Synthesis, physicochemical characterization, and self-assembly of linear, dibranched and miktoarm semi-fluorinated triphlic polymers

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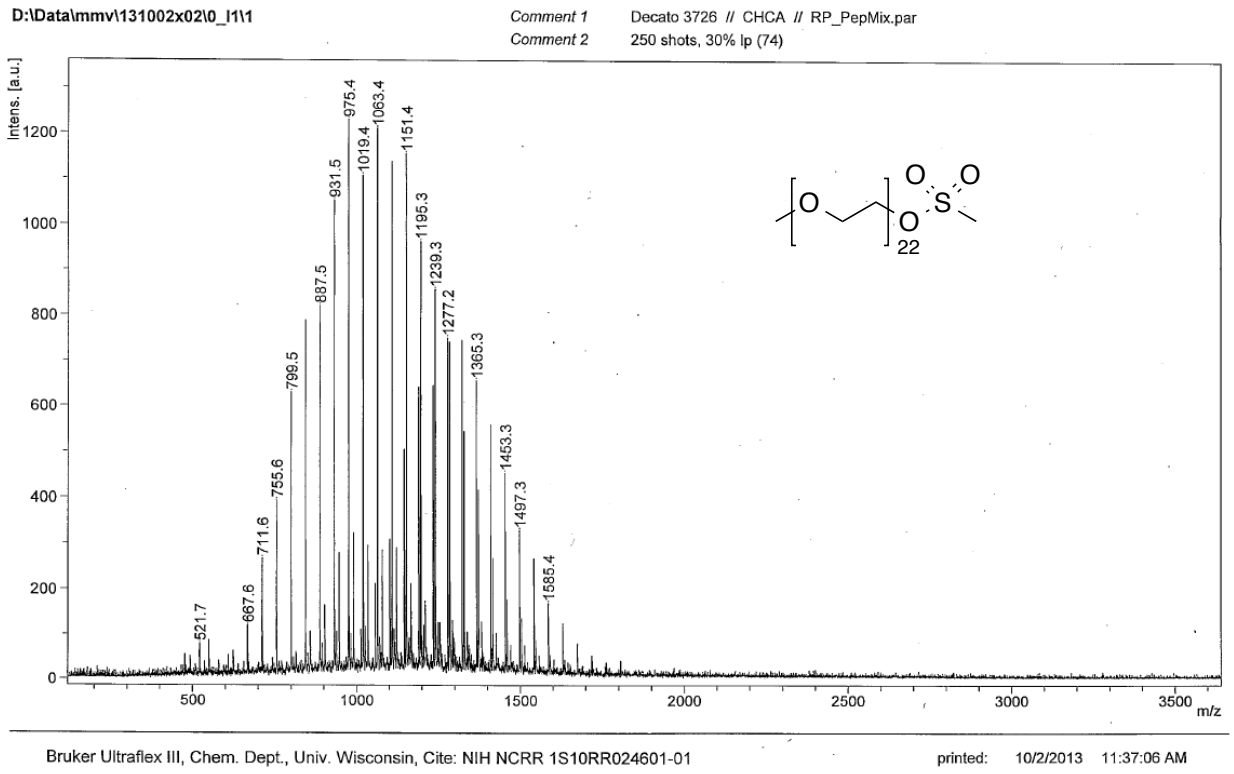
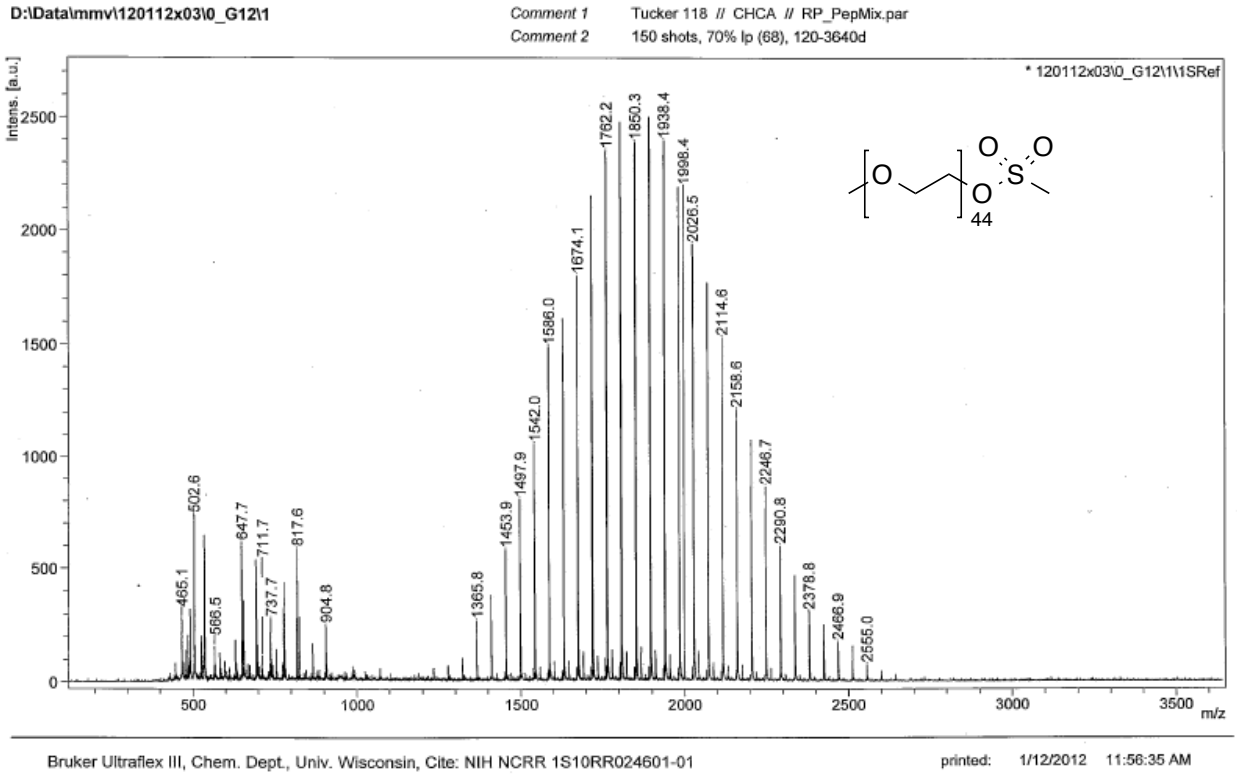
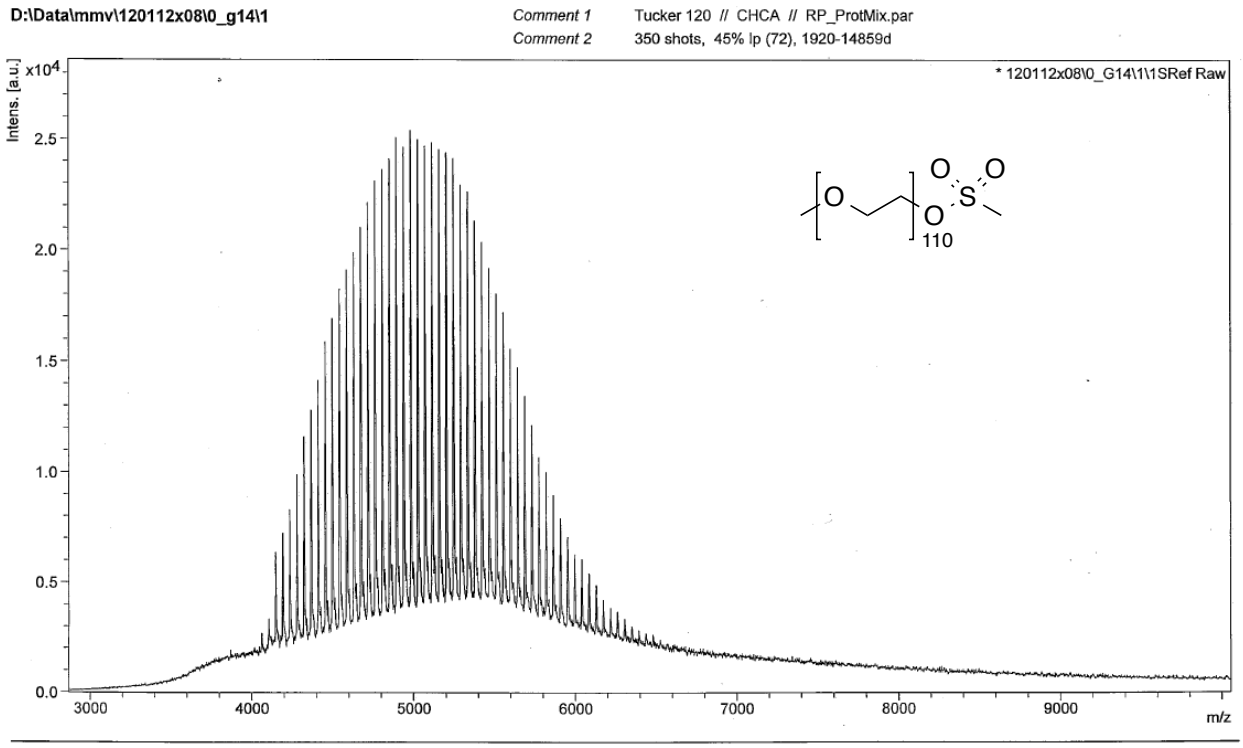
MALDI spectra



