Free Radical Formation in Novel Carotenoid Metal Ion Complexes of Astaxanthin

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Supporting Information: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for $Ast^{\bullet+}$, $\#Ast^{\bullet}(5)$, $\#Ast^{\bullet}(9)$, $\#Ast^{\bullet}(13)$, $\#Ast^{\bullet}(3)a$ and $\#Ast^{\bullet}(3)b$ neutral radicals and $Ast^{\bullet-}$ radical anion of astaxanthin; Isotropic β-methyl proton couplings and anisotropic α-proton tensors (MHz) for $Ast^{\bullet+}$, $\#Ast^{\bullet}(5)$, $\#Ast^{\bullet}(9)$, $\#Ast^{\bullet}(13)$, $\#Ast^{\bullet}(3)a$ and $\#Ast^{\bullet}(3)b$ neutral radicals and $Ast^{\bullet-}$ radical anion of astaxanthin obtained by DFT calculations; CV plot of astaxanthin in the presence of Ca and Zn salts as a function of scan rate; stability of the radical cation, dication and the neutral radical is dependent on the presence of the salt, the apparent oxidation shifts to lower oxidation potential and is dependent on the type of metal. CV plot of astaxanthin 1 mM + Ca^{2+} (20 mM) or Zn^{2+} (30 mM) in anhydrous CH_3CN (scan rate = 1000 mV/s); CV plot of astaxanthin 1 mM + $Ca(ClO_4)_2$ 20 mM in anhydrous CH_3CN (scan rate = 200 mV/s); CV plot of astaxanthin 1 mM + Ca^{2+} (20 mM) or Zn^{2+} (30 mM) in anhydrous CH_3CN (scan rate = 10 mV/s); The effect of hydrated salts in CH_3CN causing severe irreversible CV and decay of the radical species; Astaxanthin 0.1 mM in CH_3CN, Scan rate = 10 mV/sec.; The ESEEM spectra of astaxanthin radicals: the spectra show proton modulation consistent with the formation of carotenoid radicals.; The EPR spectra of astaxanthin radicals: the spectra show broadening upon irradiation indicating formation of neutral radicals. Field positions are not corrected for change in frequency before and after irradiation, samples being irradiated external to the cavity.

TABLE S1: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for $Ast^{\bullet+}$.

C	11.630156	-0.074551	0.032381
C	11.768586	1.245578	-0.314776
C	12.742373	-0.895371	0.729297
C	13.869629	0.020111	1.264505
H	14.754017	-0.586437	1.487580
H	13.543039	0.462882	2.215229
C	14.259302	1.174879	0.348026
H	14.973171	1.832571	0.850445
C	13.022232	1.997945	0.011159
C	12.144512	-1.642261	1.947494
H	11.424763	-2.411978	1.652737
H	12.946769	-2.139000	2.502650
H	11.640491	-0.950703	2.629991
C	13.327124	-1.950642	-0.246045
H	14.052610	-2.572735	0.287481
H	12.557689	-2.620309	-0.642473
H	13.851549	-1.491023	-1.084356
C	10.737509	2.084309	-1.028862
H	10.084148	1.486106	-1.665966
H	10.110660	2.635688	-0.317326
H	11.241143	2.843758	-1.629966
C	10.414384	-0.837619	-0.250766

H	10.574337	-1.888004	-0.480311
C	9.124009	-0.403137	-0.172131
H	8.931125	0.616238	0.146495
C	7.959107	-1.208946	-0.432995
C	6.719352	-0.615737	-0.241344
H	6.721375	0.419605	0.096586
C	5.450361	-1.201891	-0.433762
H	5.395533	-2.231444	-0.772860
C	4.267671	-0.515757	-0.206826
H	4.345543	0.515311	0.134357
C	2.961766	-1.032693	-0.377463
C	1.887205	-0.177260	-0.090990
H	2.147444	0.825868	0.244331
C	0.523180	-0.463471	-0.185918
H	0.201998	-1.447842	-0.516644
C	8.127875	-2.633033	-0.894327
H	7.179346	-3.132878	-1.086287
H	8.717684	-2.673509	-1.816047
H	8.664847	-3.221165	-0.141694
C	2.766187	-2.452320	-0.850260
H	3.224153	-2.599975	-1.834093
H	3.239286	-3.159360	-0.160666
H	1.716117	-2.729040	-0.933079

