Electronic Supplementary Information (ESI)

For the manuscript entitled "Cooperative Electronic Effects of Na^+ and Ca^{2+} on an Oxygenated Aromatic Model."

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Section S1. Optimized Cartesian coordinates

Optimized Cartesian coordinates (xyz) at the M06-2X/def2-TZVP level (gas phase) are provided for the representative key structures M (H), M–Na (Na), M–Ca (Ca), and M–NaCa (Na/Ca-1) reported in the main text.

Abbreviations and computational details. M denotes the oxygenated aromatic model. M–Na, M–Ca, and M–NaCa denote the Na^+, Ca^{2+}, and Na^+/Ca^{2+} ion-exchanged models, respectively. Geometry optimizations were performed at the M06-2X/def2-TZVP level in the gas phase (i.e., without an implicit solvent model).

In this ESI, the notation "RM062X/def2-TZVP" follows the software output and corresponds to the M06-2X/def2-TZVP level used here (gas phase).

Model labels: In the main manuscript, the parent and ion-exchanged models are denoted as H, Na, Ca, and Na/Ca. In this ESI, the corresponding structures are labeled M (H), M–Na (Na), M–Ca (Ca), and M–NaCa (Na/Ca). Here, M–NaCa corresponds to Na/Ca-1, i.e., the Na/Ca configuration discussed in the main text.

S1-1. H (M, neutral)

50

Optimized Cartesian coordinates (Å) at RM062X/def2-TZVP (gas phase)

C -3.396869 0.604370 -2.519379
C -3.143682 -0.163154 0.159333
C -4.532784 0.350969 -1.746414
C -2.152524 0.461960 -1.945396
C -2.010090 0.080193 -0.610141
C -4.403184 -0.031721 -0.431801
O -3.517809 0.979848 -3.815934
O -5.729282 0.510262 -2.394036
C -0.613398 -0.047673 -0.051014
C -3.037945 -0.632179 1.593922
C -0.585553 -0.915823 1.212982
C -1.637572 -0.423749 2.190689
C -4.036332 0.032721 2.520236
O -4.667756 1.028206 2.310210
O -4.118479 -0.636993 3.687534
C 0.803797 -0.885014 1.799465
O 1.031730 -0.324796 2.850704
C 1.933807 -1.538498 1.022176

C 2.786244 -0.515930 0.302951
C 4.478756 1.253404 -1.007118
C 2.818777 -0.468625 -1.098556
C 3.614112 0.348677 1.019076
C 4.482992 1.239029 0.372920
C 3.656014 0.417040 -1.756960
O 1.999923 -1.349492 -1.744147
C 1.995715 -1.332703 -3.154272
C 5.364376 2.133350 1.193242
O 3.655786 0.342953 2.372122
H -1.278760 0.657697 -2.555599
H -5.297904 -0.212329 0.153307
H -4.457827 1.045545 -4.025845
H -6.456063 0.443013 -1.768263
H -0.226106 0.945731 0.202093
H 0.048511 -0.461314 -0.812151
H -3.258439 -1.704621 1.638889
H -0.798560 -1.951248 0.920335
H -1.469585 0.639001 2.385013
H -1.560287 -0.941454 3.145581
H -4.726827 -0.145213 4.257684
H 2.549910 -2.070548 1.752513
H 1.541880 -2.253551 0.303675
H 5.135499 1.942454 -1.525109
H 3.687170 0.462908 -2.834822
H 1.282700 -2.091669 -3.465335
H 1.679761 -0.358505 -3.536421
H 2.983423 -1.574102 -3.554163
H 6.030354 1.549207 1.830265
H 4.769851 2.762975 1.856847
H 5.967774 2.771595 0.549499
H 2.814751 0.027796 2.749610

S1-2. Na (M–Na, charge-neutral)

50

Optimized Cartesian coordinates (Å) at RM062X/def2-TZVP (gas phase)

C 1.085303 3.071539 -3.585101
C -1.012638 2.517002 -1.847113
C 0.486359 4.111562 -2.871652
C 0.632964 1.779003 -3.432280
C -0.420489 1.483682 -2.564707
C -0.550837 3.822047 -2.010755

