Electronic Supplementary Information (ESI)

Effect of alkali ions on optical properties of flavins: Vibronic spectra of cryogenic M^+lumichrome ions (M=Li-Cs) in the gas phase

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Figure S1. Experimental VISPD spectra of the $S_1 \leftarrow S_0$ transition of M^+LC (M=H, Li-Cs). The spectra of H^+LC and Li^+LC are recorded with the OPO laser, while the dye laser is used for the spectra of M^+LC with M=Na-Cs.

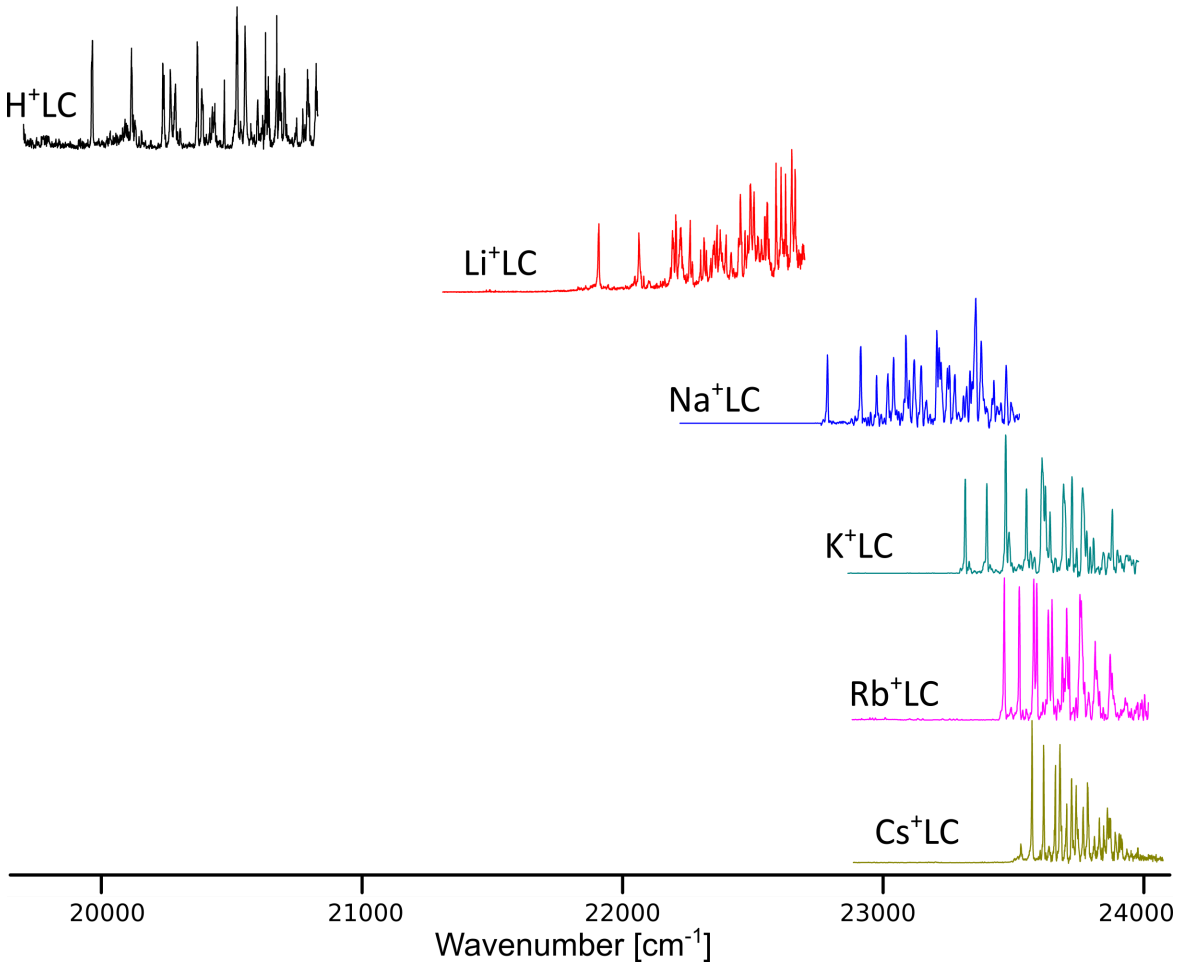


Figure S2. Experimental VISPD spectra of the $S_1 \leftarrow S_0$ transition of Cs^+LC recorded for ion trap temperatures of 25, 50, and 100 K. The Franck-Condon analysis of the intensities of the S_1 origin (0^0), the hot band and fundamental of the the in-plane Cs^+...LC bend (-42 and +45 cm^{-1}) yields a vibrational temperature of 29±3 K for a nominal trap temperature measured as 25±1 K.

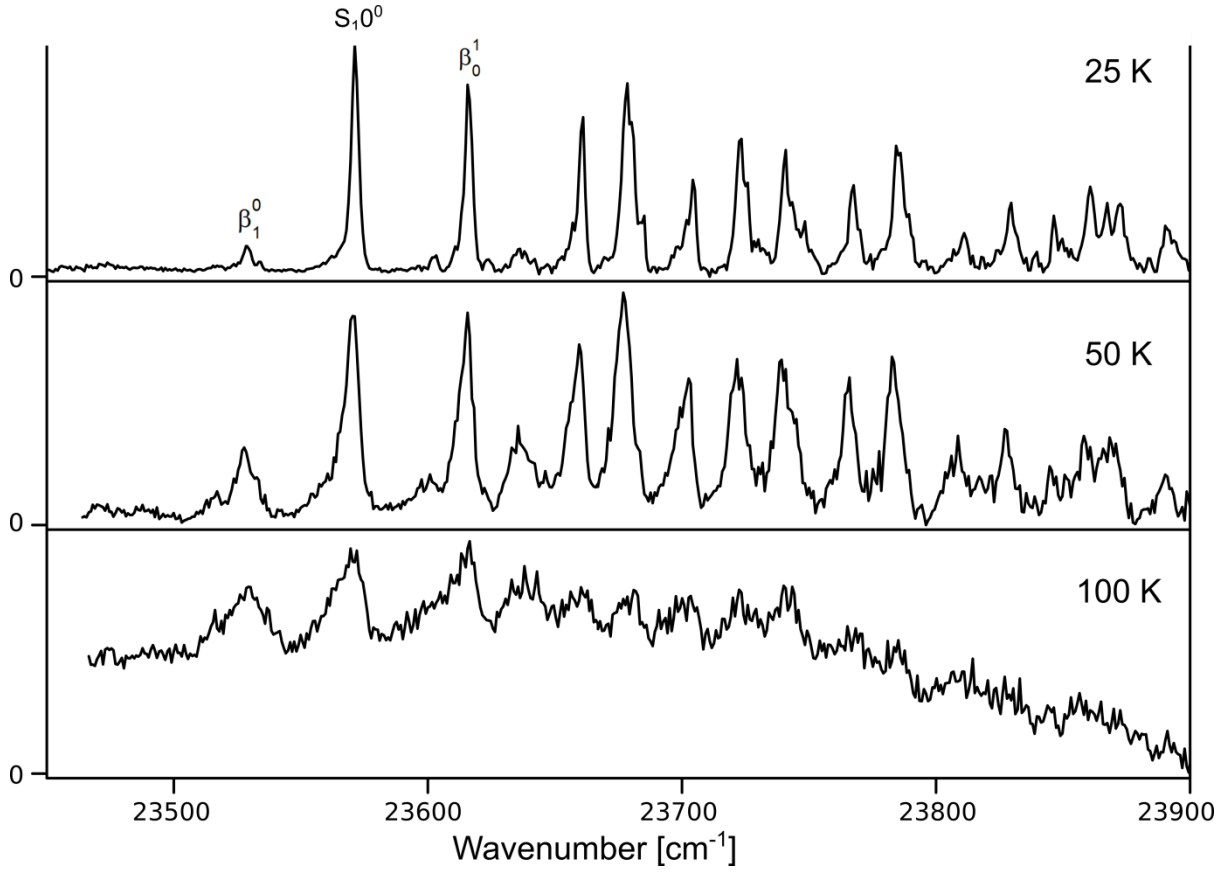
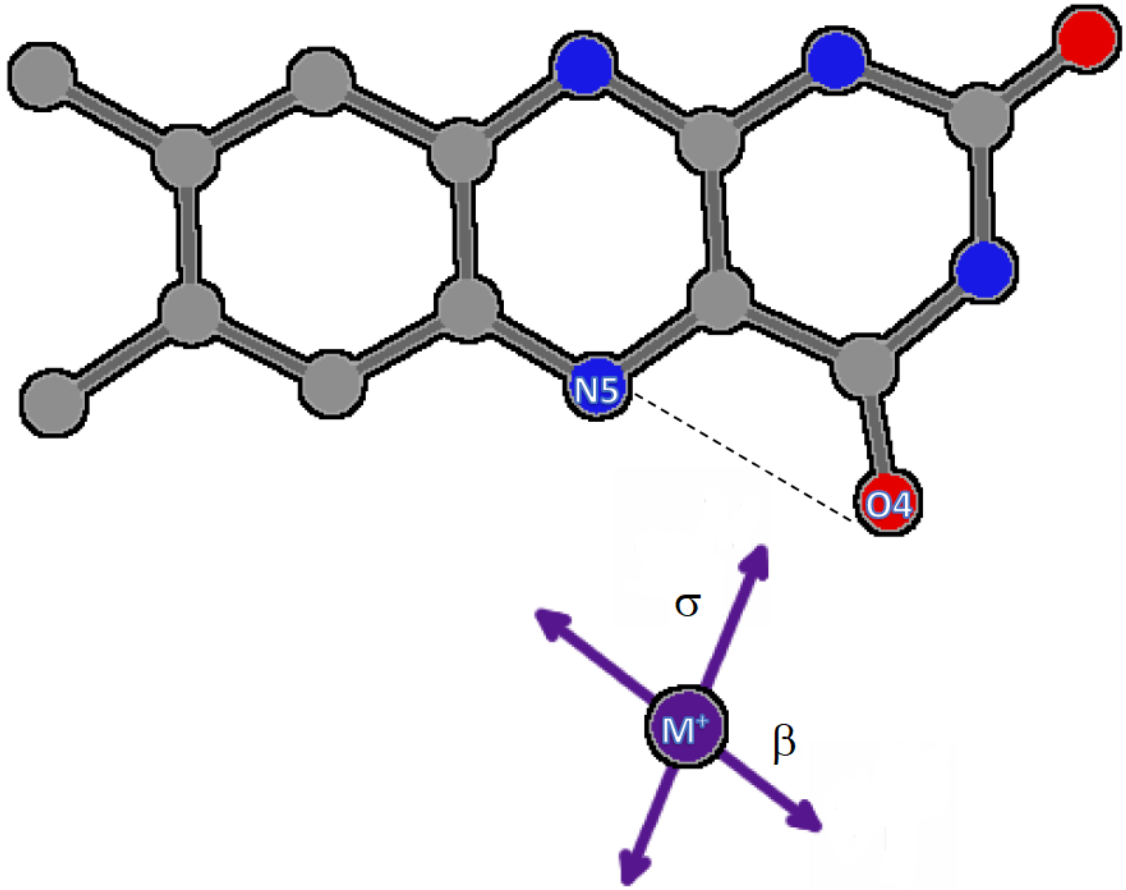
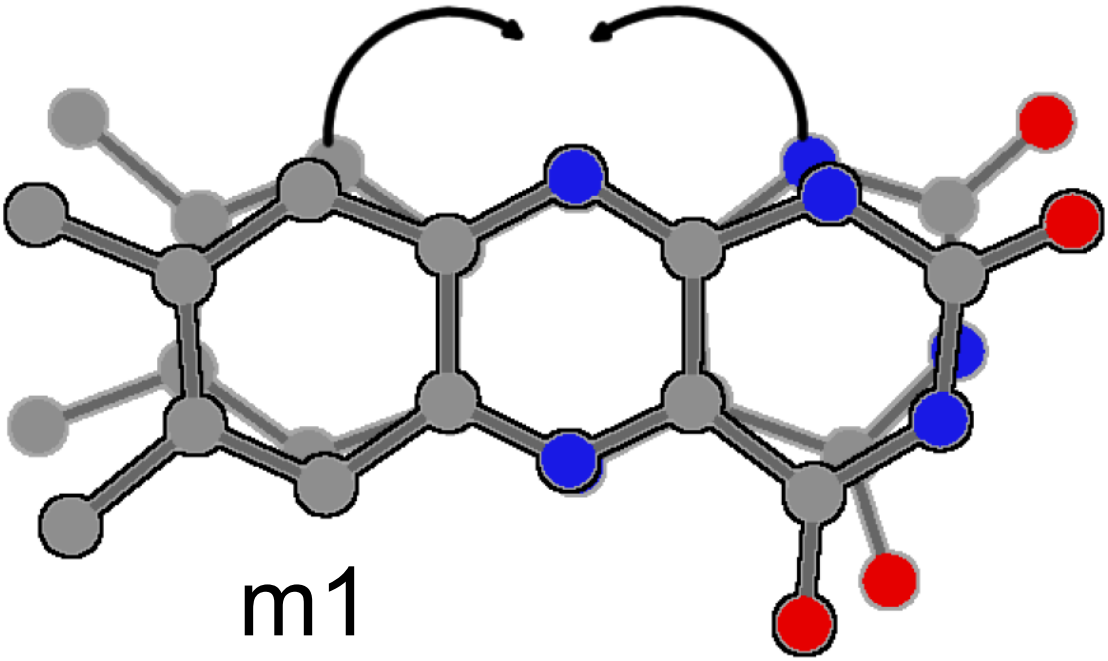


Figure S3. Schematic representation of relevant low-frequency in-plane normal coordinates in the S_1 state of $Cs^+LC(O4)$ calculated at the PBE0/cc-pVDZ level. Hydrogen atoms are omitted for the sake of simplicity. Similarly, the metal ion is not shown for vibrations of the LC moiety. Shown are the structures for maximum positive and maximum negative elongation. The arrows indicate major movements. Labels used in Table 3 are indicated.

