

Supporting Information

Use of Top-down and Bottom-up Fourier Transform Ion Cyclotron Resonance Mass Spectrometry for Mapping Calmodulin Sites modified by Platinum Anticancer Drugs

Huilin Li,[†] Tzu-Yung Lin,[‡] Steve L. Van Orden,[§] Yao Zhao,[†] Mark P. Barrow,[†] Ana M. Pizarro,[†]
Yulin Qi,[†] Peter J. Sadler,[†] Peter B. O'Connor,^{†*}

[†]Department of Chemistry, University of Warwick, Coventry, CV4 7AL, United Kingdom

[‡]School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom

[§]Bruker Daltonics, 40 Manning Road, Billerica, MA, 01821, USA

Table S-1. Peak list for Figure 1b'.

Assignments	Exp. mass (Da)	Theo. mass (Da)	Error (ppm)
$[\text{CaM}+\text{Pt}_6(\text{NH}_3)_4+\text{H}]^{13+}$	1386.677006	1386.673225	2.73
$[\text{CaM}+\text{Pt}_7(\text{NH}_3)_6-\text{H}]^{13+}$	1404.131852	1404.134884	-2.16
$[\text{CaM}+\text{Pt}_8(\text{NH}_3)_8-3\text{H}]^{13+}$	1421.673874	1421.673598	0.19
$[\text{CaM}+\text{Pt}_9(\text{NH}_3)_{10}-5\text{H}]^{13+}$	1439.059673	1439.058202	1.02
$[\text{CaM}+\text{Pt}^{10}(\text{NH}_3)_{12}-7\text{H}]^{13+}$	1456.595243	1456.596912	-1.15
Mean absolute deviation (ppm)			1.45

Table S-2. ECD Fragments of the [CaM+2Pt+12H]¹⁶⁺ ions

No.	Assignments	Exp. mass (Da)	Theo. mass (Da)	Error (ppm)
1	c ₄	487.251185	487.251089	0.20
2	c ₅ -NH ₃	571.272554	571.272066	0.85
3	c ₅	588.299110	588.298615	0.84
4	c ₆	717.341071	717.341228	-0.22
5	c ₁₃ ²⁺	781.888567	781.888477	0.12
6	c ₂₁ ³⁺	834.413684	834.414059	-0.45
7	c ₇	846.384520	846.383953	0.67
8	c ₁₄	846.910394	846.911461	-1.26
9	c ₂₃ ³⁺	891.429248	891.429057	0.21
10	c ₄₉ ⁶⁺	908.450501	908.449960	0.60
11	c ₄₁ ⁵⁺	913.256014	913.256163	-0.16
12	c ₃₃ ⁴⁺	923.205572	923.204933	0.69
13	c ₂₄ ⁴⁺	930.106823	930.105842	1.05
14	? ²⁺	933.959746		
15	c ₂₅ ³⁺	949.112602	949.112996	-0.42
16	c ₁₆ ²⁺	955.463113	955.462538	0.60
17	? ³⁺	961.785910		
18	c ₉₄ ¹¹⁺	972.469758	972.468904	0.88
19	c ₇₉ ⁹⁺	982.249595	982.250077	-0.49
20	c ₂₆ ³⁺	982.796265	982.795556	0.72
21	c ₅₃ ⁶⁺	987.315973	987.315676	0.30
22	c ₉₆ ¹¹⁺	988.202801	988.200869	1.96
23	c ₈₀ ⁹⁺	995.366295	995.365239	1.06
24	c ₉₇ ¹¹⁺	998.384463	998.386015	-1.55
25	c ₁₇ ²⁺	998.978543	998.978552	-0.01
26	c ^{45 5+}	1001.493617	1001.493358	0.26
27	? ⁵⁺	1006.899099		
28	c ₄₆ ⁵⁺	1015.700577	1015.700781	-0.20
29	c ₈₂ ⁹⁺	1019.261988	1019.262073	-0.08
30	c ₂₇ ³⁺	1020.491172	1020.490244	0.91
31	c ₉₀ ¹⁰⁺	1020.589788	1020.588878	0.89
32	c ₁₀₀ ¹¹⁺	1028.858151	1028.856488	1.62
33	c ₉₁ ¹⁰⁺	1030.495724	1030.495721	0.00
34	? ³⁺	1033.498990		
35	c ₁₀₁ ¹¹⁺	1036.676848	1036.677290	-0.43
36	c ₁₀₂ ¹¹⁺	1043.044905	1043.044017	0.85
37	c ₃₇ ⁴⁺	1045.019694	1045.019357	0.32
38	c ₉₂ ¹⁰⁺	1045.201623	1045.202563	-0.90
39	c ₁₀₃ ¹¹⁺	1049.500306	1049.501937	-1.55
40	c ₂₈ ³⁺	1054.173714	1054.172804	0.86
41	c ₆₇ ⁷⁺	1055.074252	1055.073554	0.66
42	c ₉₃ ¹⁰⁺	1056.706278	1056.705258	0.97
43	c ₇₆ ⁸⁺	1062.133808	1062.135027	-1.15

44	c ₄₈ ⁵⁺	1064.127351	1064.126113	1.16
45	c ₃₈ ⁴⁺	1066.776957	1066.777364	-0.38
46	? ³⁺	1067.181663		
47	c ₉₄ ¹⁰⁺	1069.514904	1069.514755	0.14
48	[CaM+2Pt-H ₂ O+12H] ¹⁶⁺	1073.368652	1073.367424	1.14
49	[CaM+2Pt+12H] ¹⁶⁺	1074.494353	1074.493084	1.18
50	[CaM+2Pt(NH ₃)+12H] ¹⁶⁺	1075.558402	1075.557242	1.08
51	[CaM+2Pt(NH ₃) ₂ +12H] ¹⁶⁺	1076.620720	1076.621401	-0.63
52	c ₈₆ ⁹⁺	1077.847853	1077.847672	0.17
53	c ₉₅ ¹⁰⁺	1081.019396	1081.017449	1.80
54	c ₅₉ ⁶⁺	1085.018357	1085.019890	-1.41
55	c ₉₆ ¹⁰⁺	1086.719723	1086.719596	0.12
56	c ₂₉ ³⁺	1087.856033	1087.855363	0.62
57	c ₄₉ ⁵⁺	1089.938816	1089.938497	0.29
58	c ₈₇ ⁹⁺	1092.186173	1092.185738	0.40
59	c ₇₈ ⁸⁺	1092.650223	1092.650656	-0.40
60	c ₃₉ ⁴⁺	1095.048661	1095.048374	0.26
61	? ⁸⁺	1097.152540		
62	c ₉₇ ¹⁰⁺	1098.225201	1098.224200	0.91
63	c ₈₈ ⁹⁺	1100.078004	1100.078751	-0.68
64	c ₆₀ ⁶⁺	1104.027280	1104.026745	0.48
65	c ₇₉ ⁸⁺	1105.156919	1105.156227	0.63
66	c ₇₀ ⁷⁺	1106.673577	1106.673581	0.00
67	c ₄₀ ⁴⁺	1108.802640	1108.802070	0.51
68	c ₅₀ ⁵⁺	1112.943886	1112.944782	-0.81
69	? ⁸⁺	1113.906926		
70	? ³⁺	1115.883442		
71	c ₈₉ ⁹⁺	1116.531223	1116.531154	0.06
72	c ₈₀ ⁸⁺	1119.534174	1119.534595	-0.38
73	z ₇₄ +2Pt ⁸⁺	1119.747419	1119.748572	-1.03
74	b ₁₉ ²⁺	1121.042682	1121.043222	-0.48
75	? ⁸⁺	1122.533770		
76	z ₆₅ +2Pt-H ₂ O ⁷⁺	1124.785837	1124.784931	0.81
77	z ₆₅ +2Pt ⁷⁺	1127.072093	1127.071608	0.43
78	c ₁₉ ²⁺	1129.556824	1129.556496	0.29
79	c ₈₁ ⁸⁺	1130.413850	1130.413598	0.22
80	c ₃₀ ³⁺	1130.554111	1130.553684	0.38
81	? ¹⁰⁺	1135.541130		
82	c ⁴¹ 4+	1140.817080	1140.816715	0.32
83	[CaM+2Pt+12H-H ₂ O-CH ₃ S] ¹⁵⁺	1141.791667	1141.792273	-0.53
84	[CaM+2Pt+12H-CH ₃ S] ¹⁵⁺			
85	[CaM+2Pt+12H-H ₂ O] ¹⁵⁺	1144.926094	1144.925288	0.70
86	[CaM+2Pt+12H] ¹⁵⁺	1146.126927	1146.125993	0.81
87	z ₁₀₇ +2Pt ¹¹⁺	1147.780157	1147.783193	-2.65
88	? ⁹⁺	1156.222090		
89	c ₉₂ ⁹⁺	1161.223933	1161.224262	-0.28
90	c ₅₂ ⁵⁺	1161.763879	1161.768796	-4.23