O 2.113019 3.441618 -4.414766
O 0.922551 5.388790 -3.021497
C -0.919216 0.056704 -2.495152
C -2.098737 2.244464 -0.839935
C -1.879131 -0.238950 -1.340160
C -2.846274 0.939806 -1.154130
C -1.534616 2.104390 0.583089
O -0.327011 1.752048 0.669700
O -2.330632 2.226076 1.535417
C -1.279423 -0.701646 -0.012033
O -2.014645 -0.816402 0.950261
C 0.180628 -1.085186 0.047845
C 0.640501 -1.673353 1.351799
C 1.534274 -2.837745 3.722613
C 1.065697 -3.011422 1.384279
C 0.670112 -0.946288 2.542814
C 1.121432 -1.521783 3.743707
C 1.512569 -3.597440 2.558105
O 1.005210 -3.681603 0.197009
C 1.423576 -5.025867 0.176157
C 1.152504 -0.693192 4.994929
H 1.104147 0.980296 -3.998972
H -0.995694 4.635415 -1.449304
H 2.483090 2.667356 -4.847578
H 1.655996 5.386960 -3.648867
H -0.070995 -0.629150 -2.497068
H -1.464352 -0.150842 -3.421900
H -2.820838 3.061981 -0.825292
H -2.479918 -1.112449 -1.622816
H -3.559986 0.722857 -0.360847
H -3.402956 1.066966 -2.085342
H 0.361487 -1.803760 -0.751718
H 0.738985 -0.182310 -0.220225
H 1.890081 -3.291357 4.640300
H 1.843862 -4.624346 2.582344
H 1.299240 -5.368140 -0.848240
H 2.473437 -5.118000 0.465615
H 0.811320 -5.640830 0.841023
H 0.149215 -0.393095 5.307502
H 1.716573 0.226888 4.840352
H 1.605665 -1.252166 5.812116
Na -2.030537 0.478364 2.792219

O 0.241209 0.334772 2.644571
H 0.117921 0.896732 1.783682

S1-3. Ca (M–Ca, charge-neutral)

49
Optimized Cartesian coordinates (Å) at RM062X/def2-TZVP (gas phase)
C -5.113700 1.313699 0.938512
C -3.298752 -0.200810 -0.510970
C -5.521057 0.103538 0.375909
C -3.817449 1.755653 0.773735
C -2.891445 1.002703 0.052704
C -4.610635 -0.638809 -0.348918
O -6.082046 1.994557 1.629451
O -6.797724 -0.331692 0.526952
C -1.459218 1.476030 -0.021942
C -2.328656 -0.991089 -1.344371
C -0.638853 0.920612 -1.221240
C -1.447239 -0.003308 -2.138031
C -1.402141 -1.892420 -0.540211
O -0.965414 -1.476603 0.574107
O -0.969654 -2.948217 -1.070508
C 0.674555 0.287654 -0.790829
O 1.104696 -0.697102 -1.376639
C 1.435690 0.880863 0.371721
C 2.917318 0.642369 0.368289
C 5.658984 0.283886 0.500633
C 3.783457 1.672421 -0.008037
C 3.438286 -0.595005 0.786844
C 4.840717 -0.764254 0.865834
C 5.158309 1.506764 0.055221
O 3.179872 2.826342 -0.432441
C 4.014650 3.902089 -0.788309
C 5.380116 -2.082152 1.334947
O 2.637284 -1.593911 1.098647
H -3.516718 2.699859 1.218568
H -4.941436 -1.569843 -0.793386
H -5.715228 2.796840 2.011144
H -7.276975 0.315006 1.059622
H -0.985176 1.171402 0.910335
H -1.445056 2.566868 -0.036470
H -2.863456 -1.626306 -2.049870
H -0.302397 1.777309 -1.818960

H -0.774391 -0.543499 -2.802224
H -2.115832 0.602230 -2.750806
H 1.206464 1.943200 0.446831
H 0.998355 0.397329 1.256594
H 6.734040 0.151990 0.556452
H 5.838109 2.295100 -0.229508
H 3.357375 4.718146 -1.079141
H 4.635064 4.217655 0.054686
H 4.661345 3.639527 -1.629745
H 5.108581 -2.888708 0.648564
H 4.963743 -2.348696 2.308146
H 6.466683 -2.052263 1.412856
Ca 1.018730 -2.523052 0.089802

S1-4. Na/Ca (M–NaCa, charge-neutral)

49
Optimized Cartesian coordinates (Å) at RM062X/def2-TZVP (gas phase)
C -3.504284 0.418946 -4.240558
C -2.777333 -1.103919 -2.070389
C -4.449445 -0.532702 -3.778906
C -2.270633 0.601455 -3.660478
C -1.881414 -0.154630 -2.555164
C -4.016470 -1.285805 -2.671317
O -3.898947 1.179236 -5.355193
O -5.600501 -0.685843 -4.351697
C -0.573613 0.140068 -1.862761
C -2.346374 -1.988891 -0.930656
C 0.032695 -1.063820 -1.082152
C -0.848135 -2.317940 -1.111705
C -2.515025 -1.381305 0.453114
O -2.276800 -0.146253 0.614916
O -2.724261 -2.144429 1.434259
C 0.441216 -0.691124 0.331602
O 0.290496 -1.483373 1.253542
C 1.019922 0.679493 0.596047
C 1.901648 0.784719 1.805777
C 3.541461 1.120252 4.012343
C 3.290277 0.811346 1.656856
C 1.331758 0.890855 3.087803
C 2.177081 1.080444 4.207136
C 4.123228 0.980865 2.752362
O 3.748124 0.658142 0.374833