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0.0
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5000
6000
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9000
m/z
O
O
S
O
O
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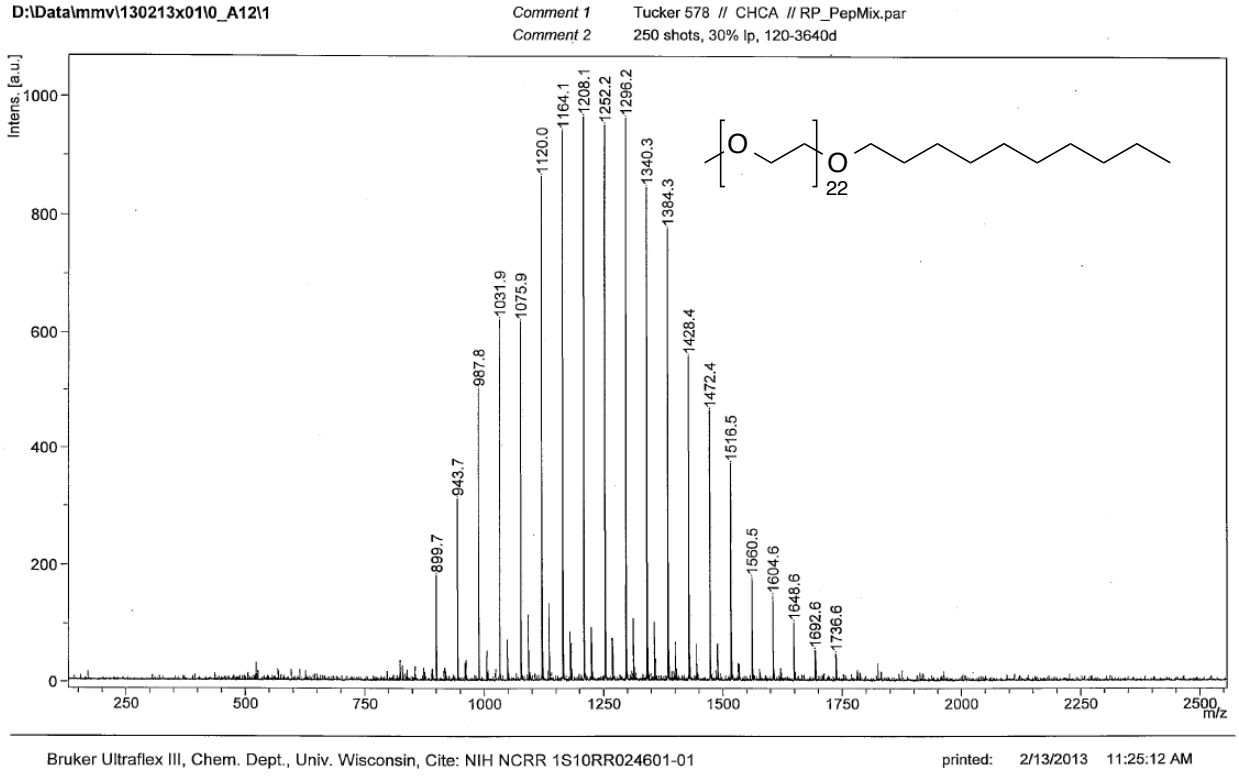
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987.8
1031.9
1075.9
1120.0
1164.1
1208.1
1252.2
1296.2
1340.3
1384.3
1428.4
1472.4
1516.5
1560.5
1604.6
1648.6
1692.6
1736.6
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500
750
1000
1250
1500
1750
2000
2250
2500
m/z
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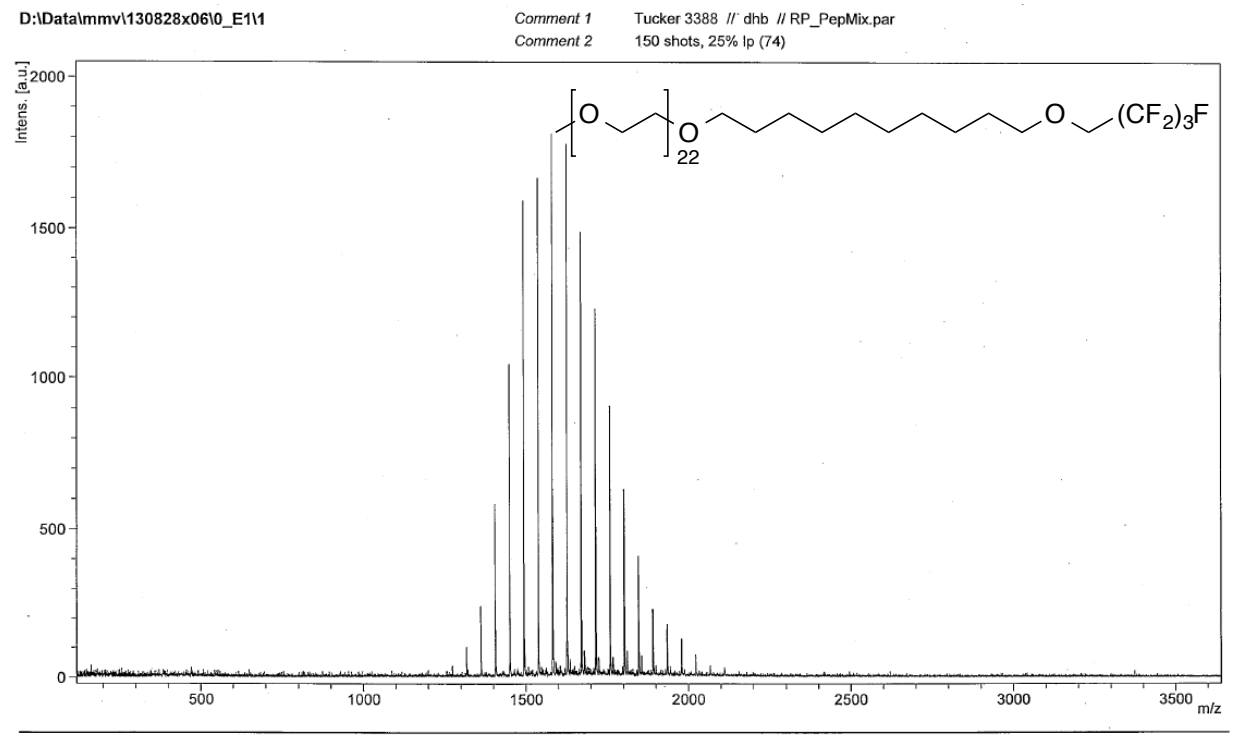
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0
O
O
22
O
(CF2)3F
500
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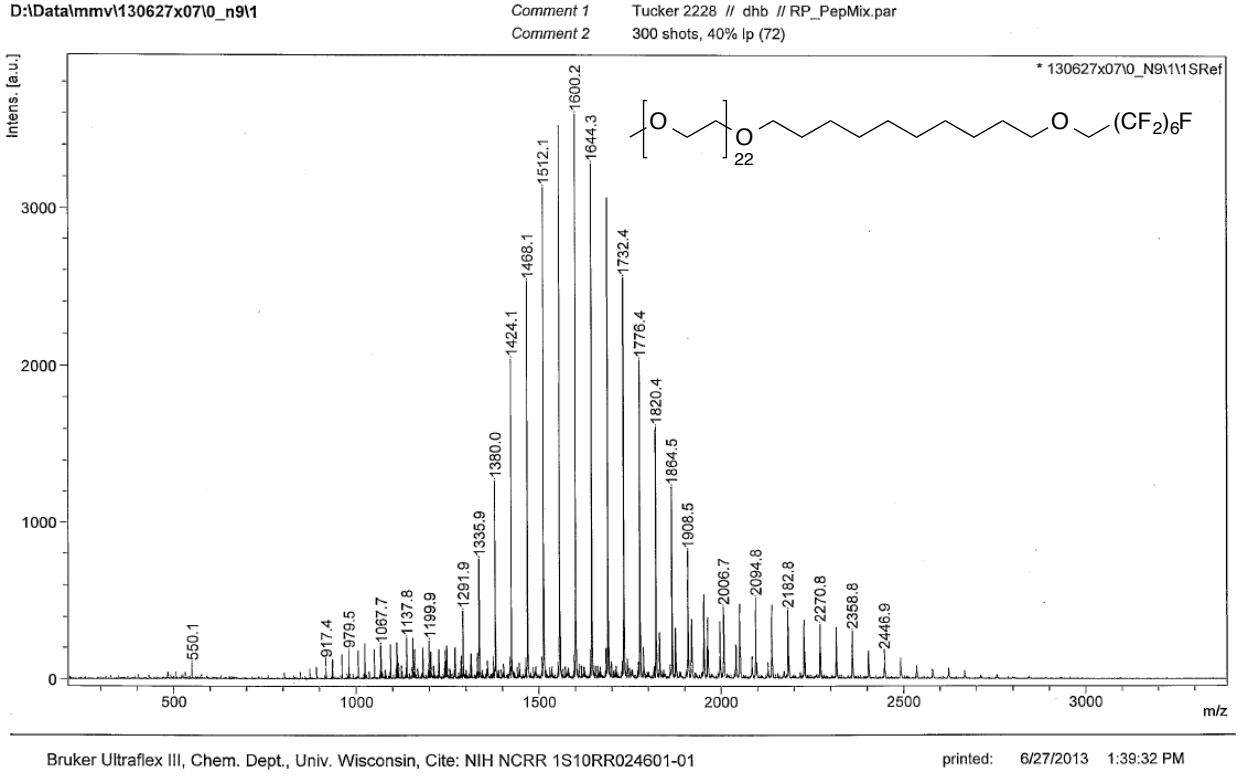
