Electronic Supplementary Material (ESI) for RSC Advances.

Practical Stability of $Au_{25}(SR)_{18}^{-1/0/+1}$

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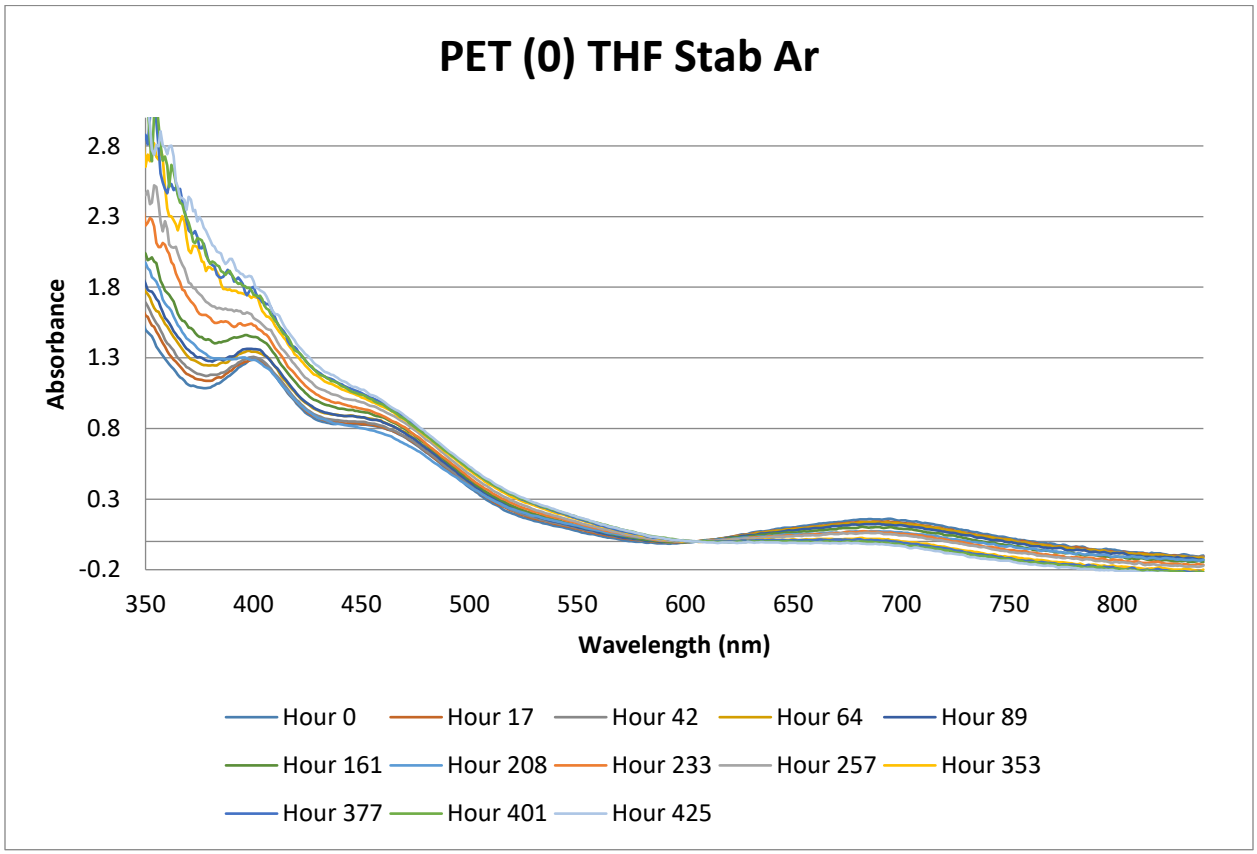
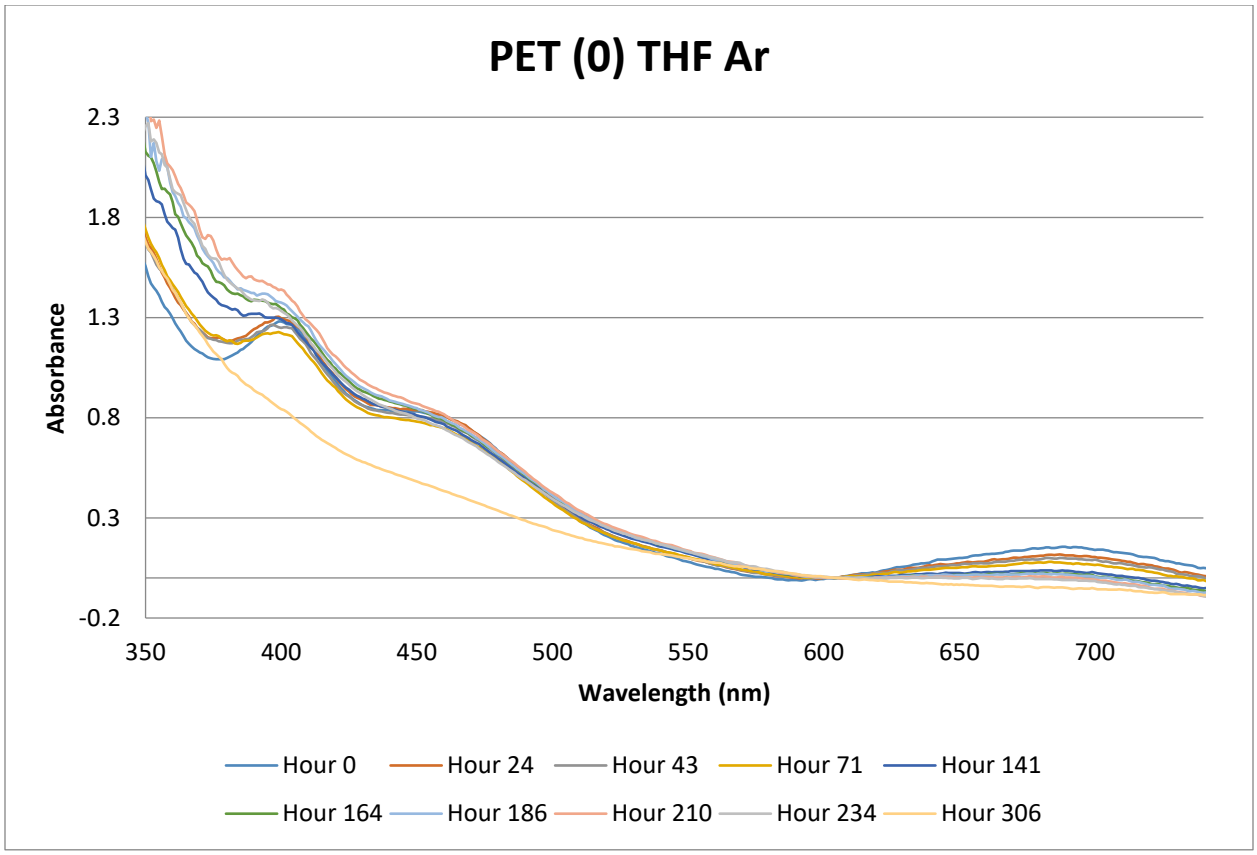
Contents

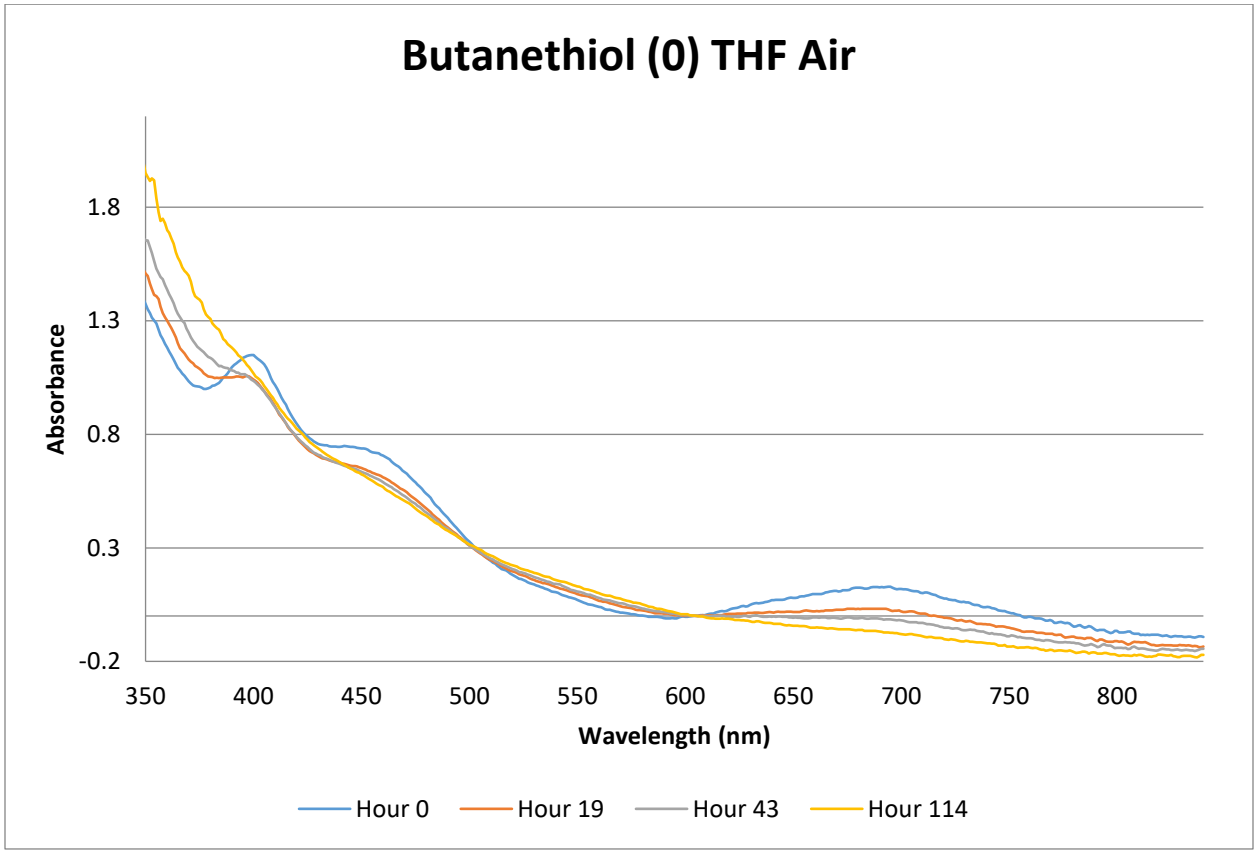
UV/Vis Spectra

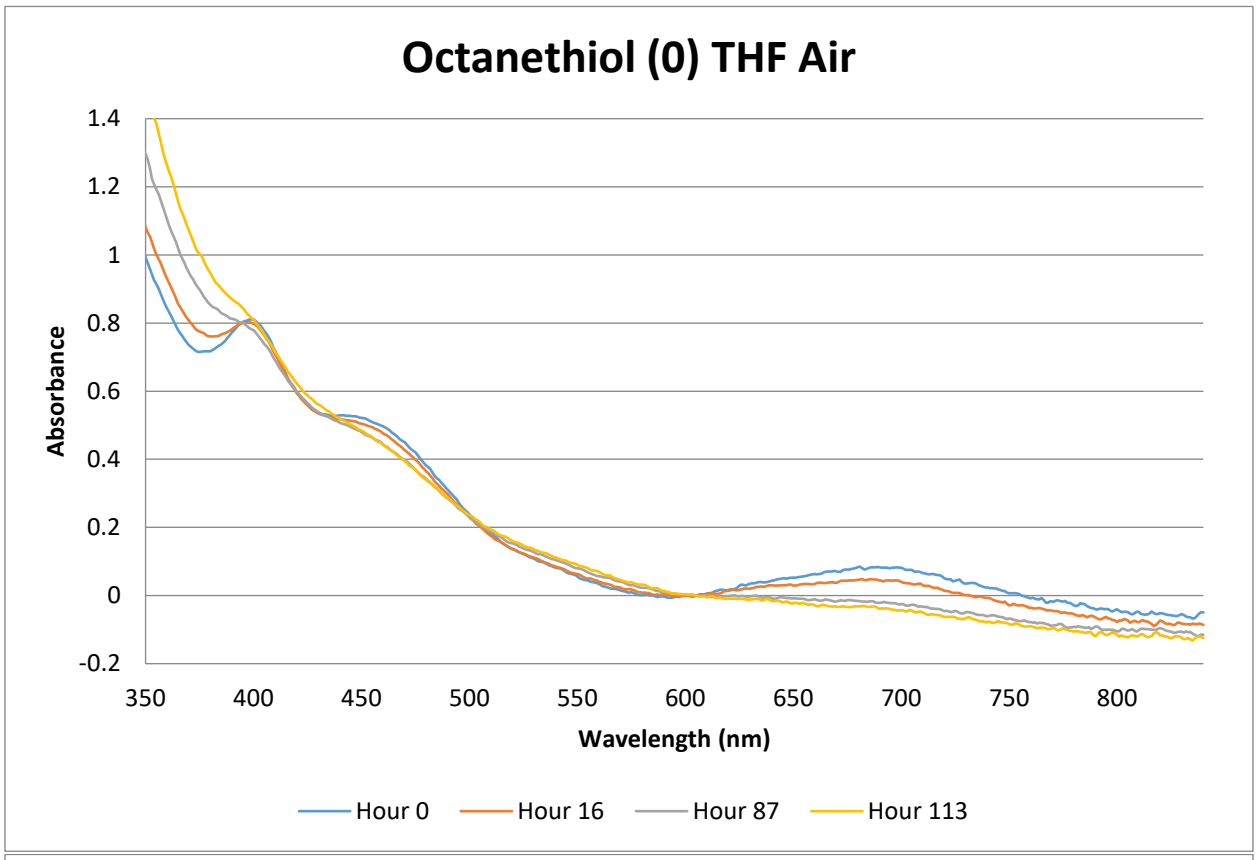
UV/Vis spectra were collected on an HP 8452A Diode Array Spectrophotometer, a ThermoFisher NanoDrop spectrophotometer in all other cases. Data were analyzed using Microsoft Excel.