C 5.139029 0.699331 0.171293
C 1.551267 1.216772 5.562679
O 0.028212 0.806759 3.256922
H -1.592714 1.350775 -4.064648
H -4.698115 -2.040667 -2.295622
H -3.191591 1.795468 -5.564049
Na -5.963056 0.566686 -5.948486
H -0.757021 0.956332 -1.164571
H 0.148918 0.507877 -2.593904
H -2.911150 -2.920637 -0.941427
H 0.994131 -1.314703 -1.549070
H -0.514886 -3.020569 -0.349243
H -0.745299 -2.797834 -2.085235
H 1.522911 1.036334 -0.301891
H 0.139058 1.319334 0.743298
H 4.189498 1.258803 4.871138
H 5.197293 1.006616 2.649993
H 5.296771 0.570114 -0.896782
H 5.558577 1.658446 0.486576
H 5.643386 -0.106115 0.711746
H 1.022985 0.303223 5.848952
H 0.810328 2.018375 5.569366
H 2.305415 1.426214 6.321188
Ca -1.388618 -0.662719 2.652165

Table S1. Selected metal–oxygen distances (Å)

In M–NaCa, Ca^{2+} is coordinated by the carboxylate oxygens (O3/O4) and an additional nonprotonated aryl-ether oxygen (O7; no attached H), while Na^{+} interacts with O2 (nonprotonated O) and O1 (phenolic O–H).

Note: Distances were measured from the optimized geometries in Spartan.
This table provides a compact summary to support the ion-binding description and reproducibility.

Model	Contact	Distance (Å)	Comment
M–Ca (M_Ca1_neutral_Gas_M062X_def2TZVP_OPT)	O4–Ca1	2.341	Carboxylate single-bond oxygen coordination to Ca (representative Ca–O contact)
M–NaCa (M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT)	O7–Ca1	2.129	Aryl-ether oxygen coordination to Ca (O7 has no H; shortest Ca–O contact)
M–NaCa (M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT)	O3–Ca1	2.282	Carboxylate carbonyl oxygen coordination to Ca
M–NaCa (M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT)	O4–Ca1	2.337	Carboxylate single-bond oxygen coordination to Ca
M–NaCa (M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT)	Na1–O2	2.062	Nonprotonated phenoxy/ether oxygen coordination to Na (shortest Na–O contact)
M–NaCa (M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT)	Na1–O1	2.233	Second phenolic oxygen (O–H

			site)/Na–O contact
M–Na (M_Na1_neutral_Gas_M062X_def2TZVP_OPT)	Na1–O4	2.174	Representative Na–O coordination distance

Atom labels (O1–O7, Na1, and Ca1) follow the Spartan atom numbering scheme shown in the figure snapshots; O7 is a nonprotonated aryl-ether oxygen (no attached H).

Section S2. Full infrared (IR) frequency tables (unscaled and scaled ×0.95)

Abbreviations and terms. IR = infrared. Mode denotes the normal-mode index. Unscaled harmonic frequencies are reported in cm^{-1}. Scaled frequencies were obtained by applying a uniform scaling factor of 0.95 (Scaled = 0.95 × Unscaled). IR intensity is reported as the value output from the frequency calculation.

Frequencies are reported as output from the frequency calculations (rounded as shown in each table). Scaled values were computed as 0.95 × Unscaled and rounded to the same precision.

Level of theory: M06-2X/def2-TZVP (gas phase).

Harmonic frequencies and IR intensities. Scaled frequencies were obtained by applying a uniform scaling factor of 0.95.

Assignments for representative vibrational modes are provided separately in Tables S6–S9 based on normal-mode inspection.

Table S2. Full list of harmonic infrared (IR) frequencies for M.

Structure: M_neutral_Gas_M062X_def2TZVP_OPT

Mode	Unscaled harmonic frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity
1	12	11	0.49
2	20	19	0.33
3	30	28	0.22
4	38	36	1.02
5	57	54	1.57
6	70	66	1.15
7	82	78	0.32
8	86	82	0.35
9	103	98	1.41
10	114	108	6.63
11	134	127	2.90
12	147	140	1.95
13	161	153	2.19
14	172	163	0.08
15	184	175	5.85
16	221	210	66.40
17	230	218	30.01
18	242	230	7.40
19	248	236	15.74
20	261	248	0.13
21	276	262	5.24
22	292	277	7.27
23	304	289	7.18
24	311	295	1.19
25	319	303	6.29