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2000
1000
0
O
O
22
O
(CF2)6F
550.1
917.4
979.5
1067.7
1137.8
1199.9
1291.9
1335.9
1380.0
1424.1
1468.1
1512.1
1600.2
1644.3
1732.4
1776.4
1820.4
1864.5
1908.5
2006.7
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500
1000
1500
2000
2500
3000
m/z
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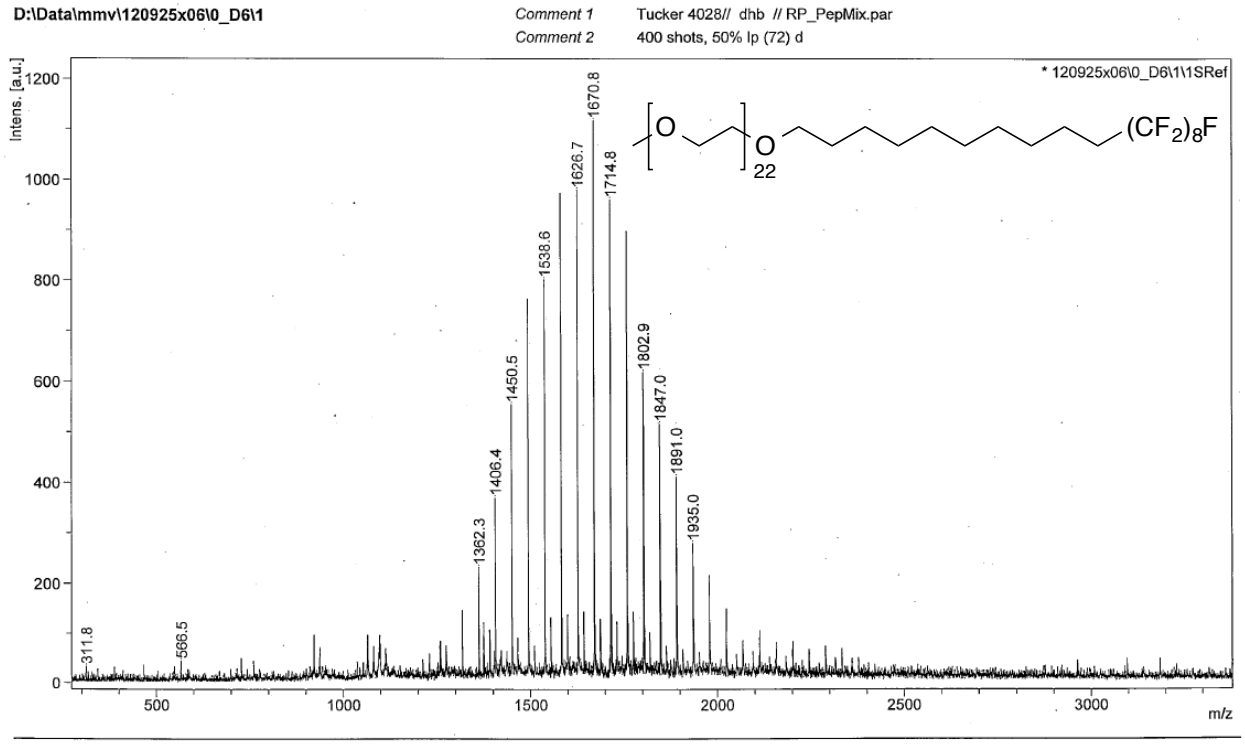
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0
500
1000
1500
2000
2500
3000
m/z
311.8
586.5
1362.3
1406.4
1450.5
1538.6
1626.7
1670.8
1714.8
1802.9
1847.0
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O
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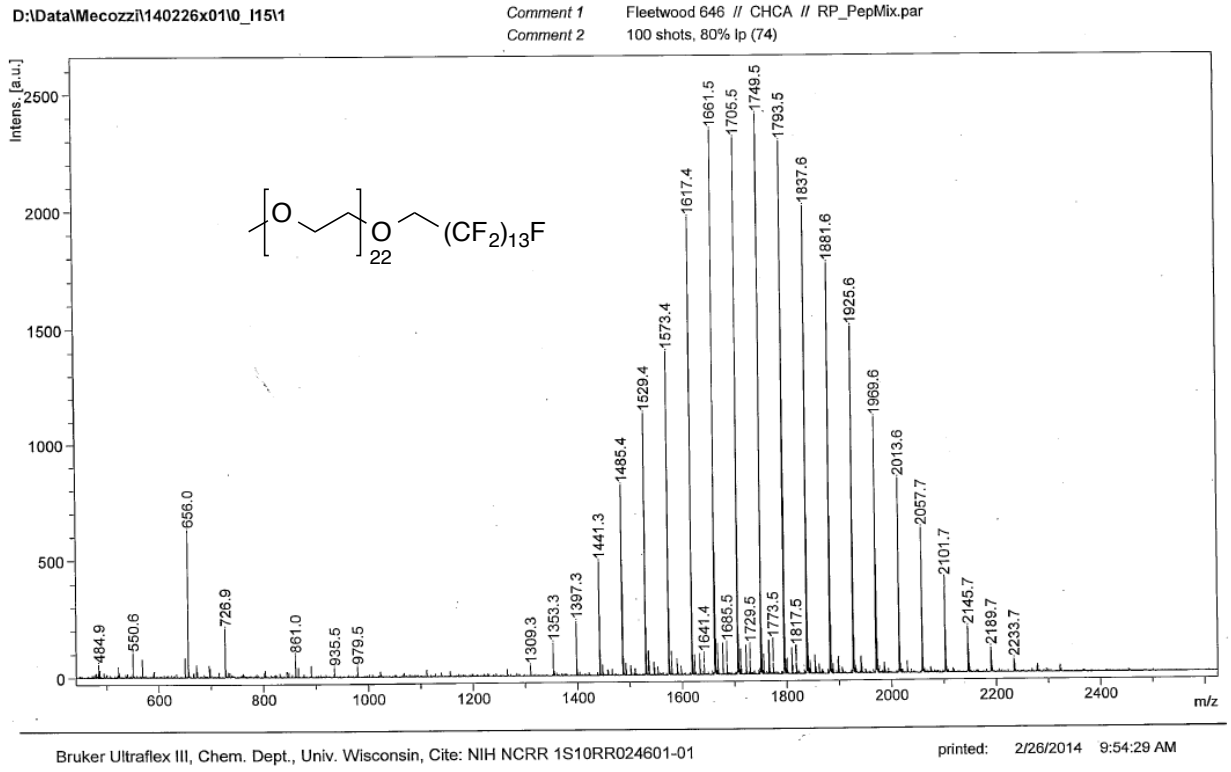
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2000
1500
1000
500
0
600
800
1000
1200
1400
1600
1800
2000
2200