91	c ₈₃ ⁸⁺	1162.675131	1162.674247	0.76
92	z ₆₇ +2Pt ⁷⁺	1163.940663	1163.940926	-0.23
93	? ⁷⁺	1165.942120		
94	c ₃₁ ³⁺	1173.234130	1173.233411	0.61
95	c ₉₃ ⁹⁺	1174.004376	1174.005033	-0.56
96	? ⁵⁺	1175.574590		
97	z ₆₈ +2Pt ⁷⁺	1176.372827	1176.373992	-0.99
98	c ₇₄ ⁷⁺	1176.419026	1176.420805	-1.51
99	z ₁₂₁ +2Pt ¹²⁺	1177.537619	1177.537189	0.37
100	? ⁷⁺	1178.377140		
101	? ⁸⁺	1180.399070		
102	? ⁹⁺	1183.016110		
103	c ₅₃ ⁵⁺	1184.577415	1184.577356	0.05
104	c ₂₀ ²⁺	1187.071101	1187.069968	0.95
105	c ₉₄ ⁹⁺	1188.238722	1188.237808	0.77
106	z ₅₉ +2Pt ⁶⁺	1190.352377	1190.352448	-0.06
107	z ₆₉ +2Pt-H ₂ O ⁷⁺	1190.377452	1190.376543	0.76
108	z ₆₉ +2Pt ⁷⁺	1192.804719	1192.806414	-1.42
109	c ₈₅ ⁸⁺	1192.938986	1192.940081	-0.92
110	c ₄₃ ⁴⁺	1194.093265	1194.092309	0.80
111	c ₇₅ ⁷⁺	1195.147411	1195.145872	1.29
112	? ⁷⁺	1194.808800		
113	? ⁹⁺	1202.240420		
114	z ₉₁ +2Pt ⁹⁺	1205.870621	1205.869506	0.92
115	z ₇₀ +2Pt ⁷⁺	1207.242180	1207.241798	0.32
116	c ₉₆ ⁹⁺	1207.353931	1207.354298	-0.30
117	c ₃₂ ³⁺	1211.262424	1211.262570	-0.12
118	c ₈₆ ⁸⁺	1212.453502	1212.452721	0.64
119	c ₇₆ ⁷⁺	1213.725382	1213.724705	0.56
120	z ₆₀ +2Pt ⁶⁺	1215.032755	1215.031015	1.43
121	c ₄₄ ⁴⁺	1219.355010	1219.354229	0.64
122	[CaM+2Pt+12H-CH ₃ S] ¹⁴⁺	1224.634869	1224.635372	-0.41
123	[CaM+2Pt+12H-CO] ¹⁴⁺	1225.992780	1225.992537	0.20
124	[CaM+2Pt+12H-H ₂ O] ¹⁴⁺	1226.706234	1226.705705	0.43
125	[CaM+2Pt+12H] ¹⁴⁺	1227.992732	1227.992174	0.45
126	c ₃₃ ³⁺	1229.935720	1229.935254	0.38
127	c ₆₇ ⁶⁺	1230.751932	1230.751267	0.54
128	c ₇₇ ⁷⁺	1232.023615	1232.023988	-0.30
129	c ₈₈ ⁸⁺	1237.461981	1237.462685	-0.57
130	? ⁷⁺	1242.000000		
131	z ₇₂ +2Pt ⁷⁺	1242.687540	1242.691819	-3.44
132	? ⁶⁺	1242.943100		
133	? ³⁺	1243.000000		
134	? ⁵⁺	1244.201300		
135	z ₆₂ +2Pt ⁶⁺	1248.375161	1248.377637	-1.98
136	c ₇₈ ⁷⁺	1248.456738	1248.456408	0.26
137	? ³⁺	1249.610000		

138	γ^{8+}	1250.000000		
139	c_{21}^{2+}	1250.615870	1250.615744	0.10
140	γ^{2+}	1251.364150		
141	c_{45}^{4+}	1251.865868	1251.865714	0.12
142	$z_{95}+2Pt^{9+}$	1251.888717	1251.888961	
143	c_{56}^{5+}	1253.204806	1253.204948	-0.11
144	γ^{7+}	1253.888000		
145	c_{89}^{8+}	1255.971803	1255.971638	0.13
146	γ^{7+}	1256.000000		
147	γ^{4+}	1258.371706		
148	γ^{10+}	1260.359460		
149	$z_{107}+2Pt-H_2O^{5+}$	1260.656613	1260.659728	-2.47
150	$z_{73}+2Pt^{7+}$	1260.837659	1260.836639	0.81
151	$z_{107}+2Pt^{5+}$	1262.561551	1262.561119	0.34
152	c_{79}^{7+}	1262.892100	1262.891791	0.24
153	c_{34}^{3+}	1263.618710	1263.617813	0.71
154	$z_{52}+2Pt^{5+}$	1264.739565	1264.739841	-0.22
155	$z_{131}+2Pt^{12+}$	1265.994248	1265.993547	0.55
156	γ^{11+}	1265.000000		
157	γ^{12+}	1266.000000		
158	c_{57}^{5+}	1267.412701	1267.412372	0.26
159	γ^{5+}	1268.000000		
160	c_{46}^{4+}	1268.873590	1268.872484	0.87
161	γ^{7+}	1272.606500		
162	$z_{132}+2Pt^{12+}$	1273.246333	1273.246219	0.09
163	γ^{12+}	1274.000000		
164	$z_{53}+2Pt-H_2O^{5+}$	1272.942707	1272.942630	0.06
165	γ^{9+}	1274.495550		
166	$z_{53}+2Pt^{5+}$	1275.944404	1275.943558	0.66
167	$z_{74}+2Pt^{7+}$	1279.710457	1279.711822	-1.07
168	c_{80}^{7+}	1279.323742	1279.324212	-0.37
169	γ^{8+}	1280.000000		
170	γ^{7+}	1282.491800		
171	c_{58}^{5+}	1290.418417	1290.417760	0.51
172	c_{70}^{6+}	1290.951358	1290.951298	0.05
173	c_{81}^{7+}	1291.756077	1291.757359	-0.99
174	$z_{64}+2Pt^{6+}$	1293.408162	1293.408711	-0.42
175	$z_{122}+2Pt^{11+}$	1294.864144	1294.865979	-1.42
176	γ^{5+}	1295.000000		
177	c_{35}^{3+}	1297.309026	1297.309517	-0.38
178	$z_{54}+2Pt^{5+}$	1299.148906	1299.149528	-0.48
179	γ^{5+}	1301.000000		
180	c_{47}^{4+}	1301.885028	1301.885641	-0.47
181	c_{59}^{5+}	1301.420330	1301.420750	-0.32
182	γ^{7+}	1303.474260		
183	c_{92}^{8+}	1306.251575	1306.251385	0.15
184	c_{22}^{2+}	1308.631393	1308.630910	0.37

