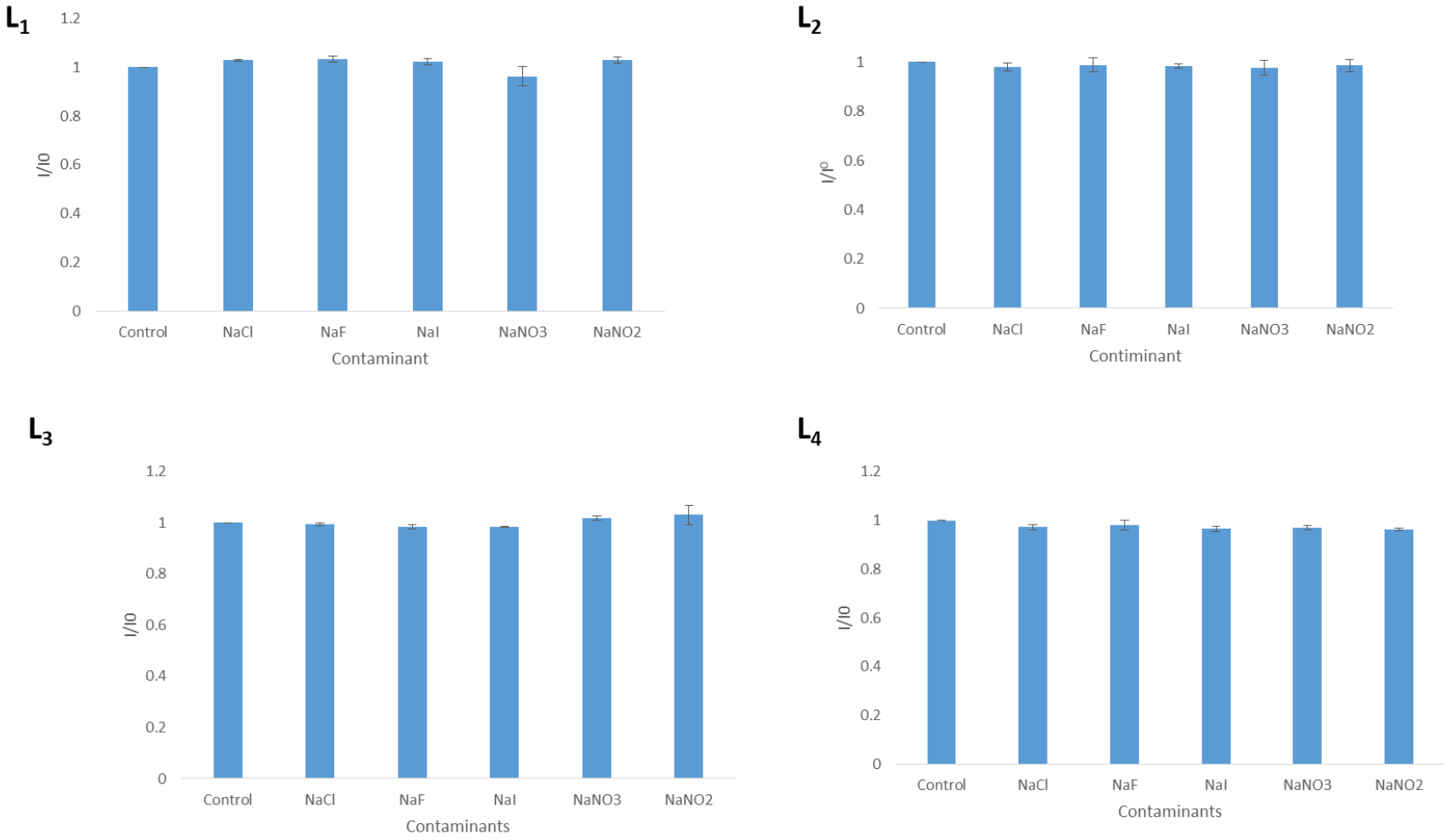
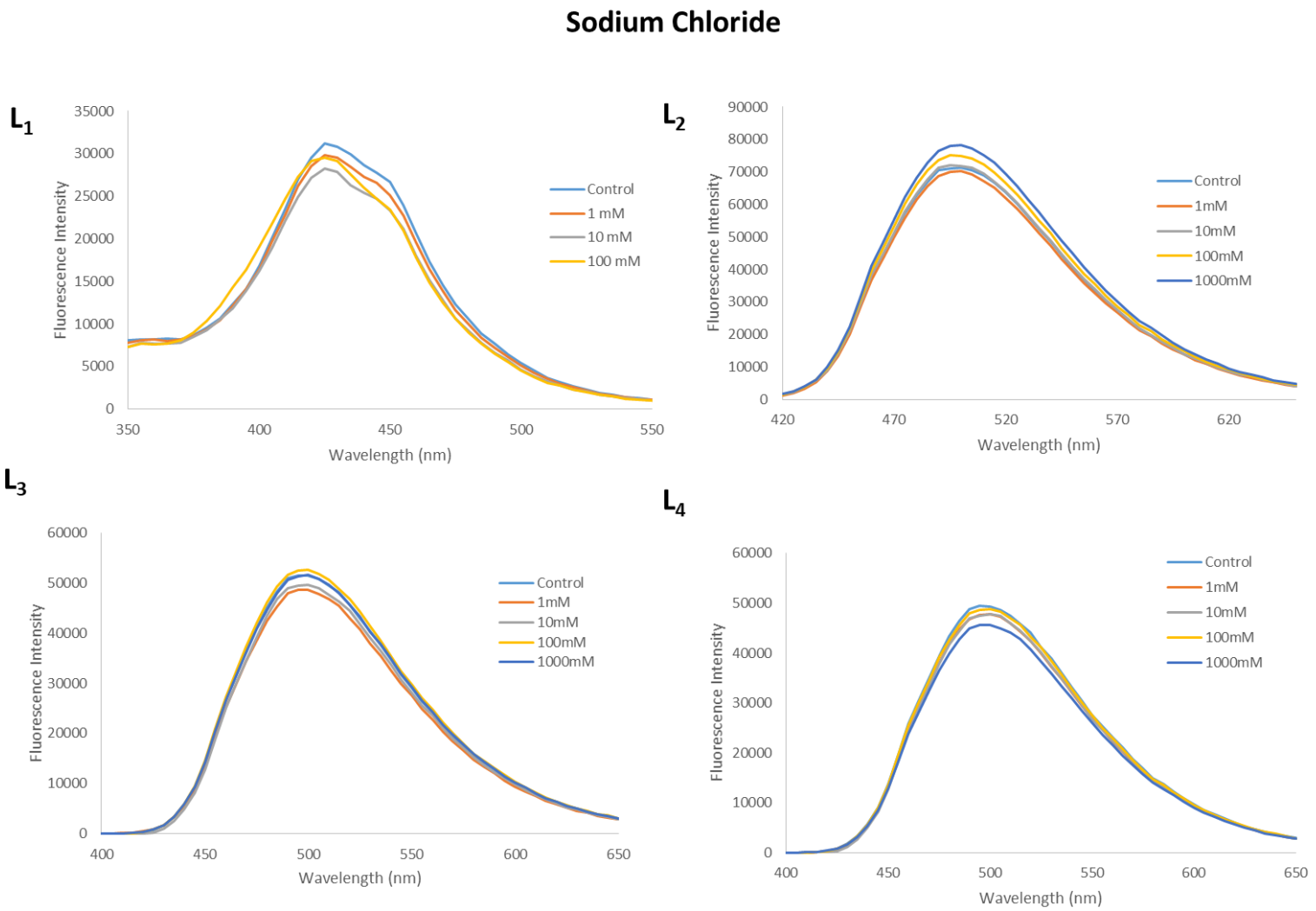
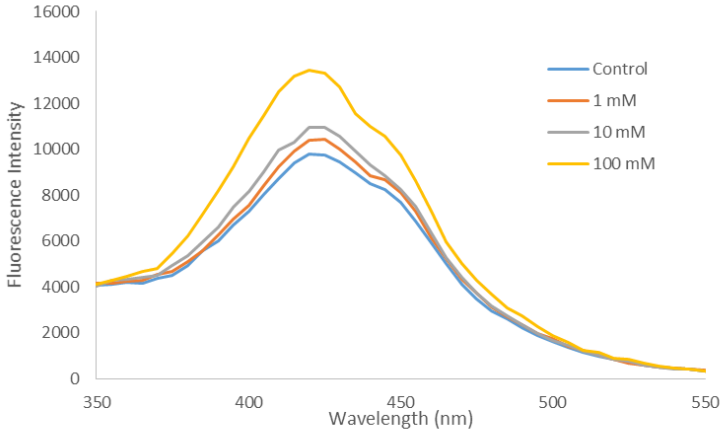


Figure S4: Ionic strength studies were performed with all L_1 (10 µM) and $L_{2\text{-}4}$ (1 mM) in the presence of 1000 mM, 100 mM, 10 mM and 1 mM solutions of NaCl, Na_2SO_4, $MgCl_2$ and $MgSO_4$. For L_1, salt concentrations at 1000 mM were not reproducible and thus omitted from the spectrum.