2400
m/z
484.9
550.6
656.0
726.9
861.0
935.5
979.5
1309.3
1353.3
1397.3
1441.3
1485.4
1529.4
1573.4
1617.4
1641.4
1661.5
1685.5
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1729.5
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1773.5
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1817.5
1837.6
1881.6
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2013.6
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2101.7
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O
22
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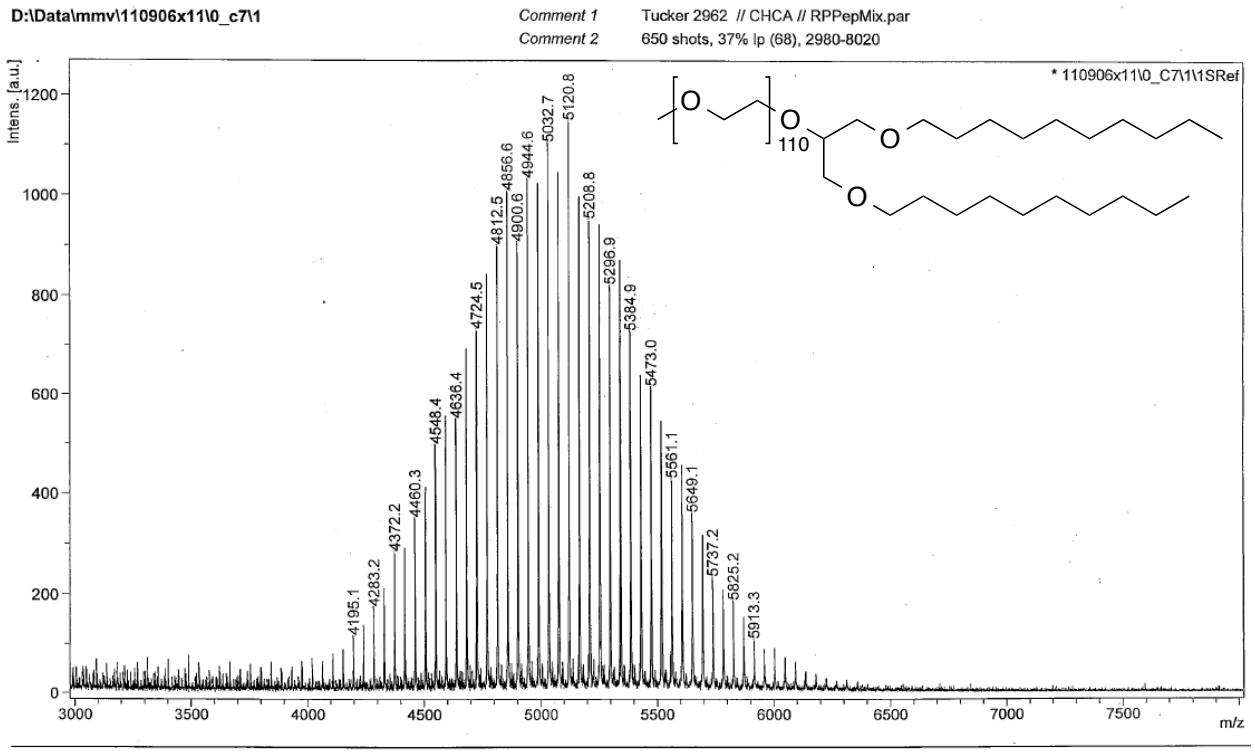
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m/z
4195.1
4283.2
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4460.3
4548.4
4636.4
4724.5
4812.5
4856.6
4900.6
4944.6
5032.7
5120.8
5208.8
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5384.9