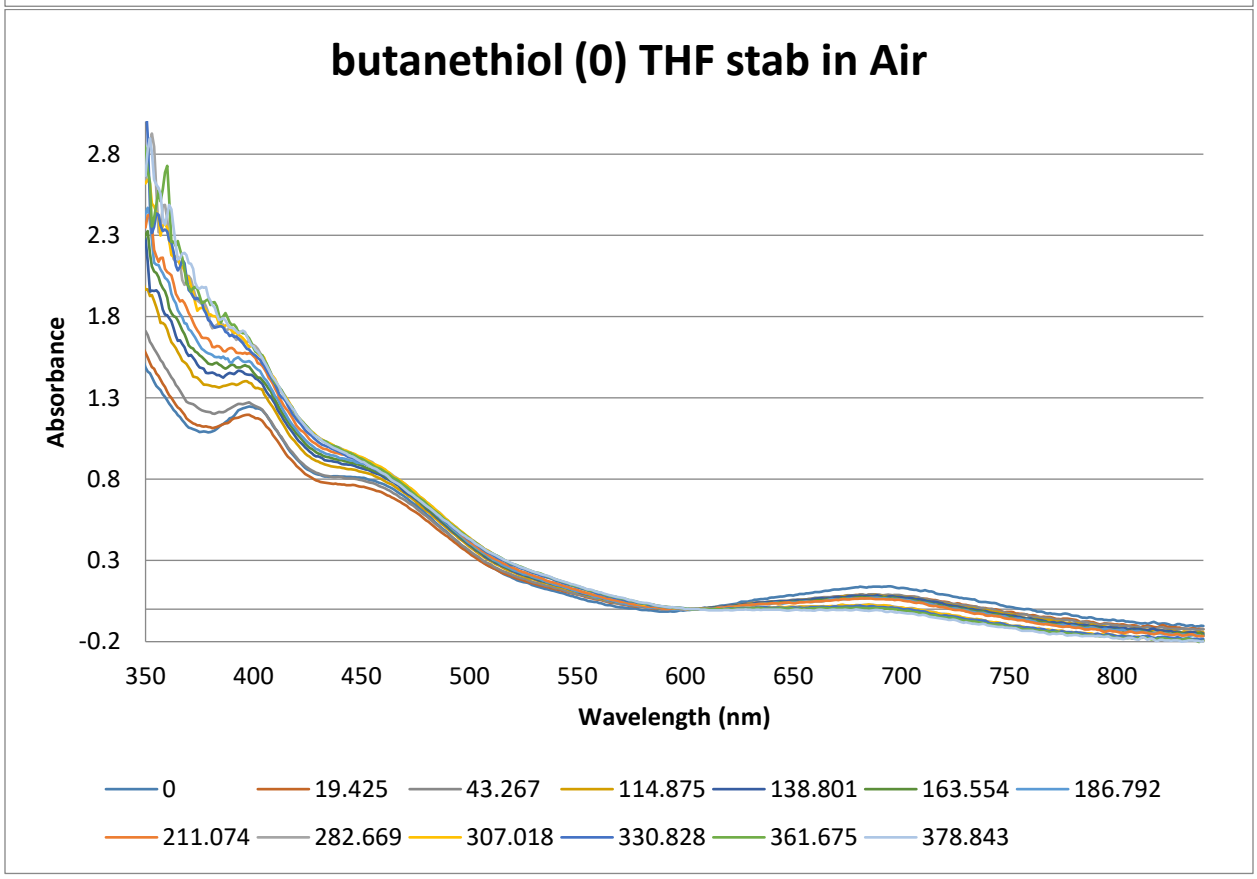
Decomposition in stabilized and unstabilized THF under argon and air

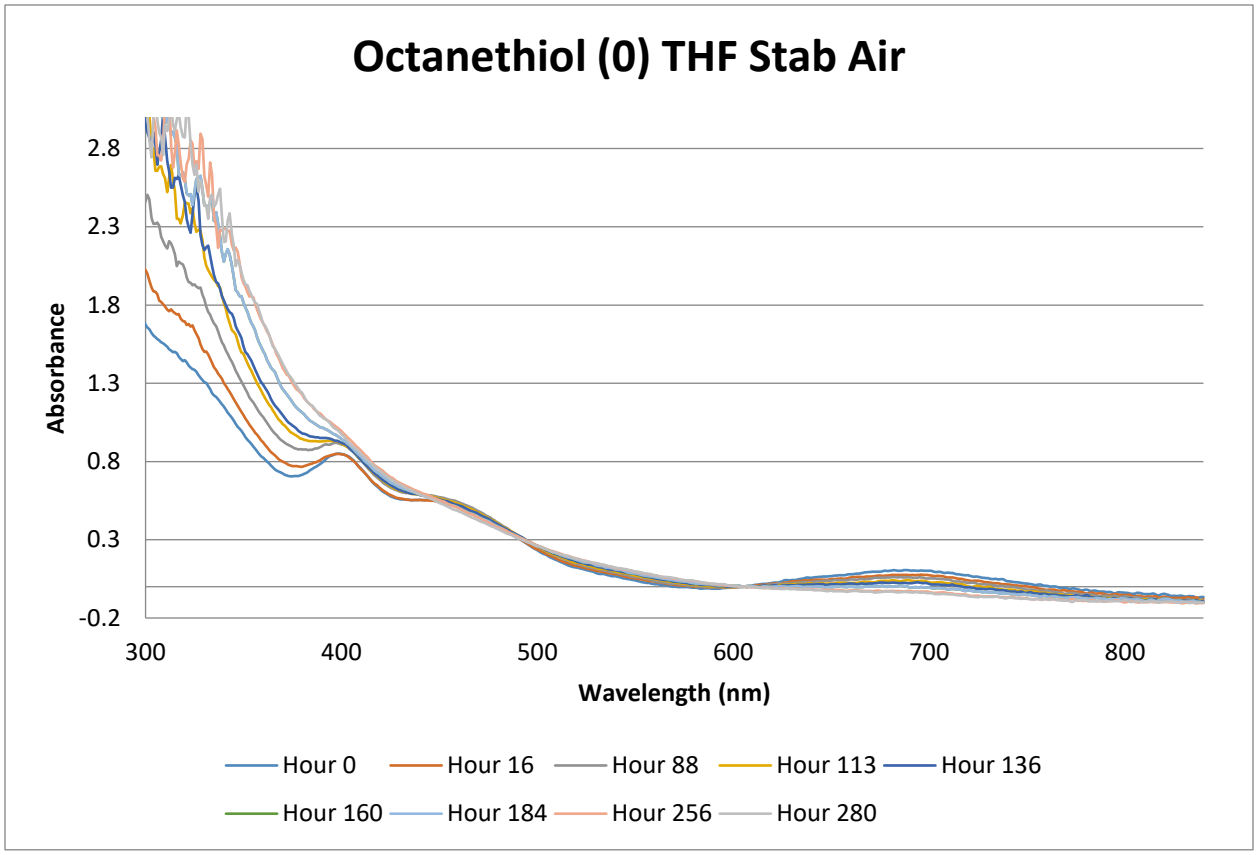


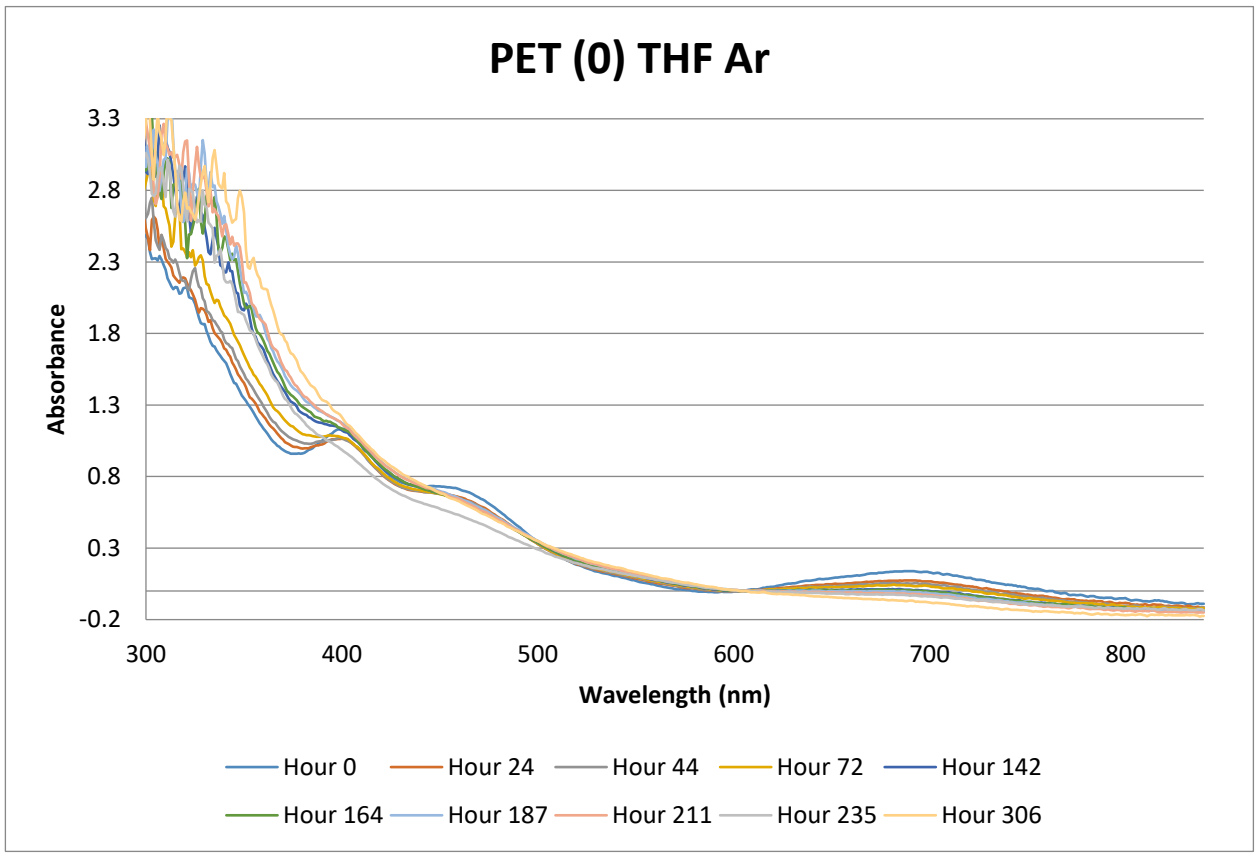

PET (0) THF Ar
Absorbance
2.3
1.8
1.3
0.8
0.3
-0.2
350
400
450
500
550
600
650
700
Wavelength (nm)
Hour 0
Hour 24
Hour 43
Hour 71
Hour 141
Hour 164
Hour 186
Hour 210
Hour 234
Hour 306