26	334	317	3.68
27	339	322	1.03
28	368	350	1.73
29	378	359	2.97
30	398	378	1.88
31	403	383	1.68
32	430	408	1.78
33	453	430	21.71
34	455	432	10.14
35	469	446	3.61
36	478	454	59.06
37	493	468	1.35
38	514	488	5.95
39	540	513	5.83
40	578	549	13.89
41	598	568	45.33
42	617	586	89.24
43	622	591	8.92
44	632	600	50.10
45	637	605	64.08
46	650	618	16.85
47	660	627	0.58
48	688	654	9.41
49	699	664	3.15
50	731	694	4.93
51	737	700	0.68
52	745	708	4.60
53	763	725	8.60
54	776	737	22.00
55	786	747	8.03
56	802	762	4.60
57	825	784	38.69
58	856	813	28.47
59	883	839	15.31
60	885	841	3.31
61	906	861	0.97
62	914	868	10.44
63	931	884	8.82
64	956	908	1.60
65	958	910	1.53
66	967	919	1.05
67	991	941	0.98
68	1001	951	1.70
69	1035	983	1.36
70	1059	1006	15.69

71	1070	1016	0.94
72	1080	1026	12.49
73	1115	1059	30.15
74	1137	1080	74.62
75	1159	1101	67.80
76	1165	1107	254.67
77	1169	1111	185.59
78	1181	1122	36.71
79	1184	1125	76.53
80	1185	1126	13.46
81	1198	1138	82.98
82	1202	1142	10.10
83	1218	1157	1.52
84	1223	1162	28.73
85	1229	1168	1.68
86	1260	1197	43.74
87	1263	1200	18.42
88	1269	1206	82.16
89	1280	1216	96.60
90	1284	1220	43.83
91	1307	1242	20.65
92	1309	1244	83.04
93	1320	1254	16.55
94	1325	1259	11.92
95	1337	1270	71.03
96	1345	1278	61.89
97	1358	1290	78.29
98	1363	1295	70.14
99	1377	1308	101.52
100	1395	1325	89.95
101	1400	1330	28.77
102	1418	1347	6.30
103	1425	1354	8.71
104	1426	1355	75.61
105	1475	1401	10.07
106	1479	1405	15.09
107	1480	1406	0.78
108	1483	1409	4.95
109	1488	1414	9.36
110	1500	1425	17.95
111	1501	1426	48.98
112	1503	1428	1.21
113	1510	1434	27.36
114	1516	1440	45.11
115	1552	1474	93.37

116	1585	1506	222.44
117	1667	1584	36.52
118	1676	1592	33.12
119	1681	1597	70.63
120	1703	1618	9.97
121	1794	1704	170.25
122	1860	1767	278.23
123	3065	2912	4.67
124	3073	2919	6.80
125	3079	2925	38.42
126	3080	2926	5.17
127	3087	2933	27.77
128	3098	2943	6.97
129	3101	2946	9.56
130	3143	2986	31.50
131	3146	2989	9.13
132	3153	2995	2.89
133	3170	3012	12.74
134	3173	3014	7.94
135	3181	3022	3.23
136	3211	3050	14.80
137	3229	3068	8.66
138	3235	3073	10.77
139	3239	3077	3.02
140	3269	3106	2.82
141	3597	3417	547.92
142	3795	3605	113.75
143	3817	3626	147.09
144	3861	3668	111.48

Table S3. Full list of harmonic IR frequencies for M–Na.

Structure: M_Na1_neutral_Gas_M062X_def2TZVP_OPT

Mode	Unscaled harmonic frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity
1	16.0	15.2	0.17
2	31.0	29.4	1.51
3	53.0	50.3	2.50
4	58.0	55.1	6.23
5	67.0	63.6	1.04
6	79.0	75.0	4.20
7	85.0	80.8	2.23
8	127.0	120.6	2.20
9	133.0	126.3	3.34
10	142.0	134.9	11.54
11	149.0	141.5	105.94
12	153.0	145.3	22.28
13	162.0	153.9	7.64
14	185.0	175.8	0.13
15	188.0	178.6	11.84
16	202.0	191.9	3.98
17	228.0	216.6	14.91
18	242.0	229.9	16.98
19	254.0	241.3	11.20
20	259.0	246.0	1.34
21	269.0	255.5	1.54
22	281.0	266.9	10.76
23	290.0	275.5	2.64
24	303.0	287.8	34.81
25	313.0	297.3	8.16
26	323.0	306.8	5.24
27	330.0	313.5	4.49
28	356.0	338.2	9.98
29	369.0	350.6	9.09
30	373.0	354.3	11.79
31	383.0	363.8	18.17
32	400.0	380.0	1.76
33	408.0	387.6	5.35
34	412.0	391.4	75.73
35	428.0	406.6	10.61
36	434.0	412.3	22.36
37	464.0	440.8	11.70
38	475.0	451.2	12.87
39	478.0	454.1	5.82
40	489.0	464.5	3.48