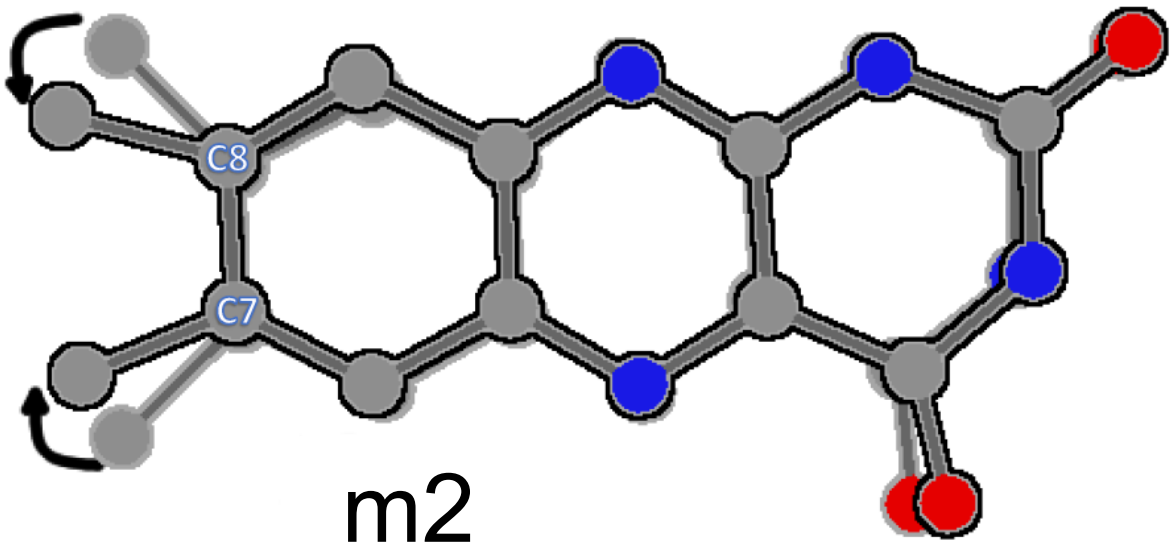
(a) modes 53 and 52



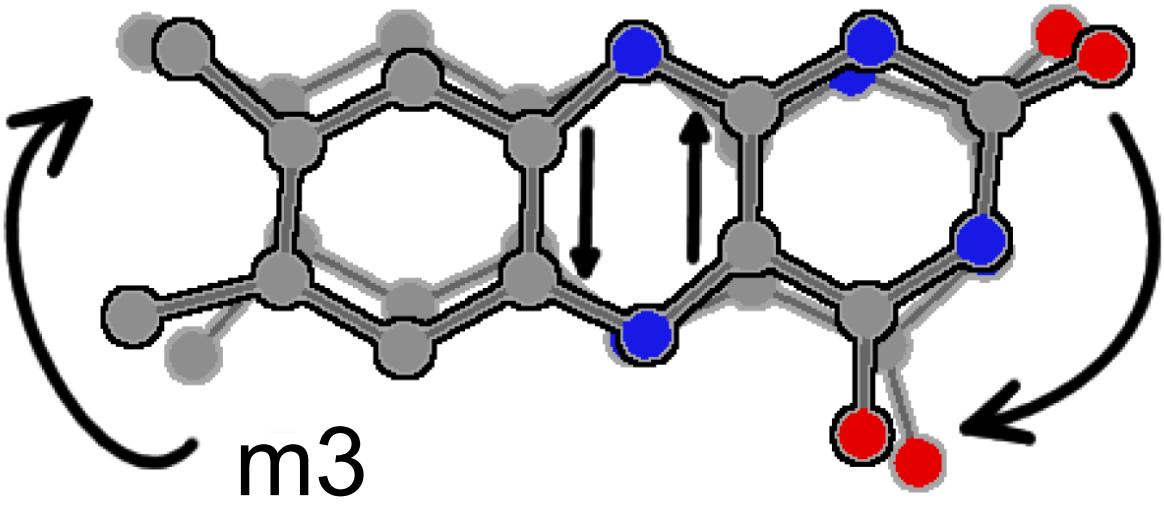
(b) mode 51



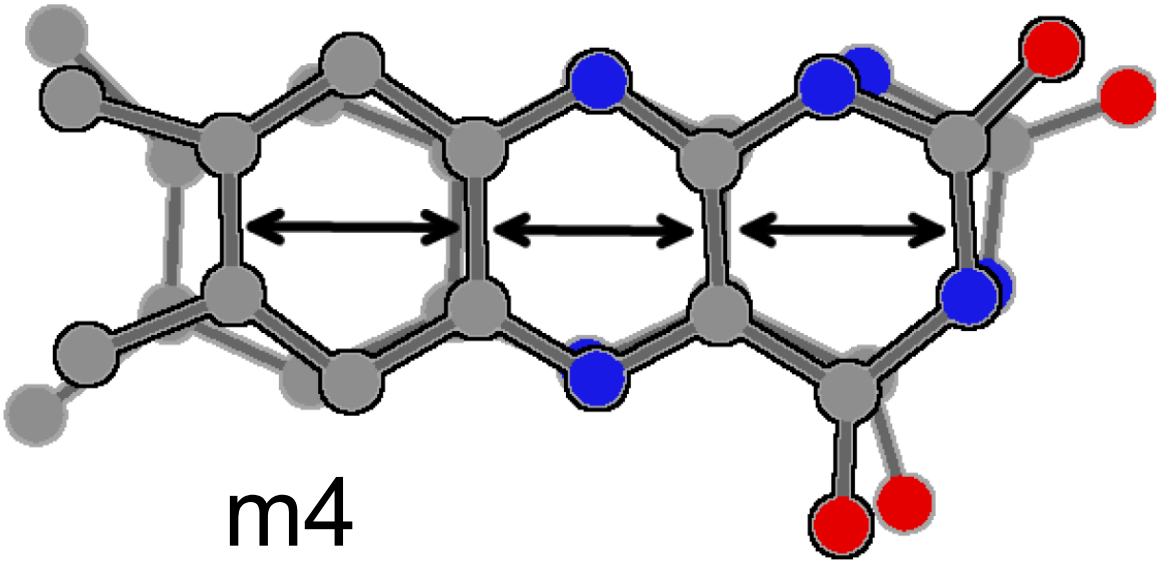
(c) mode 50



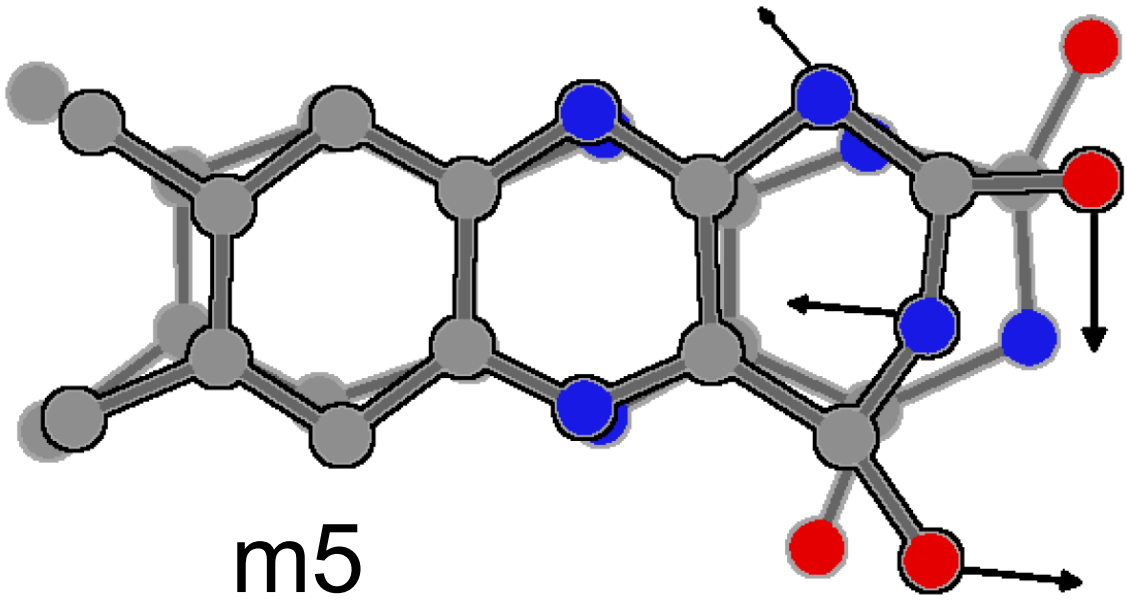
(d) mode 49



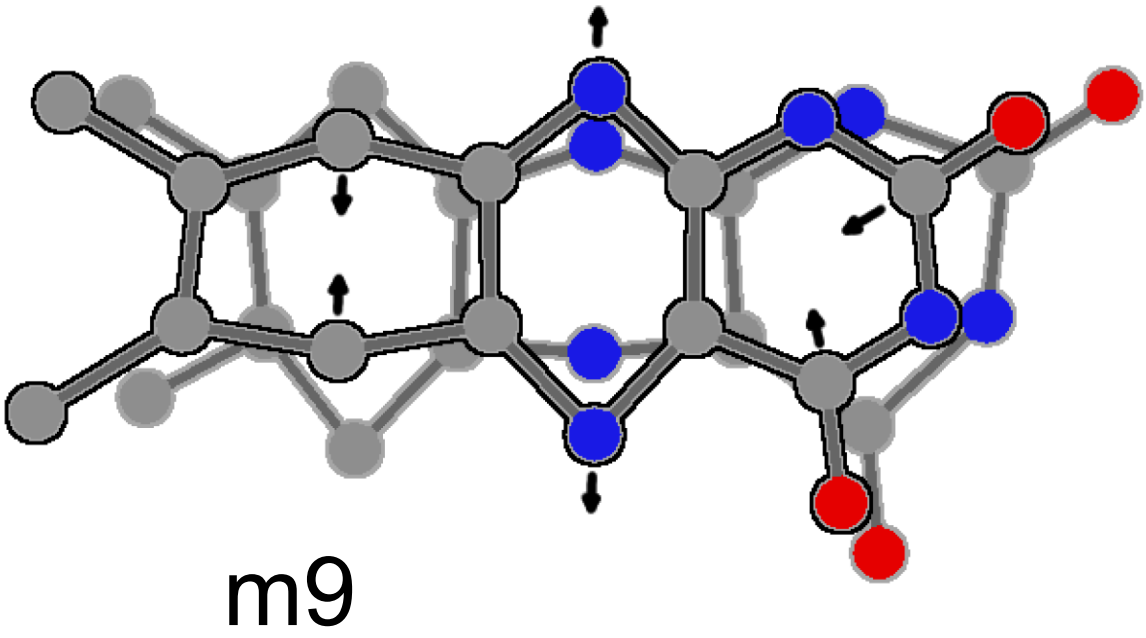
(e) mode 48



(f) mode 47



(g) mode 43



(h) mode 42

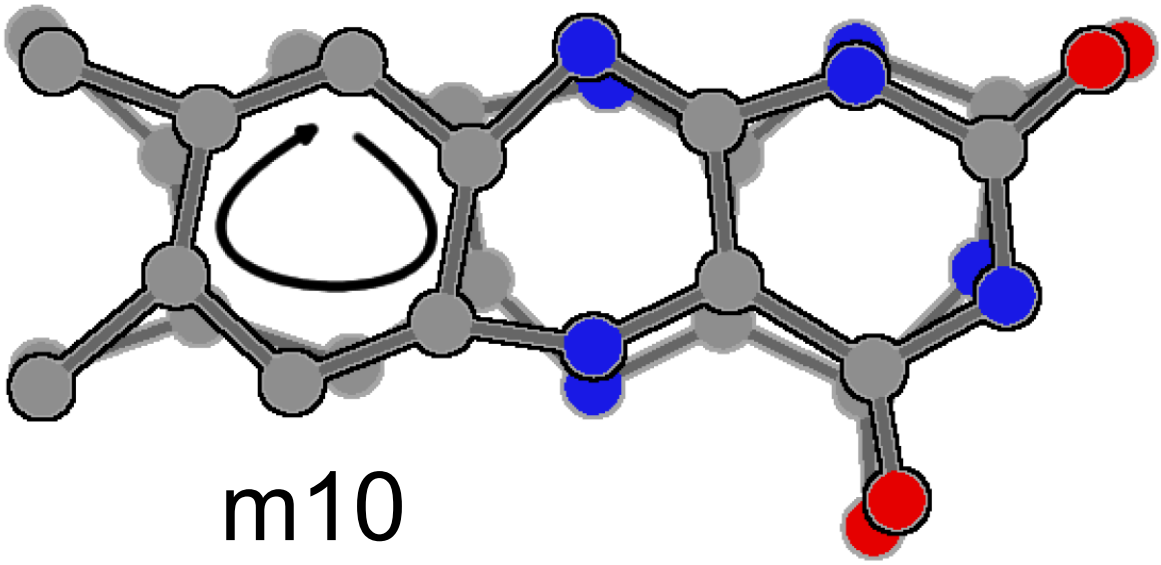