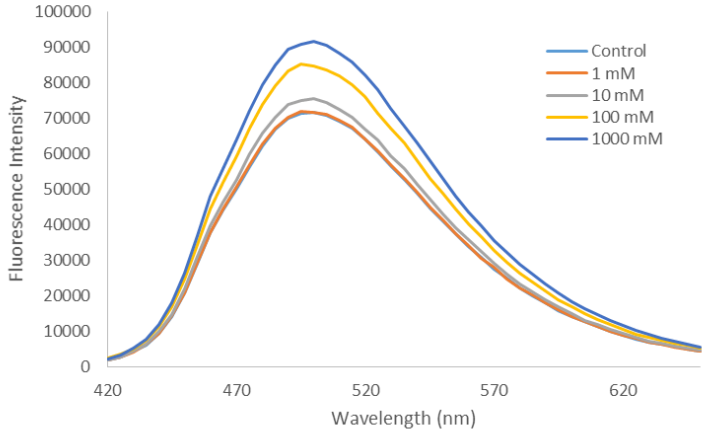


Sodium Sulfate

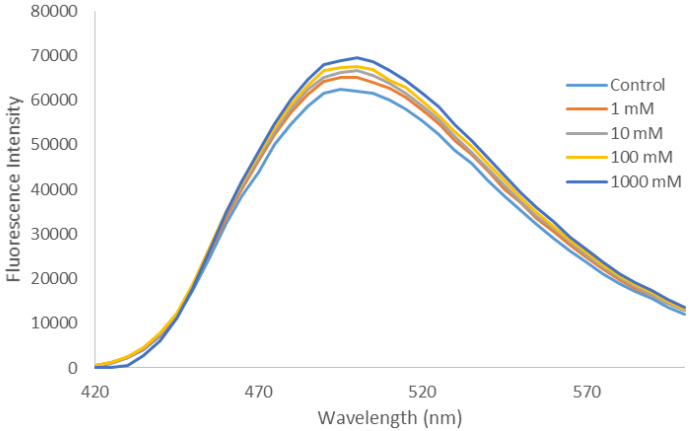
L_1



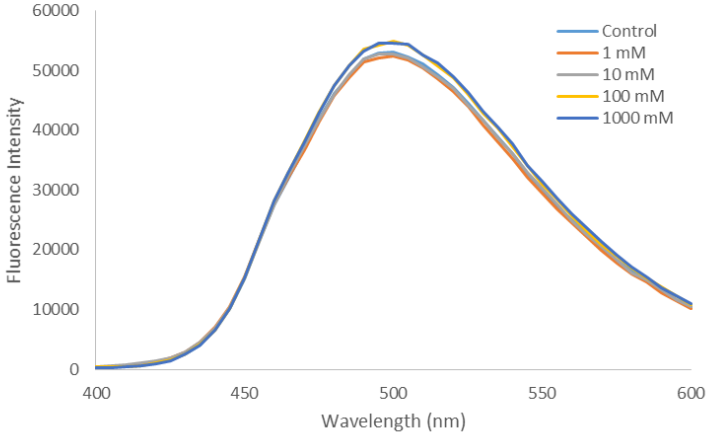
L_2



L_3

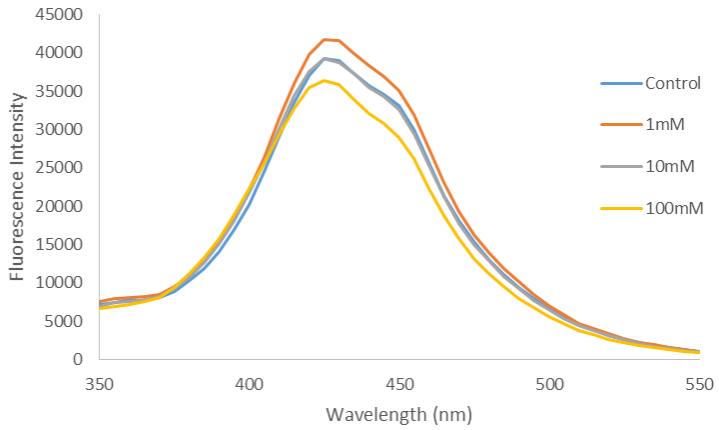


L_4

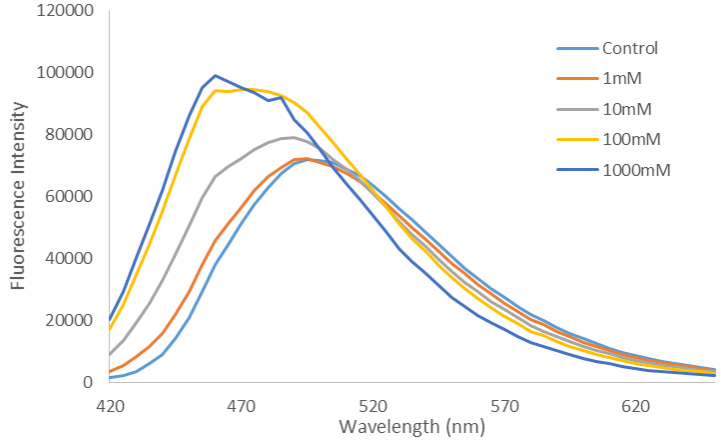


Magnesium Chloride

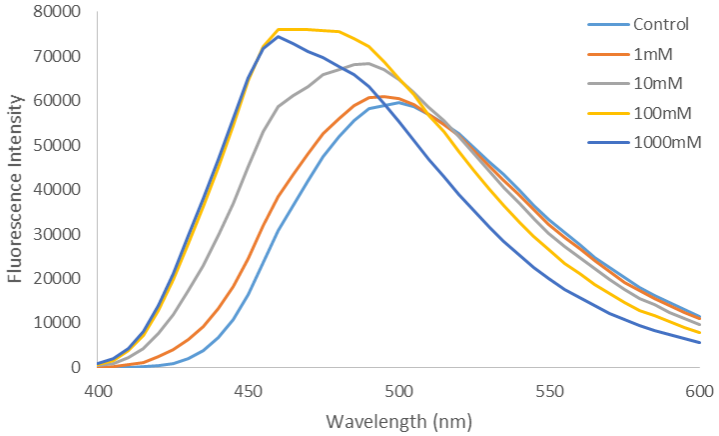
L_1



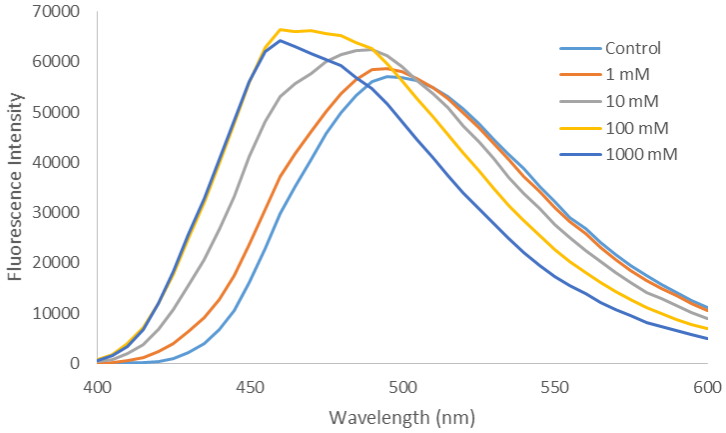
L_2



L_3

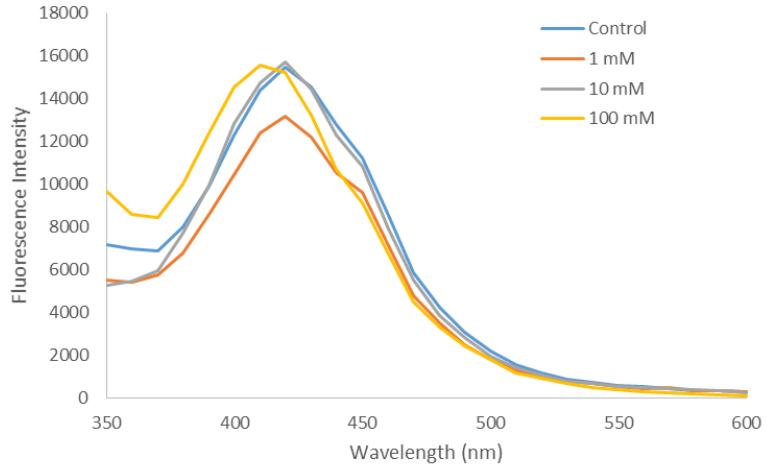


L_4

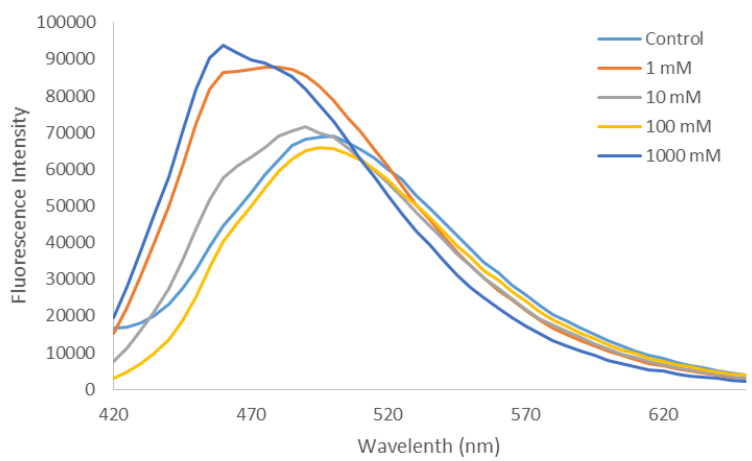


Magnesium Sulfate

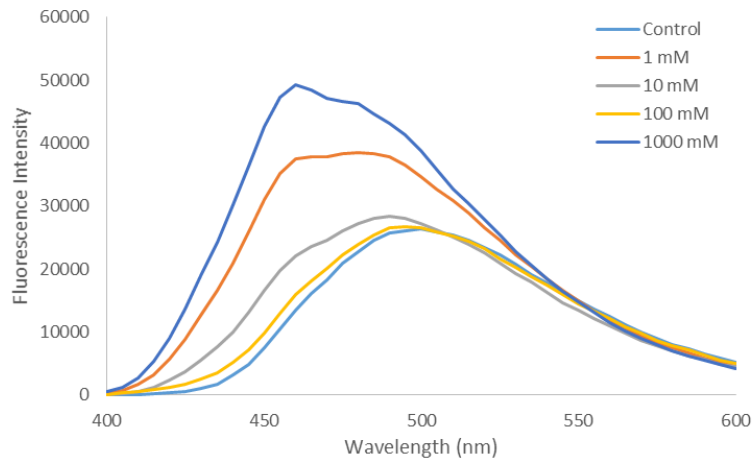
L_1



L_2



L_3



L_4

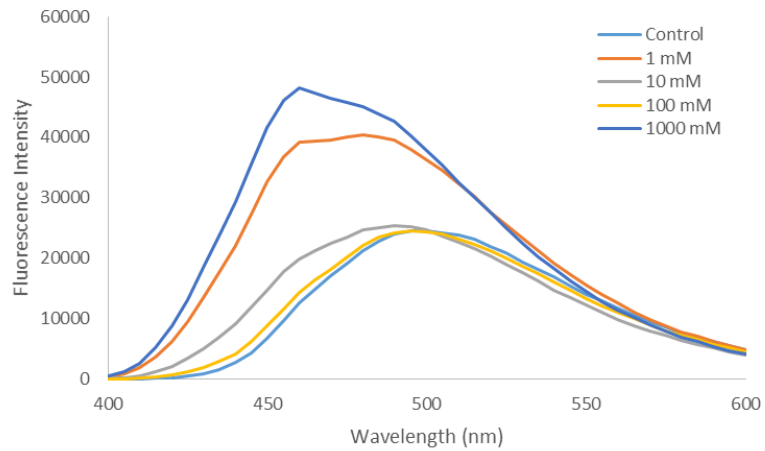