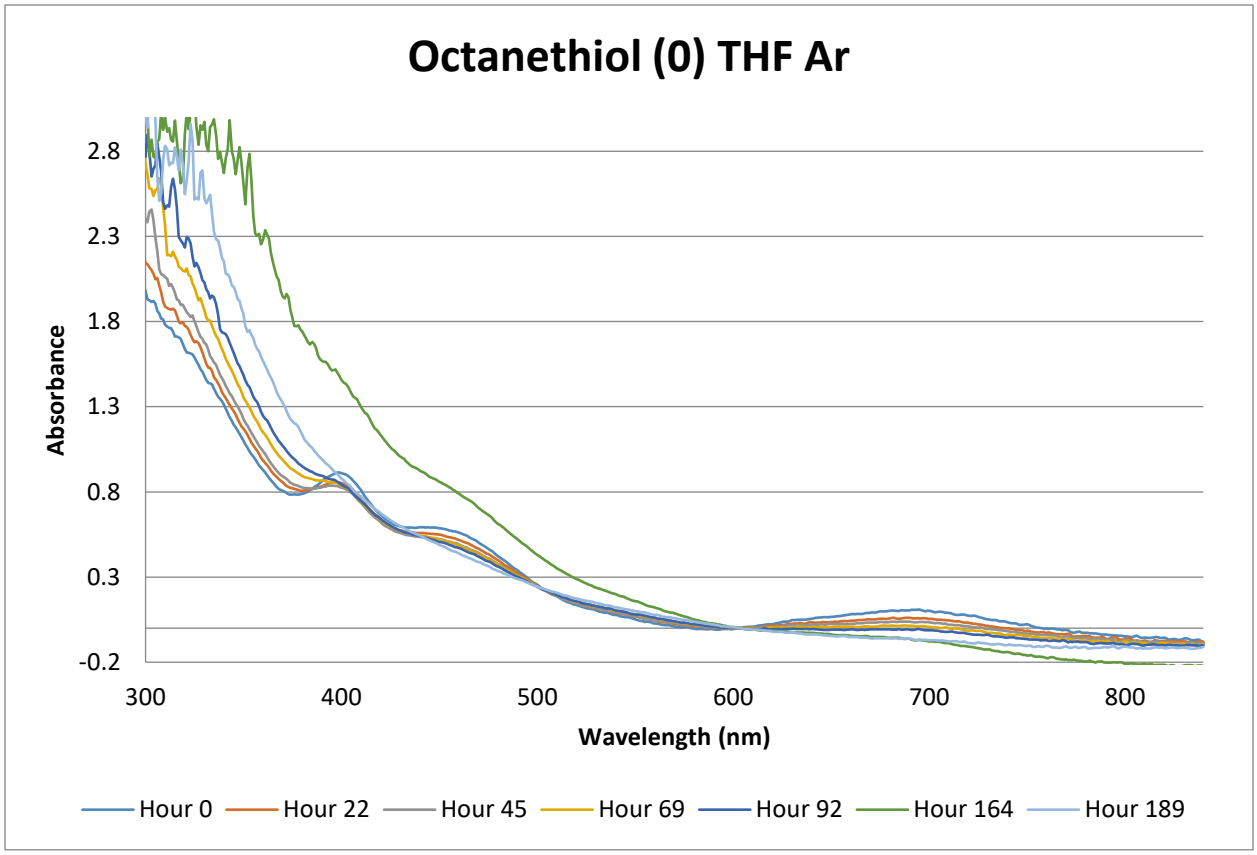

Butanethiol (0) THF Air
Absorbance
1.8
1.3
0.8
0.3
-0.2
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)
Hour 0
Hour 19
Hour 43
Hour 114

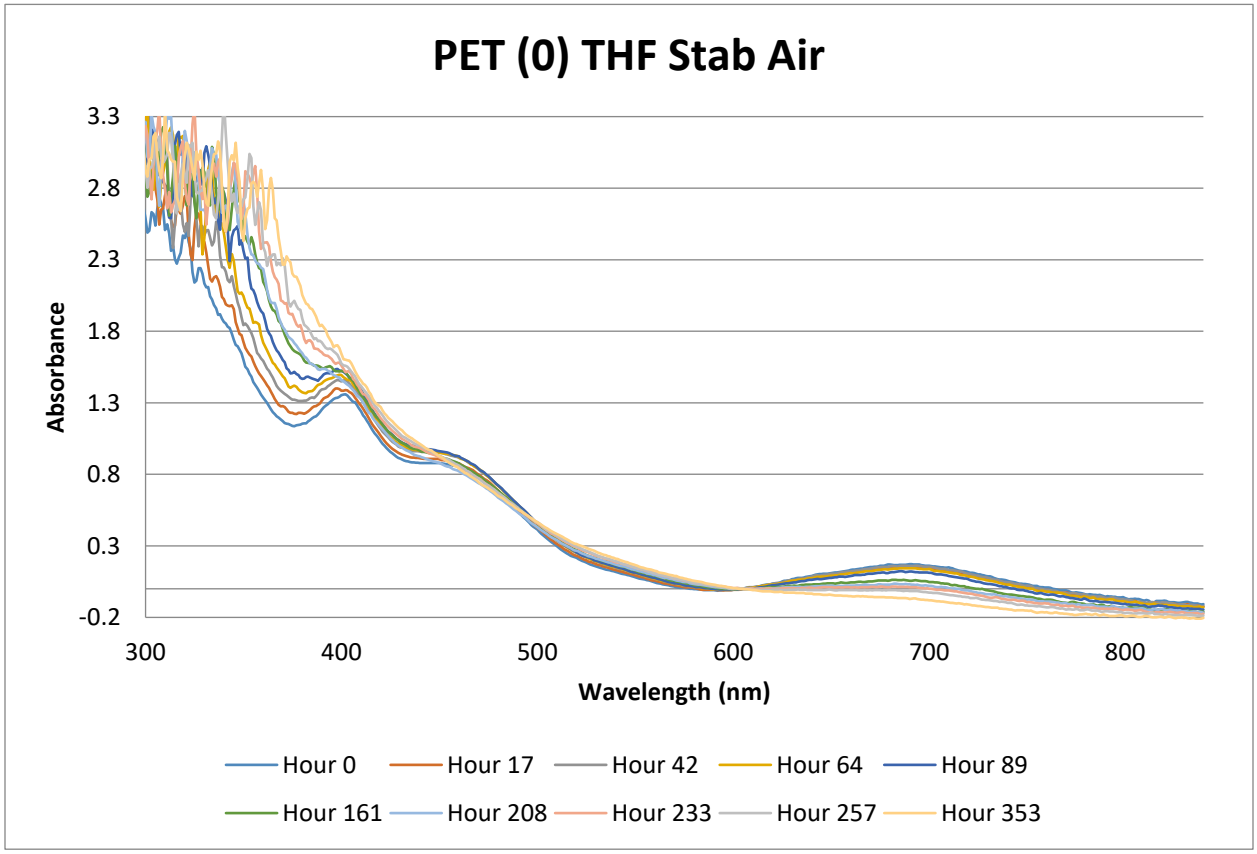

Octanethiol (0) THF Air
Absorbance
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)
Hour 0
Hour 16
Hour 87
Hour 113


butanethiol (0) THF stab in Air
Absorbance
2.8
2.3
1.8
1.3
0.8
0.3
-0.2
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)
0
19.425
43.267
114.875
138.801
163.554
186.792
211.074
282.669
307.018
330.828
361.675
378.843

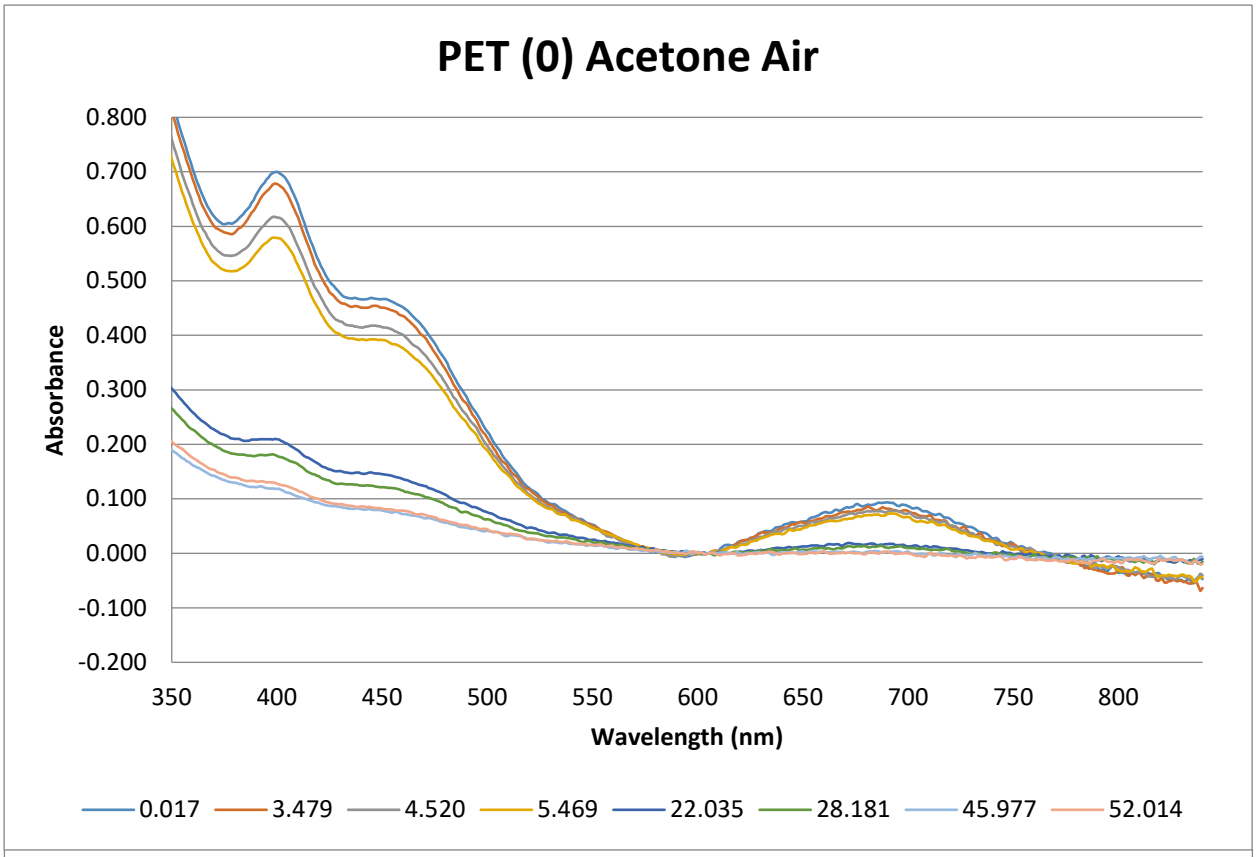

Octanethiol (0) THF Stab Air
Absorbance
2.8
2.3
1.8
1.3
0.8
0.3
-0.2
300
400
500
600
700
800
Wavelength (nm)
Hour 0
Hour 16
Hour 88
Hour 113
Hour 136
Hour 160
Hour 184
Hour 256
Hour 280

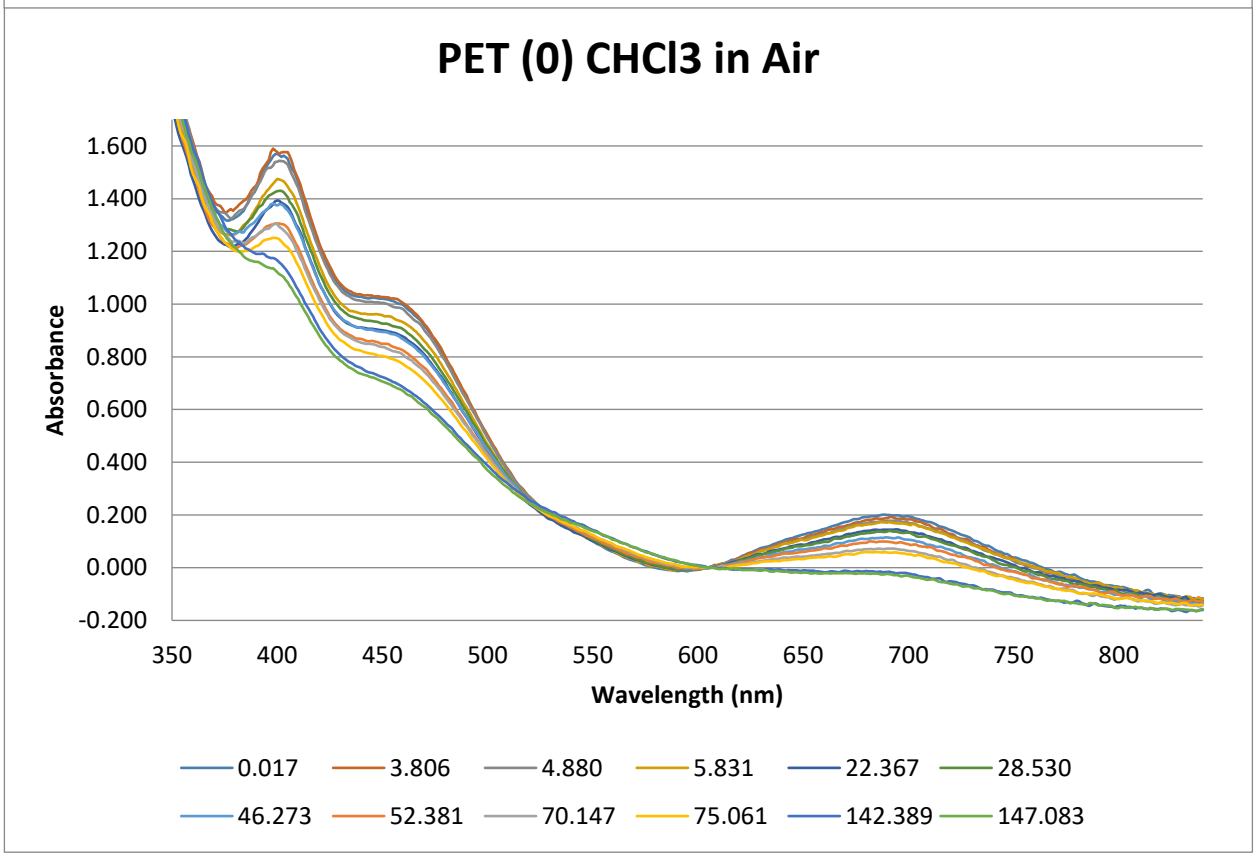

PET (0) THF Ar
Absorbance
3.3
2.8
2.3
1.8
1.3
0.8
0.3
-0.2
300
400
500
600
700
800
Wavelength (nm)
Hour 0
Hour 24
Hour 44
Hour 72
Hour 142
Hour 164
Hour 187
Hour 211
Hour 235
Hour 306