185	c ₈₂ ⁷⁺	1310.191838	1310.192015	-0.14
186	z ₇₆ +2Pt ⁷⁺	1311.441480		
187	z ₆₅ +2Pt ⁶⁺	1314.748303	1314.748996	-0.53
188	[CaM+2Pt+12H-CH ₃ S] ^{13+...}	1318.836070	1318.838135	-1.57
189	[CaM+2Pt+12H-H ₂ O] ^{13+...}	1321.067250	1321.067725	-0.36
190	[CaM+2Pt+12H] ^{13+...}	1322.453906	1322.453153	0.57
191	c ₆₀ ⁵⁺	1324.630509	1324.630639	-0.10
192	z ₅₅ +2Pt ⁵⁺	1324.770001	1324.768528	1.11
193	? ⁵⁺	1328.000000		
194	c ₈₃ ⁷⁺	1328.626544	1328.626667	-0.09
195	z ₇₇ +2Pt ⁷⁺	1330.304938	1330.304636	0.23
196	z ₆₆ +2Pt-H ₂ O ⁶⁺	1333.422287	1333.421153	0.85
197	c ₇₂ ⁶⁺	1334.631125	1334.631462	-0.25
198	c ₆₁ ⁵⁺	1336.034546	1336.034932	-0.29
199	z ₆₆ +2Pt ⁶⁺	1336.088729	1336.088891	-0.12
200	c ₉₄ ⁸⁺	1336.640563	1336.641625	-0.79
201	c ₂₃ ²⁺	1337.142104	1337.141653	0.34
202	? ⁶⁺	1338.759470		
203	c ₃₆ ³⁺	1340.321720	1340.320779	0.70
204	z ₉₀ +2Pt ⁸⁺	1342.349572	1342.349504	0.05
205	? ⁹⁺	1345.376740		
206	z ₅₆ +2Pt ⁵⁺	1347.774205	1347.773920	0.21
207	? ⁷⁺	1348.884500		
208	? ¹⁰⁺	1349.706570		
209	z ₄₃ +2Pt ⁴⁺	1351.311122	1351.311961	-0.62
210	? ⁸⁺	1352.773000		
211	z ₁₀₂ +2Pt ⁹⁺	1353.712654	1353.713556	-0.67
212	z ₉₁ +2Pt ⁸⁺	1356.477797	1356.477285	0.38
213	z ₆₇ +2Pt ⁶⁺	1357.931567	1357.930016	1.14
214	? ⁶⁺	1360.099190		
215	c ₄₉ ⁴⁺	1362.171530	1362.171302	0.17
216	c ₈₅ ⁷⁺	1363.214732	1363.216196	-1.07
217	z ₉₂ +2Pt ⁸⁺	1365.357533	1365.356925	0.45
218	c ₇₄ ⁶⁺	1372.153591	1372.155863	-1.66
219	z ₆₈ +2Pt ⁶⁺	1372.435848	1372.435355	0.36
220	? ⁶⁺	1374.771600		
221	z ₅₇ +2Pt ⁵⁺	1377.388759	1377.387797	0.70
222	c ₆₃ ⁵⁺	1378.861357	1378.861283	0.05
223	z ₄₄ +2Pt ⁴⁺	1379.334074	1379.333964	0.08
224	z ₁₃₁ +2Pt ¹¹⁺	1380.994694	1380.992299	1.73
225	z ₆₉ +2Pt-H ₂ O ⁶⁺	1388.770549	1388.771907	-0.98
226	z ₁₃₂ +2Pt ¹¹⁺	1388.996875	1388.995386	1.07
227	z ₆₉ +2Pt ⁶⁺	1391.440236	1391.439604	0.45
228	c ₃₇ ³⁺	1393.023301	1393.023384	-0.06
229	c ₇₅ ⁶⁺	1394.171361	1394.168971	1.71
230	c ₂₄ ²⁺	1394.655297	1394.655124	0.12
231	z ₅₈ +2Pt ⁵⁺	1397.202516	1397.201483	0.74

232	$z_{107}+2Pt-H_2O^{9+}$	1400.732706	1400.732594	0.08
233	$z_{81}+2Pt^{7+}$	1400.621241	1400.624647	-2.43
234	c_{64}^{5+}	1401.866275	1401.866672	-0.28
235	$z_{107}+2Pt^{9+}$	1402.736261	1402.733768	1.78
236	$z_{120}+2Pt^{10+}$	1403.139980	1403.139043	0.67
237	$?^{5+}$	1403.000000		
238	$z_{70}+2Pt^{6+}$	1408.280181	1408.280886	-0.50
239	$z_{95}+2Pt^{8+}$	1408.375197	1408.374366	0.59
240	$z_{45}+2Pt^{4+}$	1411.593647	1411.593364	0.20
241	$z_{121}+2Pt^{10+}$	1412.844525	1412.840680	2.72
242	c_{25}^{2+}	1422.664410	1422.664151	0.18
243	$z_{71}+2Pt^{6+}$	1427.617419	1427.618955	-1.08
244	$z_{59}+2Pt^{5+}$	1428.423507	1428.421708	1.26
245	$z_{46}+2Pt^{4+}$	1429.354651	1429.353902	0.52
246	c_{89}^{7+}	1435.110340	1435.108949	0.97
247	c_{77}^{6+}	1437.362678	1437.360625	1.43
248	$?^{2+}$	1442.176230		
249	$z_{47}+2Pt^{4+}$	1447.112014	1447.111927	0.06
250	$z_{72}+2Pt^{6+}$	1449.135856	1449.135271	0.40
251	c_{52}^{4+}	1451.959839	1451.959176	0.46
252	$z_{60}+2Pt^{5+}$	1457.837282	1457.835763	1.04
253	c_{39}^{3+}	1459.728326	1459.728739	-0.28
254	$z_{48}+2Pt^{4+}$	1468.871743	1468.869937	1.23
255	$z_{73}+2Pt^{6+}$	1470.978176	1470.975354	1.92
256	$z_{61}+2Pt^{5+}$	1472.045369	1472.043187	1.48
257	c_{26}^{2+}	1473.188130	1473.187990	0.10
258	c_{40}^{3+}	1478.734907	1478.735894	-0.67
259	c_{53}^{4+}	1479.969370	1479.968251	0.76
260	$?^{6+}$	1484.872660		
261	$z_{74}+2Pt^{6+}$	1492.990490	1492.990454	0.02
262	$?^{5+}$	1494.048690		
263	$z_{62}+2Pt^{5+}$	1497.851964	1497.851709	0.17
264	$z_{49}+2Pt^{4+}$	1497.141856	1497.140959	0.60
265	$?^{9+}$	1500.956880		
266	$?^{3+}$	1506.416720		
267	$?^{3+}$	1507.722080		
268	$?^{8+}$	1513.000000		
269	$?^{10+}$	1519.190850		
270	c_{41}^{3+}	1520.753210	1520.753194	0.01
271	$?^{3+}$	1521.000000		
272	$z_{131}+2Pt^{6+}$	1519.191184	1519.191177	0.00
273	$z_{89}+2Pt^{7+}$	1525.539479	1525.537512	1.29
274	c_{27}^{2+}	1529.728950	1529.730022	-0.70
275	$?^{4+}$	1532.436430		
276	$z_{50}+2Pt^{4+}$	1537.908816	1537.906876	1.26
277	c_{55}^{4+}	1537.497254	1537.497630	-0.24
278	$?^{6+}$	1542.393240		

279	γ^{11+}	1546.254890		
280	$z_{51}+2Pt^{4+}$	1552.162874	1552.162244	0.41
281	c_{13}	1562.769610	1562.769676	-0.04
282	c_{56}^{4+}	1566.254010	1566.254366	-0.23
283	γ^{2+}	1571.000000		
284	γ^{4+}	1570.000000		
285	γ^{8+}	1572.698870		
286	γ^{2+}	1573.000000		
287	γ^{4+}	1575.000000		
288	$z_{107}+2Pt-H_2O^{8+}$	1575.575603	1575.572841	1.75
289	$z_{52}+2Pt-H_2O^{4+}$	1576.420604	1576.420580	0.02
290	$z_{107}+2Pt^{8+}$	1577.826316	1577.824162	1.37
291	$z_{65}+2Pt^{5+}$	1577.497207	1577.497340	-0.08
292	$z_{107}+2Pt^{8+}$	1577.826316	1577.824162	1.37
293	$z_{52}+2Pt^{4+}$	1580.673981	1580.672982	0.63
294	c_{28}^{2+}	1580.253960	1580.253861	0.06
295	c_{57}^{4+}	1584.012975	1584.013645	-0.42
296	γ^{4+}	1584.000000		
297	$z_{53}+2Pt-H_2O^{4+}$	1590.425749	1590.425709	0.03
298	$z_{74}+2Pt^{6+}$	1492.826775	1492.829246	-1.66
299	$z_{53}+2Pt^{4+}$	1594.929601	1594.928350	0.78
300	$z_{66}+2Pt-H_2O^{5+}$	1599.703907	1599.703750	0.10
301	γ^{2+}	1599.765710		
302	$z_{66}+2Pt^{5+}$	1603.307168	1603.305863	0.81
303	$z_{95}+2Pt-H_2O^{7+}$	1607.142333	1607.140258	1.29
304	$z_{95}+2Pt^{7+}$	1609.427300	1609.426807	0.31
305	γ^{2+}	1609.000000		
306	c_{58}^{4+}	1612.772433	1612.770381	1.27
307	$z_{54}+2Pt-H_2O^{4+}$	1619.185653	1619.182450	1.98
308	$z_{54}+2Pt^{4+}$	1623.685857	1623.685091	0.47
309	c_{59}^{4+}	1627.026720	1627.025747	0.60
310	$z_{67}+2Pt^{5+}$	1629.116270	1629.114386	1.16
311	c_{29}^{2+}	1630.778140	1630.777701	0.27
312	γ^{5+}	1632.000000		
313	γ^{5+}	1643.121810		
314	γ^{4+}	1644.532710		
315	c_{74}^{5+}	1646.786809	1646.786838	-0.02
316	$z_{68}+2Pt^{5+}$	1646.522168	1646.520679	0.90
317	γ^{5+}	1649.725560		
318	$z_{55}+2Pt-H_2O^{4+}$	1651.205504	1651.206199	-0.42
319	$z_{55}+2Pt^{4+}$	1655.710480	1655.708840	0.99
320	$z_{69}+2Pt-H_2O^{5+}$	1665.921878	1665.923956	-1.25
321	c_{45}^{3+}	1668.149810	1668.149636	0.10
322	$z_{69}+2Pt^{5+}$	1669.729148	1669.726362	1.67
323	γ^{2+}	1672.819560		
324	γ^{5+}	1673.132130		
325	γ^{3+}	1677.156700		