Figure S5: Quenching spectra of L_2 (1mM) with increasing equivalence of Cu^{2+} in the a) presence of 1000 mM $MgSO_4$ and b) in the absence of 1000 mM $MgSO_4$.

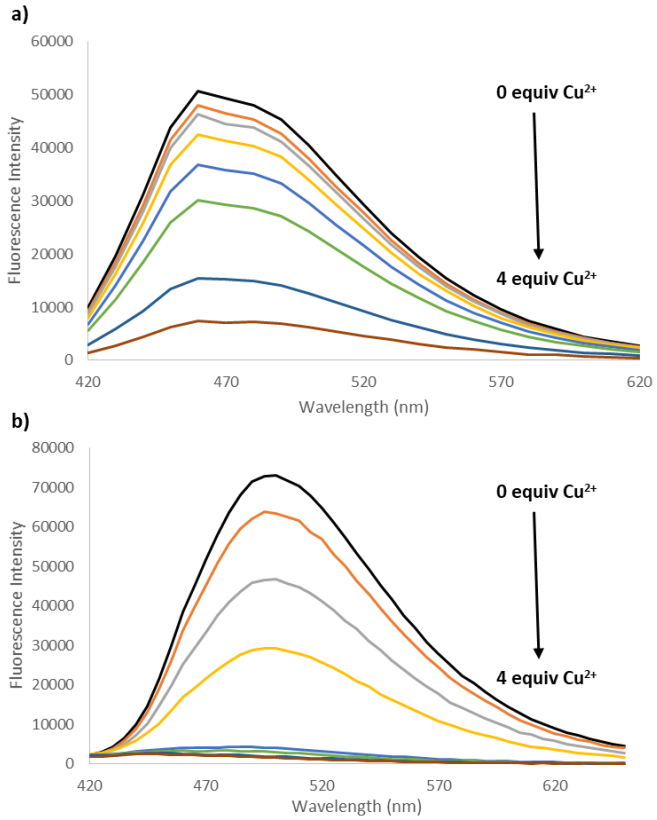
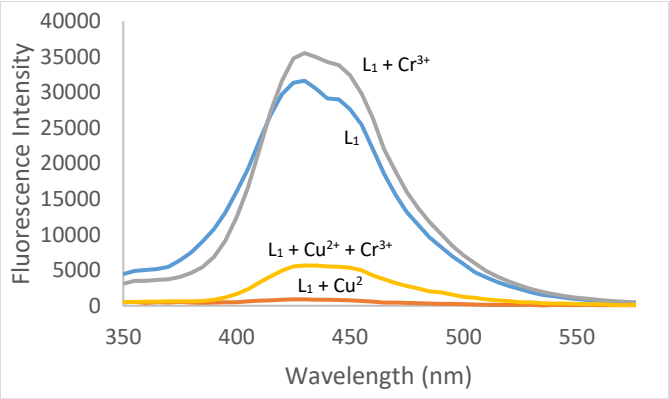


Figure S6: Competing metal ions Cu^{2+} and Cr^{3+} with L_1. The spectrum shows L_1 in the absence and presence of 1 equivalent of Cu^{2+}, 1 equivalent of Cr^{3+} and 1 equivalent of Cu^{2+} and Cr^{3+}. UV-vis and daylight phots of the compounds are shown.



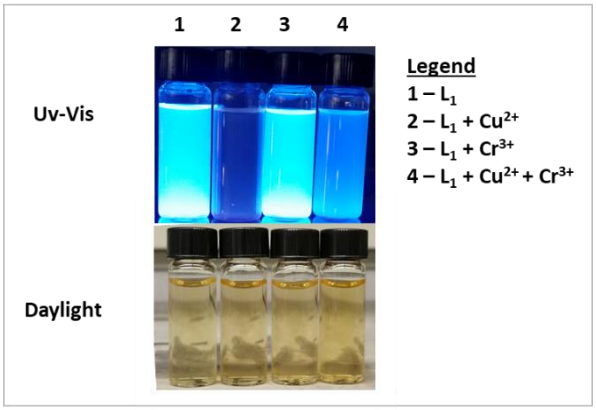
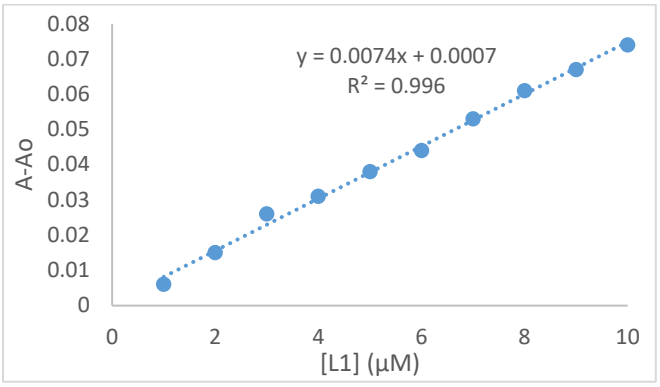
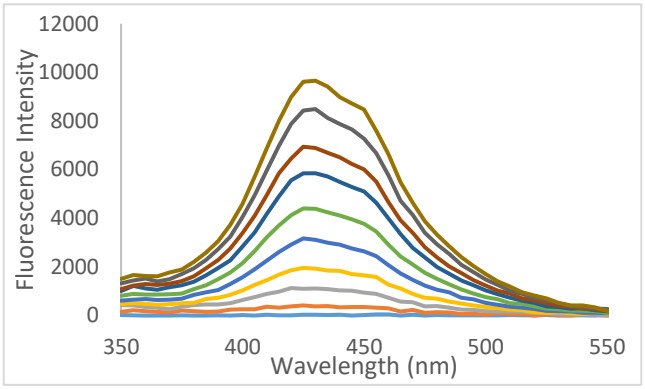