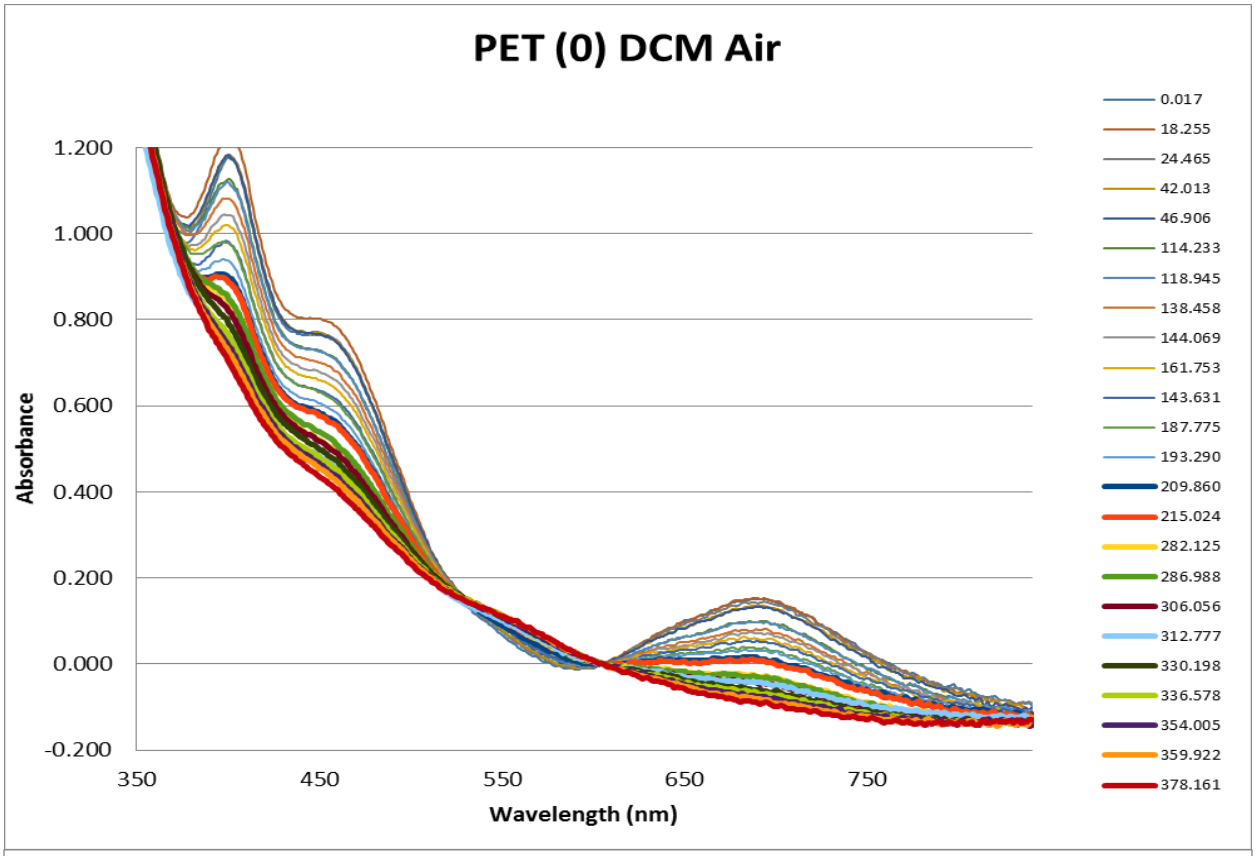

Octanethiol (0) THF Ar
Absorbance
2.8
2.3
1.8
1.3
0.8
0.3
-0.2
300
400
500
600
700
800
Wavelength (nm)
Hour 0
Hour 22
Hour 45
Hour 69
Hour 92
Hour 164
Hour 189

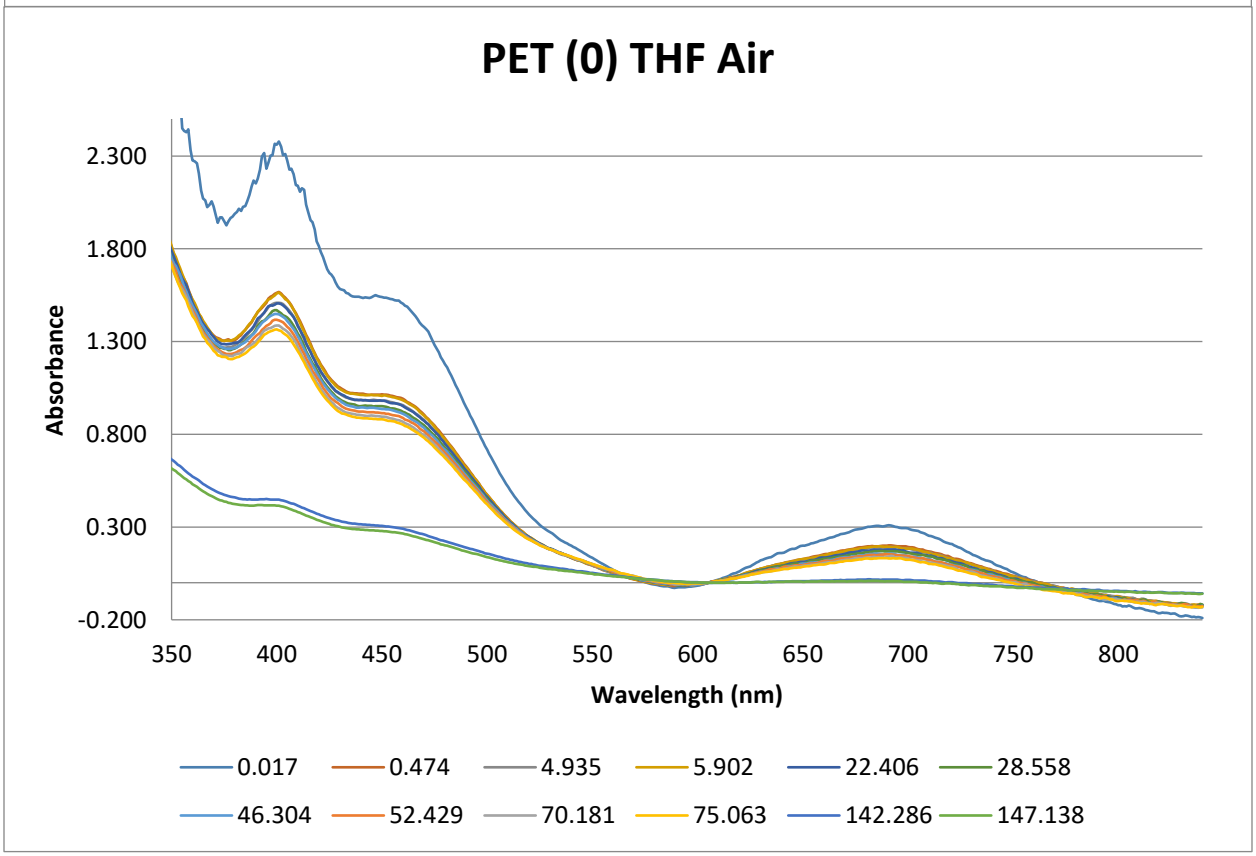

PET (0) THF Stab Air
Absorbance
3.3
2.8
2.3
1.8
1.3
0.8
0.3
-0.2
300
400
500
600
700
800
Wavelength (nm)
Hour 0
Hour 17
Hour 42
Hour 64
Hour 89
Hour 161
Hour 208
Hour 233
Hour 257
Hour 353

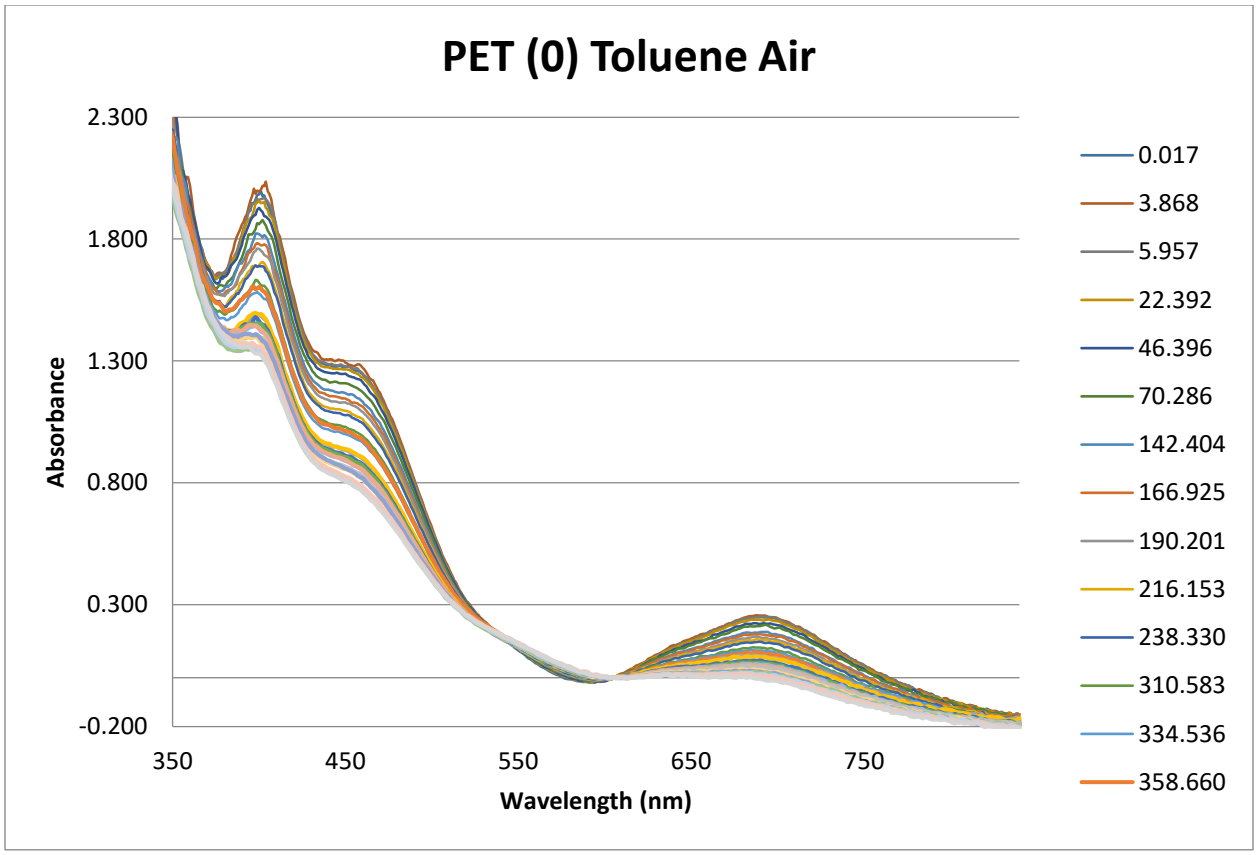
Decomposition in various solvents of the 0 charge state in air