326	$z_{56}+2Pt-H_2O^{4+}$	1680.967309	1680.970765	-2.06
327	$z_{56}+2Pt^{4+}$	1684.466917	1684.465581	0.79
328	$z_{70}+2Pt^{5+}$	1689.743351	1689.735607	4.58
329	c_{14}	1691.811880	1691.812272	-0.23
330	c_{30}^{2+}	1695.327219	1695.326888	0.20
331	$z_{71}+2Pt-H_2O^{5+}$	1709.142049	1709.138885	1.85
332	$z_{71}+2Pt^{5+}$	1712.941327	1712.941291	0.02
333	$z_{57}+2Pt^{4+}$	1721.235009	1721.232639	1.38
334	$z_{72}+2Pt-H_2O^{5+}$	1735.354705	1735.359285	-2.64
335	$z_{72}+2Pt^{5+}$	1738.157874	1738.159519	-0.95
336	$z_{58}+2Pt^{4+}$	1746.252348	1746.250034	1.33
337	c_{31}^{2+}	1759.346870	1759.346479	0.22
338	c_{15}	1762.849260	1762.849385	-0.07
339	$z_{73}+2Pt^{5+}$	1764.764988	1764.768385	-1.92
340	$z_{59}+2Pt^{4+}$	1785.277174	1785.275316	1.04
341	$z_{74}+2Pt^{5+}$	1790.992326	1790.993349	-0.57
342	$z_{43}+2Pt^{3+}$	1801.081185	1801.079272	1.06
343	c_{32}^{2+}	1815.892540	1815.888511	2.22
344	$z_{60}+2Pt^{4+}$	1822.297847	1822.293192	2.55
345	$z_{44}+2Pt^{3+}$	1838.776308	1838.776193	0.06
346	$z_{61}+2Pt^{4+}$	1840.054836	1840.052473	1.28
347	c_{33}^{2+}	1844.900046	1844.900949	-0.49
348	$?^{1+}$	1865.902360		
349	$z_{62}+2Pt^{4+}$	1872.065837	1872.062817	1.61
350	$z_{45}+2Pt^{3+}$	1881.790292	1881.788727	0.83
351	c_{34}^{2+}	1895.423669	1895.424788	-0.59
352	$z_{46}+2Pt^{3+}$	1905.802417	1905.803710	-0.68
353	c_{16}	1909.915852	1909.917799	-1.02
354	$z_{47}+2Pt^{3+}$	1929.147132	1929.146811	0.17
355	$?^{3+}$	1934.153340		
356	$z_{48}+2Pt^{3+}$	1958.160290	1958.157491	1.43
357	$z_{65}+2Pt^{4+}$	1972.125225	1972.120812	2.24
358	$z_{49}+2Pt^{3+}$	1995.513694	1995.517982	-2.15
359	c_{17}	1996.948989	1996.949828	-0.42
360	$z_{66}+2Pt^{4+}$	2003.879279	2003.880510	-0.61
361	c_{36}^{2+}	2010.979895	2010.980881	-0.49
362	$z_{50}+2Pt^{3+}$	2050.203770	2050.206842	-1.50
363	$z_{51}+2Pt^{3+}$	2069.215140	2069.213900	0.60
364	$z_{69}+2Pt-H_2O^{4+}$	2082.901128	2082.904951	-1.84
365	$z_{69}+2Pt^{4+}$	2087.408001	2087.407592	0.20
366	$z_{52}+2Pt^{3+}$	2107.230315	2107.228217	1.00
367	$z_{53}+2Pt^{3+}$	2127.241860	2127.244845	-1.40
368	$z_{54}+2Pt-H_2O^{3+}$	2158.906854	2158.907824	-0.45
369	$z_{54}+2Pt^{3+}$	2164.579285	2164.577696	0.73
370	$z_{55}+2Pt-H_2O^{3+}$	2201.933232	2201.940444	-3.28
371	$z_{55}+2Pt^{3+}$	2207.274491	2207.276028	-0.70
372	$z_{56}+2Pt^{3+}$	2245.617465	2245.618350	-0.39

373	c ₁₉	2257.101740	2257.102306	-0.25
374	c ₄₁ ²⁺	2281.633082	2281.629493	1.57
375	c ₂₀	2372.129920	2372.129249	0.28
	Mean absolute deviation (ppm)			0.59

Table S-3. ECD Fragments of the $[\text{CaM}+5\text{Pt}(\text{dien})+10\text{H}]^{20+}$ ions

No.	Assignments	Exp. mass (Da)	Theo. mass (Da)	Error (ppm)
1	$[\text{Pt}(\text{dien})-2\text{H}]^{+}$	296.060078	296.060123	-0.15
2	$[\text{Pt}(\text{dien})]^{+}$	298.075730	298.075773	-0.14
3	$[\text{Pt}(\text{dien})+\text{H}]^{+}$	299.083250	299.083598	-1.16
4	$[\text{Pt}(\text{dien})(\text{CO})-\text{H}]^{+}$	325.062743	325.062325	1.29
5	$[\text{Pt}(\text{dien})(\text{CH}_3\text{S})-\text{H}]^{+}$	344.063334	344.063506	-0.50
6	$\text{Pt}(\text{dien})(\text{CH}_3\text{S})^{+}$	345.071224	345.071331	-0.03
7	c_3	374.167161	374.167025	0.36
8	b_4	470.224588	470.22454	0.10
9	c_4	487.251057	487.251089	-0.07
10	b_5	571.272025	571.272218	-0.34
11	c_5	588.298704	588.298767	-0.11
12	$\text{z}_{12}+2\text{Pt}(\text{dien})^{3+}$	689.927521	689.927823	-0.44
13	b_6	700.314677	700.314811	-0.19
14	$\text{z}_{20}+2\text{Pt}(\text{dien})^{4+}$	717.530829	717.531519	-0.96
15	c_6	717.341075	717.34136	-0.40
16	?^{3+}	727.286910		
17	$\text{z}_{21}+2\text{Pt}(\text{dien})^{4+}$	735.290662	735.290806	-0.20
18	$\text{z}_{48}+4\text{Pt}(\text{dien})^{9+}$	741.206532	741.206553	-0.03
19	$\text{z}_{31}+3\text{Pt}(\text{dien})^{6+}$	747.458561	747.459470	-1.22
20	$\text{z}_{14}+2\text{Pt}(\text{dien})^{3+}$	765.636456	765.636859	-0.53
21	$\text{z}_{22}+2\text{Pt}(\text{dien})^{4+}$	767.550330	767.551468	-1.48
22	$\text{z}_{57}+4\text{Pt}(\text{dien})^{10+}$	769.032138	769.031759	0.49
23	$\text{z}_{51}+4\text{Pt}(\text{dien})^{9+}$	779.225319	779.225741	-0.54
24	c_{13}^{2+}	781.888045	781.88847	-0.55
25	$\text{z}_{15}+2\text{Pt}(\text{dien})^{3+}$	784.643353	784.644022	-0.85
26	$\text{z}_{65}+4\text{Pt}(\text{dien})^{11+}$	790.259691	790.261517	-2.31
27	$\text{z}_{52}+4\text{Pt}(\text{dien})^{9+}$	791.897174	791.897178	-0.01
28	$\text{z}_{59}+4\text{Pt}(\text{dien})^{10+}$	794.548943	794.548718	0.28
29	$\text{z}_{66}+4\text{Pt}(\text{dien})^{11+}$	801.990407	801.992662	-2.81
30	?^{9+}	808.900450		
31	$\text{z}_{60}+4\text{Pt}(\text{dien})^{10+}$	809.355453	809.355804	-0.43
32	$\text{z}_{54}+4\text{Pt}(\text{dien})^{9+}$	811.013047	811.013315	-0.33
33	$\text{z}_{46}+4\text{Pt}(\text{dien})^{8+}$	815.097114	815.097816	-0.86
34	?^{3+}	816.314700		
35	$\text{z}_{16}+2\text{Pt}(\text{dien})^{3+}$	822.985996	822.986351	-0.43
36	$\text{z}_{55}+4\text{Pt}(\text{dien})^{9+}$	825.357039	825.357484	-0.54
37	?^{5+}	825.328810		
38	$\text{z}_{69}+4\text{Pt}(\text{dien})^{11+}$	832.091926	832.092520	-0.71
39	$\text{z}_{35}+3\text{Pt}(\text{dien})^{6+}$	833.343887	833.346139	-2.70
40	$\text{z}_{48}+4\text{Pt}(\text{dien})^{8+}$	834.856114	834.856462	-0.42
41	$\text{z}_{56}+4\text{Pt}(\text{dien})^{9+}$	838.025275	838.026872	-1.91
42	$\text{z}_{17}+2\text{Pt}(\text{dien})^{3+}$	841.992622	841.993513	-1.06
43	c_7	846.383316	846.383953	-0.75