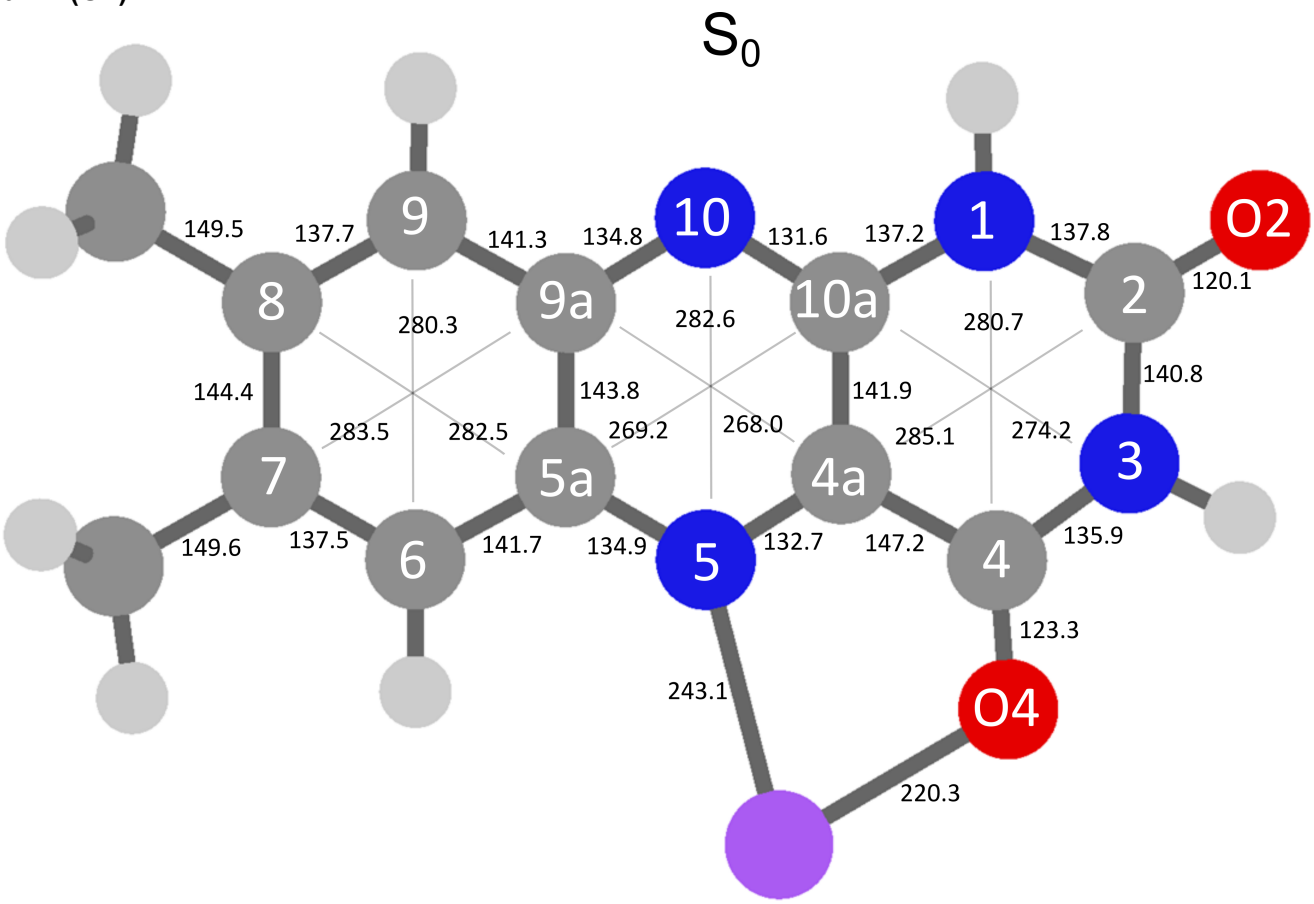
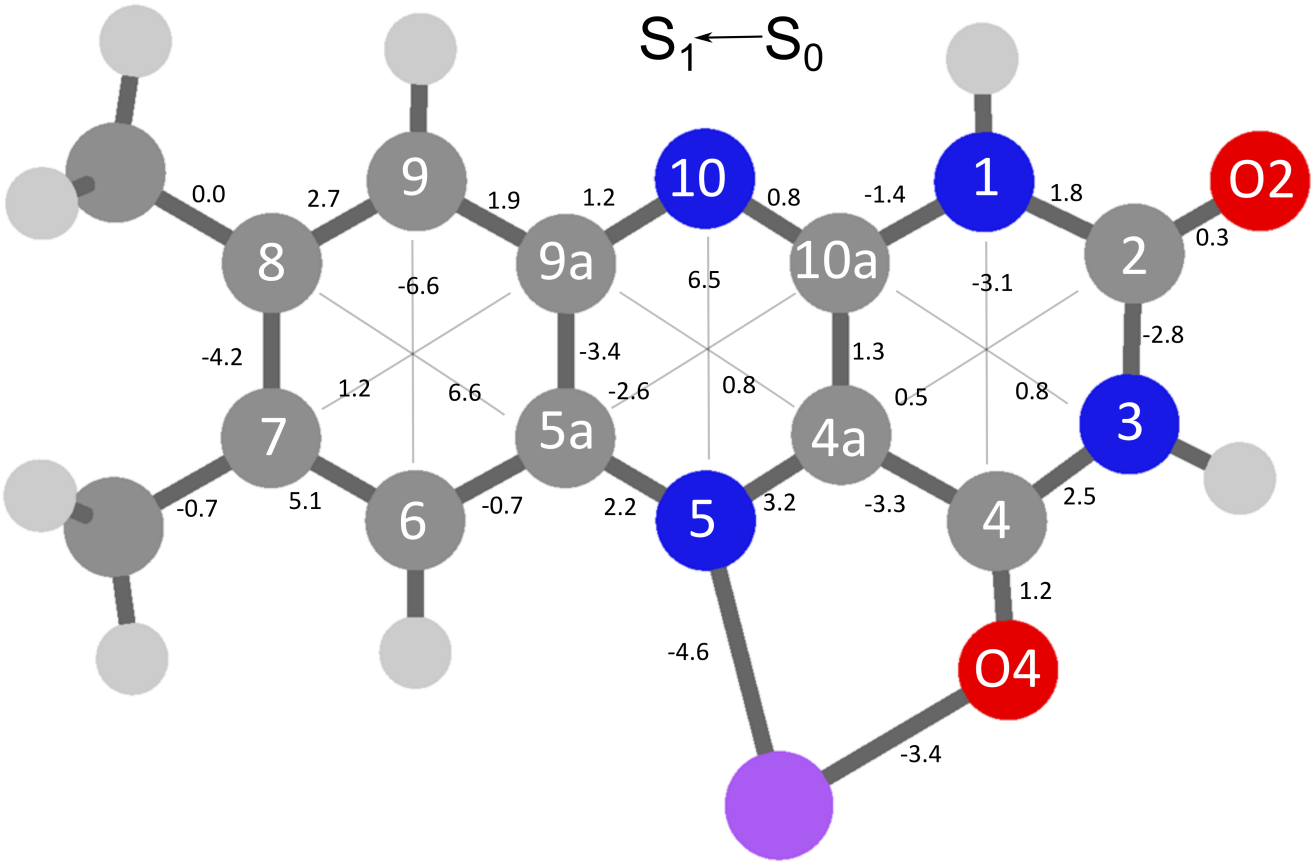


Figure S4. Ground state S_0 (top, absolute distances) and S_1 excited state geometries (bottom, distances relative to S_0) of $M^+LC(O4)$ calculated at the PBE0/cc-pVDZ level. All values are given in pm. Positive values correspond to elongations; negative values indicate contractions upon S_1 excitation.