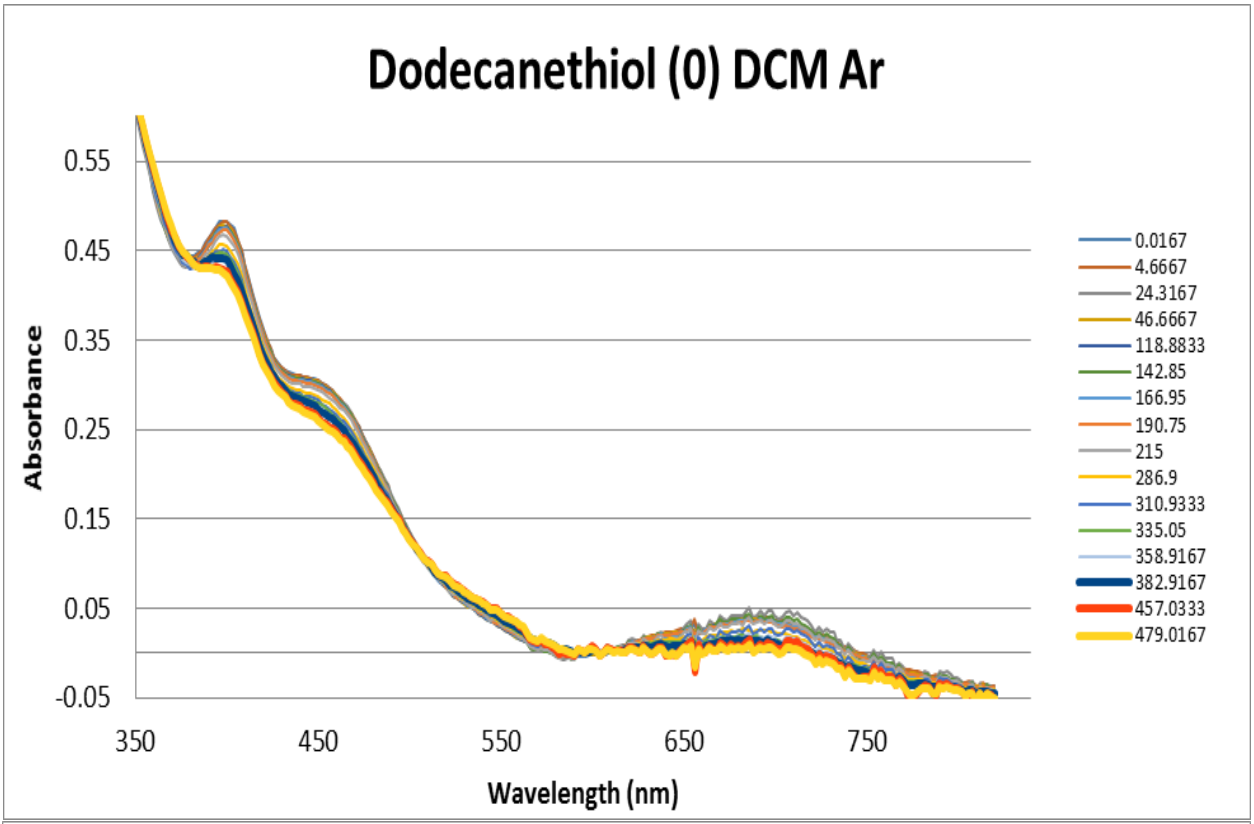


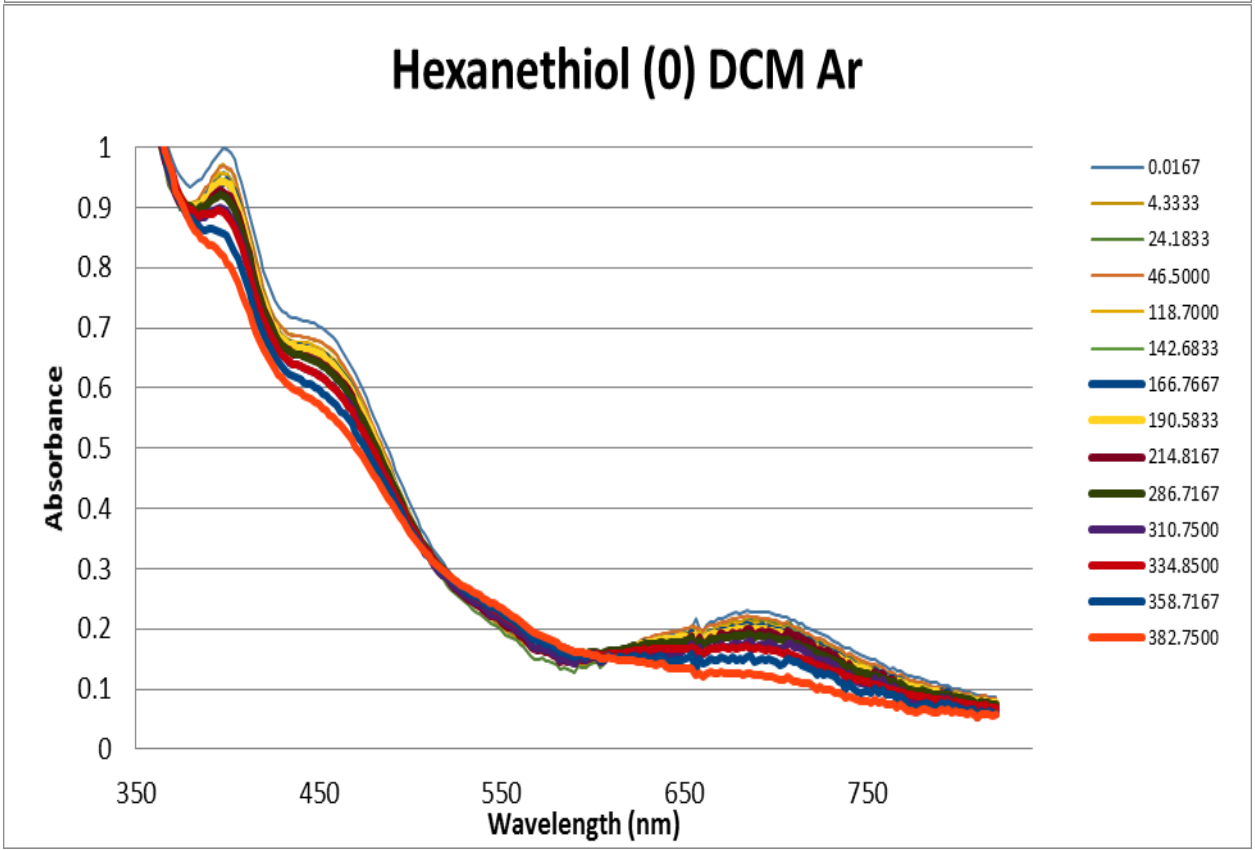

PET (0) DCM Air
Absorbance
1.200
1.000
0.800
0.600
0.400
0.200
0.000
-0.200
350
450
550
650
750
Wavelength (nm)
0.017
18.255
24.465
42.013
46.906
114.233
118.945
138.458
144.069
161.753
143.631
187.775
193.290
209.860
215.024
282.125
286.988
306.056
312.777
330.198
336.578
354.005
359.922
378.161

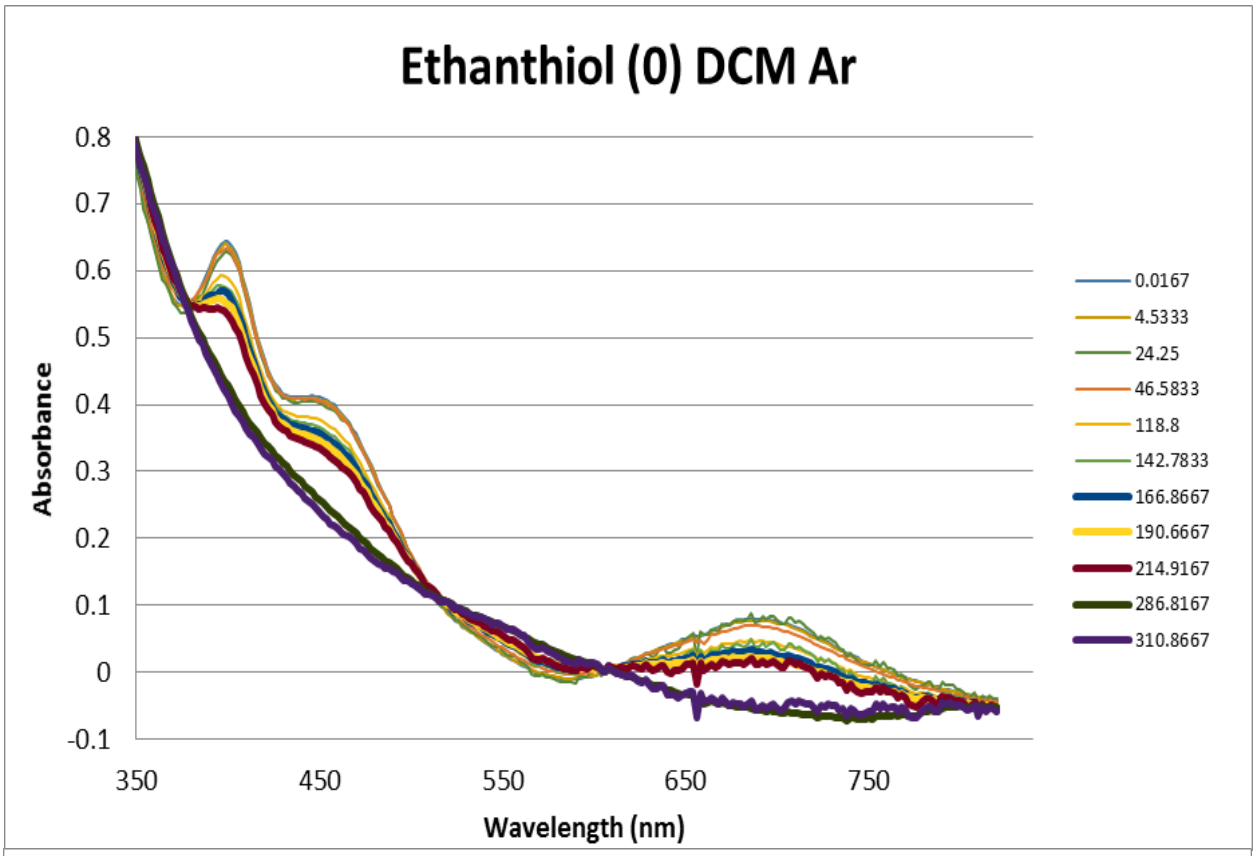

PET (0) THF Air
Absorbance
2.300
1.800
1.300
0.800
0.300
-0.200
350
400
450
500
550
600
650
700
750
800
Wavelength (nm)
0.017
0.474
4.935
5.902
22.406
28.558
46.304
52.429
70.181
75.063
142.286
147.138