44	$z_{29}+3Pt(dien)^{5+}$	848.135954	848.136442	-0.58
45	$z_{57}+4Pt(dien)^{9+}$	854.367353	854.3678131	-0.54
46	$z_{65}+4Pt(dien)^{10+}$	869.185226	869.186941	-1.97
47	$z_{30}+3Pt(dien)^{5+}$	873.943514	873.944980	-1.68
48	$z_{51}+4Pt(dien)^{8+}$	876.502434	876.503049	-0.70
49	$z_{18}+2Pt(dien)^{3+}$	880.335063	880.3358423	-0.89
50	$z_{66}+4Pt(dien)^{10+}$	882.090974	882.091200	-0.26
51	c_{15}^{2+}	881.928653	881.928331	0.37
52	c_{23}^{3+}	891.429015	891.429057	-0.05
53	$z_{31}+3Pt(dien)^{5+}$	896.949295	896.950374	-1.20
54	$z_{68}+4Pt(dien)^{10+}$	903.597184	903.598053	-0.96
55	$[CaM+5Pt(dien)-H_2O+10H]^{20+}$	913.665494	913.665499	-0.01
56	$[CaM+5Pt(dien)+10H]^{20+}$	914.566326	914.566027	0.33
57	$z_{19}+2Pt(dien)^{3+}$	918.030147	918.030603	-0.50
58	$z_{55}+4Pt(dien)^{8+}$	928.526216	928.526327	-0.12
59	$z_{65}+3Pt(dien)^{9+}$	932.64424	932.644262	-0.02
60	$z_{33}+3Pt(dien)^{5+}$	939.775017	939.776735	-1.83
61	$?^{5+}$	942.579640		
62	$?^{9+}$	946.761680		
63	c_{25}^{3+}	948.777807	948.778526	-0.76
64	$z_{48}+4Pt(dien)^{7+}$	953.978085	953.977774	0.33
65	c_{16}^{2+}	955.461835	955.462538	-0.74
66	$z_{20}+2Pt(dien)^{3+}$	956.372235	956.372933	-0.73
67	$[CaM+5Pt(dien)-CH_3S-H_2O+10H]^{19+}$	959.278132	959.280302	-2.26
68	$[CaM+5Pt(dien)-CH_3S+10H]^{19+}$	960.226745	960.228227	-1.54
69	$[CaM+5Pt(dien)-H_2O+10H]^{19+}$	961.753196	961.753735	-0.56
70	$[CaM+5Pt(dien)+10H]^{19+}$	962.700602	962.701660	-1.10
71	$z_{65}+4Pt(dien)^{9+}$	965.539523	965.539553	-0.03
72	$?^{9+}$	970.988670		
73	$z_{58}+4Pt(dien)^{8+}$	973.545398	973.546739	-1.38
74	$?^{7+}$	975.140160		
75	$z_{11}+2Pt(dien)^{2+}$	976.866016	976.865640	0.38
76	$z_{21}+2Pt(dien)^{3+}$	980.052277	980.051983	0.30
77	c_{26}^{3+}	982.460682	982.461086	-0.41
78	c_{17}^{2+}	998.978327	998.978552	-0.23
79	$[CaM+4Pt(dien)-CH_3S-H_2O+10H]^{18+}$	995.958021	995.957715	0.31
80	$[CaM+4Pt(dien)-CH_3S+10H]^{18+}$	996.958369	996.958303	0.07
81	$[CaM+4Pt(dien)-H_2O+10H]^{18+}$	998.624525	998.624222	0.30
82	$[CaM+4Pt(dien)+10H]^{18+}$	999.624754	999.624809	-0.06
83	$[CaM+5Pt(dien)-CH_3S-H_2O+10H]^{18+}$	1012.517103	1012.517504	-0.40
84	$[CaM+5Pt(dien)-CH_3S+10H]^{18+}$	1013.571719	1013.573751	-2.00
85	$[CaM+5Pt(dien)-H_2O+10H]^{18+}$	1015.182782	1015.184009	-1.21
86	$[CaM+5Pt(dien)+10H]^{18+}$	1016.183387	1016.184596	-1.19
87	$[CaM+4Pt(dien)-CH_3S-H_2O+10H]^{17+}$	1054.601115	1054.602528	-1.34
88	$[CaM+4Pt(dien)-CH_3S+10H]^{17+}$	1055.602001	1055.603038	-0.98
89	$[CaM+4Pt(dien)-H_2O+10H]^{17+}$	1057.365952	1057.366953	-0.95
90	$[CaM+4Pt(dien)+10H]^{17+}$	1058.425060	1058.426398	-1.26

91	$c_{117}+2Pt(dien)^{13+}$	1061.812279	1061.812756	-0.45
92	c_{38}^{4+}	1066.526508	1066.526542	-0.03
93	b_9	1070.499605	1070.500046	-0.41
94	$[CaM+5Pt(dien)-CH_3S-H_2O+10H]^{17+...}$	1072.135116	1072.136355	-1.16
95	$[CaM+5Pt(dien)-CH_3S+10H]^{17+...}$	1073.192642	1073.195801	-2.94
96	$[CaM+5Pt(dien)-H_2O+10H]^{17+...}$	1074.959298	1074.959711	-0.38
97	$c_{93}+Pt(dien)^{10+}$	1086.310822	1086.311212	-0.36
98	c_{49}^{5+}	1089.536692	1089.537162	-0.43
99	$z_{30}+3Pt(dien)^{4+}$	1092.179897	1092.179818	0.07
100	$c_{94}+Pt(dien)^{10+}$	1099.119676	1099.120709	-0.94
101	c_{40}^{4+}	1108.802188	1108.802070	0.11
102	$c_{86}+Pt(dien)^{9+}$	1110.852945	1110.854621	-1.51
103	$c_{77}+Pt(dien)^{8+}$	1115.153248	1115.154333	-0.97
104	$c_{96}+Pt(dien)^{10+}$	1116.324985	1116.325551	-0.51
105	$[CaM+4Pt(dien)-CH_3S-H_2O+10H]^{16+...}$	1120.513669	1120.515187	-1.35
106	$[CaM+4Pt(dien)-CH_3S+10H]^{16+...}$	1121.575870	1121.578228	-2.10
107	$[CaM+4Pt(dien)-H_2O+10H]^{16+...}$	1123.389994	1123.389771	0.20
108	$[CaM+4Pt(dien)+10H]^{16+...}$	1124.515018	1124.515431	-0.37
109	$c_{97}+Pt(dien)^{10+}$	1127.727591	1127.729845	-2.00
110	c_{19}^{2+}	1129.053648	1129.054791	-1.01
111	$c_{78}+Pt(dien)^{8+}$	1129.408078	1129.407317	0.67
112	c_{30}^{3+}	1130.218559	1130.219214	-0.58
113	c_{41}^{4+}	1140.816085	1140.816715	-0.55
114	$c_{79}+Pt(dien)^{8+}$	1142.161889	1142.163663	-1.55
115	$c_{80}+Pt(dien)^{8+}$	1156.540502	1156.542032	-1.32
116	c_{10}	1158.563786	1158.563708	0.07
117	$c_{100}+Pt(dien)^{10+}$	1161.046132	1161.046734	-0.52
118	$c_{81}+Pt(dien)^{8+}$	1167.420970	1167.421036	-0.06
119	$c_{101}+Pt(dien)^{10+}$	1169.747148	1169.749938	-2.39
120	c_{31}^{3+}	1173.233902	1173.233411	0.42
121	$c_{82}+Pt(dien)^{8+}$	1183.550084	1183.551362	-1.08
122	c_{53}^{5+}	1184.176463	1184.176056	0.34
123	c_{20}^{2+}	1186.568598	1186.568263	0.28
124	$[CaM+4Pt(dien)-CH_3S-H_2O+10H]^{15+...}$	1195.214402	1195.216345	-1.63
125	$[CaM+4Pt(dien)-CH_3S+10H]^{15+...}$	1196.415953	1196.417050	-0.92
126	$c_{83}+Pt(dien)^{8+}$	1199.680959	1199.681688	-0.61
127	$c_{93}+Pt(dien)^{9+}$	1206.899263	1206.900538	-1.06
128	c_{32}^{3+}	1210.927075	1210.928099	-0.85
129	c_{44}^{4+}	1218.851827	1218.852557	-0.60
130	$c_{94}+Pt(dien)^{9+}$	1221.132951	1221.133313	-0.30
131	$c_{85}+Pt(dien)^{8+}$	1230.073049	1230.072898	0.12
132	c_{33}^{3+}	1229.934715	1229.935254	-0.44
133	$c_{96}+Pt(dien)^{9+}$	1240.24939	1240.249804	-0.33
134	$c_{86}+Pt(dien)^{8+}$	1249.459456	1249.460165	-0.57
135	c_{21}^{2+}	1250.615729	1250.615744	-0.01
136	c_{45}^{4+}	1251.865782	1251.865714	0.05
137	c_{56}^{4+}	1253.204701	1253.204948	-0.20