5473.0
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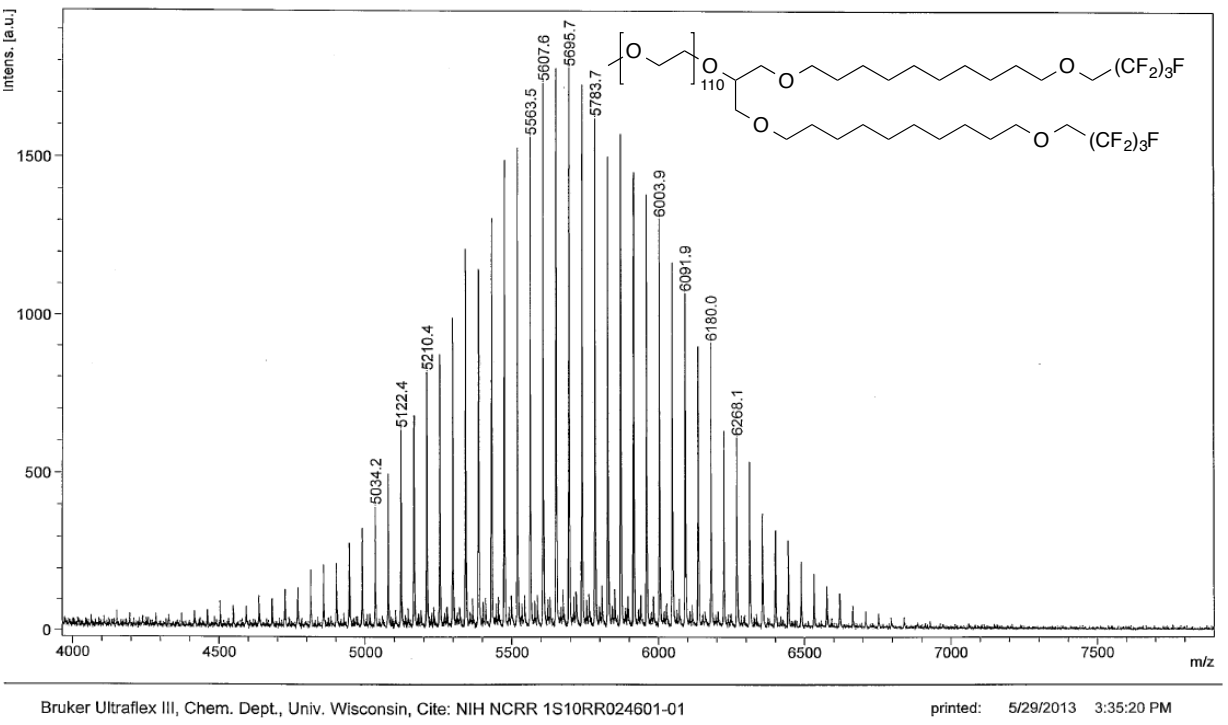
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m/z
5034.2
5122.4
5210.4
5563.5
5607.6
5695.7
5783.7
6003.9
6091.9
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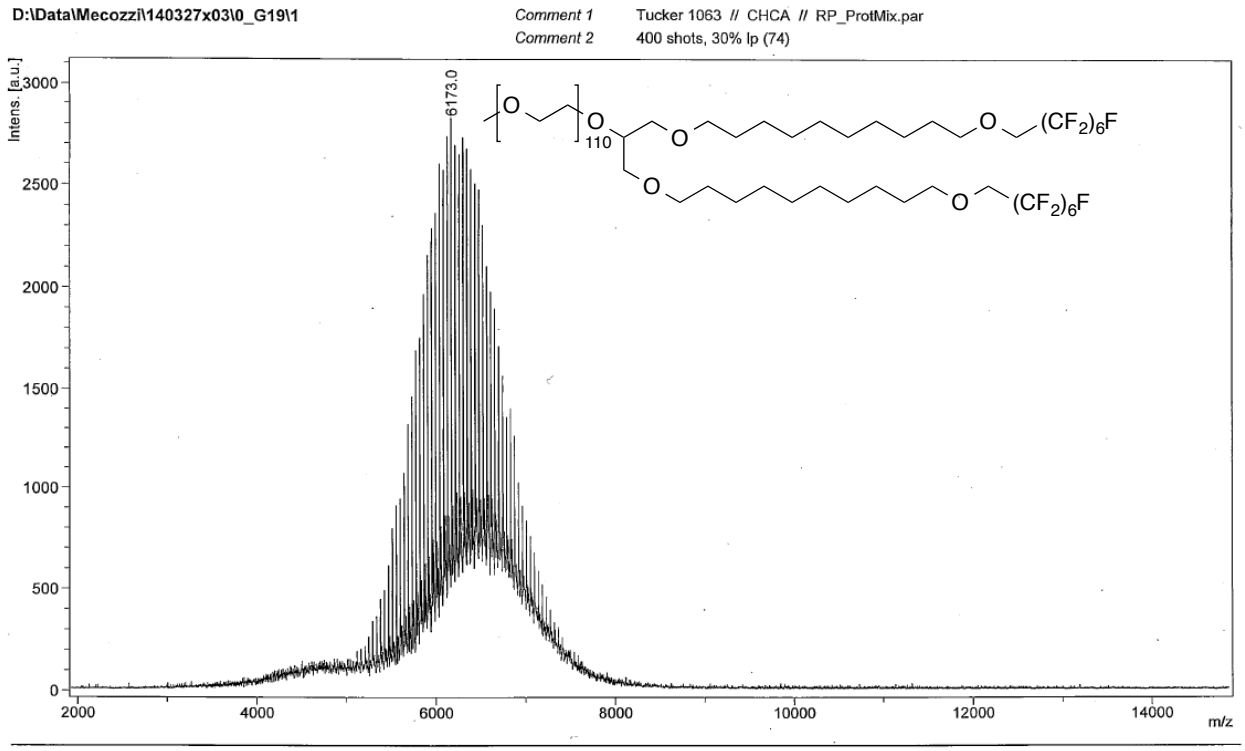
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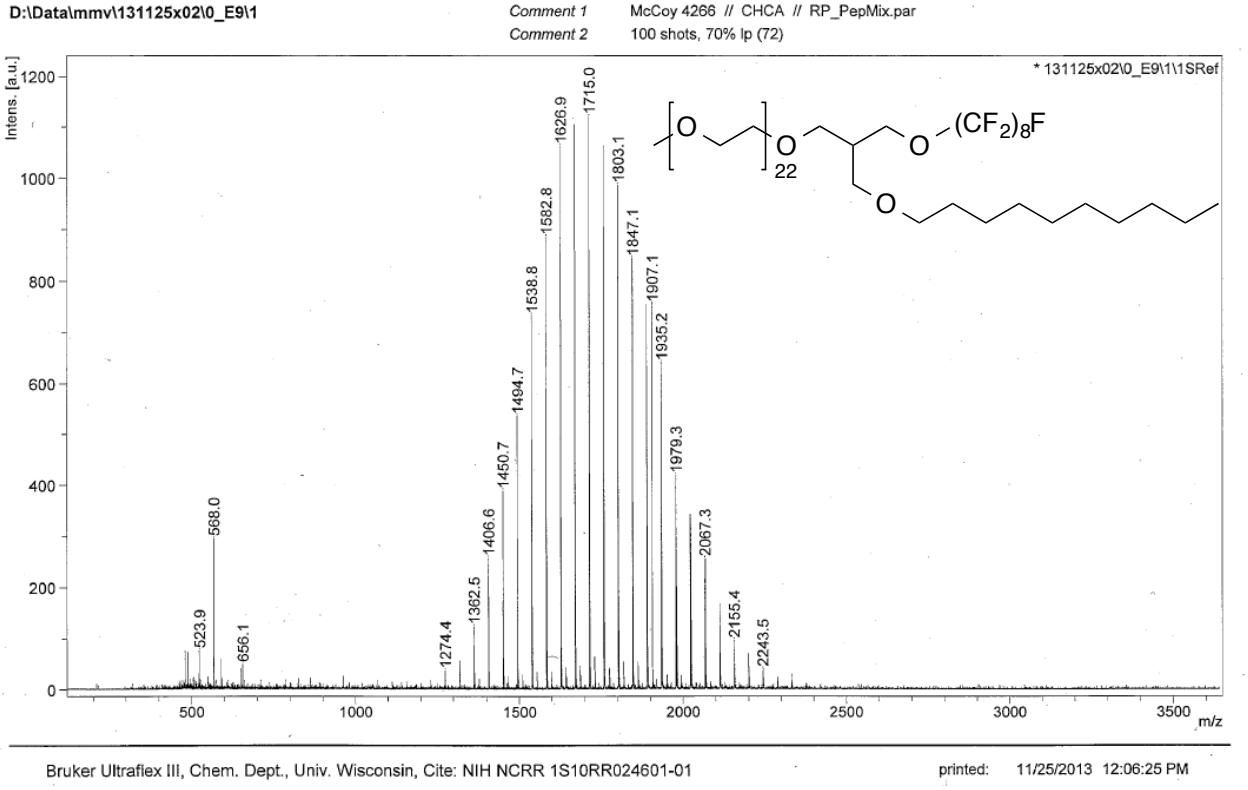
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1803.1
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1847.1
1538.8
1907.1
1935.2
1494.7
1979.3
1450.7
2067.3
1406.6
2155.4
1362.5
2243.5
1274.4
568.0
523.9
656.1
22
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m/z
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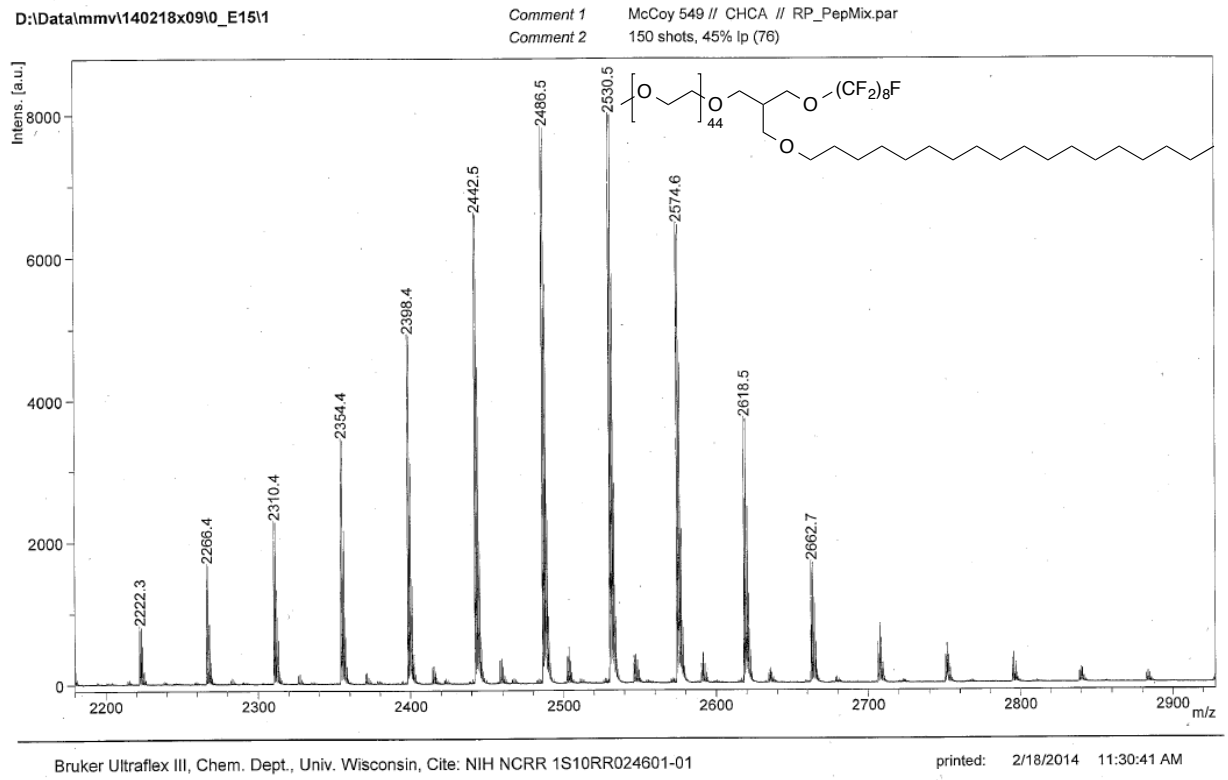