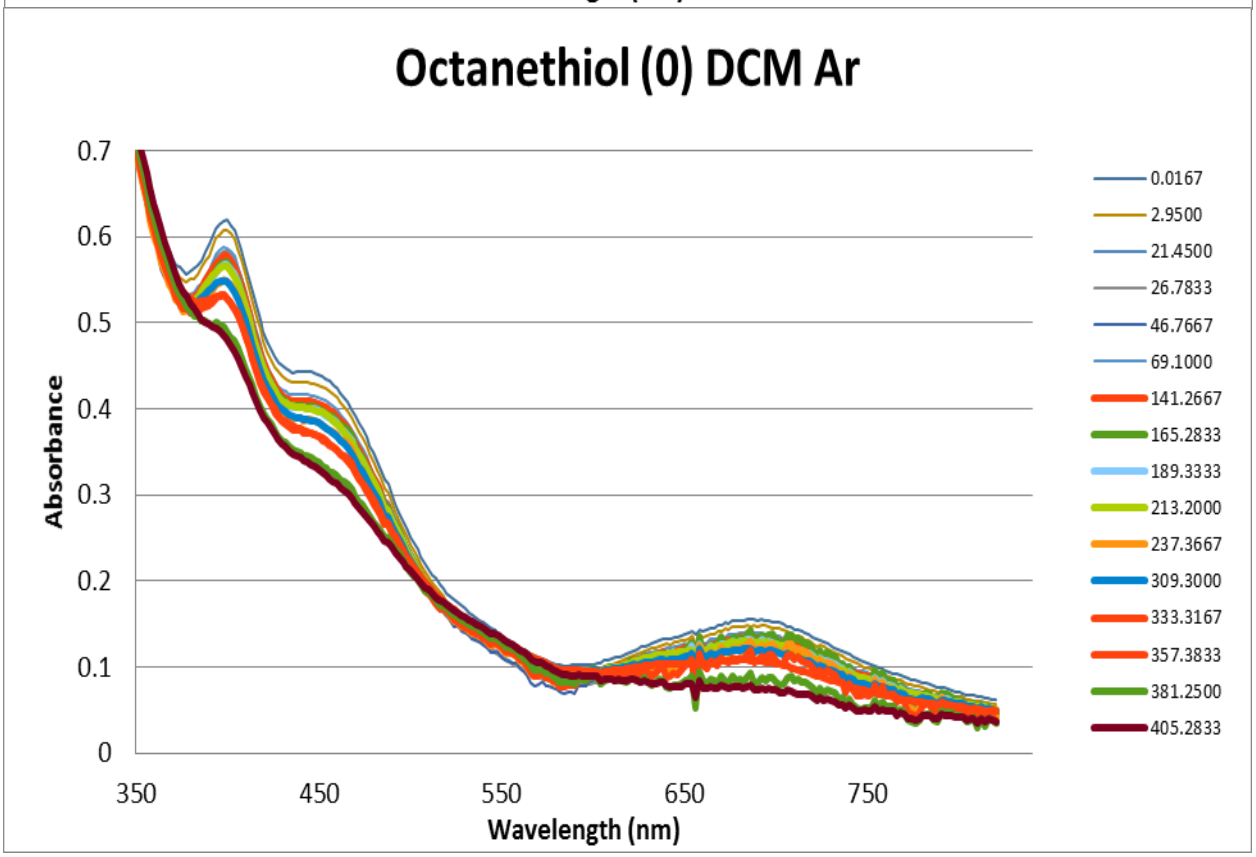

PET (0) Toluene Air
2.300
1.800
1.300
0.800
0.300
-0.200
Absorbance
350
450
550
650
750
Wavelength (nm)
0.017
3.868
5.957
22.392
46.396
70.286
142.404
166.925
190.201
216.153
238.330
310.583
334.536
358.660

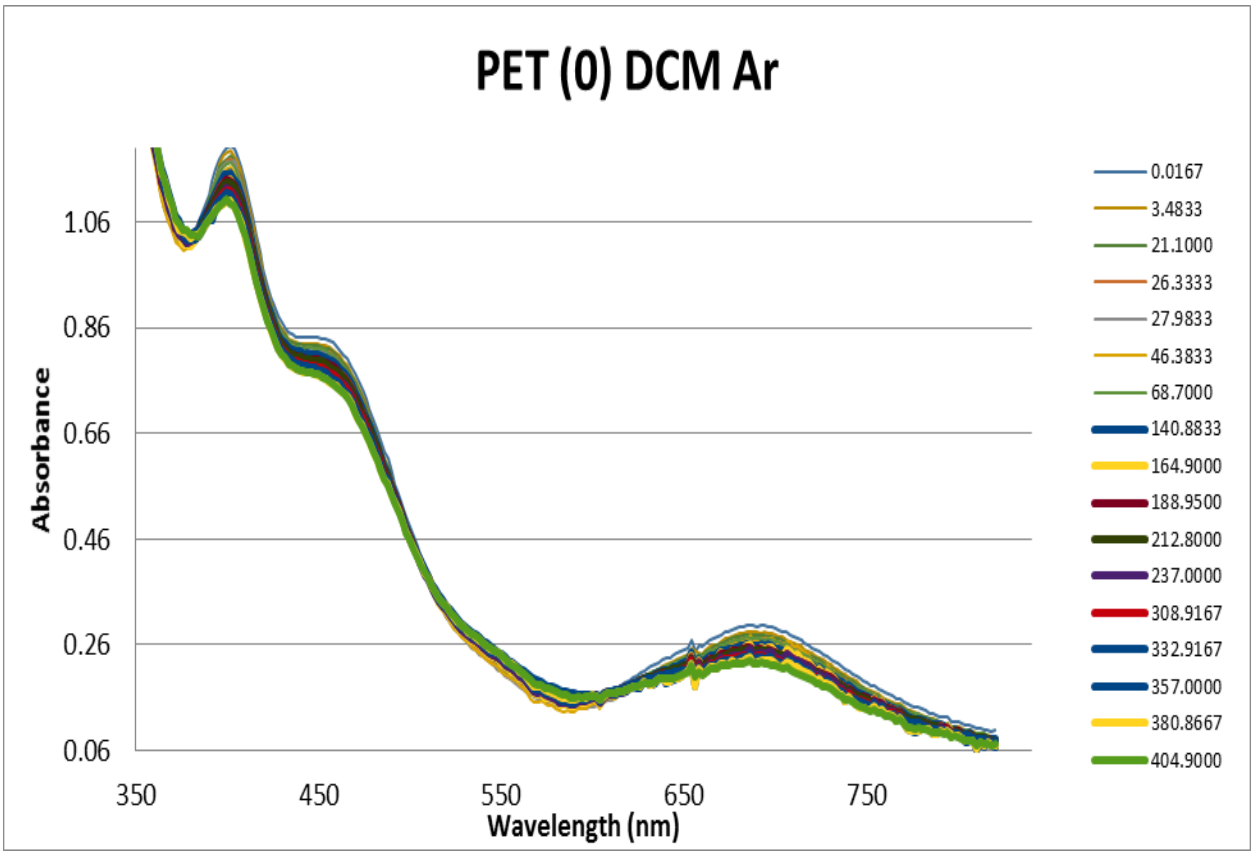
Decomposition of 0 charge state with different ligand in DCM under argon





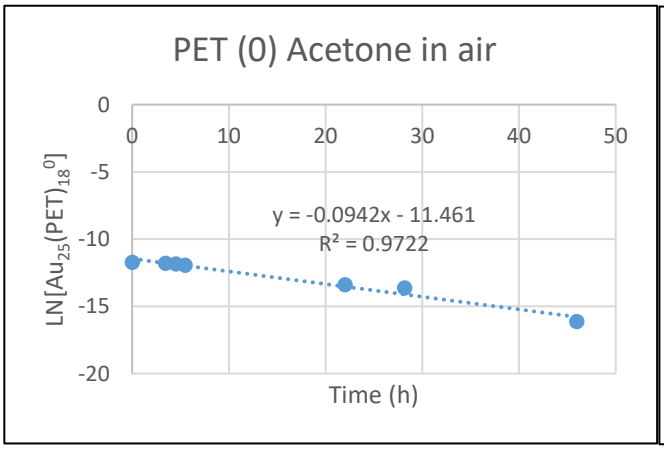

Ethanthiol (0) DCM Ar
Absorbance
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
350
450
550
650
750
Wavelength (nm)
0.0167
4.5333
24.25
46.5833
118.8
142.7833
166.8667
190.6667
214.9167
286.8167
310.8667

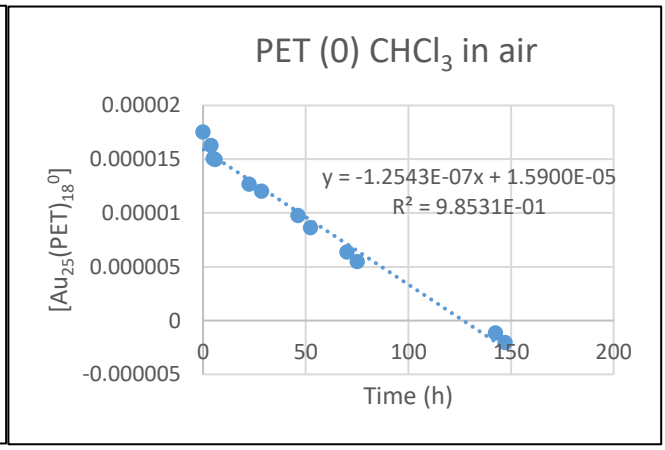

Octanethiol (0) DCM Ar
Absorbance
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
350
450
550
650
750
Wavelength (nm)
0.0167
2.9500
21.4500
26.7833
46.7667
69.1000
141.2667
165.2833
189.3333
213.2000
237.3667
309.3000
333.3167
357.3833
381.2500
405.2833

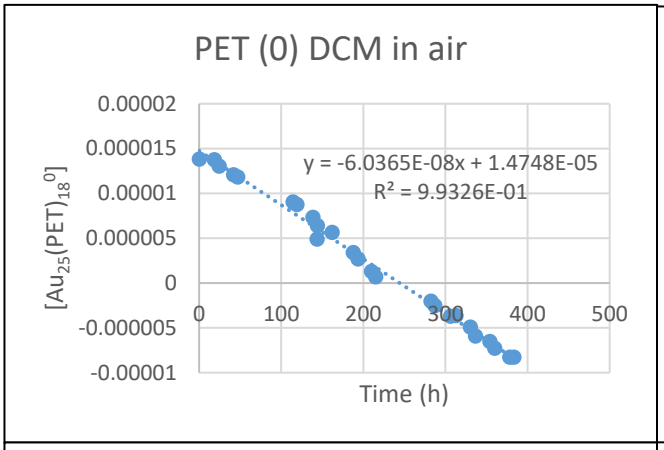


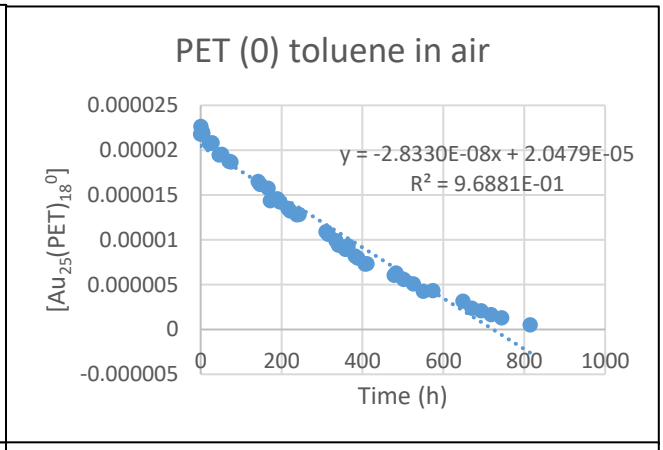
Linear fits of rate laws to the absorbance data

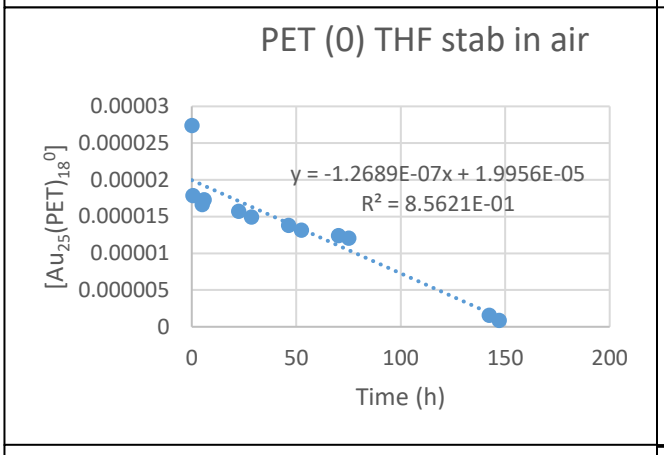
Concentration was calculated using the molar absorptivity of 8800 $cm^{-1}M^{-1}$ at 680nm. This concentration data was then fit to integrated rate laws using Microsoft Excel and the best fits were chosen to report the reactant order of gold for that set of conditions. The graphs are labeled with the ligand layer charge state solvent then atmosphere.