138	η^{16+}	1255.796560			
139	η^{4+}	1257.869450			
140	c_{34}^{3+}	1263.617647	1263.617813	-0.13	
141	$c_{87}+\text{Pt}(\text{dien})^{8+}$	1265.590347	1265.590490	-0.11	
142	η^{5+}	1267.211670			
143	c_{46}^{4+}	1268.871561	1268.872484	-0.73	
144	$c_{77}+\text{Pt}(\text{dien})^{7+}$	1274.173891	1274.174901	-0.79	
145	η^{9+}	1284.938490			
146	c_{11}	1287.601493	1287.606302	-3.73	
147	$c_{100}+\text{Pt}(\text{dien})^{9+}$	1289.940532	1289.940007	0.41	
148	$c_{55}+\text{Pt}(\text{dien})^{5+}$	1290.015016	1290.012598	1.87	
149	$c_{89}+\text{Pt}(\text{dien})^{8+}$	1292.853160	1292.853686	-0.41	
150	c_{35}^{3+}	1296.640610	1296.640618	-0.01	
151	η^{7+}	1298.468630			
152	c_{47}^{4+}	1301.133767	1301.133132	0.49	
153	c_{59}^{5+}	1301.419784	1301.42075	-0.74	
154	$c_{79}+\text{Pt}(\text{dien})^{7+}$	1305.184872	1305.186004	-0.87	
155	c_{22}^{2+}	1308.128919	1308.129216	-0.23	
156	$c_{90}+\text{Pt}(\text{dien})^{8+}$	1312.618001	1312.61709	0.69	
157	η^{7+}	1314.899920			
158	$c_{80}+\text{Pt}(\text{dien})^{7+}$	1321.618669	1321.618426	0.18	
159	$c_{81}+\text{Pt}(\text{dien})^{7+}$	1334.051096	1334.051574	-0.36	
160	c_{23}^{2+}	1336.639751	1336.639947	-0.15	
161	c_{36}^{3+}	1340.319966	1340.320779	-0.61	
162	$c_{92}+\text{Pt}(\text{dien})^{8+}$	1343.258450	1343.258826	-0.28	
163	η^{7+}	1345.910930			
164	$c_{82}+\text{Pt}(\text{dien})^{7+}$	1352.486454	1352.486231	0.16	
165	c_{49}^{4+}	1361.669998	1361.669633	0.27	
166	η^{7+}	1364.348310			
167	$c_{83}+\text{Pt}(\text{dien})^{7+}$	1370.920160	1370.920890	-0.53	
168	$c_{94}+\text{Pt}(\text{dien})^{8+}$	1373.647589	1373.649068	-1.08	
169	c_{63}^{5+}	1378.456444	1378.459977	-2.56	
170	η^{7+}	1382.925310			
171	c_{50}^{4+}	1390.677257	1390.677203	0.04	
172	c_{37}^{3+}	1392.353599	1392.354483	-0.63	
173	c_{24}^{2+}	1394.153161	1394.153419	-0.19	
174	$c_{96}+\text{Pt}(\text{dien})^{8+}$	1394.281455	1394.280491	0.69	
175	η^{2+}	1401.159230			
176	c_{64}^{5+}	1401.867273	1401.866672	0.43	
177	$c_{85}+\text{Pt}(\text{dien})^{7+}$	1405.509923	1405.510416	-0.35	
178	$c_{25}-\text{H}_2\text{O}^{2+}$	1414.160925	1414.160574	0.25	
179	η^{1+}	1417.646743			
180	c_{38}^{3+}	1421.698617	1421.699630	-0.71	
181	c_{25}^{2+}	1422.663974	1422.664151	-0.12	
182	$c_{86}+\text{Pt}(\text{dien})^{7+}$	1427.667162	1427.667273	-0.08	
183	η^{12+}	1442.175260			
184	$c_{87}+\text{Pt}(\text{dien})^{7+}$	1446.244955	1446.245235	-0.19	

185	c ₅₂ ⁴⁺	1451.456024	1451.457506	-1.02
186	c ₃₉ ³⁺	1459.395113	1459.394030	0.74
187	? ³⁺	1471.608450		
188	c ₂₆ ²⁺	1473.187500	1473.187990	-0.33
189	c ₈₉ +Pt(dien) ⁷⁺	1477.549534	1477.546458	2.08
190	c ₄₀ ³⁺	1478.401710	1478.401457	0.17
191	c ₅₃ ⁴⁺	1479.967559	1479.968251	-0.47
192	? ³⁺	1493.915950		
193	? ³⁺	1506.415980		
194	? ²⁺	1507.705720		
195	c ₄₁ ³⁺	1520.753519	1520.753194	0.21
196	c ₂₇ ²⁺	1529.730215	1529.730022	0.13
197	c ₉₂ +Pt(dien) ⁷⁺	1534.05336		
198	c ₅₅ ⁴⁺	1536.996711	1536.996003	0.46
199	? ²⁺	1549.242880		
200	c ₁₃	1562.770080	1562.769676	0.26
201	c ₅₆ ⁴⁺	1566.253023	1566.254366	-0.85
202	? ⁶⁺	1570.072130		
203	c ₈₂ +Pt(dien) ⁶⁺	1577.565060	1577.565535	-0.30
204	c ₂₈ ²⁺	1580.253955	1580.253861	0.06
205	c ₅₇ ⁴⁺	1583.510552	1583.512017	-0.93
206	? ⁶⁺	1591.735880		
207	c ₈₃ +Pt(dien) ⁶⁺	1598.238236	1598.239825	-0.99
208	? ²⁺	1599.765740		
209	? ²⁺	1608.769190		
210	c ₅₈ ⁴⁺	1612.266469	1612.268753	-1.42
211	c ₄₄ ³⁺	1625.135842	1625.135439	0.25
212	c ₅₉ ⁴⁺	1626.776576	1626.774944	1.00
212	c ₂₉ ²⁺	1630.778168	1630.777701	0.29
213	c ₄₅ ³⁺	1668.150143	1668.149636	0.30
214	c ₆₁ ⁴⁺	1669.793779	1669.791846	1.16
215	? ²⁺	1672.818790		
216	? ³⁺	1677.161210		
217	c ₁₄	1691.812455	1691.812272	0.11
218	c ₃₀ ²⁺	1694.825403	1694.825182	0.13
219	c ₃₁ ²⁺	1759.347762	1759.346479	0.73
220	c ₁₅	1762.850828	1762.849385	0.82
221	c ₃₂ ²⁺	1815.893164	1815.888511	2.56
222	c ₃₃ ²⁺	1844.397857	1844.399242	-0.75
223	? ¹⁺	1865.904520		
224	? ²⁺	1873.420190		
225	c ₃₄ ²⁺	1894.924541	1894.923082	0.77
226	c ₁₆	1909.918207	1909.917780	0.22
227	c ₁₇	1996.950698	1996.949828	0.44
228	? ²⁺	2010.477840		
229	c ₁₈	2110.036609	2110.033892	1.29
230	c ₁₉	2257.105508	2257.102306	1.42

231	γ^{1+}	2281.622640		
232	c_{20}	2372.127611	2372.129249	-0.69
233	c_{21}	2500.226977	2500.224212	1.11
	Mean absolute deviation (ppm)			0.60
	Standard deviation (ppm)			0.88