C	-0.471334	0.465584	0.127783
H	-0.149921	1.449552	0.459412
C	-1.835219	0.179774	0.033151
H	-2.096096	-0.822178	-0.305218
C	-2.909618	1.034332	0.325065
C	-4.215140	0.518729	0.154060
H	-4.294378	-0.509481	-0.195337
C	-5.397638	1.203180	0.392013
H	-5.340698	2.228915	0.742038
C	-6.666704	0.620452	0.198598
H	-6.671844	-0.410101	-0.153639
C	-7.905871	1.211958	0.407769
C	-9.072148	0.412209	0.143792
H	-8.885060	-0.600689	-0.198615
C	-2.712551	2.451277	0.805587
H	-3.163216	2.591845	1.793851
H	-1.662279	2.728864	0.882503
H	-3.191578	3.162202	0.124233
C	-10.362513	0.845880	0.247018
H	-10.521762	1.889459	0.505945
C	-11.579247	0.090359	-0.027692
C	-11.719796	-1.230572	0.319008
C	-13.029908	-1.914527	0.132437

C	-14.144899	-1.257994	-0.683304
H	-14.475955	-2.007696	-1.418401
C	-13.690774	-0.003914	-1.409079
H	-14.575526	0.557725	-1.727206
H	-13.168314	-0.317973	-2.321161
C	-12.747397	0.919798	-0.608283
C	-8.069311	2.628600	0.893519
H	-8.643818	2.653511	1.825401
H	-7.118618	3.127182	1.077623
H	-8.619750	3.226807	0.158971
C	-10.687413	-2.074612	1.022008
H	-10.077060	-2.639288	0.305614
H	-10.014792	-1.479841	1.642387
H	-11.201443	-2.812381	1.640553
C	-13.494373	1.619038	0.554459
H	-12.818452	2.258258	1.133562
H	-14.290147	2.255831	0.154136
H	-13.954918	0.891980	1.224208
C	-12.237072	1.994893	-1.596628
H	-11.606137	1.558966	-2.378218
H	-13.092207	2.472580	-2.084717
H	-11.668395	2.788065	-1.102776
O	13.051543	3.216608	-0.056690

O	-13.270637	-2.988448	0.673151
O	14.900734	0.761610	-0.864898
H	14.223671	0.561391	-1.524978
O	-15.214508	-0.942627	0.205946
H	-15.418756	-1.758742	0.687579

TABLE S2: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for #Ast$^{\bullet}$(5).

C	11.566069	-0.045585	0.100032
C	11.715000	1.243187	-0.356406
C	12.667033	-0.786075	0.898416
C	13.778818	0.179524	1.373849
H	14.661165	-0.398692	1.671725
H	13.427863	0.704358	2.273019
C	14.180381	1.249348	0.366740
H	14.876911	1.958868	0.821880
C	12.946304	2.026633	-0.081739
C	12.050942	-1.421275	2.169815
H	11.345176	-2.222013	1.934461
H	12.847718	-1.850145	2.787638
H	11.523015	-0.672865	2.769257
C	13.283478	-1.923932	0.042441
H	13.997149	-2.490842	0.649850
H	12.525248	-2.628062	-0.312406

H	13.828100	-1.537230	-0.819751
C	10.688221	1.998244	-1.167164
H	10.095611	1.329500	-1.795078
H	9.995059	2.559010	-0.528056
H	11.192489	2.740585	-1.788929
C	10.364150	-0.845960	-0.130068
H	10.533191	-1.917320	-0.196412
C	9.068079	-0.424291	-0.165085
H	8.853295	0.627950	-0.006219
C	7.912448	-1.270958	-0.337352
C	6.665525	-0.682867	-0.273572
H	6.647373	0.394257	-0.104643
C	5.393785	-1.302858	-0.390942
H	5.350668	-2.375633	-0.552634
C	4.208174	-0.600156	-0.298712
H	4.279276	0.475832	-0.138412
C	2.897070	-1.136818	-0.384642
C	1.812702	-0.258960	-0.261599
H	2.066270	0.791294	-0.113983
C	0.448740	-0.558455	-0.298845
H	0.130518	-1.589437	-0.437633
C	8.115717	-2.748067	-0.568383
H	7.178068	-3.279944	-0.729818