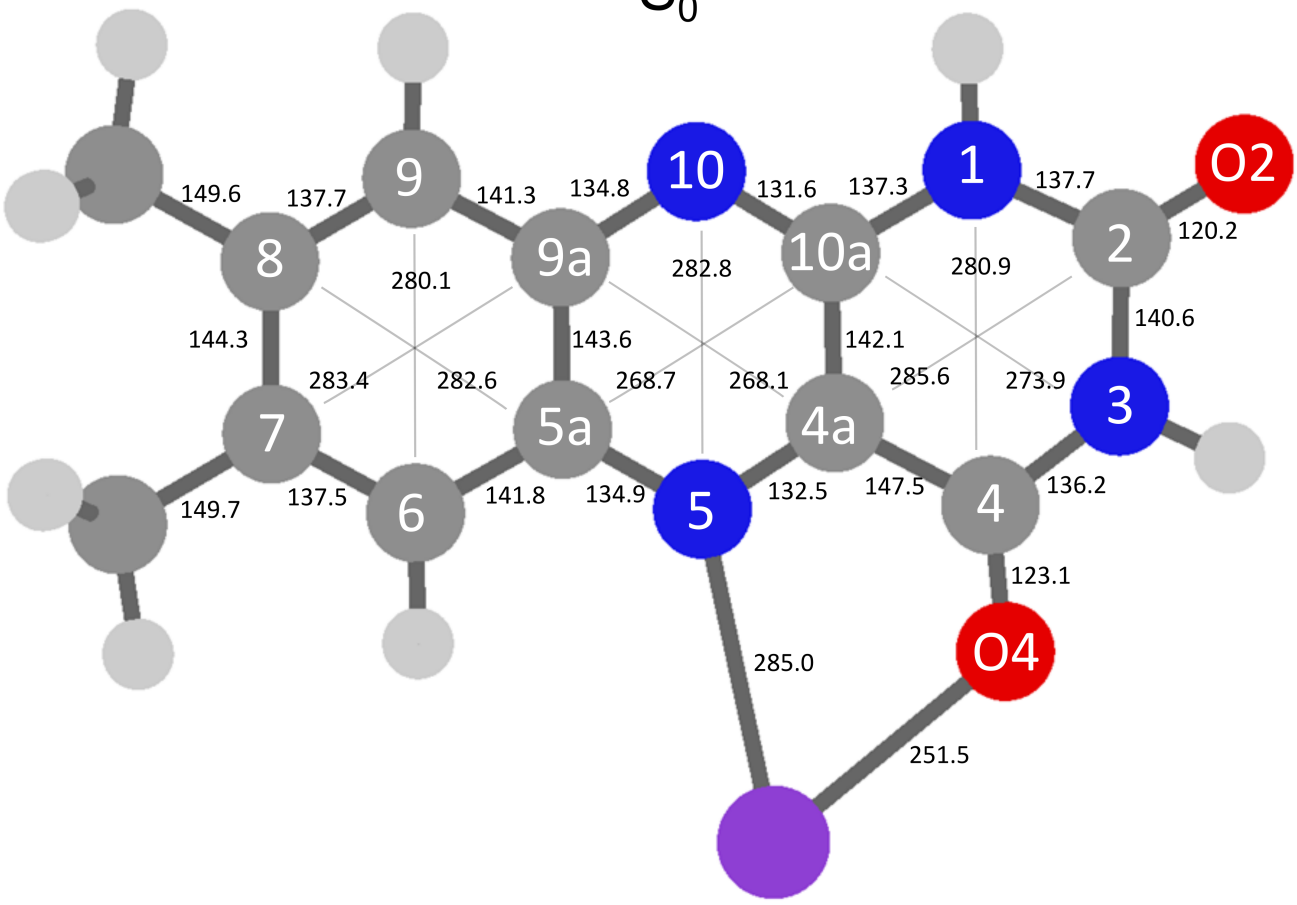
$Na^+LC(O4)$



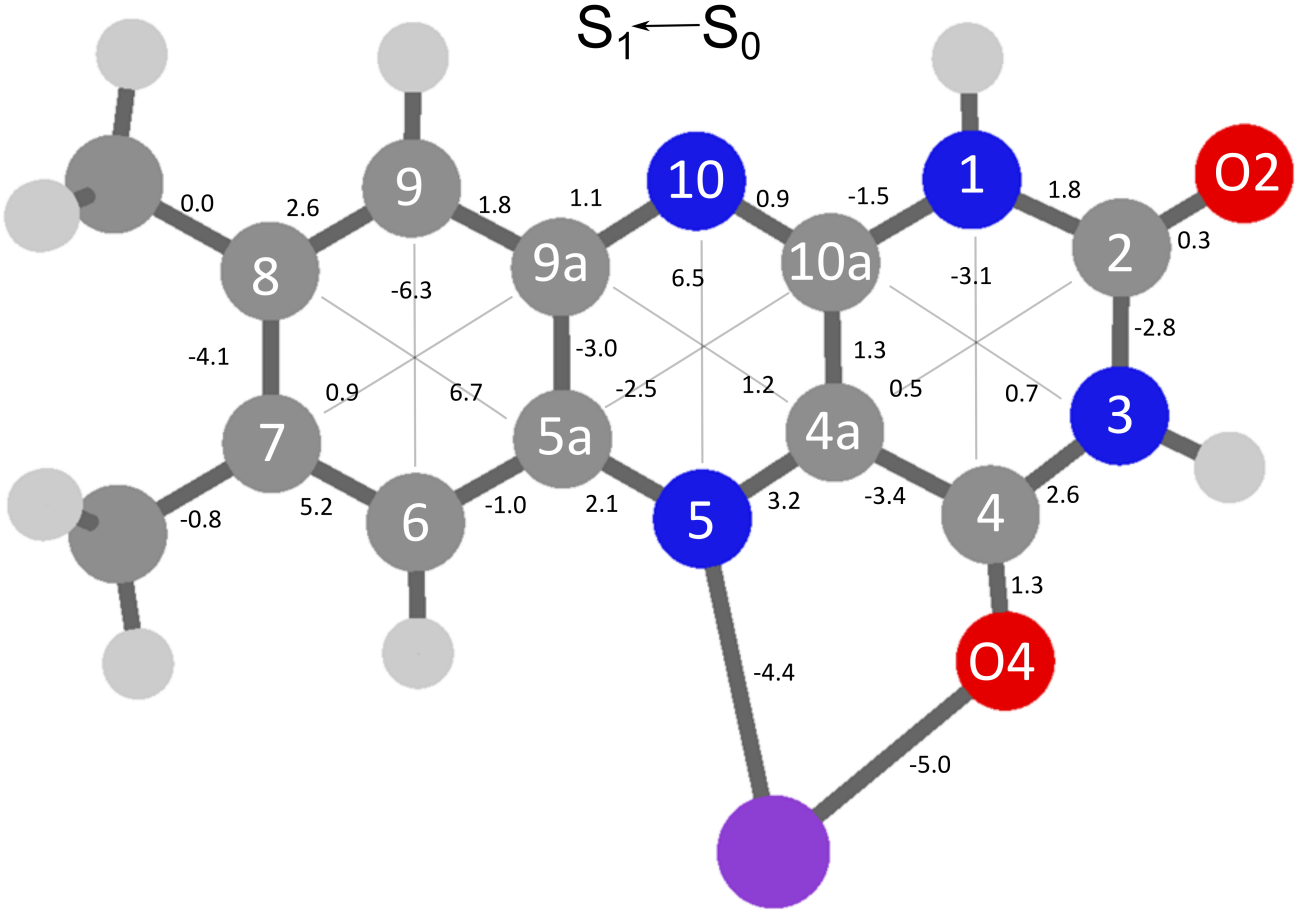


$K^+LC(O4)$

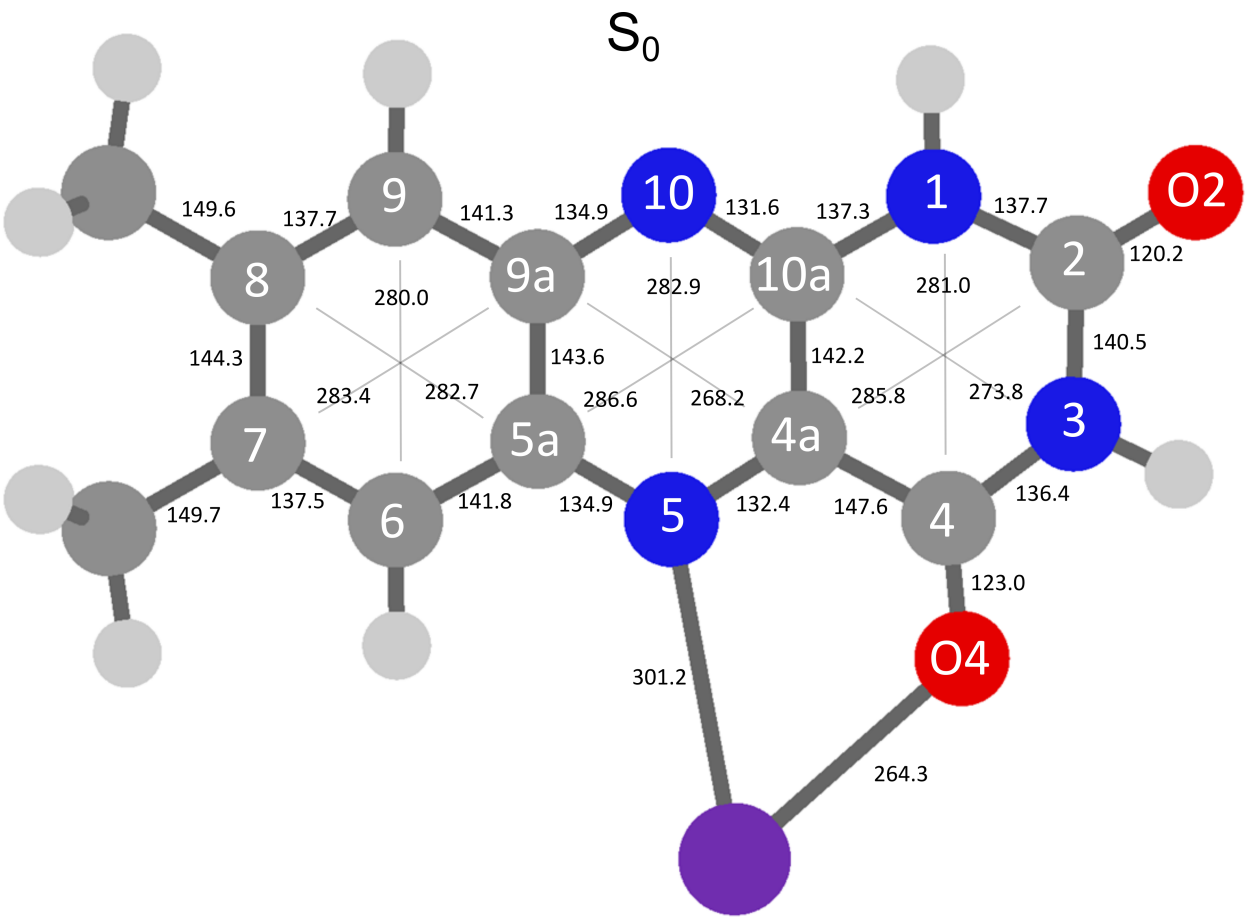
S_0

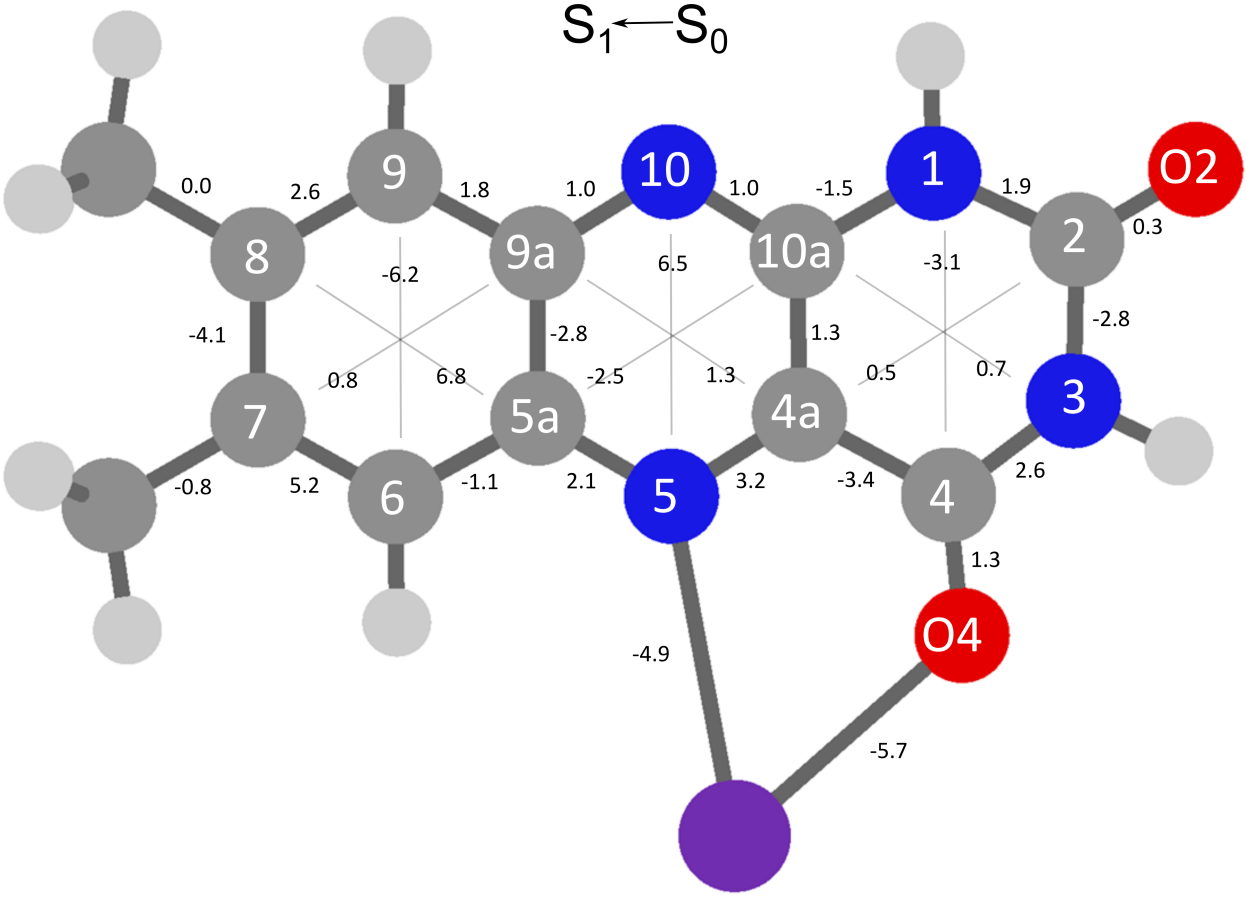


$S_1 \leftarrow S_0$

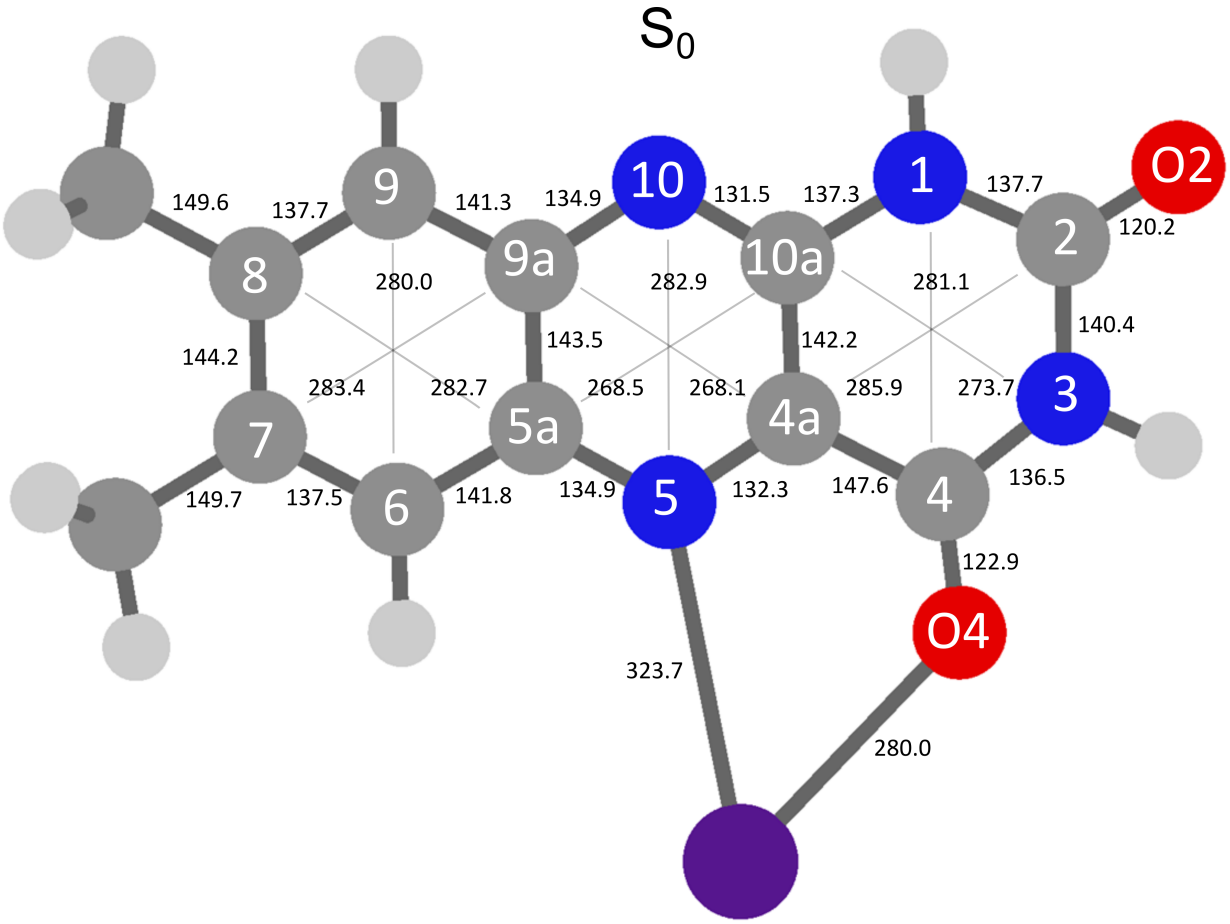


$Rb^{+}LC(O4)$


S0
149.6
137.7
141.3
134.9
131.6
137.3
137.7
120.2
280.0
282.9
281.0
144.3
143.6
142.2
140.5
283.4
282.7
286.6
268.2
285.8
273.8
149.7
137.5
141.8
134.9
132.4
147.6
136.4
123.0
301.2
264.3
O2
O4
1
2
3
4
5
6
7
8
9
10
9a
10a
5a
4a


S1←S0
0.0
2.6
1.8
1.0
1.0
-1.5
1.9
0.3
-6.2
6.5
-3.1
-4.1
-2.8
1.3
-2.8
0.8
6.8
-2.5
1.3
0.5
0.7
-0.8
5.2
-1.1
2.1
3.2
-3.4
2.6
1.3
-4.9
-5.7
O2
O4
1
2
3
4
5
6
7
8
9
10
9a
10a
5a
4a

$Cs^{+}LC(O4)$


S0
149.6
137.7
141.3
134.9
131.5
137.3
137.7
120.2
140.4
144.2
280.0
282.9
281.1
143.5
142.2
283.4
282.7
268.5
268.1
285.9
273.7
149.7
137.5
141.8
134.9
132.3
147.6
136.5
122.9
323.7
280.0
O2
O4
1
2
3
4
5
6
7
8
9
10
9a
10a
4a
5a

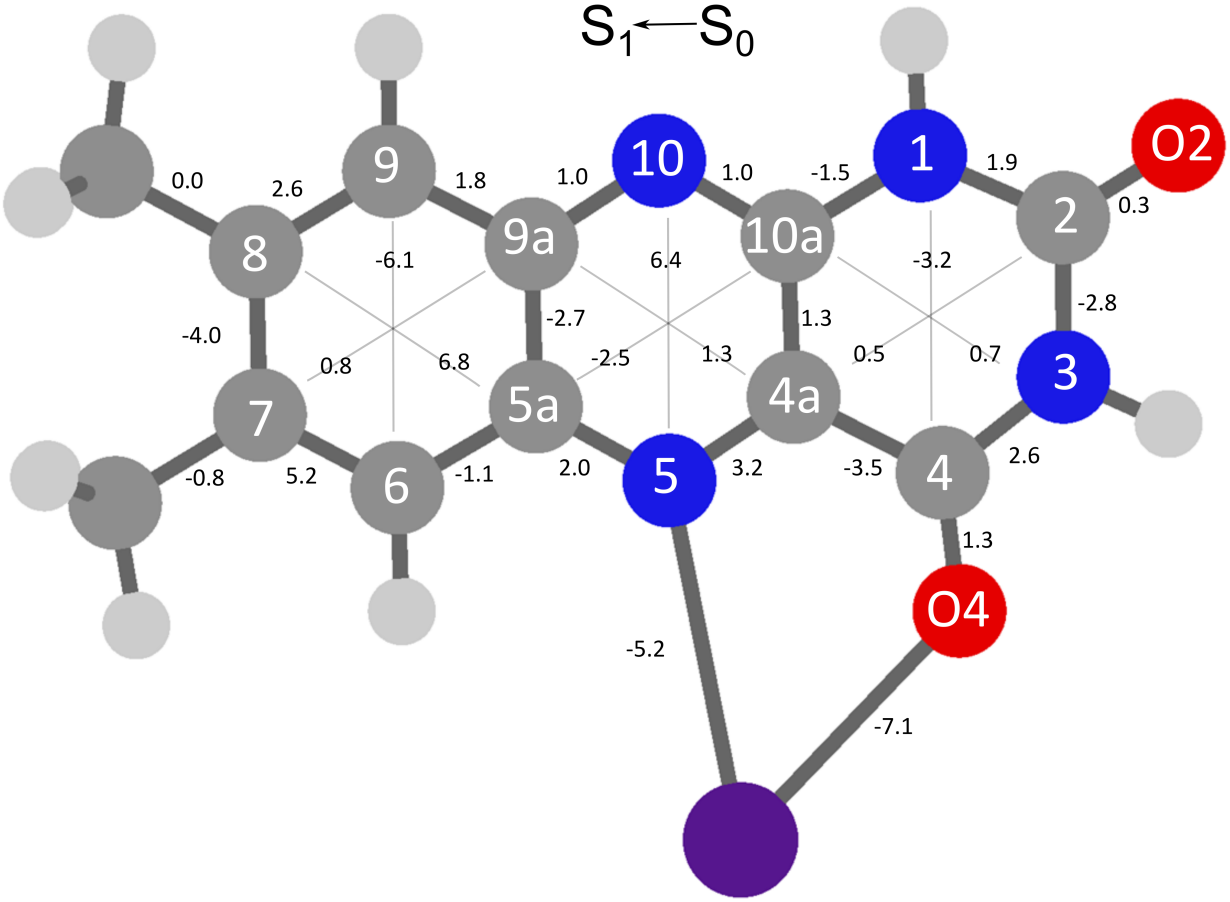

S1←S0
0.0
2.6
1.8
1.0
1.0
-1.5
1.9
0.3
-2.8
-4.0
-6.1
6.4
-3.2
-2.7
1.3
0.8
6.8
-2.5
1.3
0.5
0.7
-0.8
5.2
-1.1
2.0
3.2
-3.5
2.6
1.3
-5.2
-7.1
O2
O4
1
2
3
4
5
6
7
8
9
10
9a
10a
4a
5a

Table S1. Experimental frequencies for vibronic transitions (in cm^{-1}) observed in the VISPD spectrum of the S_1 state of M^+LC compared to harmonic frequencies of the $M^+LC(O4)$ isomer computed at the PBE0/cc-pVDZ level, along with the mode assignment.

(a) $Li^+LC(O4)$

Band	ν (exp)	ν (calc)	Assignment