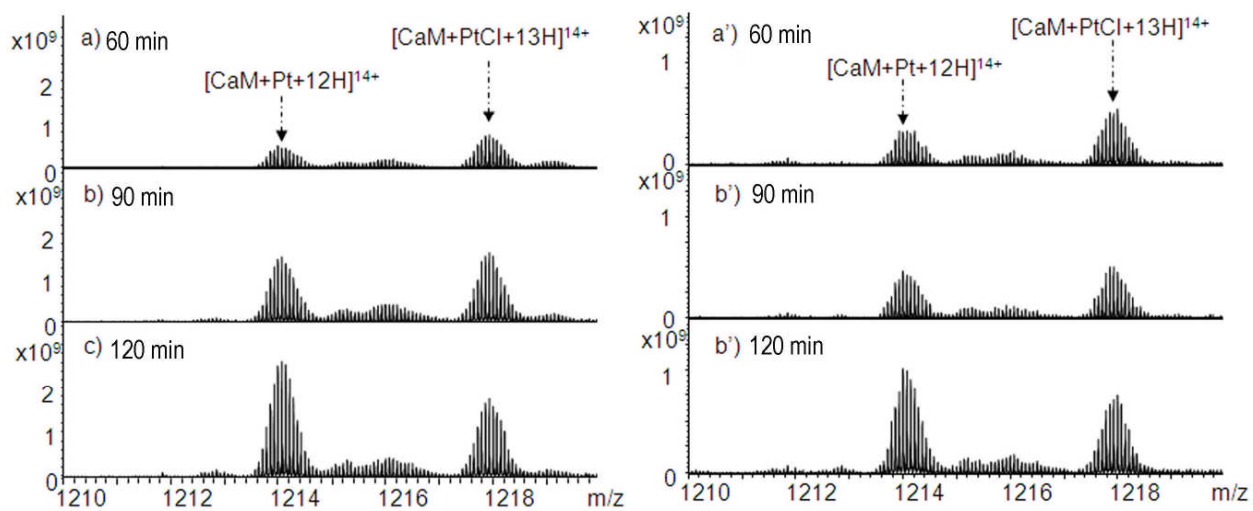


Figure S-1. ESI-FTMS analyses of anti-cancer platinum drug-CaM mixtures after different reaction times. CaM:Pt₁ (1:2) at (a) 60min, (b) 90min, and (c) 120min; CaM:Pt₃ (1:1) at (a') 60min, (b') 90min, and (c') 120min.

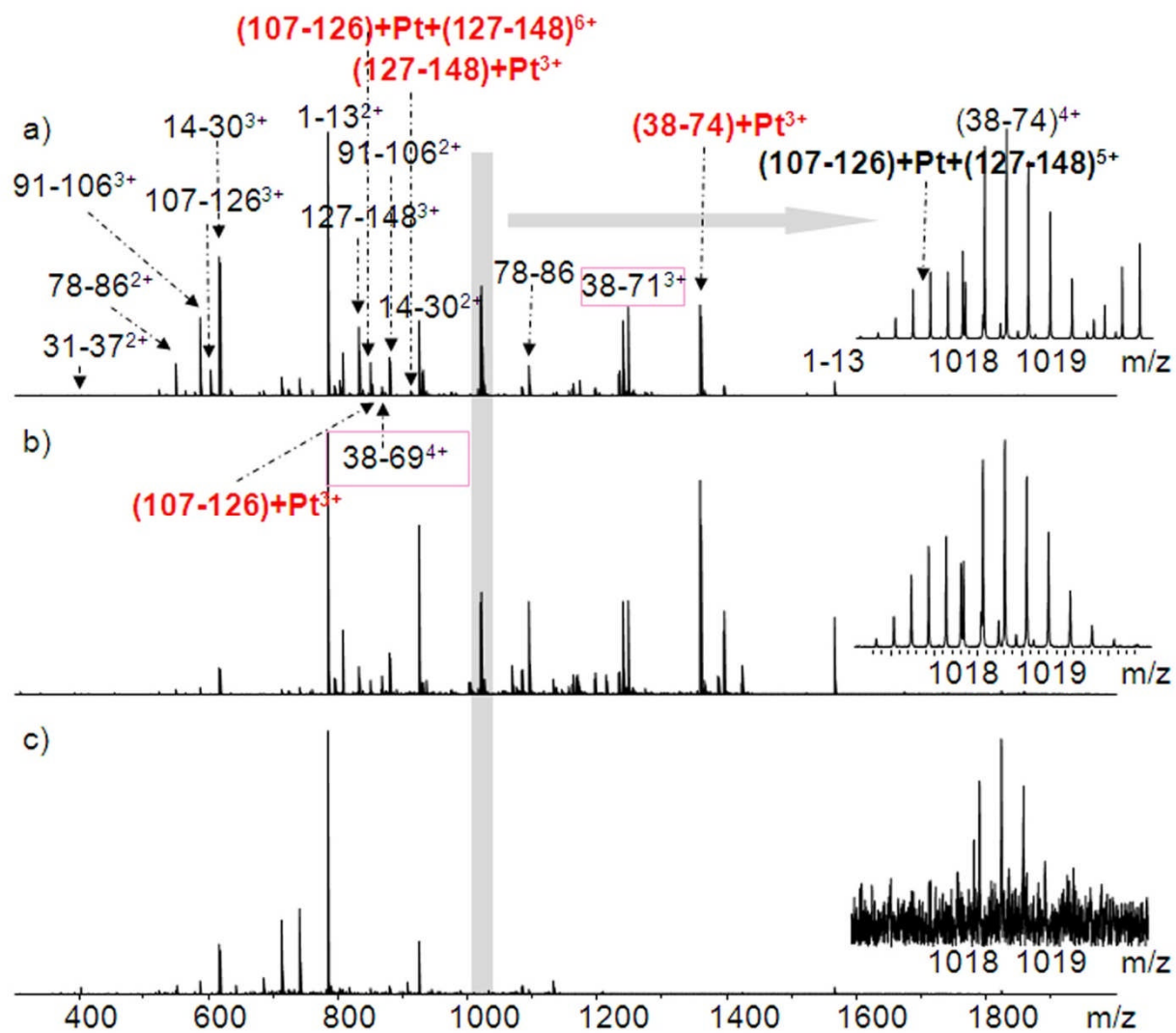


Figure S-2. ESI-FTMS analyses of trypsin-digested CaM-cisplatin (Pt₁) samples at different molar ratios. (a) CaM:Pt₁ (1:1); (b) CaM:Pt₁ (1:2); (c) CaM:Pt₁ (1:8).