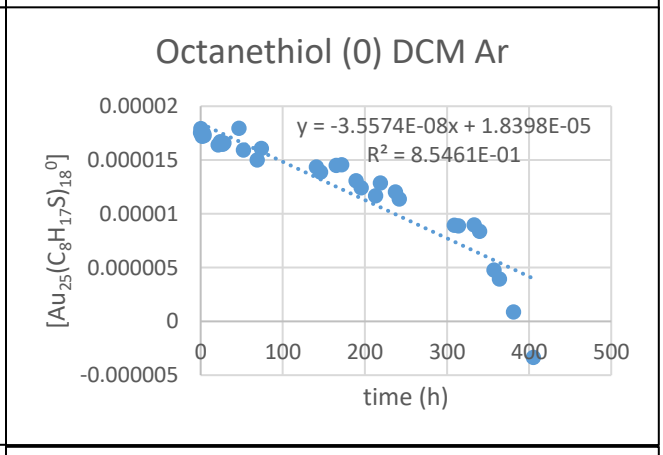


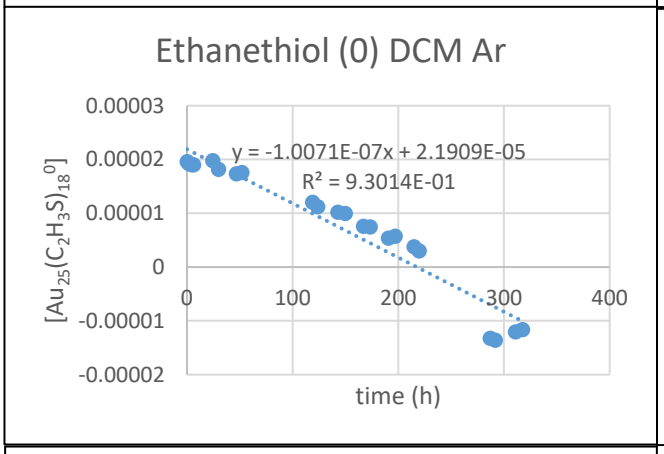


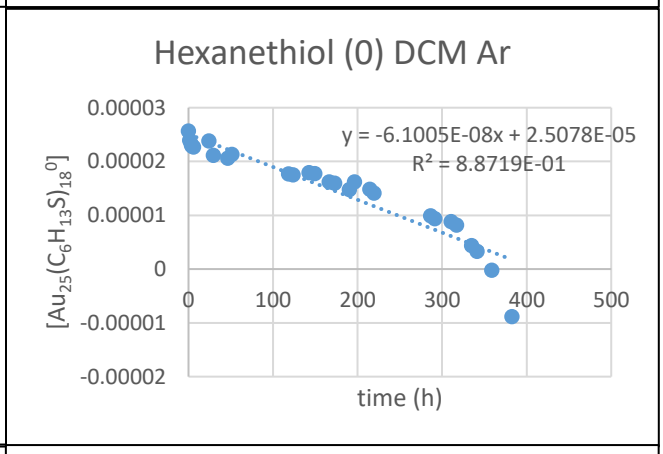

PET (0) DCM in air
y = -6.0365E-08x + 1.4748E-05
R² = 9.9326E-01
[Au25(PET)18 0]
Time (h)

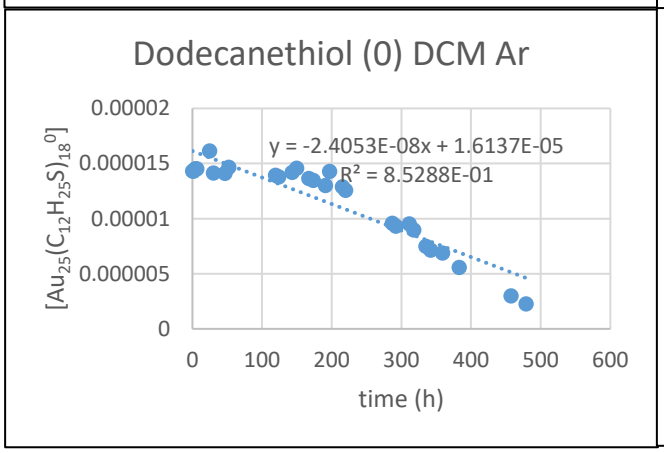

PET (0) toluene in air
y = -2.8330E-08x + 2.0479E-05
R² = 9.6881E-01
[Au25(PET)18 0]
Time (h)

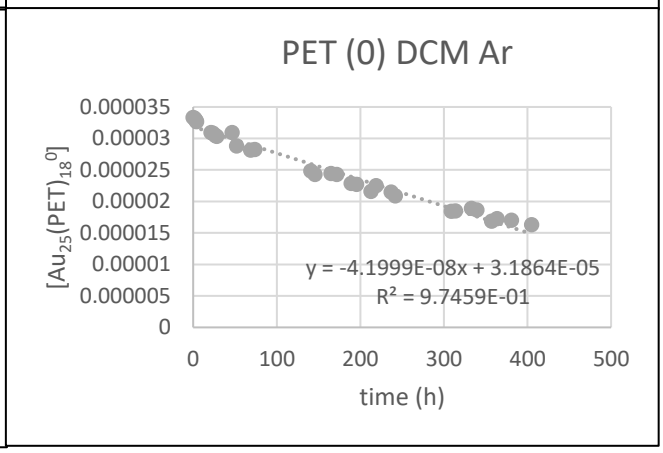

PET (0) THF stab in air
y = -1.2689E-07x + 1.9956E-05
R² = 8.5621E-01
[Au25(PET)18 0]
Time (h)

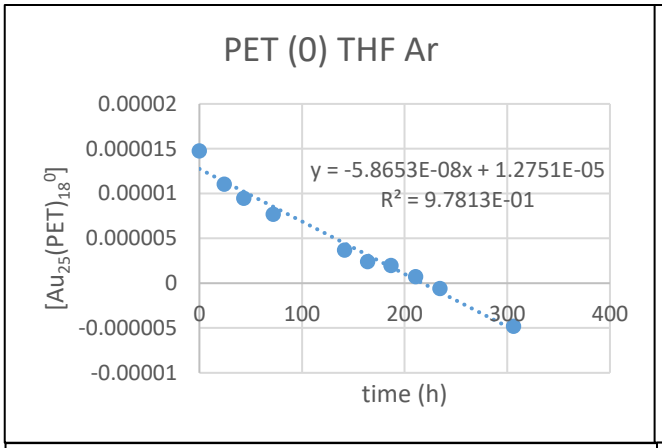

Octanethiol (0) DCM Ar
y = -3.5574E-08x + 1.8398E-05
R² = 8.5461E-01
[Au25(C8H17S)18 0]
time (h)

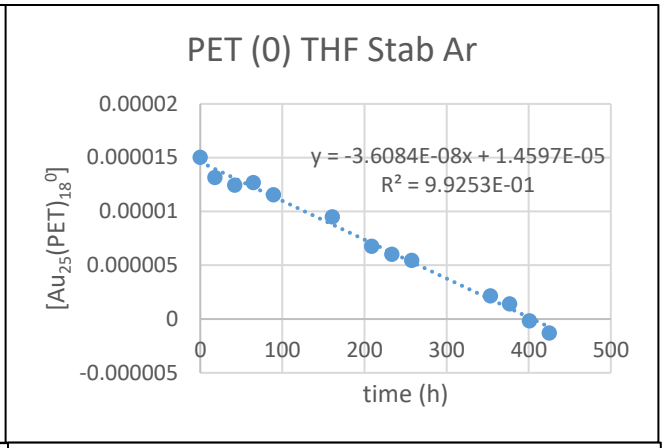

Ethanethiol (0) DCM Ar
y = -1.0071E-07x + 2.1909E-05
R² = 9.3014E-01
[Au25(C2H3S)18 0]
time (h)

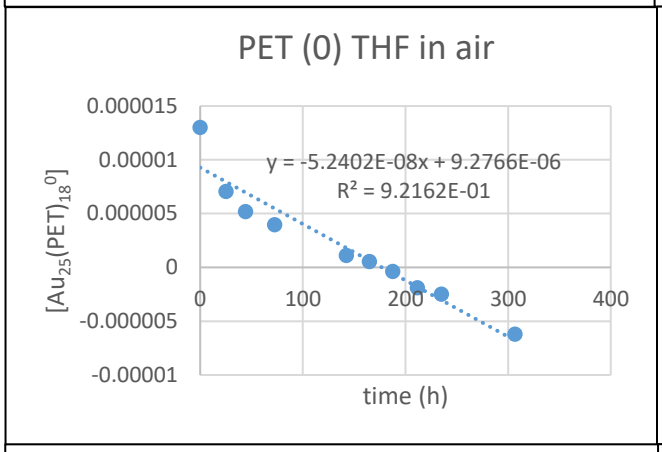

Hexanethiol (0) DCM Ar
y = -6.1005E-08x + 2.5078E-05
R² = 8.8719E-01
[Au25(C6H13S)18 0]
time (h)

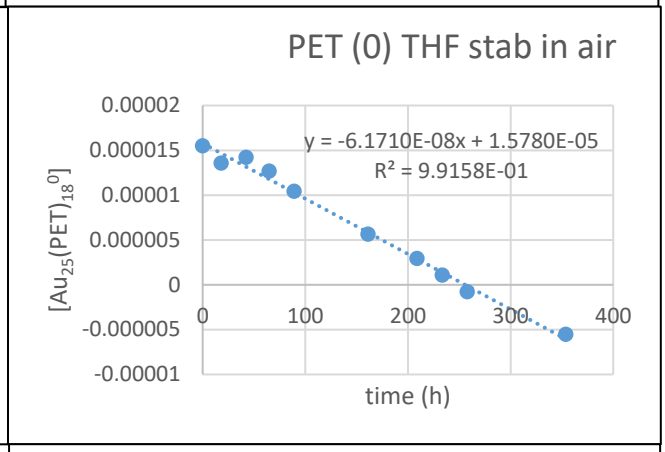

Dodecanethiol (0) DCM Ar
y = -2.4053E-08x + 1.6137E-05
R² = 8.5288E-01
[Au25(C12H25S)18 0]
time (h)

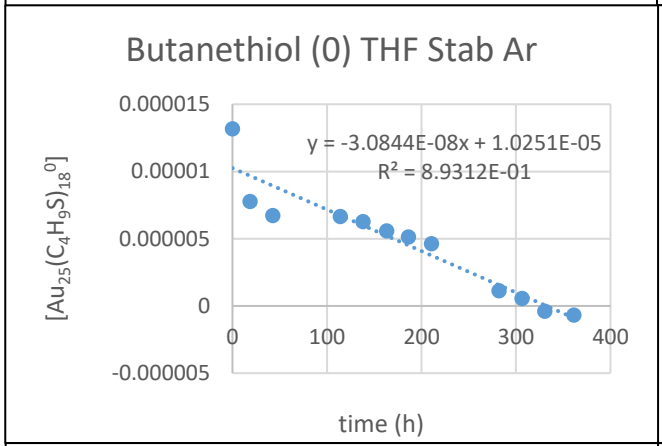

PET (0) DCM Ar
y = -4.1999E-08x + 3.1864E-05
R² = 9.7459E-01
[Au25(PET)18 0]
time (h)

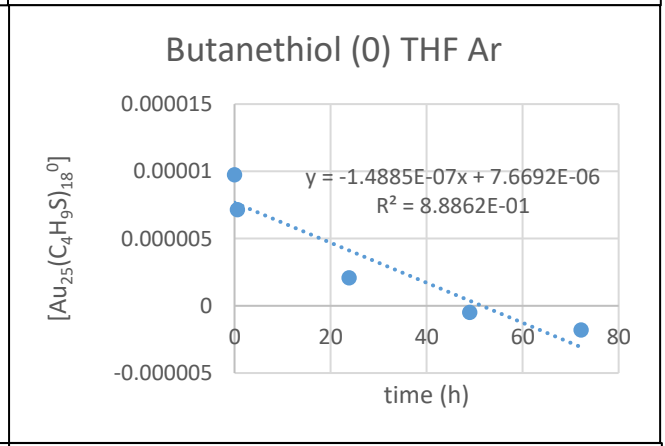

PET (0) THF Ar
y = -5.8653E-08x + 1.2751E-05
R² = 9.7813E-01
[Au25(PET)18 0]
time (h)

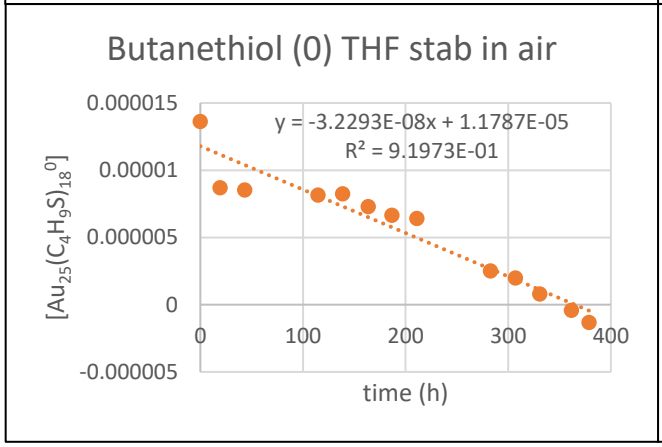

PET (0) THF Stab Ar
y = -3.6084E-08x + 1.4597E-05
R² = 9.9253E-01
[Au25(PET)18 0]
time (h)