	21911	20757	0^0
A	157	161	m1
B	288	307	m3
C	299	314	m4
D	319	322	2m1
E	350	373	β
F	403	418	m5
G	470	468	m1+m3
H	454	475	m1+m4
I	466	483	3m1
J	507	534	m1+β
K	548	569	m10
L	561	579	m1+ m5
M	581	607	m9
N	595	615	σ

(b) $Na^{+}LC(O4)$

Band	ν (exp)	ν (calc)	Assignment
	22786	21817	0^{0}
A	128	132	β
B	189	195	m1
C	232	240	σ
D	254	264	2β
E	301	307	m3
F	314	327	m1+β
G	333	342	m4
H	360	372	σ+β
I	379	396	3β
J	420	428	m5
K	429	435 439	m1+σ m3+β
L	436 443	445 459	m6 m1+2β
M	460	474	m4+β
N	468	480	2σ
O	489	504	σ+2β
P	522	537	m1+m4
Q	534	538	m8
R	547	560	m5+β
S	569	582	m9
T	590	601	m10

(c) $K^+LC(O4)$

Band	ν (exp)	ν (calc)	assignment
	23315	22360	0^0
A	83	86	β
B	155	161	σ
C	168	172	2β
D	235	247	σ+β
E	295	303	m3
F	308	322	2σ
G	325	328 333	m4 σ+2β
H	377	389	m3+β
I	410	408 419 419	2σ+β σ+3β m5
J	450	464	m3+σ
K	466	476 475	m7 m3+2β
L	480	489	m4+σ
M	492	505	m5+β
N	565	579 580	m9 m5+σ

(d) $Rb^{+}LC(O4)$

Band	ν (exp)	ν (calc)	assignment
	23465	22584	0^{0}
A	57	60	β
B	113	120	2β
C	125	132	σ
D	169 Shoulder: 182	180 180	3β m1
E	183	192	σ+β
F	223 Shoulder:230	240 240	m1+β 4β
G	239	252	σ+2β
H	249	264	2σ
I	293	301 312 312	m3 m1+σ σ+3β
J	323	324 325	2σ+β m4

(e) $Cs^{+}LC(O4)$

Band	ν (exp)	ν (calc)	assignment
	23571	22717	0^{0}
A	45	45	β
B	90	90	2β
C	108	114	σ
D	133	135	3β
E	152	159	σ+β
F	170	174	m1
G	196	204	σ+2β
H	214	228	2σ
I	240	249	σ+3β

Table S2. Calculated vibrations (in cm^{-1}) for the S_0 and S_1 states of the $M^+LC(O4)$ isomers, $H^+LC(N5)$, and LC.