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2442.5
2486.5
2530.5
2574.6
2618.5
2662.7
O
O
44
O
O
(CF2)8F
m/z
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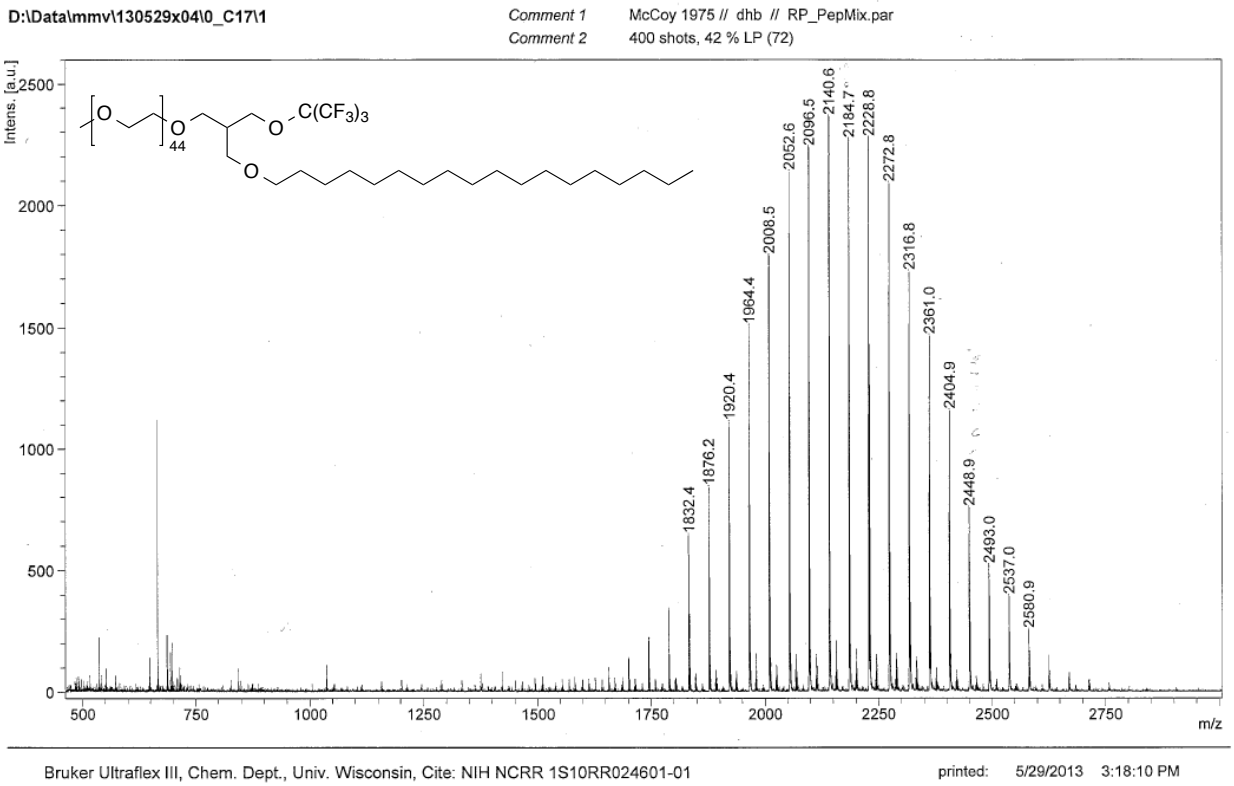
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1876.2
1920.4
1964.4
2008.5
2052.6
2096.5
2140.6
2184.7
2228.8
2272.8
2316.8
2361.0
2404.9
2448.9
2493.0
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2580.9
O
O
44
O
C(CF3)3
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m/z
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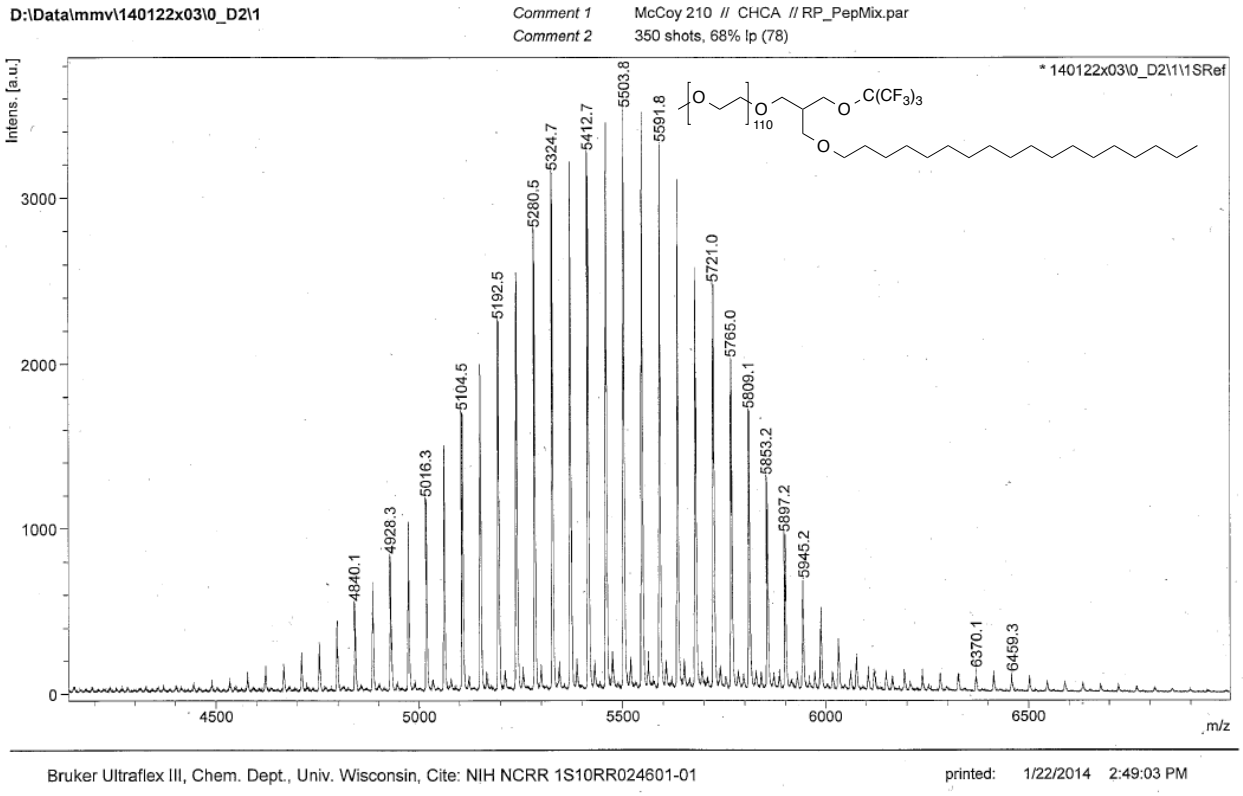
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5192.5
5280.5
5324.7
5412.7
5503.8
5591.8
5721.0
5765.0
5809.1
5853.2
5897.2
5945.2
6370.1
6459.3
O
O
110
O
C(CF3)3
O
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Surface tension data