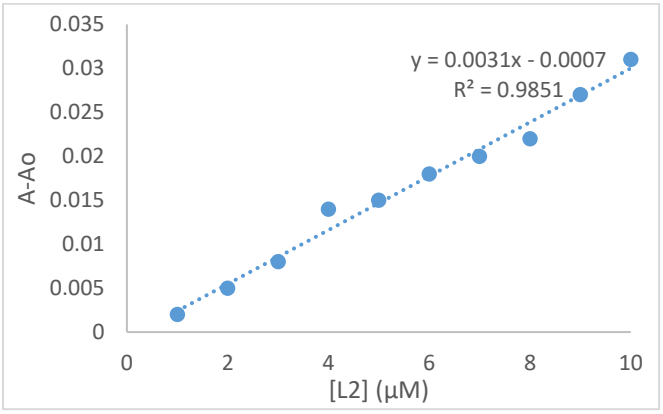
Figure S7: Detection Limit of L_1-L_4. L_1 was excited at 300 nm, L_2 was excited at 380 nm and L_3 and L_4 were excited at 375 nm.

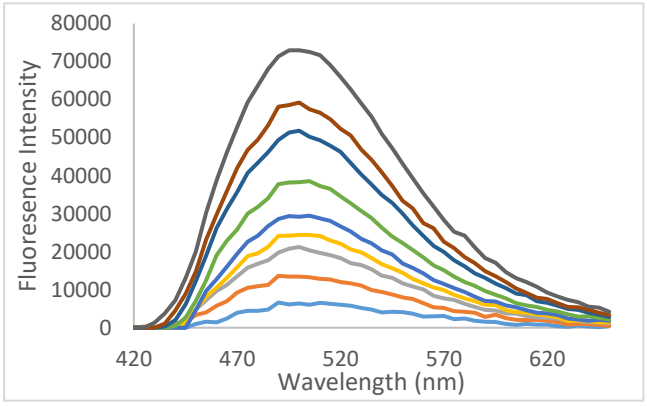
L_1



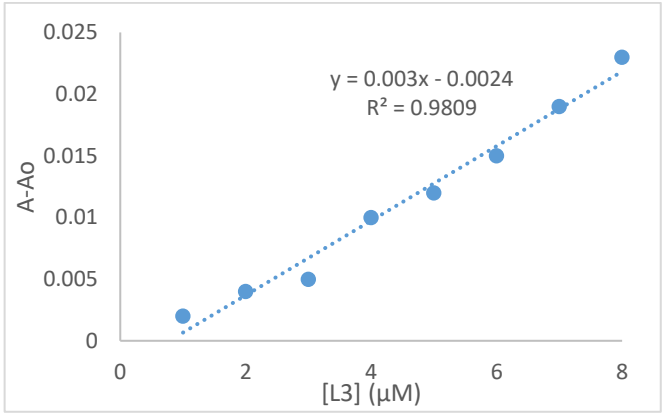


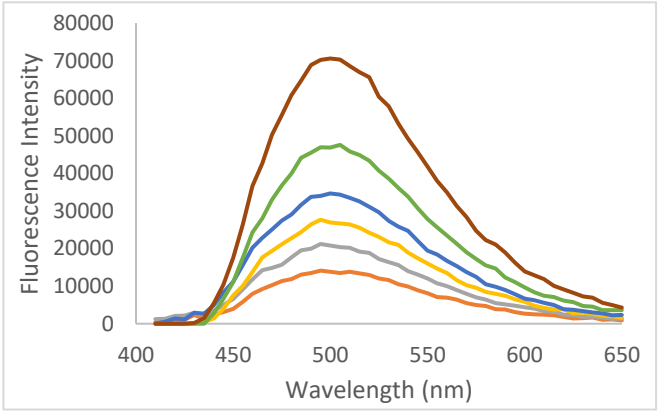
L_2



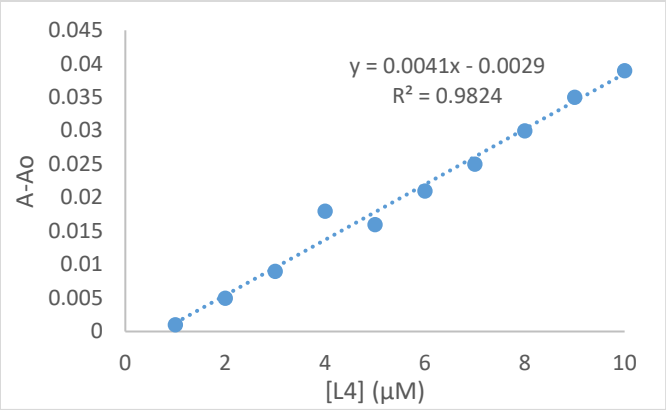


L_3





L_4


y = 0.0041x - 0.0029
R² = 0.9824
A-Ao
[L4] (µM)
0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
0
2
4
6
8
10

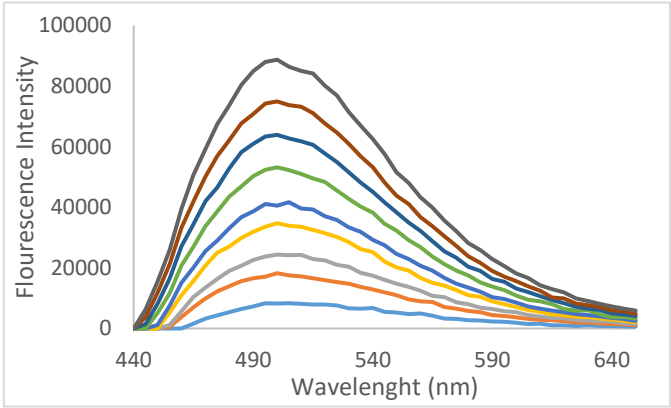

Flourescence Intensity
Wavelenght (nm)
100000
80000
60000
40000
20000
0
440
490
540
590
640

Figure S8: Absorbance spectrum of L_{1-4} at different pH in 10 mM KH_2PO_4 buffer.