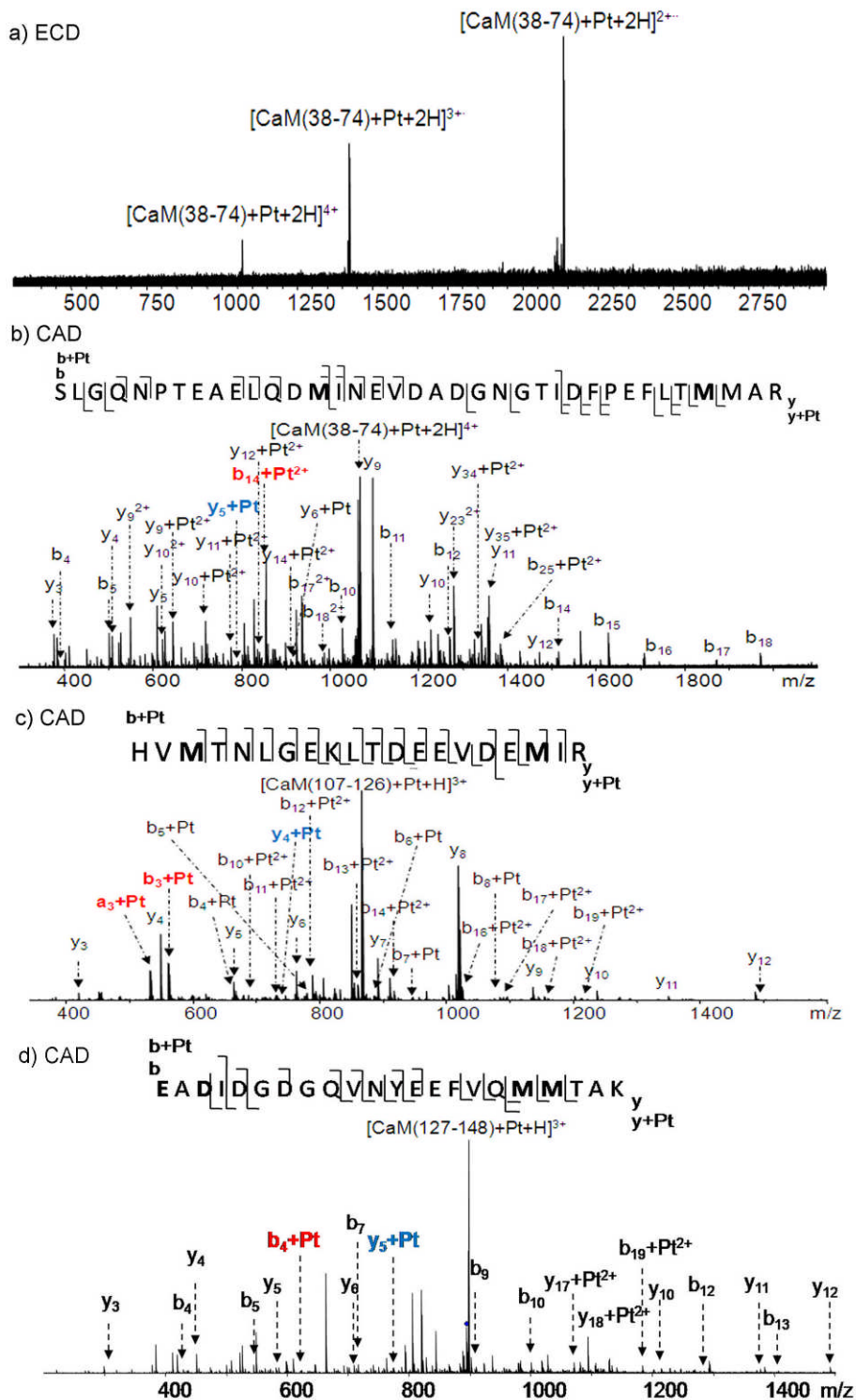


Figure S-3. Bottom-up MS/MS spectra of CaM:cisplatin (1:2). (a) ECD spectrum of $[\text{CaM}(38-74)+\text{Pt}+2\text{H}]^{4+}$ ion at m/z 1066; (b) CAD spectrum of $[\text{CaM}(38-74)+\text{Pt}+2\text{H}]^{4+}$ ion at m/z 1066; the observation of $b_{14}+\text{Pt}^{2+}$ and $y_5+\text{Pt}$ ions suggests that Pt cross-links Met51 and Met71 or Met72. (c) CAD spectrum of $[\text{CaM}(107-126)+\text{Pt}+\text{H}]^{3+}$ ion at m/z 865; the observation of $b_3+\text{Pt}$ and $y_4+\text{Pt}$ suggests that Pt cross-links Met109 and Met124 (d) CAD spectrum of

[CaM(127-148)+Pt+H]³⁺ ion at m/z 895. The detection of b₄+Pt and y₅+Pt ions suggests that Pt cross-links E127 or D129 with Met144 and Met145.

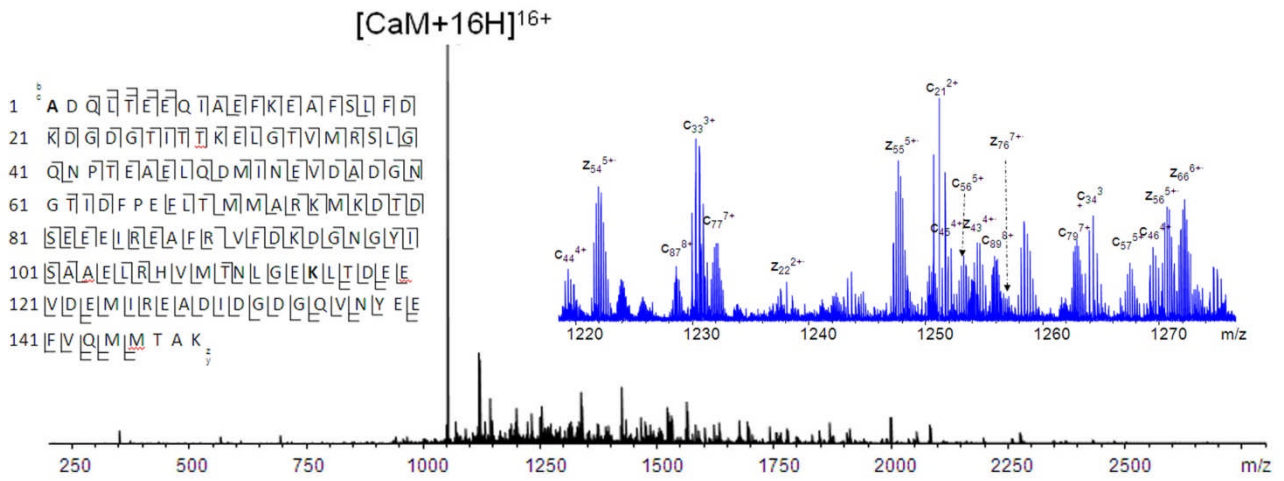


Figure S-4. ECD spectra of $[\text{CaM}+16\text{H}]^{16+}$ ions at m/z 1050 in a CaM sample. The insert is shown to compare with Figure 2b, which indicates that the intra-chain cross-linking of Pt between CaM(109) and CaM(144) contributes to repressed detections of cleavages in the region of CaM(106-148) in the top-down analyses. 91% backbone cleavage efficiency was achieved.

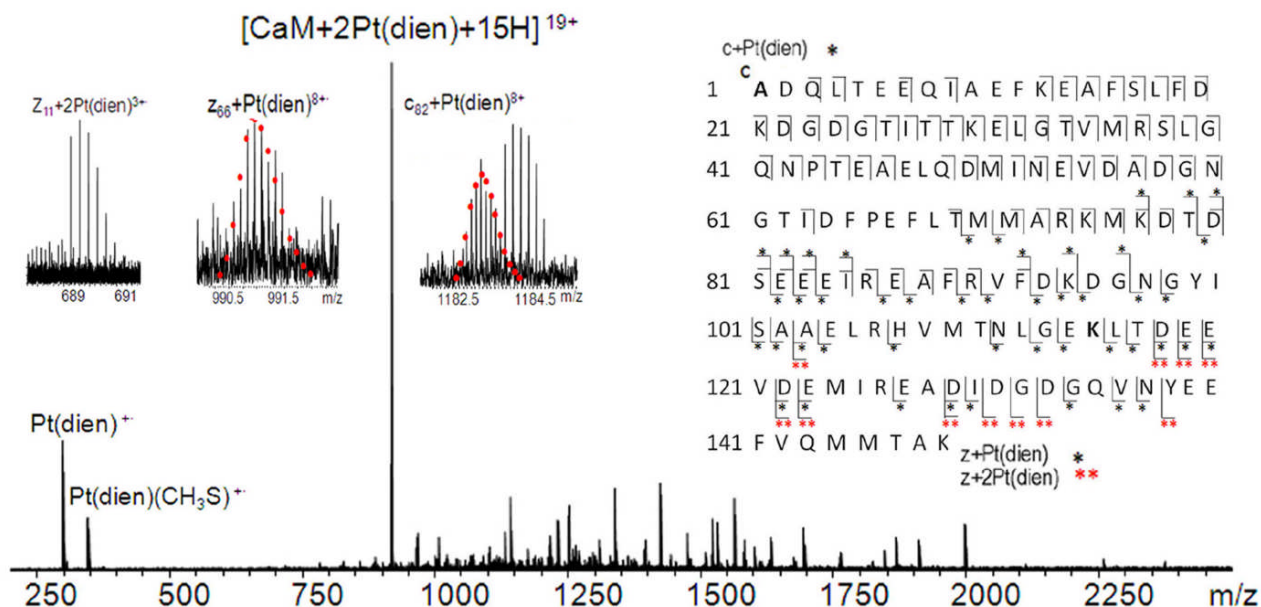


Figure S-5. ECD spectrum of $[\text{CaM}+2\text{Pt}(\text{dien})+15\text{H}]^{19+}$ ions at m/z 916 in the sample of CaM: cisplatin (1:2). The left inserts are the complimentary c/z^* ion pair, $c_{82}+\text{Pt}(\text{dien})^{8+}$ and $z_{66}+\text{Pt}(\text{dien})^{8+}$; the right insert is the fragmentation map of the ECD spectrum of CaM+2Pt(dien). Single dot represent singly Pt(dien)-modified fragments; two dots represent doubly Pt(dien)-modified fragments.

[CaM(107-126)+2Pt(dien)+H]⁵⁺ ion at m/z 600; (c) CAD spectrum of [CaM(127-148)+Pt(dien)+2H]⁴⁺ ion at m/z 697. Single stars represent singly Pt(dien)-modified fragments; double stars represent doubly Pt(dien)-modified fragments.