M5diH10

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-1.93	33.968	0.128
-2.93	34.628	0.193
-3.93	34.585	0.087
-4.93	45.578	0.463
-5.93	54.657	0.211
-6.93	65.677	0.132
-7.93	72.330	0.400
-8.93	72.230	0.124
-9.93	72.063	0.100

M5diH10-O-F3

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	40.300	0.966
-2.98	39.104	0.566
-3.87	39.236	0.049
-4.87	44.913	0.114
-5.87	54.169	0.042
-6.87	69.256	0.067
-7.87	72.245	0.076
-8.87	72.248	0.209
-9.87	72.380	0.108

M1H10

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	36.491	0.550
-2.50	35.170	0.245
-3.00	36.054	0.689
-3.50	42.887	0.243
-4.00	48.846	0.185
-4.50	56.902	0.204
-5.00	59.178	0.560
-6.00	62.912	0.155
-7.00	68.616	0.147
-8.00	72.051	0.175
-9.00	72.198	0.126

M1H10-O-F3

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	34.978	0.227
-3.00	35.366	0.145
-3.50	35.349	0.065
-4.00	38.230	0.149
-5.00	48.457	0.214
-6.00	58.153	0.027
-7.00	72.238	0.117
-8.00	71.986	0.141
-9.00	72.094	0.156

M1H10-O-F6

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	16.436	0.138
-3.00	16.730	0.263
-4.00	17.441	0.348
-5.00	26.609	1.100
-6.00	53.668	0.210
-7.00	71.598	0.102
-8.00	71.744	0.059
-9.00	71.865	0.051
-10.00	72.065	0.093
-11.00	72.058	0.139
-12.00	72.204	0.571

M1H10F8

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	27.736	0.131
-3.00	31.598	0.203
-4.00	33.664	0.181
-5.00	35.687	0.057
-5.90	42.873	0.365
-6.00	50.397	0.180
-6.15	71.696	0.045
-6.50	71.758	0.150
-7.00	71.993	0.115
-8.00	72.101	0.158
-9.00	72.145	0.139

M1F13

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-4.67	35.509	0.238
-5.45	35.971	0.333
-5.84	36.405	0.305
-6.15	38.529	0.140
-6.62	48.849	0.255
-7.01	59.954	0.131
-7.78	70.854	0.218
-8.56	71.610	0.186
-9.34	71.217	0.165

M1μH10F8

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.97	21.138	0.079
-3.26	21.206	0.057
-3.61	22.341	0.059
-4.01	21.708	0.115
-4.30	22.566	0.095
-4.66	23.337	0.102
-5.05	24.638	0.156
-5.34	25.737	0.082
-5.70	30.190	0.205
-6.09	59.424	0.103
-6.38	70.603	0.077
-6.74	72.757	0.197
-7.14	72.805	0.107
-7.42	72.877	0.086
-7.78	72.704	0.420
-8.18	72.922	0.089
-8.46	72.876	0.133
-8.82	72.706	0.153

M2μH18F8

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.00	31.816	0.122
-3.00	34.337	0.230
-4.00	36.876	0.199
-5.00	44.580	0.079
-6.00	60.375	0.140
-7.00	71.180	0.044
-8.00	71.699	0.165
-9.00	72.085	0.126
-10.00	71.891	0.123
-11.00	71.816	0.148
-12.00	71.674	0.150

M2μH18PftB

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-2.44	42.980	1.425
-3.57	45.346	1.976
-3.63	44.365	0.475
-4.61	43.736	0.655
-5.65	55.222	0.661
-6.32	64.032	0.243
-6.69	66.661	0.113
-7.07	70.915	0.101
-7.73	71.937	0.130
-8.78	71.983	0.024
-9.82	71.824	0.207

M5μH18PftB

log(M)	Ave. S.T. (mN/m)	Std. Dev.
-3.34	49.134	1.440
-3.40	47.805	0.646
-3.48	49.808	0.461
-3.66	49.563	3.055
-4.38	48.806	1.110
-4.52	48.180	0.116
-4.70	49.474	0.096
-5.43	51.235	0.212
-5.49	50.559	0.082
-5.56	53.418	0.146
-5.74	54.535	0.218
-6.47	59.606	0.183
-6.53	63.624	0.152
-7.51	71.656	0.111
-7.57	71.972	0.129
-8.55	72.455	0.075
-8.61	72.229	0.024

Each sample was measured in quadruplicate. The average and standard deviation were then calculated. The CMC value was determined from the intersection of the slope at the crossover point and the slope at high concentrations. The error in the CMC measurement was calculated by applying a weighted, least-squares analysis to the linear sections of interest. The individual uncertainties of the two slopes and intercepts produced by the weighted least squares analysis were then propagated through as follows:

$$x_{\log(M)} = \frac{b_2 - b_1}{m_2 - m_1}$$

$$\sigma_{x_{\log(m)}} = \sqrt{x_{\log(m)}{}^2 \left[\left(\frac{\sigma_{b2-b1}}{b_2 - b_1} \right)^2 + \left[\left(\frac{\sigma_{m1-m2}}{m_1 - m_2} \right)^2 \right] \right]}$$

where

$$\sigma_{m1-m2} = \sqrt{\sigma_{m1}{}^2 + \sigma_{m2}{}^2}, \qquad \sigma_{b2-b1} = \sqrt{\sigma_{b2}{}^2 + \sigma_{b1}{}^2}$$

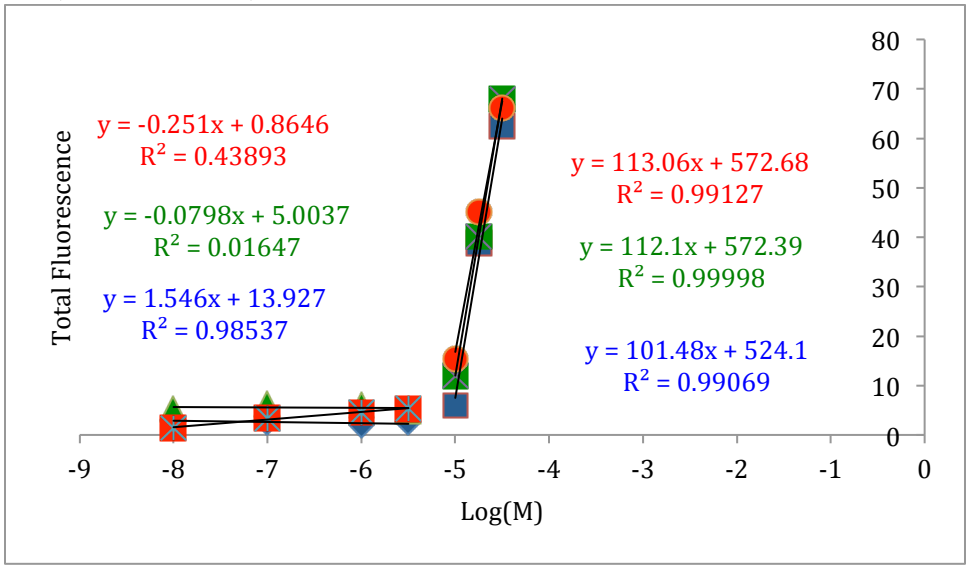
The weighted, least-squares analysis was chosen because the uncertainty of each individual data point was known.

Pyrene CMC data

M5diH10-O-F6

Log(M)	Total Fluorescence	Total Fluorescence	Total Fluorescence
-8	2.99	5.16	1.39
-7	2.56	6.18	3.41
-6	1.97	6.04	4.58
-5.499	2.59	4.75	5.36
-4.999	5.96	11.93	15.38
-4.749	38.82	40.16	45.01
-4.499	62.49	67.98	66.12

Plot, with linear fit, for each data



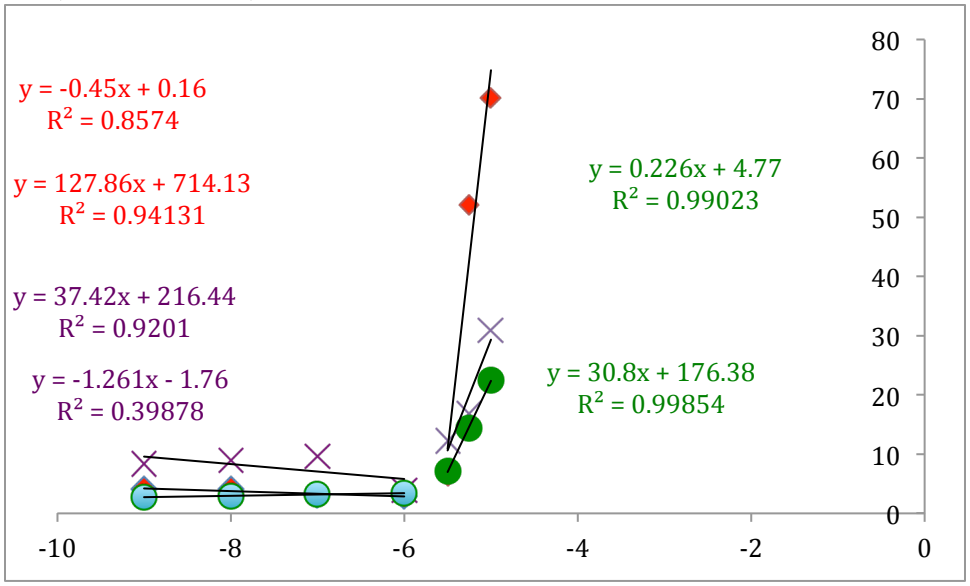
Average of crossover points

-5.070	Ave
0.031	Std. dev.