(a) $Li^+LC(O4)$

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
159.4	53	56.1	81	161.3	53	54.2	81
293.7	52	67.1	80	280.4	52	66.2	80
310.2	51	120.2	79	306.5	51	102.0	79
325.3	50	136.7	78	313.8	50	117.9	78
354.3	49	149.0	77	372.9	49	137.7	77
414.1	48	171.0	76	417.9	48	153.7	76
446.0	47	200.2	75	445.5	47	169.4	75
481.0	46	203.8	74	480.0	46	205.1	74
496.5	45	252.5	73	504.6	45	226.6	73
568.1	44	315.0	72	568.6	44	292.0	72
598.4	43	392.5	71	607.0	43	346.9	71
622.7	42	466.8	70	615.0	42	380.6	70
661.8	41	517.1	69	659.6	41	454.4	69
710.9	40	625.4	68	711.8	40	590.7	68
754.1	39	645.3	67	763.1	39	619.2	67
806.6	38	681.3	66	810.4	38	668.7	66
858.7	37	733.7	65	856.9	37	689.8	65
903.7	36	774.6	64	905.6	36	716.2	64
1005.7	35	791.4	63	1001.3	35	767.0	63
1017.9	34	835.2	62	1010.6	34	784.6	62
1026.7	33	872.6	61	1021.6	33	884.0	61
1170.3	32	914.2	60	1156.7	32	903.4	60
1185.7	31	1031.6	59	1178.4	31	1005.2	59
1220.7	30	1051.7	58	1222.6	30	1037.7	58
1257.2	29	1438.8	57	1236.8	29	1429.5	57
1286.0	28	1454.4	56	1274.0	28	1448.1	56
1315.9	27	3134.9	55	1296.4	27	3112.5	55
1340.2	26	3137.4	54	1330.6	26	3129.6	54
1380.2	25			1349.8	25		
1387.9	24			1353.5	24		
1392.1	23			1375.3	23		
1399.4	22			1389.2	22		
1427.7	21			1392.6	21		
1433.3	20			1429.5	20		
1457.1	19			1446.0	19		
1467.3	18			1460.0	18		
1488.5	17			1472.1	17		
1529.0	16			1496.8	16		
1547.5	15			1510.8	15		
1576.0	14			1576.9	14		
1641.4	13			1595.3	13		
1643.6	12			1625.1	12		
1709.3	11			1691.6	11		
1758.9	10			1710.6	10		
1906.5	9			1878.0	9		
3062.4	8			3047.2	8		
3063.5	7			3057.9	7		
3175.8	6			3179.8	6		
3182.5	5			3181.2	5		
3202.1	4			3208.0	4		
3233.8	3			3224.5	3		
3592.5	2			3602.7	2		
3613.6	1			3619.2	1		

(b) $Na^{+}LC(O4)$

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
123.2	53	50.1	81	132.1	53	48.1	81
186.8	52	64.8	80	194.8	52	63.6	80
232.8	51	78.9	79	239.5	51	73.4	79
303.1	50	126.8	78	288.7	50	102.1	78
314.2	49	138.7	77	306.5	49	126.4	77
343.9	48	166.6	76	341.8	48	146.0	76
428.1	47	176.6	75	427.8	47	162.0	75
444.8	46	200.5	74	445.4	46	175.4	74
478.9	45	253.9	73	476.9	45	223.4	73
541.3	44	316.0	72	538.2	44	290.8	72
585.7	43	391.9	71	582.1	43	343.1	71
615.7	42	466.0	70	601.0	42	380.8	70
656.6	41	512.6	69	653.7	41	448.0	69
703.4	40	625.0	68	699.7	40	592.9	68
754.8	39	646.3	67	759.0	39	617.9	67
804.6	38	681.3	66	780.6	38	671.0	66
854.6	37	733.0	65	848.7	37	691.5	65
901.4	36	773.7	64	903.5	36	715.8	64
1007.0	35	790.9	63	1001.9	35	767.5	63
1022.8	34	835.3	62	1010.3	34	806.7	62
1027.0	33	867.9	61	1027.0	33	880.9	61
1168.4	32	914.8	60	1156.1	32	902.5	60
1177.7	31	1031.8	59	1169.7	31	1004.7	59
1217.6	30	1052.6	58	1219.4	30	1038.4	58
1254.9	29	1439.5	57	1235.9	29	1430.1	57
1288.8	28	1455.2	56	1266.2	28	1449.5	56
1313.9	27	3134.3	55	1291.4	27	3111.8	55
1337.1	26	3136.8	54	1325.2	26	3129.2	54
1375.4	25			1352.4	25		
1388.3	24			1357.7	24		
1394.9	23			1375.4	23		
1403.0	22			1391.1	22		
1427.5	21			1395.7	21		
1434.4	20			1426.4	20		
1456.7	19			1446.0	19		
1465.8	18			1456.1	18		
1479.9	17			1467.5	17		
1527.6	16			1493.7	16		
1544.8	15			1500.1	15		
1572.5	14			1574.0	14		
1638.6	13			1582.7	13		
1646.4	12			1614.4	12		
1710.5	11			1679.4	11		
1773.6	10			1720.5	10		
1902.8	9			1871.3	9		
3062.0	8			3046.8	8		
3062.8	7			3057.7	7		
3172.6	6			3177.4	6		
3181.2	5			3179.6	5		
3193.5	4			3202.2	4		
3232.3	3			3223.2	3		
3600.0	2			3602.7	2		
3617.2	1			3625.3	1		

(c) $K^+LC(O4)$

S_0				S_1			
v	sym(a')	v	sym (a")	v	sym(a')	v	sym (a")
78.9	53	38.9	81	86.0	53	37.0	81
156.1	52	60.0	80	160.7	52	59.5	80
189.5	51	67.4	79	198.7	51	62.5	79
298.6	50	125.0	78	285.0	50	101.9	78
309.4	49	138.4	77	302.5	49	124.7	77
336.0	48	161.1	76	328.4	48	144.8	76
418.8	47	172.6	75	418.6	47	155.7	75
440.3	46	199.1	74	436.6	46	170.6	74
478.0	45	253.4	73	475.7	45	221.8	73
539.0	44	315.8	72	535.0	44	287.4	72
584.7	43	391.1	71	578.5	43	337.6	71
613.0	42	464.9	70	598.3	42	380.1	70
654.6	41	509.0	69	651.1	41	441.5	69
701.3	40	624.1	68	696.9	40	593.4	68
754.7	39	646.1	67	756.3	39	615.2	67
804.2	38	680.9	66	805.6	38	668.4	66
852.2	37	731.4	65	844.3	37	691.0	65
900.0	36	772.7	64	902.1	36	713.5	64
1006.8	35	790.4	63	1001.6	35	767.1	63
1024.1	34	835.5	62	1009.9	34	779.3	62
1027.3	33	867.4	61	1028.3	33	878.6	61
1167.0	32	914.3	60	1155.4	32	900.8	60
1174.2	31	1031.9	59	1165.0	31	1004.4	59
1215.2	30	1052.9	58	1216.1	30	1038.8	58
1253.0	29	1439.8	57	1235.5	29	1430.5	57
1288.7	28	1455.4	56	1261.6	28	1450.2	56
1312.5	27	3133.5	55	1288.7	27	3111.1	55
1335.0	26	3135.8	54	1321.6	26	3128.7	54
1372.2	25			1352.0	25		
1388.3	24			1361.6	24		
1395.3	23			1375.4	23		
1404.0	22			1391.2	22		
1427.1	21			1395.8	21		
1434.3	20			1424.7	20		
1455.9	19			1446.1	19		
1464.2	18			1453.8	18		
1478.4	17			1466.1	17		
1526.7	16			1490.6	16		
1543.0	15			1500.5	15		
1570.7	14			1571.8	14		
1636.8	13			1575.5	13		
1648.4	12			1610.6	12		
1711.2	11			1671.8	11		
1771.5	10			1717.5	10		
1900.2	9			1867.9	9		
3061.4	8			3046.3	8		
3061.9	7			3057.3	7		
3170.2	6			3175.8	6		
3180.0	5			3178.3	5		
3193.7	4			3202.2	4		
3230.6	3			3222.1	3		
3603.1	2			3603.0	2		
3619.0	1			3628.2	1		

(d) $Rb^{+}LC(O4)$

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
54.9	53	33.1	81	59.8	53	31.5	81
122.4	52	58.1	80	131.5	52	57.6	80
175.9	51	66.8	79	179.6	51	62.4	79
296.8	50	124.8	78	283.4	50	100.3	78
308.3	49	138.3	77	301.4	49	124.8	77
334.0	48	158.8	76	324.6	48	144.6	76
416.4	47	172.0	75	415.8	47	153.8	75
439.8	46	199.1	74	435.1	46	170.1	74
477.8	45	253.6	73	475.3	45	221.0	73
538.2	44	316.0	72	533.9	44	286.1	72
584.4	43	391.1	71	577.2	43	336.5	71
612.4	42	464.6	70	597.7	42	379.8	70
654.3	41	508.7	69	650.8	41	440.6	69
700.7	40	623.8	68	696.0	40	593.5	68
754.9	39	646.1	67	755.4	39	614.3	67
804.0	38	680.5	66	805.2	38	668.3	66
851.9	37	730.8	65	843.5	37	691.1	65
899.8	36	772.3	64	901.7	36	712.9	64
1006.9	35	790.6	63	1001.5	35	767.1	63
1024.4	34	835.5	62	1009.8	34	778.3	62
1027.8	33	868.2	61	1028.7	33	878.2	61
1166.6	32	914.4	60	1155.1	32	900.3	60
1173.2	31	1032.1	59	1164.1	31	1004.1	59
1214.3	30	1053.1	58	1215.4	30	1038.9	58
1252.3	29	1440.0	57	1235.5	29	1430.4	57
1289.2	28	1455.7	56	1260.7	28	1450.7	56
1312.2	27	3133.3	55	1288.3	27	3110.8	55
1334.7	26	3135.5	54	1321.0	26	3128.5	54
1371.4	25			1352.3	25		
1388.4	24			1363.4	24		
1395.6	23			1375.0	23		
1404.7	22			1391.4	22		
1427.4	21			1396.1	21		
1434.4	20			1424.0	20		
1455.7	19			1446.0	19		
1463.6	18			1453.2	18		
1478.3	17			1465.7	17		
1526.6	16			1489.9	16		
1543.3	15			1500.8	15		
1570.3	14			1571.2	14		
1636.9	13			1573.2	13		
1649.5	12			1608.9	12		
1711.7	11			1670.0	11		
1776.5	10			1721.0	10		
1899.2	9			1866.8	9		
3061.3	8			3046.0	8		
3061.6	7			3057.3	7		
3169.4	6			3175.2	6		
3179.7	5			3178.0	5		
3195.6	4			3203.2	4		
3230.2	3			3221.6	3		
3605.5	2			3603.4	2		
3619.9	1			3629.8	1		

(e) $Cs^{+}LC(O4)$

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
42.0	53	29.4	81	45.2	53	28.8	81
103.7	52	57.5	80	113.5	52	56.9	80
171.4	51	66.6	79	173.5	51	62.0	79
295.6	50	124.7	78	282.7	50	101.6	78
307.6	49	138.6	77	300.7	49	124.3	77
332.9	48	157.9	76	322.4	48	144.8	76
414.3	47	171.7	75	413.2	47	153.1	75
439.3	46	199.2	74	434.3	46	169.5	74
477.7	45	253.7	73	475.2	45	221.0	73
537.5	44	316.0	72	532.9	44	285.0	72
584.1	43	391.2	71	576.1	43	335.5	71
611.8	42	464.5	70	597.2	42	380.2	70
653.8	41	508.1	69	650.3	41	440.3	69
700.1	40	623.6	68	695.4	40	593.5	68
754.9	39	646.1	67	754.7	39	613.2	67
804.0	38	680.7	66	805.3	38	667.4	66
851.2	37	730.8	65	842.5	37	690.8	65
899.5	36	772.2	64	901.9	36	712.5	64
1006.9	35	791.2	63	1001.4	35	767.0	63
1024.3	34	836.2	62	1009.6	34	778.8	62
1028.0	33	869.1	61	1028.8	33	878.8	61
1166.3	32	914.4	60	1155.1	32	899.9	60
1172.2	31	1032.1	59	1163.0	31	1004.1	59
1213.4	30	1053.3	58	1214.1	30	1039.1	58
1251.5	29	1440.2	57	1235.5	29	1430.7	57
1289.3	28	1455.9	56	1260.1	28	1450.9	56
1311.8	27	3133.1	55	1287.8	27	3110.5	55
1334.0	26	3135.1	54	1320.4	26	3128.4	54
1370.5	25			1352.2	25		
1388.4	24			1364.5	24		
1395.6	23			1374.9	23		
1404.7	22			1391.1	22		
1427.3	21			1395.9	21		
1434.3	20			1423.8	20		
1455.6	19			1446.3	19		
1463.3	18			1452.9	18		
1478.0	17			1465.7	17		
1526.3	16			1489.5	16		
1543.1	15			1501.1	15		
1569.9	14			1570.2	14		
1636.4	13			1571.9	13		
1650.0	12			1608.5	12		
1711.9	11			1668.2	11		
1774.7	10			1718.0	10		
1898.4	9			1866.3	9		
3061.0	8			3045.9	8		
3061.3	7			3057.2	7		
3168.7	6			3175.1	6		
3179.3	5			3177.6	5		
3197.8	4			3204.8	4		
3229.8	3			3221.6	3		
3607.1	2			3603.6	2		
3620.3	1			3631.2	1		