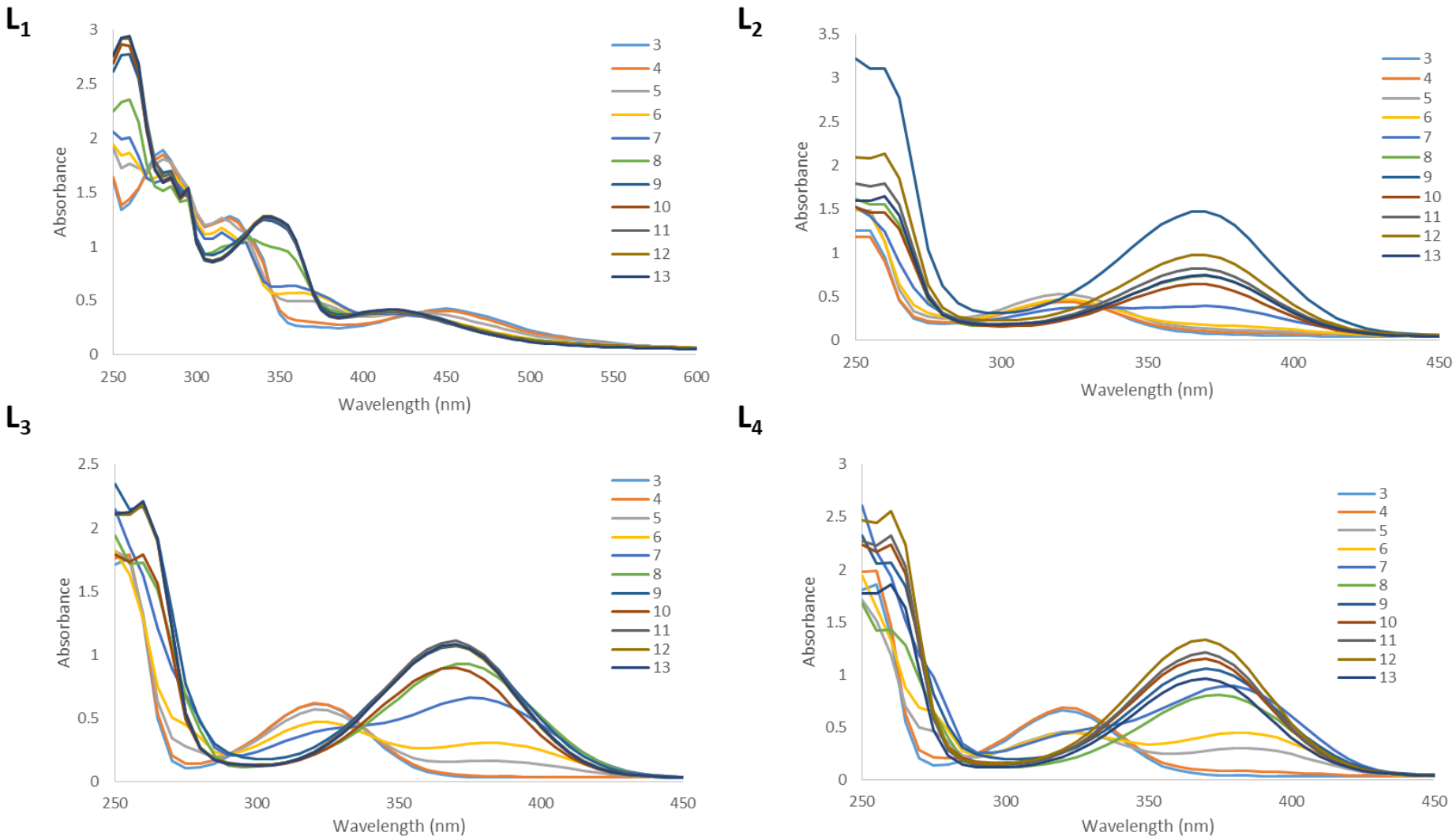


Figure S9: Plot of the integrated fluorescence intensity for the emission of L_1-L_4 in the absence (orange bar) and presence (gray, yellow and blue bar) of 1 equivalent of the metal ion against pH. L_1 was excited at 300 nm and read from 350-600 