41	531.0	504.4	2.59
42	553.0	525.4	6.37
43	577.0	548.1	2.13
44	603.0	572.9	5.87
45	624.0	592.8	46.72
46	645.0	612.8	2.43
47	653.0	620.4	44.89
48	663.0	629.9	6.58
49	694.0	659.3	9.51
50	717.0	681.1	2.80
51	725.0	688.8	62.42
52	744.0	706.8	7.15
53	749.0	711.5	7.82
54	771.0	732.4	5.12
55	771.0	732.4	0.84
56	792.0	752.4	21.53
57	816.0	775.2	17.12
58	835.0	793.2	44.29
59	859.0	816.0	3.13
60	864.0	820.8	31.85
61	869.0	825.5	7.60
62	898.0	853.1	17.71
63	910.0	864.5	1.57
64	930.0	883.5	10.22
65	941.0	893.9	5.29
66	951.0	903.4	28.11
67	954.0	906.3	1.76
68	981.0	931.9	2.29
69	1005.0	954.8	7.65
70	1013.0	962.3	1.01
71	1039.0	987.0	16.42
72	1064.0	1010.8	17.86
73	1066.0	1012.7	0.79
74	1107.0	1051.6	5.11
75	1131.0	1074.5	32.03
76	1148.0	1090.6	325.33
77	1153.0	1095.3	102.96
78	1160.0	1102.0	65.38
79	1167.0	1108.6	60.62
80	1183.0	1123.8	79.52
81	1187.0	1127.6	0.48
82	1194.0	1134.3	21.47
83	1198.0	1138.1	46.44
84	1213.0	1152.3	55.54
85	1219.0	1158.0	1.13

86	1229.0	1167.5	3.45
87	1249.0	1186.5	15.33
88	1260.0	1197.0	9.79
89	1264.0	1200.8	20.42
90	1274.0	1210.3	26.19
91	1286.0	1221.7	325.66
92	1300.0	1235.0	39.47
93	1307.0	1241.6	41.76
94	1313.0	1247.3	53.32
95	1317.0	1251.1	98.98
96	1347.0	1279.6	260.45
97	1355.0	1287.2	33.64
98	1360.0	1292.0	296.26
99	1365.0	1296.8	209.26
100	1374.0	1305.3	93.56
101	1385.0	1315.8	49.03
102	1392.0	1322.4	14.69
103	1416.0	1345.2	54.83
104	1420.0	1349.0	2.16
105	1451.0	1378.5	34.43
106	1464.0	1390.8	141.23
107	1477.0	1403.1	16.99
108	1483.0	1408.8	8.72
109	1484.0	1409.8	7.19
110	1487.0	1412.6	44.23
111	1496.0	1421.2	15.89
112	1500.0	1425.0	8.47
113	1507.0	1431.6	18.83
114	1512.0	1436.4	19.47
115	1519.0	1443.0	65.51
116	1541.0	1463.9	80.21
117	1582.0	1502.9	225.49
118	1655.0	1572.2	530.96
119	1666.0	1582.7	35.68
120	1678.0	1594.1	7.04
121	1681.0	1596.9	85.29
122	1703.0	1617.8	14.92
123	1773.0	1684.3	182.67
124	2485.0	2360.8	2651.37
125	3042.0	2889.9	12.90
126	3068.0	2914.6	51.31
127	3074.0	2920.3	21.66
128	3080.0	2926.0	16.21
129	3080.0	2926.0	28.13
130	3107.0	2951.6	25.85

131	3127.0	2970.6	21.38
132	3132.0	2975.4	26.29
133	3141.0	2983.9	11.44
134	3142.0	2984.9	16.74
135	3158.0	3000.1	10.42
136	3176.0	3017.2	9.36
137	3181.0	3021.9	11.76
138	3194.0	3034.3	13.73
139	3200.0	3040.0	18.90
140	3229.0	3067.5	10.84
141	3241.0	3078.9	2.27
142	3273.0	3109.3	4.44
143	3812.0	3621.4	135.66
144	3860.0	3667.0	94.37

Table S4. Full list of harmonic IR frequencies for M–Ca.