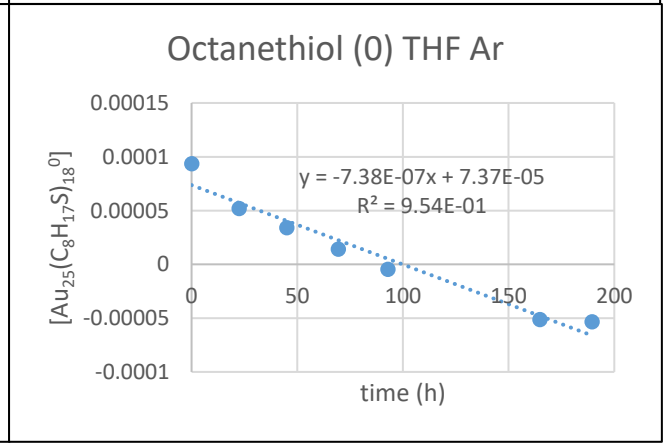

PET (0) THF in air
y = -5.2402E-08x + 9.2766E-06
R² = 9.2162E-01
[Au25(PET)18 0]
time (h)

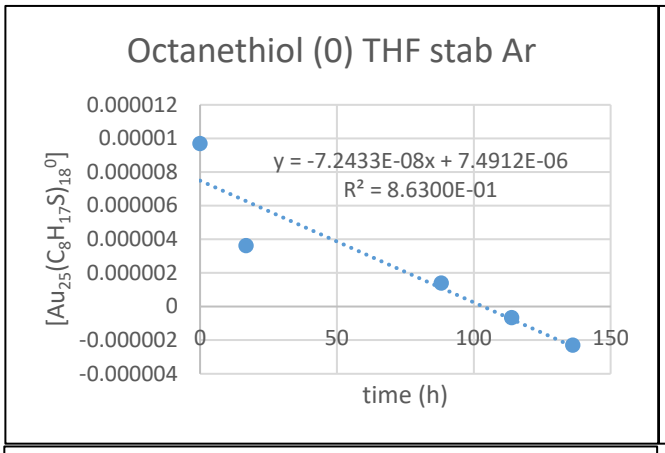

PET (0) THF stab in air
y = -6.1710E-08x + 1.5780E-05
R² = 9.9158E-01
[Au25(PET)18 0]
time (h)

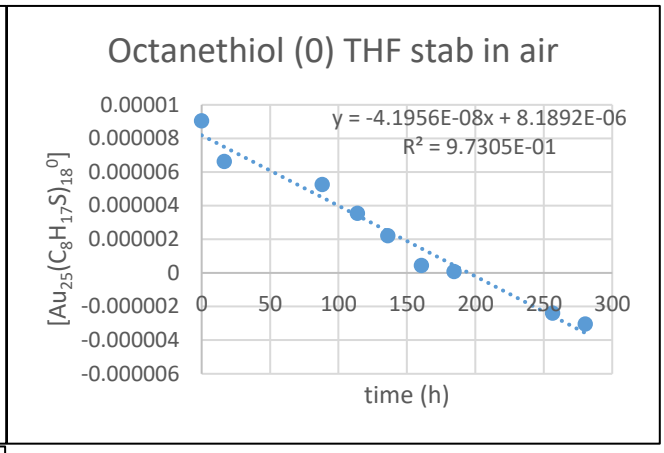

Butanethiol (0) THF Stab Ar
y = -3.0844E-08x + 1.0251E-05
R² = 8.9312E-01
[Au25(C4H9S)18 0]
time (h)

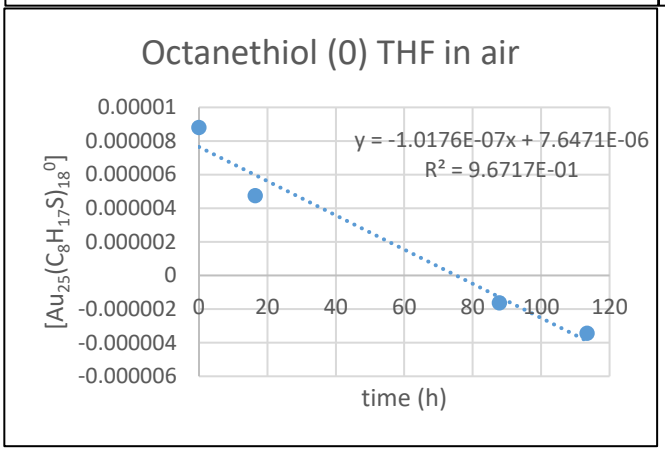

Butanethiol (0) THF Ar
y = -1.4885E-07x + 7.6692E-06
R² = 8.8862E-01
[Au25(C4H9S)18 0]
time (h)


Butanethiol (0) THF stab in air
y = -3.2293E-08x + 1.1787E-05
R² = 9.1973E-01
[Au25(C4H9S)18 0]
time (h)

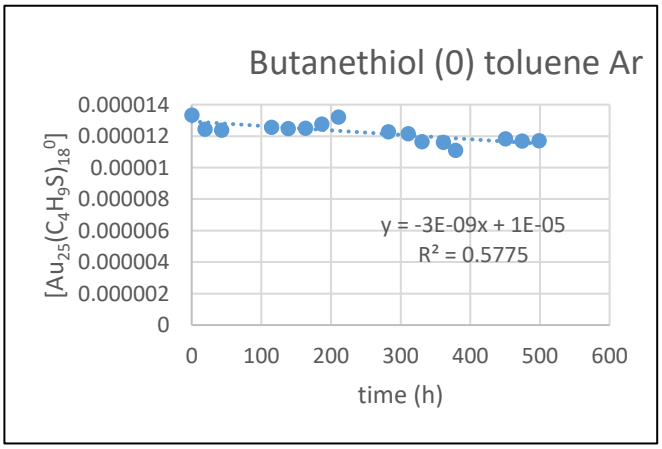

Octanethiol (0) THF Ar
y = -7.38E-07x + 7.37E-05
R² = 9.54E-01
[Au25(C8H17S)18 0]
time (h)

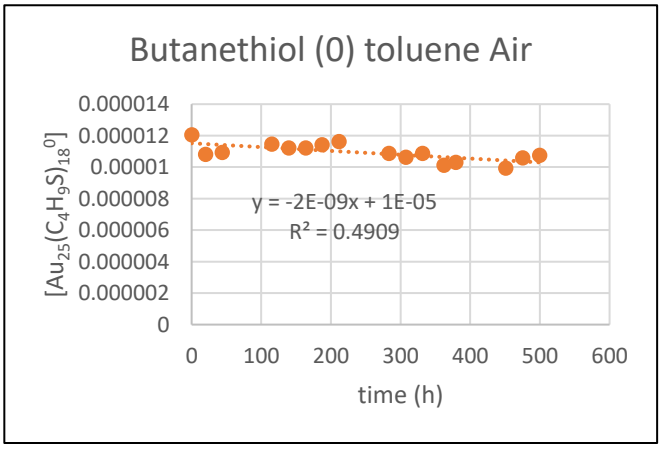






Conditions resulting in little to no decay over ~20 days observed





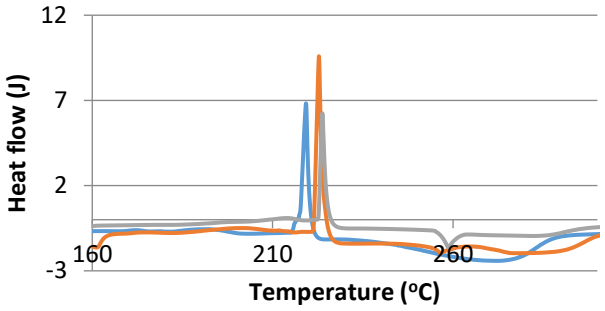
Summary of reactant order determination

Ligand	Atm	Charge	solvent	order for cluster	rate constant k	[A]0 (M)	Half life (h)
PET	air	0	Acetone	1st	0.0942	8E-06	7.35825032
PET	air	0	CHCl3	0th	1.254E-07	1.8E-05	69.9277464
PET	air	0	DCM	0th	6.04E-08	1.4E-05	114.517995
PET	air	0	THF	0th	1.27E-07	2.7E-05	107.820329
PET	air	0	Toluene	0th	2.83E-08	2.2E-05	384.403513
Ethanethiol	Ar	0	DCM	0th	1.0071E-07	2E-05	97.3768065
hexanethiol	Ar	0	DCM	0th	6.1005E-08	2.6E-05	210.272134
octanethiol	Ar	0	DCM	0th	3.5574E-08	1.8E-05	246.498549
dodecanethiol	Ar	0	DCM	0th	2.4053E-08	1.4E-05	297.63817
PET	Ar	0	DCM	0th	4.20E-08	3.33E-05	396.744656
hexanethiol	Ar	-1	DCM	0th	1.1223E-07	2.5E-05	110.602145
PET	Ar	-1	DCM	0th	3.42E-08	3.5E-05	511.806663
PET	air	-1	Acetone	1st	0.0147	1.6E-05	47.1528694
PET	air	-1	CHCl3	0th	9.96E-08	1.6E-05	81.5378285
PET	air	-1	DCM	0th	1.48E-07	1.9E-05	63.156831
PET	air	-1	MeCN	1st	0.0591	1.7E-05	11.7283787
PET	air	-1	THF stab	0th	2.14E-08	1.6E-05	365.628776
PET	air	-1	Toluene	0th	7.48E-08	1.3E-05	86.635093

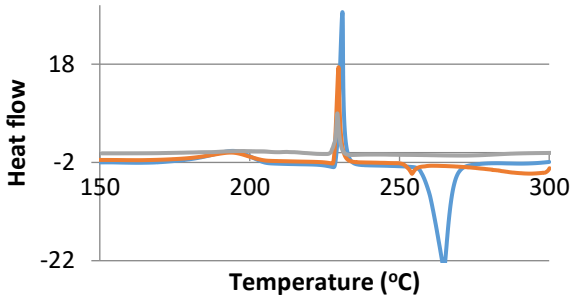
Differential Scanning calorimetry data

All differential calorimetry scanning measurements (DSC) were taken using TA Instrument's 2920 modulated DSC. All products were re-dissolved in a minimal amount of DCM and then deposited into an aluminum hermetic DSC pan and allowed to air dry in order to achieve uniform coverage of the pan. Once the products were dry enough to stick to the DSC pan they were put under vacuum for 10 min to ensure the complete removal of the solvent.

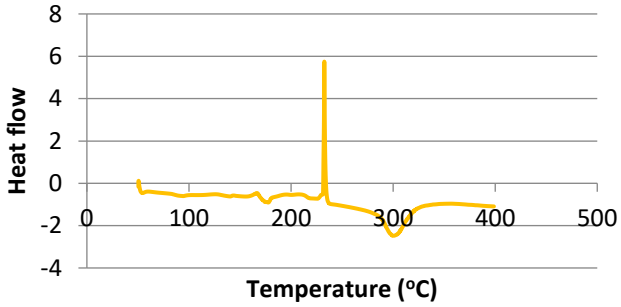
Hexanethiol (0) DSC



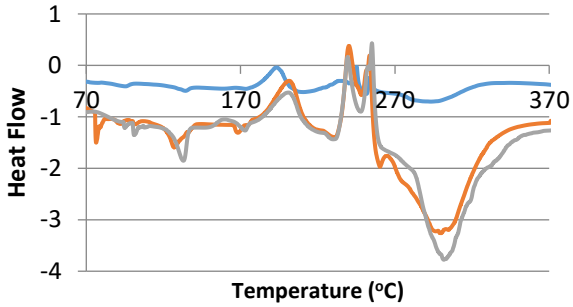
Hexanethiol (-1) DSC



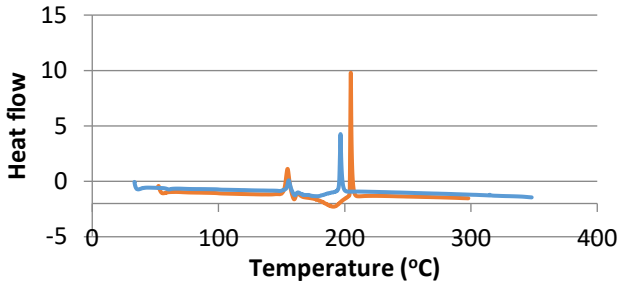
PET (0) DSC



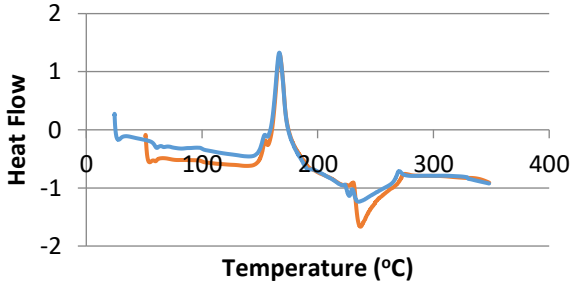
PET (-1) DSC



Propanethiol (0) DSC



Propanethiol (-1) DSC



Ethanethiol (-1) DSC