(f) LC

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
158.7	51	53.3	78	158.5	51	52.6	78
289.1	50	65.4	77	278.1	50	58.7	77
302.7	49	120.9	76	295.7	49	89.6	76
327.9	48	136.9	75	314.3	48	114.9	75
406.4	47	142.3	74	404.0	47	130.9	74
436.2	46	170.5	73	430.1	46	135.9	73
474.8	45	196.9	72	471.2	45	159.3	72
528.6	44	252.9	71	522.0	44	202.0	71
580.7	43	319.1	70	563.7	43	212.4	70
607.3	42	392.9	69	592.3	42	308.3	69
653.1	41	462.2	68	646.9	41	383.6	68
691.9	40	507.7	67	683.3	40	437.1	67
758.0	39	605.9	66	741.6	39	592.1	66
803.8	38	642.2	65	799.8	38	614.4	65
848.2	37	675.2	64	837.3	37	672.6	64
899.0	36	722.6	63	896.5	36	677.7	63
1006.0	35	770.0	62	998.3	35	719.9	62
1021.7	34	798.8	61	1006.3	34	768.1	61
1035.1	33	843.9	60	1027.2	33	775.8	60
1150.0	32	902.3	59	1131.5	32	872.4	59
1163.5	31	920.2	58	1156.4	31	904.0	58
1208.0	30	1035.5	57	1204.5	30	1003.8	57
1244.1	29	1056.6	56	1234.3	29	1039.2	56
1294.2	28	1443.3	55	1242.6	28	1433.7	55
1307.4	27	1458.9	54	1286.3	27	1453.6	54
1320.6	26	3122.4	53	1309.0	26	3101.5	53
1356.5	25	3124.5	52	1352.1	25	3114.6	52
1387.1	24			1371.4	24		
1396.1	23			1381.0	23		
1406.7	22			1390.2	22		
1427.0	21			1397.9	21		
1434.1	20			1418.1	20		
1450.2	19			1431.4	19		
1461.8	18			1451.7	18		
1480.6	17			1461.4	17		
1522.4	16			1478.3	16		
1545.5	15			1499.5	15		
1561.6	14			1538.1	14		
1638.9	13			1566.4	13		
1661.8	12			1573.0	12		
1715.3	11			1655.7	11		
1854.0	10			1800.0	10		
1871.3	9			1844.1	9		
3053.2	8			3039.6	8		
3054.4	7			3047.5	7		
3165.6	6			3163.6	6		
3167.3	5			3172.9	5		
3218.2	4			3210.6	4		
3220.7	3			3216.4	3		
3629.4	2			3618.4	2		
3642.1	1			3643.5	1		

(g) H^+LC (N5)

S_0				S_1			
v	sym(a')	v	sym (a'')	v	sym(a')	v	sym (a'')
152.8	53	56.8	81	153.1	53	53.4	81
282.6	52	68.3	80	273.9	52	67.3	80
304.5	51	121.5	79	289.0	51	104.7	79
329.7	50	134.8	78	314.7	50	121.7	78
412.9	49	158.1	77	411.7	49	142.2	77
431.6	48	169.0	76	430.8	48	155.1	76
473.6	47	200.1	75	471.5	47	172.7	75
525.3	46	246.5	74	519.9	46	220.1	74
572.8	45	314.2	73	569.8	45	287.3	73
609.5	44	391.1	72	598.6	44	329.6	72
651.4	43	439.7	71	649.2	43	369.2	71
694.8	42	489.6	70	690.9	42	424.1	70
749.0	41	612.9	69	759.5	41	585.6	69
798.0	40	635.4	68	800.5	40	617.2	68
847.4	39	664.5	67	850.4	39	632.9	67
898.7	38	720.0	66	895.4	38	672.6	66
1003.8	37	768.0	65	999.7	37	687.4	65
1013.7	36	773.4	64	1010.0	36	719.5	64
1025.0	35	815.6	63	1013.2	35	762.8	63
1151.5	34	861.4	62	1142.9	34	767.3	62
1175.9	33	910.2	61	1165.9	33	877.5	61
1210.7	32	929.0	60	1212.7	32	903.9	60
1257.2	31	1029.6	59	1227.2	31	1006.1	59
1265.8	30	1049.0	58	1269.1	30	1035.4	58
1310.2	29	1436.3	57	1287.5	29	1429.6	57
1341.1	28	1452.1	56	1301.1	28	1444.1	56
1375.4	27	3137.6	55	1342.7	27	3116.6	55
1385.3	26	3137.8	54	1353.6	26	3127.9	54
1386.8	25			1377.6	25		
1398.6	24			1381.1	24		
1406.2	23			1387.9	23		
1428.4	22			1418.2	22		
1438.0	21			1426.7	21		
1448.1	20			1443.9	20		
1462.2	19			1463.7	19		
1492.9	18			1480.6	18		
1531.3	17			1492.2	17		
1557.6	16			1545.0	16		
1602.8	15			1576.6	15		
1639.3	14			1601.1	14		
1693.1	13			1649.8	13		
1712.8	12			1726.7	12		
1846.5	11			1806.1	11		
1905.1	10			1863.7	10		
3063.9	9			3050.1	9		
3064.5	8			3056.1	8		
3183.3	7			3182.4	7		
3185.9	6			3184.8	6		
3214.9	5			3210.0	5		
3239.5	4			3228.0	4		
3455.3	3			3554.6	3		
3593.6	2			3600.2	2		
3615.4	1			3612.6	1		

Table S3. Optimized geometries for the S_0 and S_1 states of the $M^+LC(O4)$ isomers, $H^+LC(N5)$ and $H^+LC(O4)$, LC, and iso-LC.

(a) $Li^+LC(O4)$

S_0				S_1			
	x	y	z		x	y	z
C	-3.17	-0.46	0.00	C	-3.22	-0.44	0.00
C	-1.94	-1.08	0.00	C	-1.94	-1.06	0.00
C	-0.74	-0.34	0.00	C	-0.71	-0.36	0.00
C	-0.79	1.10	0.00	C	-0.77	1.04	0.00
C	-2.06	1.72	0.00	C	-2.06	1.67	0.00
C	-3.23	0.99	0.00	C	-3.28	0.97	0.00
C	1.47	1.22	0.00	C	1.47	1.19	0.00
C	1.54	-0.19	0.00	C	1.57	-0.23	0.00
C	2.85	-0.86	0.00	C	2.87	-0.85	0.00
C	3.91	1.38	0.00	C	3.92	1.37	0.00
H	-1.89	-2.17	0.00	H	-1.90	-2.16	0.00
H	-2.08	2.81	0.00	H	-2.07	2.76	0.00
H	4.85	-0.45	0.00	H	4.88	-0.43	0.00
H	2.59	2.94	0.00	H	2.57	2.92	0.00
N	0.32	1.86	0.00	N	0.32	1.85	0.00
N	2.64	1.93	0.00	N	2.62	1.90	0.00
N	3.92	-0.04	0.00	N	3.95	-0.01	0.00
N	0.46	-0.96	0.00	N	0.48	-1.04	0.00
O	2.95	-2.10	0.00	O	3.01	-2.10	0.00
O	4.92	2.01	0.00	O	4.90	2.07	0.00
C	-4.55	1.67	0.00	C	-4.58	1.69	0.00
H	-5.15	1.39	0.88	H	-5.19	1.43	0.88
H	-4.44	2.77	0.00	H	-4.44	2.78	0.00
H	-5.15	1.39	-0.88	H	-5.19	1.43	-0.88
C	-4.43	-1.25	0.00	C	-4.45	-1.27	0.00
H	-5.05	-1.02	0.88	H	-5.08	-1.04	0.88
H	-5.05	-1.02	-0.88	H	-5.08	-1.04	-0.88
H	-4.23	-2.33	0.00	H	-4.23	-2.34	0.00
Li	1.24	-2.87	0.00	Li	1.33	-2.86	0.00

(b) $Na^+LC(O4)$

S_0				S_1			
	x	y	z		x	y	z
C	-3.43	0.49	0.00	C	3.32	0.28	0.00
C	-2.21	1.13	0.00	C	2.02	0.86	0.00
C	-1.00	0.41	0.00	C	0.82	0.12	0.00
C	-1.04	-1.03	0.00	C	0.94	-1.28	0.00
C	-2.30	-1.67	0.00	C	2.25	-1.86	0.00
C	-3.47	-0.95	0.00	C	3.44	-1.12	0.00
C	1.22	-1.11	0.00	C	-1.30	-1.50	0.00
C	1.29	0.30	0.00	C	-1.46	-0.07	0.00
C	2.60	0.97	0.00	C	-2.80	0.48	0.00
C	3.66	-1.28	0.00	C	-3.73	-1.81	0.00
H	-2.17	2.22	0.00	H	1.95	1.95	0.00
H	-2.31	-2.76	0.00	H	2.29	-2.96	0.00
H	4.60	0.55	0.00	H	-4.78	-0.06	0.00
H	2.34	-2.84	0.00	H	-2.30	-3.28	0.00
N	0.08	-1.77	0.00	N	-0.13	-2.12	0.00
N	2.40	-1.83	0.00	N	-2.41	-2.27	0.00
N	3.67	0.13	0.00	N	-3.84	-0.44	0.00
N	0.19	1.05	0.00	N	-0.39	0.76	0.00
O	2.73	2.20	0.00	O	-3.05	1.70	0.00
O	4.68	-1.91	0.00	O	-4.67	-2.56	0.00
C	-4.79	-1.65	0.00	C	4.77	-1.79	0.00
H	-5.39	-1.38	-0.88	H	5.36	-1.51	0.88
H	-4.67	-2.74	0.00	H	4.66	-2.89	0.00
H	-5.39	-1.38	0.88	H	5.36	-1.51	-0.88
C	-4.71	1.28	0.00	C	4.52	1.16	0.00
H	-5.32	1.04	-0.88	H	5.16	0.96	0.88
H	-5.32	1.04	0.88	H	5.16	0.96	-0.88
H	-4.52	2.36	0.00	H	4.26	2.22	0.00
Na	0.88	3.38	0.00	Na	-1.29	2.97	0.00

(c) $K^+LC(O4)$

S_0				S_1			
	x	y	z		x	y	z
C	-3.46	0.38	0.00	C	-3.42	0.15	0.00
C	-2.22	0.97	0.00	C	-2.09	0.67	0.00
C	-1.03	0.20	0.00	C	-0.93	-0.14	0.00
C	-1.13	-1.23	0.00	C	-1.12	-1.53	0.00
C	-2.42	-1.82	0.00	C	-2.46	-2.04	0.00
C	-3.56	-1.06	0.00	C	-3.61	-1.24	0.00
C	1.13	-1.40	0.00	C	1.10	-1.86	0.00
C	1.24	0.02	0.00	C	1.34	-0.44	0.00
C	2.58	0.63	0.00	C	2.70	0.03	0.00
C	3.55	-1.66	0.00	C	3.51	-2.31	0.00
H	-2.14	2.06	0.00	H	-1.96	1.75	0.00
H	-2.47	-2.91	0.00	H	-2.56	-3.13	0.00
H	4.56	0.12	0.00	H	4.65	-0.62	0.00
H	2.17	-3.17	0.00	H	1.99	-3.70	0.00
N	-0.04	-2.02	0.00	N	-0.10	-2.42	0.00
N	2.27	-2.16	0.00	N	2.17	-2.70	0.00
N	3.62	-0.26	0.00	N	3.69	-0.94	0.00
N	0.18	0.80	0.00	N	0.31	0.44	0.00
O	2.78	1.84	0.00	O	3.03	1.23	0.00
O	4.54	-2.34	0.00	O	4.41	-3.12	0.00
C	-4.91	-1.71	0.00	C	-4.97	-1.84	0.00
H	-5.49	-1.41	-0.88	H	-5.55	-1.53	-0.88
H	-4.82	-2.80	0.00	H	-4.93	-2.94	0.00
H	-5.49	-1.41	0.88	H	-5.55	-1.53	0.88
C	-4.71	1.21	0.00	C	-4.57	1.09	0.00
H	-5.33	1.00	-0.88	H	-5.22	0.92	-0.88
H	-5.33	1.00	0.88	H	-5.22	0.92	0.88
H	-4.47	2.29	0.00	H	-4.25	2.14	0.00
K	0.93	3.55	0.00	K	1.36	3.04	0.00