Structure: M_Ca1_neutral_Gas_M062X_def2TZVP_OPT

Mode	Unscaled harmonic frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity
1	27	25.6	0.44
2	28	26.6	0.06
3	52	49.4	0.70
4	57	54.1	0.77
5	70	66.5	6.27
6	88	83.6	1.42
7	97	92.1	4.32
8	104	98.8	7.36
9	134	127.3	3.24
10	139	132.0	1.55
11	149	141.5	0.80
12	154	146.3	1.92
13	169	160.5	3.58
14	181	171.9	24.75
15	205	194.8	0.20
16	229	217.5	22.66
17	252	239.4	6.03
18	252	239.4	9.03
19	258	245.1	6.17
20	272	258.4	0.75
21	281	266.9	110.30
22	282	267.9	7.59
23	291	276.4	38.63
24	309	293.6	6.01
25	314	298.3	8.46
26	317	301.1	0.24
27	338	321.1	31.49
28	360	342.0	7.87
29	369	350.6	0.64
30	377	358.1	1.95
31	393	373.3	5.94
32	402	381.9	14.72
33	413	392.3	57.29
34	416	395.2	68.47
35	420	399.0	15.30
36	437	415.1	72.49
37	457	434.1	3.78
38	479	455.0	8.93
39	483	458.8	8.14
40	519	493.0	11.01

41	531	504.4	7.94
42	568	539.6	21.22
43	593	563.4	40.67
44	612	581.4	2.70
45	630	598.5	73.42
46	639	607.0	18.61
47	669	635.5	12.06
48	688	653.6	1.41
49	694	659.3	11.50
50	728	691.6	4.24
51	738	701.1	7.34
52	753	715.4	34.12
53	762	723.9	2.83
54	776	737.2	1.48
55	778	739.1	8.43
56	793	753.3	24.40
57	813	772.3	4.10
58	837	795.1	26.40
59	851	808.4	11.16
60	860	817.0	14.61
61	877	833.1	17.59
62	897	852.1	15.37
63	915	869.2	11.23
64	929	882.5	9.58
65	937	890.1	43.01
66	944	896.8	1.03
67	967	918.6	8.96
68	975	926.2	4.93
69	1005	954.8	2.61
70	1014	963.3	3.48
71	1038	986.1	17.79
72	1062	1008.9	0.76
73	1068	1014.6	14.72
74	1106	1050.7	26.89
75	1138	1081.1	60.89
76	1154	1096.3	118.86
77	1168	1109.6	92.37
78	1175	1116.2	77.96
79	1187	1127.6	2.12
80	1188	1128.6	54.87
81	1194	1134.3	1.27
82	1212	1151.4	67.83
83	1220	1159.0	23.86
84	1224	1162.8	15.39
85	1225	1163.8	10.71

86	1239	1177.0	24.12
87	1252	1189.4	3.33
88	1269	1205.5	33.23
89	1277	1213.1	15.53
90	1297	1232.1	178.50
91	1302	1236.9	50.89
92	1311	1245.5	54.78
93	1318	1252.1	27.92
94	1330	1263.5	24.46
95	1343	1275.8	133.72
96	1356	1288.2	30.60
97	1366	1297.7	249.84
98	1370	1301.5	21.14
99	1385	1315.8	19.64
100	1398	1328.1	38.82
101	1411	1340.5	6.75
102	1413	1342.3	52.72
103	1439	1367.0	27.33
104	1472	1398.4	152.75
105	1474	1400.3	27.70
106	1475	1401.2	22.75
107	1480	1406.0	13.00
108	1485	1410.8	33.51
109	1498	1423.1	102.86
110	1499	1424.0	7.51
111	1508	1432.6	92.91
112	1509	1433.5	20.20
113	1520	1444.0	73.22
114	1540	1463.0	110.87
115	1580	1501.0	245.88
116	1612	1531.4	355.47
117	1643	1560.8	88.42
118	1672	1588.4	89.35
119	1680	1596.0	29.51
120	1701	1615.9	13.39
121	1743	1655.8	190.42
122	3054	2901.3	30.55
123	3056	2903.2	10.88
124	3061	2907.9	53.88
125	3078	2924.1	47.68
126	3113	2957.3	18.06
127	3117	2961.1	16.07
128	3122	2965.9	26.93
129	3133	2976.3	21.98
130	3155	2997.2	8.24

131	3167	3008.6	5.14
132	3169	3010.5	16.46
133	3169	3010.5	5.49
134	3184	3024.8	6.40
135	3189	3029.5	21.81
136	3209	3048.5	12.63
137	3217	3056.1	18.05
138	3246	3083.7	2.34
139	3266	3102.7	5.08
140	3812	3621.4	144.99
141	3867	3673.6	100.05

Table S5. Full list of harmonic IR frequencies for M–NaCa.