nm; L_2 was excited at 380 nm and read from 420-600 nm; L_3 and L_4 were excited at 375 nm and read from 400-350 nm.

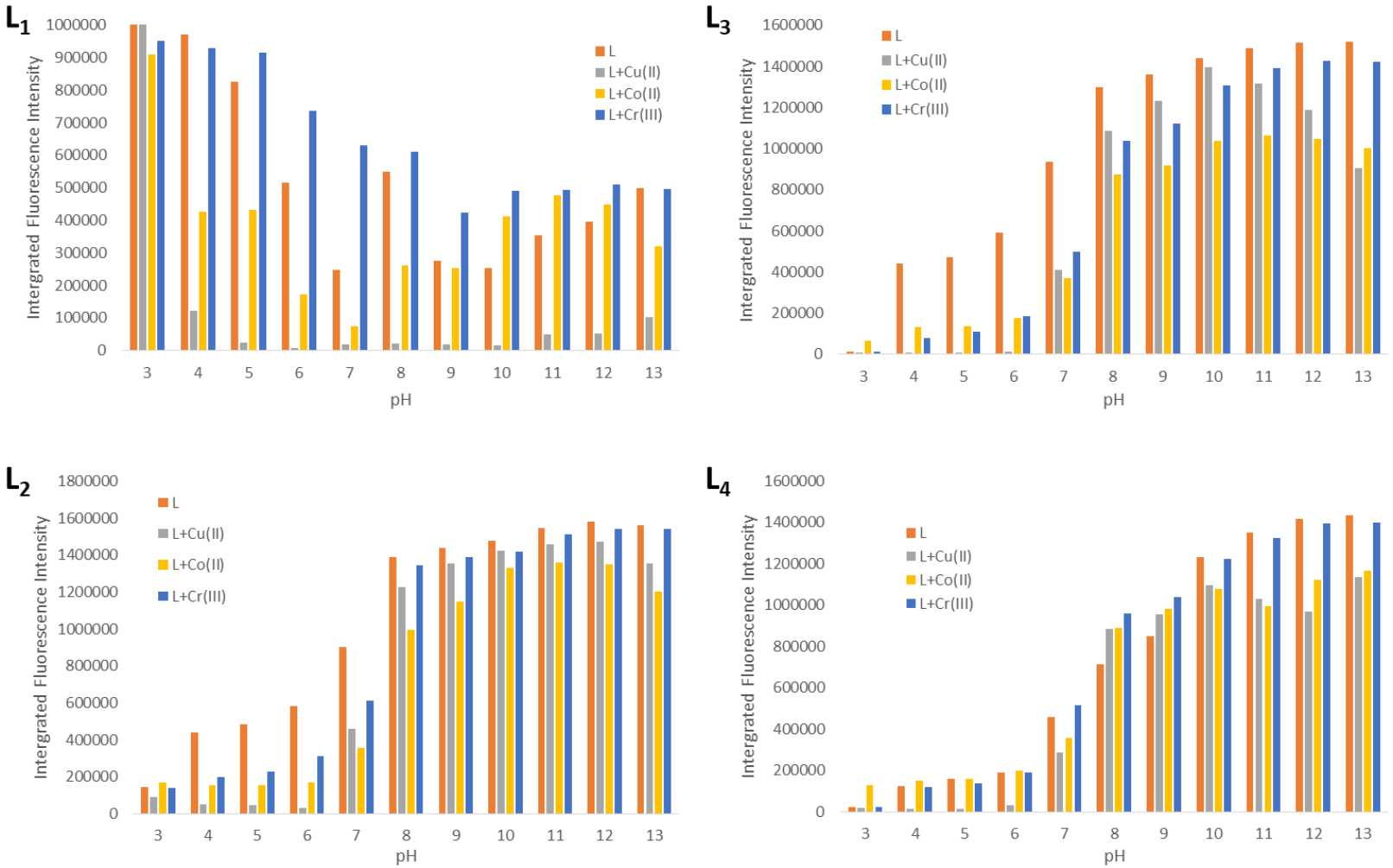
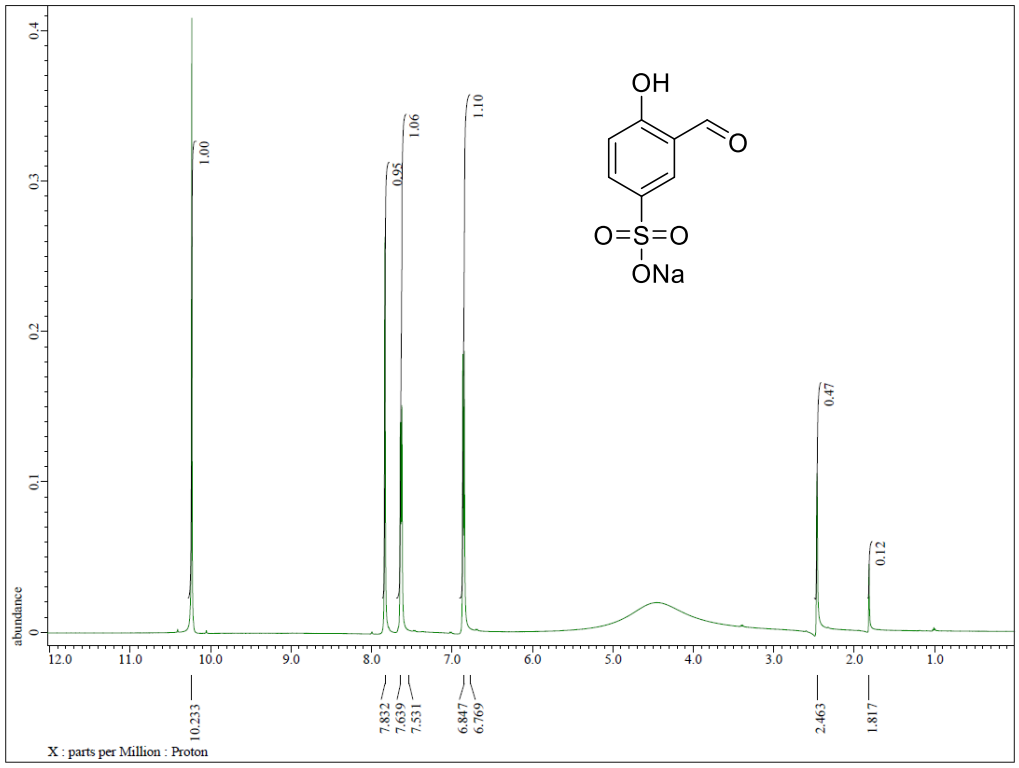
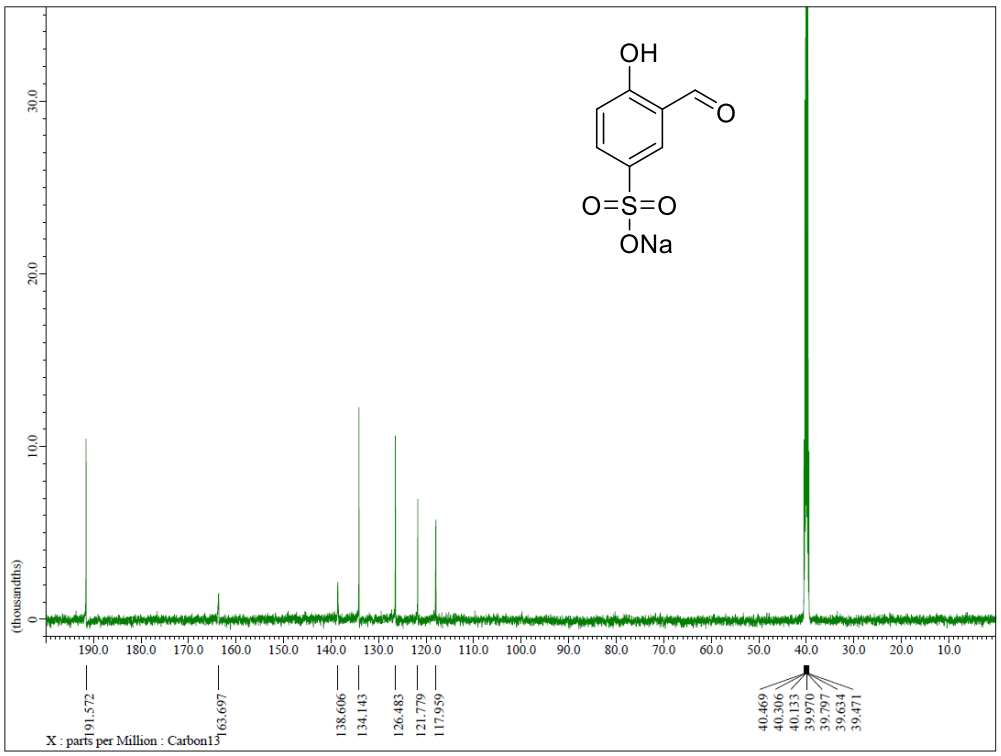
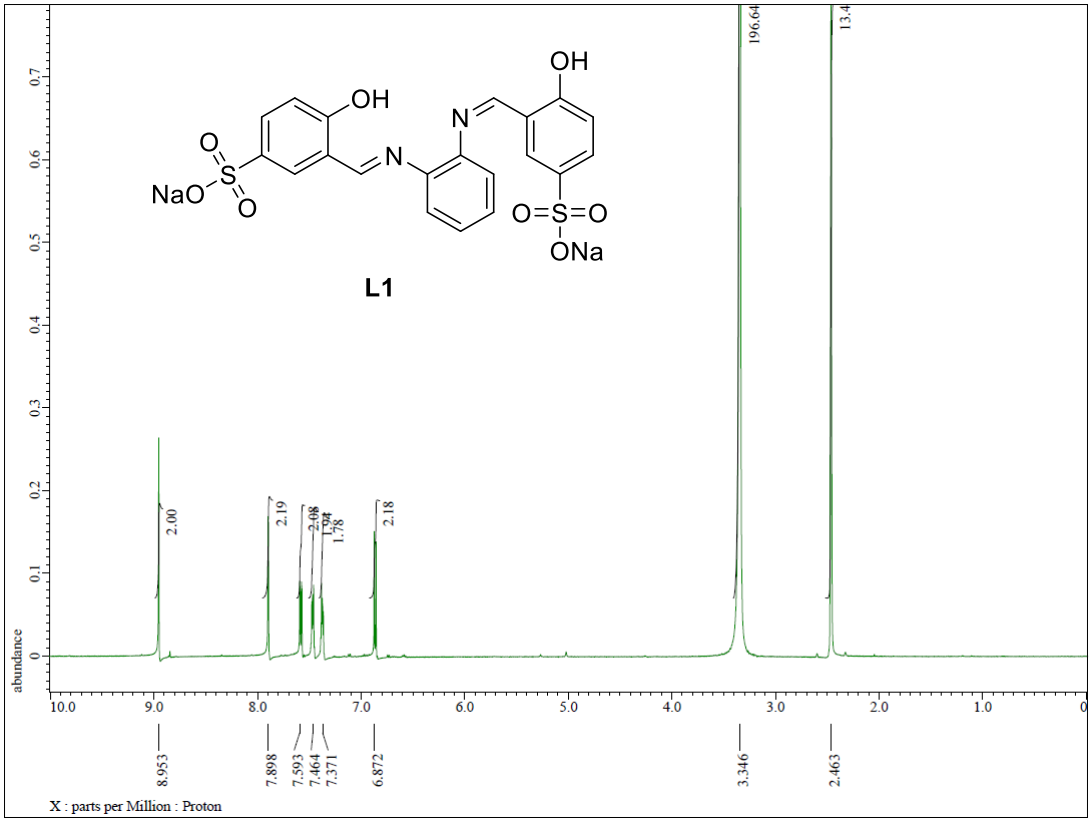