(d) $Rb^+LC(O4)$

S_0				S_1			
	x	y	z		x	y	z
C	3.54	-0.03	0.00	C	-3.62	0.48	0.00
C	2.22	-0.41	0.00	C	-2.24	0.87	0.00
C	1.17	0.55	0.00	C	-1.16	-0.03	0.00
C	1.50	1.94	0.00	C	-1.48	-1.40	0.00
C	2.87	2.32	0.00	C	-2.86	-1.79	0.00
C	3.87	1.38	0.00	C	-3.93	-0.89	0.00
C	-0.70	2.48	0.00	C	0.70	-1.93	0.00
C	-1.04	1.10	0.00	C	1.07	-0.54	0.00
C	-2.47	0.71	0.00	C	2.47	-0.19	0.00
C	-3.05	3.14	0.00	C	3.06	-2.60	0.00
H	1.96	-1.47	0.00	H	-2.02	1.94	0.00
H	3.09	3.39	0.00	H	-3.05	-2.87	0.00
H	-4.33	1.54	0.00	H	4.35	-1.02	0.00
H	-1.44	4.40	0.00	H	1.42	-3.84	0.00
N	0.55	2.90	0.00	N	-0.54	-2.38	0.00
N	-1.70	3.42	0.00	N	1.69	-2.86	0.00
N	-3.34	1.76	0.00	N	3.36	-1.25	0.00
N	-0.12	0.15	0.00	N	0.12	0.43	0.00
O	-2.86	-0.45	0.00	O	2.91	0.97	0.00
O	-3.91	3.97	0.00	O	3.88	-3.48	0.00
C	5.31	1.80	0.00	C	-5.35	-1.37	0.00
H	5.84	1.41	-0.88	H	-5.89	-1.00	-0.88
H	5.40	2.90	0.00	H	-5.40	-2.46	0.00
H	5.84	1.41	0.88	H	-5.89	-1.00	0.88
C	4.63	-1.05	0.00	C	-4.68	1.52	0.00
H	5.28	-0.94	-0.88	H	-5.34	1.41	-0.88
H	5.28	-0.94	0.88	H	-5.34	1.41	0.88
H	4.23	-2.07	0.00	H	-4.27	2.54	0.00
Rb	-1.33	-2.61	0.00	Rb	1.43	3.09	0.00

(e) Cs^{+}LC(O4)

S_0				S_1			
	x	y	z		x	y	z
C	-3.75	-0.21	0.00	C	-3.85	-0.30	0.00
C	-2.38	-0.37	0.00	C	-2.43	-0.43	0.00
C	-1.50	0.74	0.00	C	-1.54	0.66	0.00
C	-2.05	2.06	0.00	C	-2.12	1.95	0.00
C	-3.46	2.21	0.00	C	-3.54	2.07	0.00
C	-4.30	1.12	0.00	C	-4.42	0.98	0.00
C	0.03	2.94	0.00	C	-0.07	2.88	0.00
C	0.60	1.63	0.00	C	0.55	1.58	0.00
C	2.06	1.48	0.00	C	1.99	1.50	0.00
C	2.25	3.97	0.00	C	2.12	3.98	0.00
H	-1.95	-1.38	0.00	H	-2.01	-1.44	0.00
H	-3.85	3.23	0.00	H	-3.94	3.09	0.00
H	3.77	2.60	0.00	H	3.69	2.68	0.00
H	0.46	4.96	0.00	H	0.28	4.89	0.00
N	-1.26	3.16	0.00	N	-1.38	3.09	0.00
N	0.87	4.03	0.00	N	0.72	3.98	0.00
N	2.76	2.66	0.00	N	2.67	2.72	0.00
N	-0.16	0.55	0.00	N	-0.19	0.45	0.00
O	2.64	0.40	0.00	O	2.65	0.45	0.00
O	2.97	4.93	0.00	O	2.76	5.00	0.00
C	-5.78	1.31	0.00	C	-5.90	1.18	0.00
H	-6.24	0.84	0.88	H	-6.37	0.72	0.88
H	-6.05	2.38	0.00	H	-6.16	2.25	0.00
H	-6.24	0.84	-0.88	H	-6.37	0.72	-0.88
C	-4.66	-1.40	0.00	C	-4.70	-1.53	0.00
H	-5.32	-1.39	0.88	H	-5.37	-1.54	0.88
H	-5.32	-1.39	-0.88	H	-5.37	-1.54	-0.88
H	-4.10	-2.34	0.00	H	-4.11	-2.45	0.00
Cs	1.57	-2.19	0.00	Cs	1.70	-2.11	0.00

(f) LC

S_0				S_2			
	x	y	z		x	y	z
C	-3.38	0.66	0.00	C	-3.41	0.63	0.00
C	-2.18	1.34	0.00	C	-2.16	1.33	0.00
C	-0.94	0.65	0.00	C	-0.92	0.68	0.00
C	-0.94	-0.78	0.00	C	-0.93	-0.74	0.00
C	-2.18	-1.46	0.00	C	-2.18	-1.43	0.00
C	-3.37	-0.78	0.00	C	-3.42	-0.77	0.00
C	1.32	-0.76	0.00	C	1.32	-0.73	0.00
C	1.33	0.66	0.00	C	1.36	0.70	0.00
C	2.62	1.40	0.00	C	2.64	1.38	0.00
C	3.77	-0.84	0.00	C	3.77	-0.85	0.00
H	-2.14	2.43	0.00	H	-2.15	2.42	0.00
H	-2.15	-2.55	0.00	H	-2.14	-2.52	0.00
H	4.64	1.00	0.00	H	4.67	0.96	0.00
H	2.51	-2.45	0.00	H	2.44	-2.43	0.00
N	0.22	-1.48	0.00	N	0.21	-1.47	0.00
N	2.52	-1.43	0.00	N	2.49	-1.42	0.00
N	3.73	0.55	0.00	N	3.76	0.51	0.00
N	0.21	1.36	0.00	N	0.22	1.42	0.00
O	2.74	2.60	0.00	O	2.83	2.58	0.00
O	4.80	-1.46	0.00	O	4.76	-1.56	0.00
C	-4.67	-1.53	0.00	C	-4.71	-1.54	0.00
H	-5.28	-1.27	-0.88	H	-5.32	-1.31	-0.88
H	-4.50	-2.61	0.00	H	-4.52	-2.63	0.00
H	-5.28	-1.27	0.88	H	-5.32	-1.31	0.88
C	-4.68	1.41	0.00	C	-4.68	1.42	0.00
H	-5.29	1.16	-0.88	H	-5.30	1.17	-0.88
H	-5.29	1.16	0.88	H	-5.30	1.17	0.88
H	-4.51	2.49	0.00	H	-4.50	2.50	0.00

e) iso-LC

S_0				S_1			
	x	y	z		x	y	z
C	-3.37	0.68	0.00	C	-3.37	0.66	0.00
C	-2.15	1.33	0.00	C	-2.16	1.35	0.00
C	-0.93	0.63	0.00	C	-0.91	0.70	0.00
C	-0.96	-0.78	0.00	C	-0.96	-0.74	0.00
C	-2.19	-1.45	0.00	C	-2.18	-1.44	0.00
C	-3.38	-0.74	0.00	C	-3.39	-0.77	0.00
C	1.45	-0.80	0.00	C	1.42	-0.72	0.00
C	1.36	0.66	0.00	C	1.39	0.70	0.00
C	2.66	1.39	0.00	C	2.67	1.38	0.00
C	3.75	-0.87	0.00	C	3.74	-0.89	0.00
H	-2.09	2.42	0.00	H	-2.14	2.44	0.00
H	-2.20	-2.55	0.00	H	-2.16	-2.53	0.00
H	4.66	0.97	0.00	H	4.68	0.92	0.00
N	0.24	-1.44	0.00	N	0.24	-1.39	0.00
N	2.53	-1.53	0.00	N	2.49	-1.52	0.00
N	3.74	0.54	0.00	N	3.76	0.48	0.00
N	0.25	1.33	0.00	N	0.23	1.41	0.00
O	2.76	2.60	0.00	O	2.87	2.58	0.00
O	4.81	-1.45	0.00	O	4.76	-1.56	0.00
C	-4.69	-1.48	0.00	C	-4.68	-1.52	0.00
H	-5.29	-1.22	-0.88	H	-5.30	-1.28	-0.88
H	-4.54	-2.57	0.00	H	-4.51	-2.61	0.00
H	-5.29	-1.22	0.88	H	-5.30	-1.28	0.88
C	-4.65	1.45	0.00	C	-4.66	1.42	0.00
H	-5.27	1.22	-0.88	H	-5.27	1.17	-0.88
H	-5.27	1.22	0.88	H	-5.27	1.17	0.88
H	-4.46	2.54	0.00	H	-4.49	2.51	0.00
H	0.28	-2.45	0.00	H	0.31	-2.40	0.00

f) H^+LC(N5)

S_0				S_1			
	x	y	z		x	y	z
C	-3.38	0.65	0.00	C	-3.44	0.62	0.00
C	-2.19	1.34	0.00	C	-2.20	1.31	0.00
C	-0.98	0.64	0.00	C	-0.96	0.64	0.00
C	-0.94	-0.80	0.00	C	-0.92	-0.76	0.00
C	-2.18	-1.48	0.00	C	-2.18	-1.44	0.00
C	-3.38	-0.80	0.00	C	-3.43	-0.78	0.00
C	1.34	-0.81	0.00	C	1.34	-0.79	0.00
C	1.37	0.59	0.00	C	1.40	0.62	0.00
C	2.63	1.37	0.00	C	2.65	1.36	0.00
C	3.79	-0.83	0.00	C	3.80	-0.83	0.00
H	-2.19	2.44	0.00	H	-2.21	2.40	0.00
H	-2.15	-2.57	0.00	H	-2.14	-2.53	0.00
H	4.65	1.03	0.00	H	4.68	1.01	0.00
H	2.56	-2.47	0.00	H	2.54	-2.46	0.00
N	0.21	-1.49	0.00	N	0.22	-1.50	0.00
N	2.55	-1.46	0.00	N	2.53	-1.44	0.00
N	3.74	0.57	0.00	N	3.77	0.55	0.00
N	0.23	1.26	0.00	N	0.24	1.31	0.00
O	2.62	2.58	0.00	O	2.68	2.58	0.00
O	4.82	-1.44	0.00	O	4.81	-1.49	0.00
C	-4.67	-1.54	0.00	C	-4.69	-1.57	0.00
H	-5.28	-1.28	-0.88	H	-5.31	-1.33	-0.88
H	-4.51	-2.63	0.00	H	-4.50	-2.65	0.00
H	-5.28	-1.28	0.88	H	-5.31	-1.33	0.88
C	-4.68	1.39	0.00	C	-4.72	1.39	0.00
H	-5.29	1.12	-0.88	H	-5.33	1.14	-0.88
H	-5.29	1.12	0.88	H	-5.33	1.14	0.88
H	-4.54	2.47	0.00	H	-4.55	2.48	0.00
H	0.32	2.28	0.00	H	0.32	2.33	0.00

g) H^+LC(O4)

S_0				S_1			
	x	y	z		x	y	z
C	-3.38	0.66	0.00	C	-3.42	0.63	0.00
C	-2.18	1.34	0.00	C	-2.17	1.31	0.00
C	-0.94	0.64	0.00	C	-0.93	0.65	0.00
C	-0.94	-0.81	0.00	C	-0.94	-0.75	0.00
C	-2.18	-1.48	0.00	C	-2.21	-1.44	0.00
C	-3.37	-0.79	0.00	C	-3.44	-0.77	0.00
C	1.32	-0.83	0.00	C	1.31	-0.81	0.00
C	1.31	0.58	0.00	C	1.34	0.62	0.00
C	2.56	1.27	0.00	C	2.60	1.26	0.00
C	3.76	-0.86	0.00	C	3.77	-0.87	0.00
H	-2.15	2.43	0.00	H	-2.16	2.41	0.00
H	-2.16	-2.57	0.00	H	-2.17	-2.53	0.00
H	4.59	1.04	0.00	H	4.64	0.99	0.00
H	2.54	-2.49	0.00	H	2.50	-2.49	0.00
N	0.20	-1.53	0.00	N	0.19	-1.51	0.00
N	2.53	-1.48	0.00	N	2.50	-1.47	0.00
N	3.69	0.57	0.00	N	3.73	0.52	0.00
N	0.21	1.32	0.00	N	0.23	1.37	0.00
O	2.62	2.57	0.00	O	2.72	2.56	0.00
O	4.82	-1.41	0.00	O	4.79	-1.50	0.00
C	-4.67	-1.53	0.00	C	-4.72	-1.54	0.00
H	-5.27	-1.26	-0.88	H	-5.33	-1.29	-0.88
H	-4.52	-2.61	0.00	H	-4.54	-2.62	0.00
H	-5.27	-1.26	0.88	H	-5.33	-1.29	0.88
C	-4.67	1.40	0.00	C	-4.69	1.42	0.00
H	-5.28	1.14	-0.88	H	-5.30	1.17	-0.88
H	-5.28	1.14	0.88	H	-5.30	1.17	0.88
H	-4.52	2.49	0.00	H	-4.51	2.50	0.00
H	1.68	2.88	0.00	H	1.80	2.92	0.00