Structure: M_Na1Ca1_neutral_Gas_M062X_def2TZVP_OPT

Mode	Unscaled harmonic frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity
1	23	22	2.58
2	35	33	0.55
3	45	43	10.82
4	52	49	0.86
5	64	61	24.78
6	70	66	3.86
7	88	84	1.73
8	91	86	3.54
9	101	96	4.16
10	134	127	13.29
11	138	131	1.52
12	150	142	1.38
13	157	149	6.50
14	170	162	1.69
15	177	168	7.15
16	195	185	24.56
17	211	200	13.88
18	230	218	15.96
19	248	236	8.11
20	257	244	40.14
21	263	250	13.42
22	267	254	4.25
23	277	263	3.57
24	289	275	6.32
25	294	279	11.27
26	300	285	53.10
27	314	298	6.59
28	333	316	8.41
29	341	324	56.77
30	362	344	5.14
31	369	351	3.29
32	387	368	11.62
33	394	374	5.19
34	402	382	22.67
35	411	390	47.73
36	418	397	7.86
37	431	409	64.38
38	449	427	11.94
39	466	443	33.89
40	480	456	18.74

41	498	473	13.27
42	527	501	2.91
43	545	518	11.64
44	566	538	62.93
45	598	568	11.28
46	617	586	2.60
47	634	602	39.18
48	646	614	43.59
49	670	636	11.75
50	690	656	1.32
51	702	667	28.95
52	731	694	0.38
53	751	713	36.25
54	754	716	8.31
55	764	726	4.48
56	771	732	8.84
57	776	737	1.08
58	792	752	24.50
59	817	776	6.03
60	841	799	31.51
61	849	807	12.66
62	865	822	6.32
63	873	829	10.65
64	894	849	23.87
65	904	859	20.49
66	926	880	6.20
67	937	890	0.95
68	941	894	36.18
69	968	920	10.85
70	973	924	2.11
71	1003	953	4.05
72	1017	966	2.42
73	1037	985	22.10
74	1062	1009	1.31
75	1066	1013	17.92
76	1104	1049	43.95
77	1133	1076	52.18
78	1150	1092	150.92
79	1164	1106	94.42
80	1180	1121	90.59
81	1186	1127	12.58
82	1188	1129	65.14
83	1194	1134	3.33
84	1209	1149	65.81
85	1217	1156	2.98

86	1223	1162	34.67
87	1236	1174	13.11
88	1253	1190	3.92
89	1263	1200	8.82
90	1266	1203	20.90
91	1282	1218	74.49
92	1292	1227	13.36
93	1293	1228	169.45
94	1315	1249	8.29
95	1327	1261	48.34
96	1331	1264	19.78
97	1343	1276	68.26
98	1356	1288	6.14
99	1368	1300	122.28
100	1380	1311	31.92
101	1397	1327	26.06
102	1409	1339	6.29
103	1431	1359	371.65
104	1435	1363	8.53
105	1472	1398	112.34
106	1474	1400	23.88
107	1477	1403	59.04
108	1482	1408	23.22
109	1484	1410	41.57
110	1493	1418	32.85
111	1499	1424	126.99
112	1501	1426	9.43
113	1508	1433	95.59
114	1517	1441	65.73
115	1539	1462	104.60
116	1572	1493	501.66
117	1606	1526	366.25
118	1628	1547	0.28
119	1639	1557	86.69
120	1672	1588	96.54
121	1683	1599	112.05
122	1736	1649	192.87
123	3060	2907	15.85
124	3062	2909	56.86
125	3068	2915	27.09
126	3074	2920	48.47
127	3096	2941	28.76
128	3120	2964	15.62
129	3122	2966	29.88
130	3131	2974	23.66

131	3138	2981	11.09
132	3149	2992	4.79
133	3163	3005	25.58
134	3168	3010	17.91
135	3171	3012	6.41
136	3177	3018	8.80
137	3196	3036	23.51
138	3216	3055	8.19
139	3222	3061	19.39
140	3265	3102	6.10
141	3859	3666	65.12

Section S3. Key IR peak assignments (scaled by 0.95×)

Assignments were confirmed by normal-mode inspection. Definitions of terms and abbreviations used in this section are given in Section S2.

Table S6. Key IR peak assignments for M.

Mode	Unscaled frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity	Assignment
76.0	1165.0	1107	254.67	ν(C–O(H)) stretching of COOH (confirmed by normal-mode inspection).
121.0	1794.0	1704	170.25	ν(C=O) stretching of COOH (localized; confirmed by normal-mode inspection).
141.0	3597.0	3417	547.92	ν(O–H) stretching (confirmed by normal-mode inspection).

Table S7. Key IR peak assignments for M–Na.

Mode	Unscaled frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity
124	2485	2361	ν(O–H) stretching strongly red-shifted by Na^+ coordination and intramolecular hydrogen bonding (confirmed by normal-mode inspection).
118	1655	1572	Mixed δ(C=O–O) bending coupled with ν(C–O/C=O) stretching in the C(=O)–O–Na moiety (confirmed by normal-mode inspection).
117	1582	1503	Aromatic ring ν(C=C) stretching coupled with phenolic ν(C–O(H)) stretching (confirmed by normal-mode inspection).
76	1148	1091	Phenolic ν(C–O) stretching coupled with O–H bending/torsional motion (confirmed by normal-mode inspection).