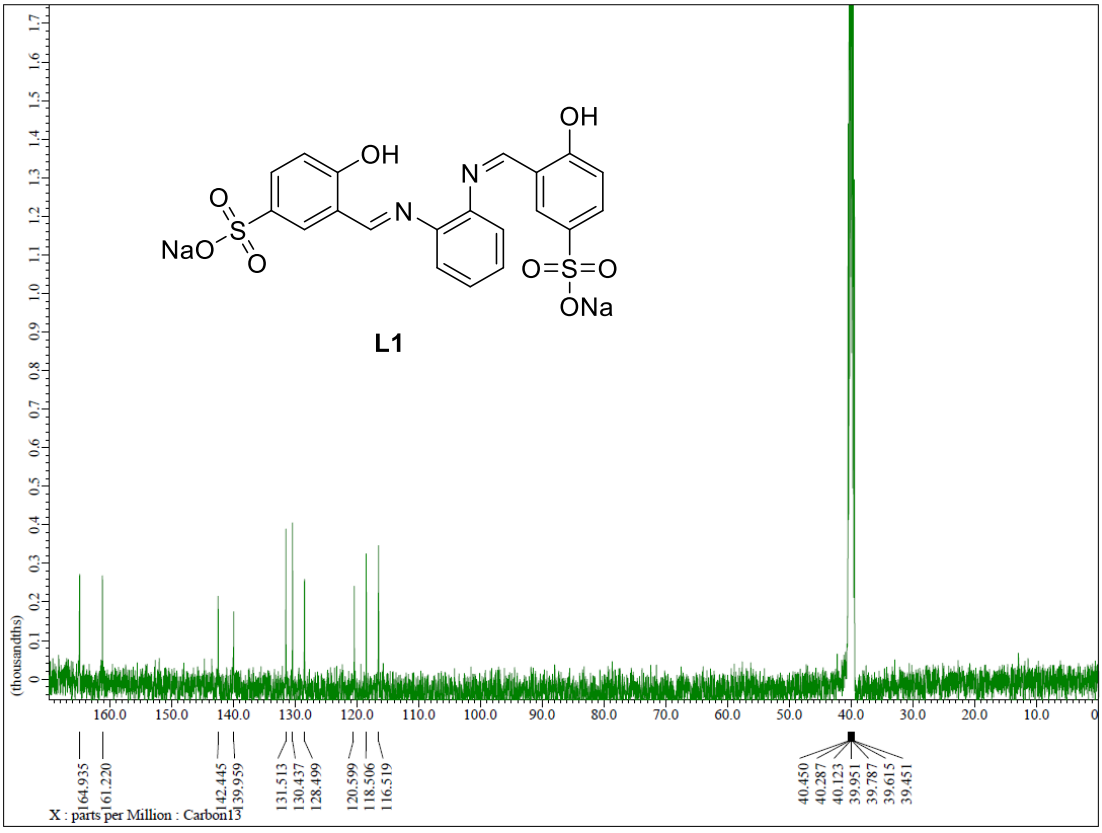
Figure S10: NMRs

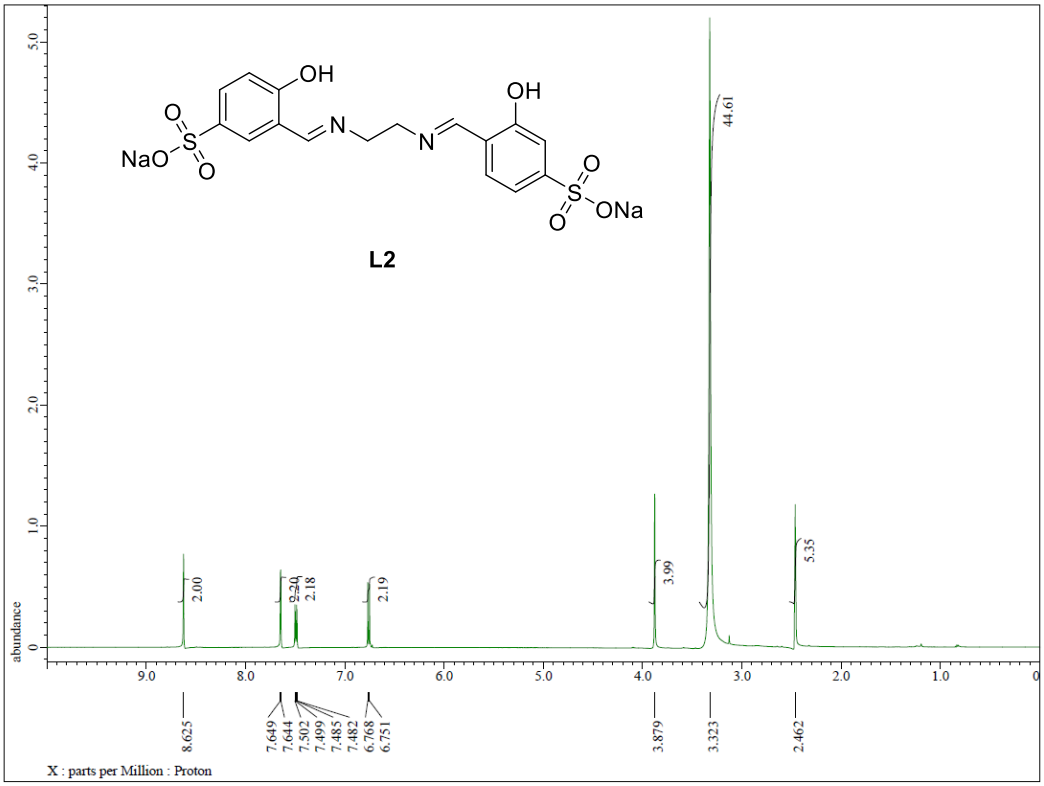
NMR Precursor

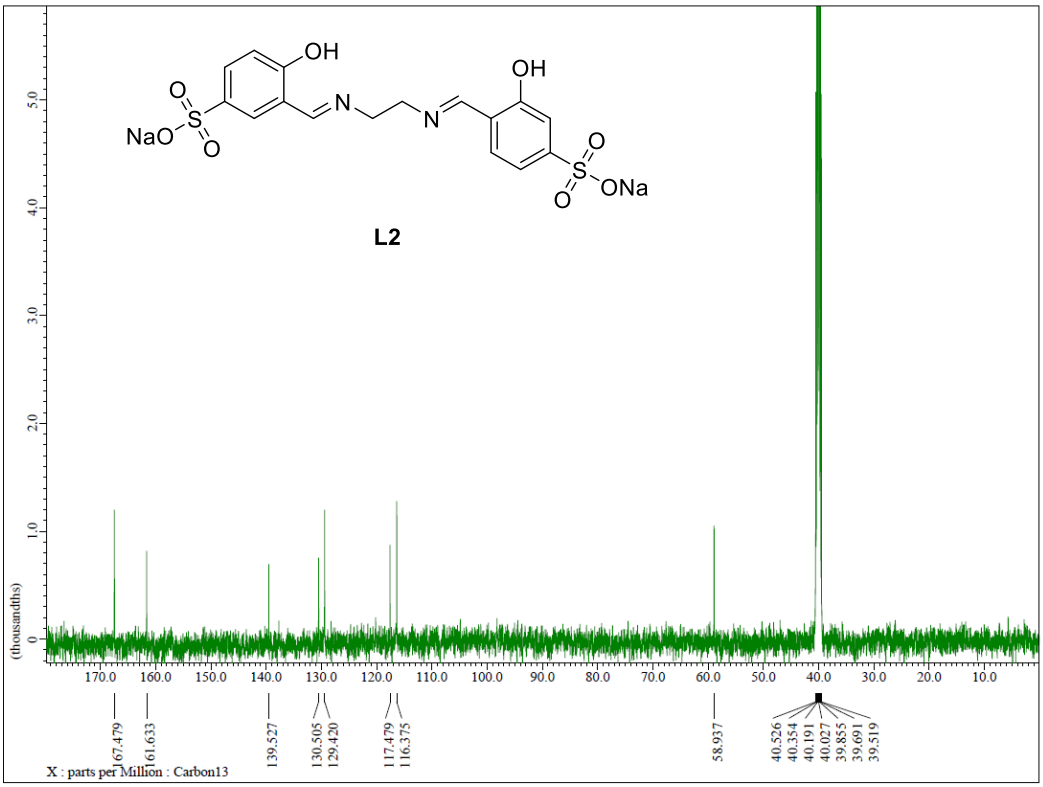


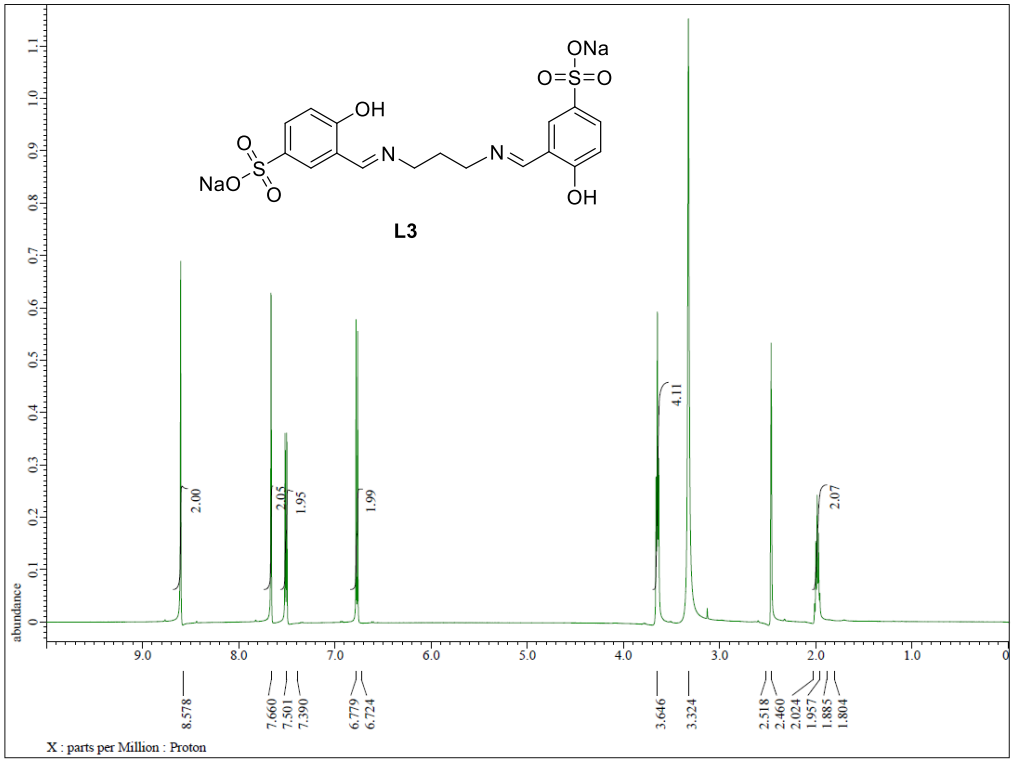


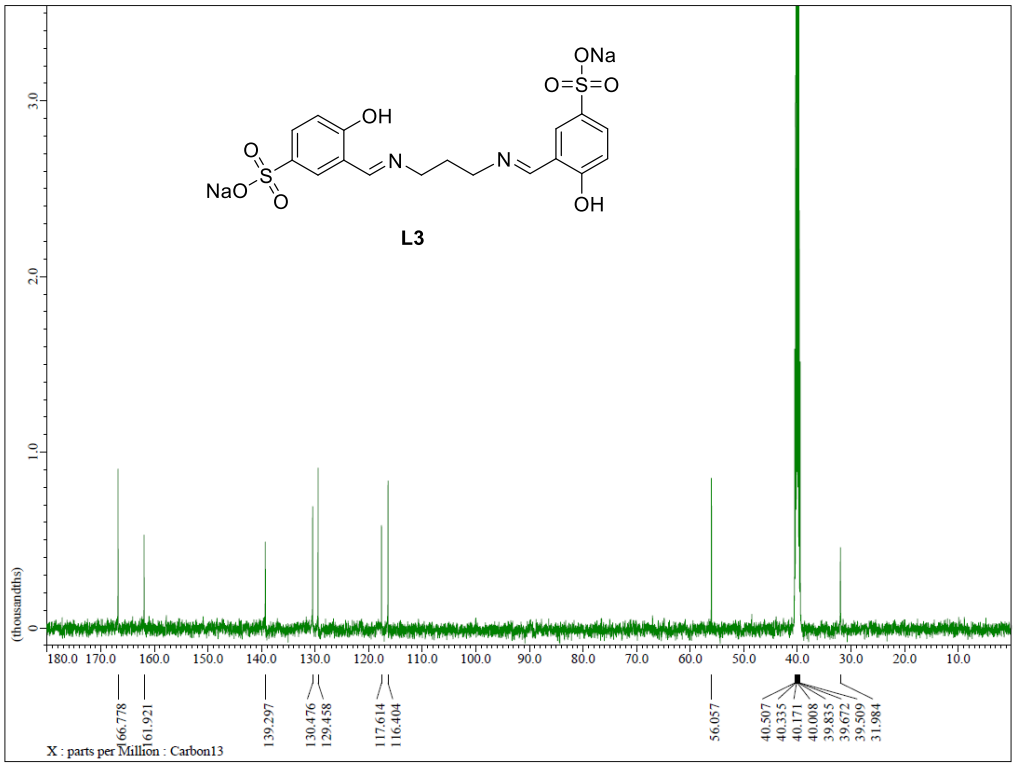

OH
OH
N
N
O
S
NaO
O
O=S=O
ONa
L1
196.64
13.4
2.00
2.19
2.08
1.94
1.78
2.18
abundance
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.953
7.898
7.593
7.464
7.371
6.872
3.346
2.463
X : parts per Million : Proton

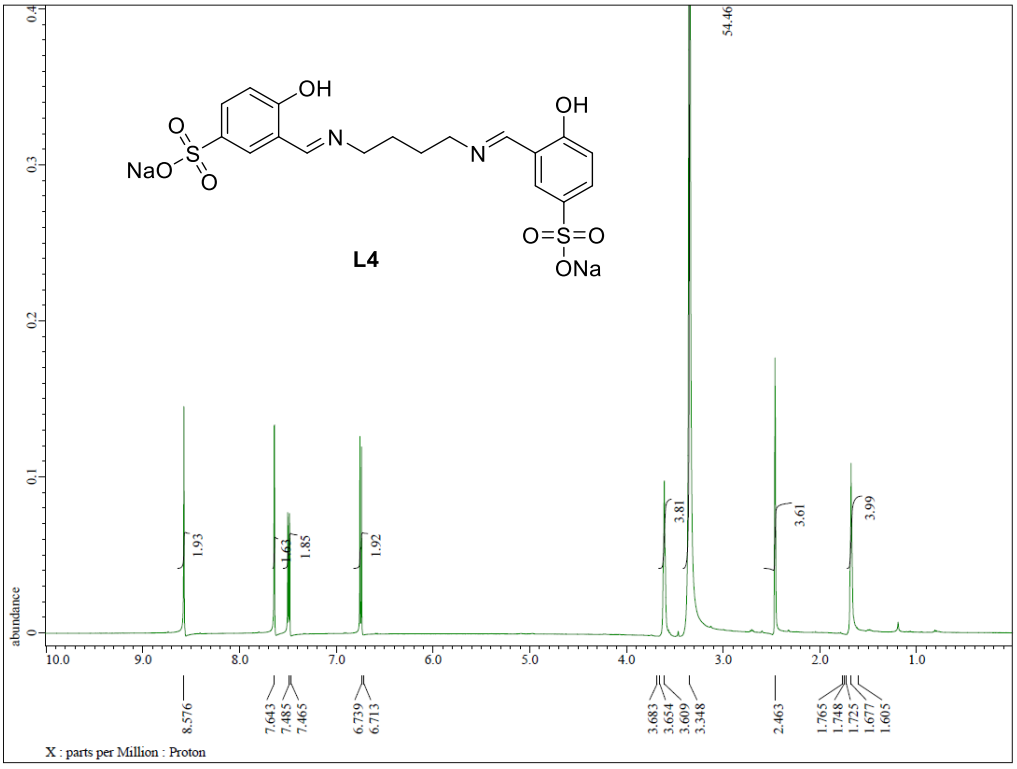

OH
OH
N
N
O
S
NaO
O
O=S=O
ONa
L1
(thousandths)
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
164.935
161.220
142.445
139.959
131.513
130.437
128.499
120.599
118.506
116.519
40.450
40.287
40.123
39.951
39.787
39.615
39.451
X : parts per Million : Carbon13

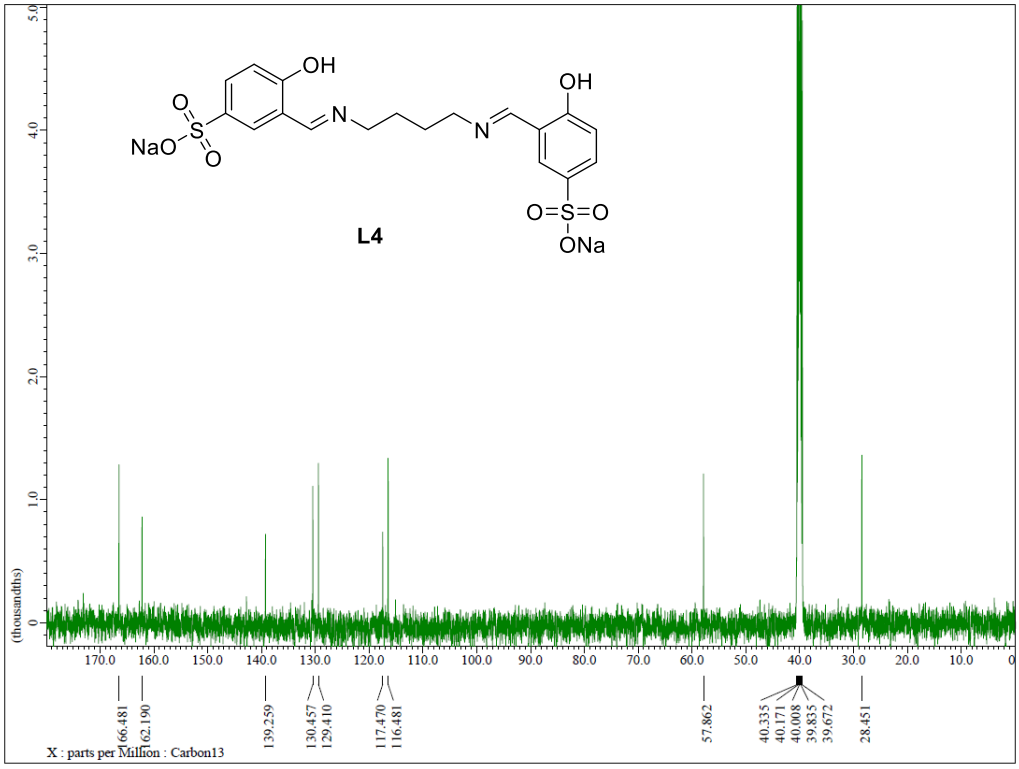

OH
OH
NaO
ONa
L2
abundance
X : parts per Million : Proton


OH
OH
NaO
ONa
L2
(thousandths)
X : parts per Million : Carbon13


ONa
O=S=O
OH
O
NaO
S
O
N
N
OH
L3
abundance
2.00
2.05
1.95
1.99
4.11
2.07
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
8.578
7.660
7.501
7.390
6.779
6.724
3.646
3.324
2.518
2.460
2.024
1.957
1.885
1.804
X : parts per Million : Proton


ONa
O=S=O
OH
O
NaO
S
O
N
N
OH
L3
(thousandths)
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0
166.778
161.921
139.297
130.476
129.458
117.614
116.404
56.057
40.507
40.335
40.171
40.008
39.835
39.672
39.509
31.984
X : parts per Million : Carbon13


OH
O
S
NaO
O
N
N
OH
O=S=O
ONa
L4
abundance
54.46
1.93
1.63
1.85
1.92
3.81
3.61
3.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
8.576
7.643
7.485
7.465
6.739
6.713
3.683
3.654
3.609
3.348
2.463
1.765
1.748
1.725
1.677
1.605
X : parts per Million : Proton


OH
O
S
NaO
O
N
N
OH
O=S=O
ONa
L4
(thousandths)
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
166.481
162.190
139.259
130.457
129.410
117.470
116.481
57.862
40.335
40.171
40.008
39.835
39.672
28.451
X : parts per Million : Carbon13