M5H10F8

Log(M)	Total Fluorescence	Total Fluorescence	Total Fluorescence
-9	4.08	8.35	2.76
-8	4.07	8.91	2.92
-7	3.08	9.62	3.2
-6	2.91	3.91	3.42
-5.5	6.29	12.22	7.15
-5.25	52.08	16.8	14.34
-5	70.22	30.93	22.55

Plot, with linear fit, for each data



Average of crossover points

Ave	-5.606
Std. dev.	0.039

Microviscosity data

M1H10

376	*480*	*Im/Ie Ratio*	
1.95	0.72	2.71	
2.34	0.81	2.89	
2.22	0.83	2.66	
		2.75	Ave
		0.11	Std. Dev.

M1H10-O-F3

376	*480*	*Im/Ie Ratio*	
2.77	0.46	6.06	
3.89	0.62	6.28	
3.59	0.64	5.65	
		5.99	Ave
		0.32	Std. Dev.

M1H10-o-F6

376	*480*	*Im/Ie Ratio*	
3.53	0.57	6.23	
2.30	0.35	6.47	
2.38	0.39	6.09	
		6.26	Ave
		0.19	Std. Dev.

M1H10F8

376	*480*	*Im/Ie Ratio*	
2.55	0.37	6.91	
2.78	0.41	6.81	
2.54	0.38	6.70	
		6.81	Ave
		0.11	Std. Dev.

M1F13

376	*480*	*Im/Ie Ratio*	
1.54	0.44	3.50	
1.50	0.47	3.19	
1.40	0.40	3.50	
		3.40	Ave
		0.18	Std. Dev.

M5diH10

376	*480*	*Im/Ie Ratio*	
1.59	0.47	3.38	
1.48	0.39	3.79	
1.54	0.41	3.76	
		3.64	Ave
		0.23	Std. Dev.

M5diH10-O-F3

376	*480*	*Im/Ie Ratio*	
2.83	0.41	6.90	
2.96	0.44	6.73	
2.26	0.34	6.65	
		6.76	Ave
		0.13	Std. Dev.

M5diH10-O-F6

376	*480*	*Im/Ie Ratio*	
2.06	0.31	6.68	
2.32	0.33	7.01	
2.47	0.36	6.79	
		6.83	Ave
		0.17	Std. Dev.

M1μH10F8

376	*480*	*Im/Ie Ratio*	
2.59	0.51	5.12	
2.22	0.44	5.01	
2.31	0.45	5.12	
		5.08	Ave
		0.06	Std. Dev.

M2μH18F8

376	*480*	*Im/Ie Ratio*	
2.11	0.39	5.45	
2.54	0.48	5.30	
2.28	0.42	5.39	
		5.38	Ave
		0.08	Std. Dev.

M2μH18PftB

376	*480*	*Im/Ie Ratio*	
2.25	0.51	4.45	
2.31	0.51	4.50	
1.98	0.46	4.34	
		4.43	Ave
		0.08	Std. Dev.

M2DSPE

376	*480*	*Im/Ie Ratio*	
2.63	0.46	5.72	
3.21	0.60	5.35	
2.53	0.44	5.75	
		5.61	Ave
		0.22	Std. Dev.

M5μH18PftB

376	*480*	*Im/Ie Ratio*	
2.36	0.55	4.28	
2.62	0.63	4.17	
2.11	0.49	4.30	
		4.25	Ave
		0.07	Std. Dev.

M5DSPE

376	*480*	*Im/Ie Ratio*	
1.51	0.29	5.21	
2.02	0.39	5.22	
2.32	0.44	5.27	
		5.23	Ave
		0.03	Std. Dev.

FRET stability data

M1H10 was not analyzed because it did not form micelles

M1F13 was not analyzed because the lipophilic FRET dyes could not be encapsulated

FRET Ratio: $\frac{I_{565}}{(I_{501}+I_{565})}$, where I_{501} = emission of donor dye and I_{565} = emission of acceptor dye

	M1H10-O-F3		M1H10-O-F6		M1H10F8	
Min.	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**
0	0.742	0.017	0.816	0.025	0.813	0.007
15	0.702	0.008	0.811	0.008	0.814	0.012
30	0.692	0.038	0.801	0.004	0.816	0.013
45	0.680	0.014	0.804	0.005	0.815	0.009
60	0.680	0.024	0.784	0.007	0.808	0.008
75	0.669	0.012	0.749	0.006	0.757	0.005
90	0.661	0.003	0.732	0.004	0.750	0.008
105	0.617	0.008	0.728	0.001	0.733	0.003
120	0.587	0.030	0.710	0.005	0.692	0.001

	M5diH10		M5diH10F3		M5diH10-O-F6	
Min.	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**
0	0.642	0.124	0.892	0.064	0.843	0.119
15	0.499	0.081	0.658	0.022	0.800	0.036
30	0.471	0.042	0.531	0.023	0.749	0.016
45	0.459	0.071	0.459	0.010	0.724	0.035
60	0.451	0.042	0.448	0.023	0.673	0.039
75	0.441	0.020	0.446	0.006	0.638	0.029
90	0.439	0.035	0.429	0.025	0.612	0.035
105	0.436	0.039	0.422	0.012	0.609	0.030
120	0.427	0.024	0.415	0.011	0.608	0.049

	M1brF8H10		M2mH18F8		M2brPftBH18	
Min.	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**
0	0.523	0.03	0.658	0.005	0.666	0.043
15	0.463	0.004	0.596	0.004	0.526	0.006
30	0.448	0.003	0.565	0.002	0.500	0.004
45	0.439	0.002	0.519	0.001	0.485	0.003
60	0.440	0.003	0.494	0.003	0.484	0.000
75	0.437	0.003	0.476	0.003	0.484	0.001
90	0.428	0.001	0.452	0.002	0.473	0.003
105	0.432	0.002	0.423	0.002	0.456	0.002
120	0.423	0.004	0.430	0.002	0.469	0.001

	M2DSPE		M5brPftBH18		M5DSPE	
Min.	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**	**FRET Ratio**	**Std. Dev.**
0	0.789	0.013	0.661	0.014	0.702	0.027
15	0.723	0.018	0.530	0.013	0.589	0.125
30	0.695	0.011	0.459	0.007	0.548	0.125
45	0.660	0.014	0.411	0.006	0.533	0.077
60	0.634	0.010	0.385	0.005	0.504	0.046
75	0.621	0.016	0.359	0.003	0.481	0.022
90	0.616	0.013	0.346	0.003	0.471	0.039
105	0.626	0.003	0.334	0.010	0.452	0.042
120	0.626	0.011	0.321	0.001	0.444	0.027

Paclitaxel encapsulation data

M1H10 not analyzed as it does not form micelles.

Amphiphile	Initial Encapsulation μg/mL (ave ± S.D.) PTX	Remaining After 24 h μg/mL (ave ± S.D.) PTX
M2DSPE	229.61 ± 5.38	215.83 ± 6.51
M5DSPE	187.59 ± 2.93	184.84 ± 8.08
M1F13	0	0
M5diH10	152.17 ± 31.21	16.94 ± 0.67
M5diH10F3	199.86 ± 5.65	125.94 ± 26.75
M5diH10F6	208.38 ± 15.81	157.15 ± 17.19
M1H10-o-F3	152.50 ± 9.10	19.11 ± 6.61
M1H10-o-F6	173.43 ± 5.59	52.10 ± 8.19
M1H10F8	192.08 ± 6.25	80.21 ± 27.53
M1μH10F8	188.44 ± 6.62	47.27 ± 6.46
M2μH18F8	166.13 ± 23.39	115.13 ± 8.75
M2μH18PFtB	162.22 ± 18.40	34.78 ± 11.48
M5μH18PFtB	185.41 ± 20.84	44.74 ± 16.60