Table S8. Key IR peak assignments for M–Ca.

Mode	Unscaled frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity	Assignment
116	1612	1531.4	355.47	v(C=O)/v(C–O) of Ca-coordinated carboxyl group (C(=O)–O–Ca), confirmed by normal-mode inspection.
115	1580	1501.0	245.88	Aromatic ring v(C=C) stretching coupled with phenolic C–O stretching/O–H in-plane deformation (two phenolic OH groups), confirmed by normal-mode inspection.
121	1743	1655.8	190.42	v(C=O) stretching of the central carbonyl group, confirmed by normal-mode inspection.
97	1366	1297.7	249.84	Mixed skeletal deformation/in-plane bending involving the overall framework (global angle/deformation mode), confirmed by normal-mode inspection.
104	1472	1398.4	152.75	Coupled aromatic ring C–C stretching and carboxylate-group skeletal motion involving

				the C(=O)–O–Ca moiety, confirmed by normal-mode inspection.
76	1154	1096.3	118.86	Phenolic O–H in-plane bending (δ(O–H)) on the aromatic ring, confirmed by normal-mode inspection.

Table S9. Key IR peak assignments for M–NaCa.

Mode	Unscaled frequency (cm^{-1})	Scaled frequency (0.95×) (cm^{-1})	IR intensity	Assignment
103.0	1431.0	1359	371.65	Aromatic ring mode coupled with $Ar–O^-–Na^+$ motion (confirmed by normal-mode inspection).
116.0	1572.0	1493	501.66	ν($Ar–O^-–Na^+$) stretching (phenolate; confirmed by normal-mode inspection).
117.0	1606.0	1526	366.25	ν_as($COO^-–Ca^{2+}$) (Ca-bound carboxylate; confirmed by normal-mode inspection).

Section S4. Post-processing and plotting procedure

The harmonic vibrational frequencies were initially obtained from the quantum chemical calculations as raw (unscaled) values. For comparison and discussion purposes, a uniform scaling factor of 0.95 was applied to the raw frequencies.

Key IR peak assignments were not generated automatically but were confirmed by visual inspection of the corresponding normal-mode animations using Spartan.

For comparison with experiments, scaled frequencies reported in the IR tables were obtained by applying a uniform scaling factor of 0.95 in the postprocessing stage.

Single-point calculations using the polarizable continuum model (PCM; water) confirm that the inclusion of solvent effects does not qualitatively alter the relative energetic trends discussed in this study. Absolute total energies are reported to document the PCM single-point checks; direct comparison of stability across systems with different compositions is not intended.

Table S10. Absolute total energies obtained from single-point PCM (water) calculations.

Model	SCF total energy (hartree)
M	−1340.1105713
M–Na	−1501.8685914
M–Ca	−2016.6596756
M–NaCa	−2178.3877174

Note: Absolute total energies are listed to document the PCM single-point calculations.
These PCM single-point energies are reported solely to document the solvent-sensitivity check; no thermodynamic stabilization upon metal binding is inferred from these absolute values.
Direct comparison of energetic stability across systems with different compositions is not intended.

Section S5. Limited quantitative deviation analysis for selected experimental reference bands

To provide a compact quantitative indicator for the agreement between calculated and experimental IR peak positions discussed in Table 3 of the main manuscript, mean absolute error (MAE) and root-mean-square deviation (RMSD) were evaluated for a limited set of key experimental reference bands (1705 cm^{-1} and the 1570/1400 cm^{-1} region). For the 1570/1400 cm^{-1} region, |Δ| was evaluated against the closer experimental band.

Table S11. Limited quantitative errors (MAE and RMSD) for the key experimental reference bands used in Table 3.

Method	Structure	Calculated peak (scaled 0.95×, cm^{-1})	Experimental reference (cm^{-1})	|Δ| (cm^{-1})
HF/6-311G*	H (M)	1910	1705	205
HF/6-311G*	Ca (M–Ca)	1643	1570 or 1400	73
HF/6-311G*	Na/Ca (M–NaCa)	1632	1570 or 1400	62
HF/6-311G*	MAE / RMSD	–	–	MAE = 113.3; RMSD = 130.6
B3LYP/6-31G*	H (M)	1664	1705	41
B3LYP/6-31G*	Ca (M–Ca)	1435	1570 or 1400	35
B3LYP/6-31G*	Na/Ca (M–NaCa)	1423	1570 or 1400	23
B3LYP/6-31G*	MAE / RMSD	–	–	MAE = 33.0; RMSD = 33.8