H	8.751360	-2.923040	-1.444060
H	8.617346	-3.214776	0.288321
C	2.717525	-2.620946	-0.599721
H	3.182368	-2.939065	-1.540223
H	3.194656	-3.193681	0.203984
H	1.668861	-2.916082	-0.635510
C	-0.560727	0.407647	-0.160148
H	-0.243309	1.440326	-0.025993
C	-1.917414	0.119751	-0.180777
H	-2.201228	-0.924205	-0.312954
C	-2.983230	1.050768	-0.042089
C	-4.285385	0.570453	-0.073398
H	-4.398735	-0.506126	-0.202576
C	-5.494595	1.304020	0.047003
H	-5.436007	2.381843	0.166718
C	-6.734212	0.712704	0.021729
H	-6.772362	-0.370147	-0.096471
C	-8.003891	1.377927	0.138818
C	-9.143451	0.608451	0.114690
H	-8.999901	-0.465819	0.030446
C	-2.658827	2.516769	0.136557
H	-2.037041	2.673763	1.025175
H	-2.095719	2.900719	-0.721685

H	-3.550729	3.133443	0.247529
C	-10.503311	1.073088	0.149333
H	-10.641120	2.142481	0.037853
C	-11.636949	0.316442	0.240451
C	-11.594440	-1.149876	0.442665
C	-12.525238	-2.014245	-0.366678
C	-13.867793	-1.398536	-0.796595
H	-14.149218	-1.887206	-1.740207
C	-13.792813	0.117792	-0.996406
H	-14.815149	0.510247	-1.098806
H	-13.296742	0.307546	-1.957687
C	-13.042183	0.921735	0.103958
C	-8.016644	2.880818	0.297771
H	-9.022779	3.284870	0.409531
H	-7.444526	3.181483	1.183035
H	-7.551539	3.370718	-0.565553
C	-10.799795	-1.782822	1.326042
H	-10.147763	-1.239995	2.001185
H	-10.820951	-2.865591	1.391444
C	-13.770005	0.835729	1.469608
H	-13.242558	1.445522	2.210476
H	-14.792371	1.222150	1.381776
H	-13.831673	-0.187858	1.839359

C	-13.030321	2.396191	-0.336648
H	-12.497409	2.537908	-1.282265
H	-14.058792	2.745869	-0.474598
H	-12.569476	3.041218	0.418039
O	13.000131	3.233857	-0.286304
O	-12.266233	-3.170386	-0.640026
O	-14.768703	-1.786798	0.245286
O	14.857944	0.727699	-0.787145
H	-15.639094	-1.427274	0.026739
H	14.188709	0.479093	-1.439059

TABLE S3: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for #Ast$^{\bullet}$(9).

C	11.594690	-0.094041	0.060345
C	11.728905	1.251985	-0.185301
C	12.715310	-0.948206	0.703803
C	13.850053	-0.067343	1.280262
H	14.739233	-0.684710	1.452074
H	13.536831	0.314820	2.261543
C	14.218492	1.143162	0.432455
H	14.942932	1.770822	0.958519
C	12.972861	1.983699	0.169273
C	12.128465	-1.761089	1.884385
H	11.401655	-2.508304	1.554082

H	12.935713	-2.288162	2.405010
H	11.630944	-1.105750	2.606284
C	13.298723	-1.950141	-0.327371
H	14.022037	-2.603643	0.171846
H	12.526454	-2.590981	-0.762473
H	13.826196	-1.443254	-1.136298
C	10.677446	2.126716	-0.826494
H	10.061073	1.569569	-1.535365
H	10.008378	2.572541	-0.080244
H	11.161890	2.962898	-1.334449
C	10.387192	-0.851520	-0.268745
H	10.557077	-1.892033	-0.532443
C	9.091610	-0.435735	-0.192777
H	8.883622	0.568318	0.163935
C	7.929366	-1.233847	-0.500773
C	6.687029	-0.665134	-0.303815
H	6.678445	0.356208	0.077925
C	5.410165	-1.239535	-0.535366
H	5.356712	-2.253772	-0.919386
C	4.231004	-0.561484	-0.290608
H	4.313363	0.452674	0.100569
C	2.915573	-1.050509	-0.494564
C	1.839947	-0.210524	-0.172043

H	2.105942	0.772498	0.217781
C	0.474594	-0.473732	-0.284683
H	0.143184	-1.436405	-0.667856
C	8.120926	-2.637083	-1.019592
H	7.178132	-3.124533	-1.268195
H	8.743666	-2.638810	-1.921531
H	8.631160	-3.263860	-0.277904
C	2.718108	-2.443988	-1.042436
H	3.222914	-2.559233	-2.008335
H	3.142761	-3.195344	-0.366310
H	1.666932	-2.691574	-1.190085
C	-0.524327	0.448500	0.076281
H	-0.193275	1.410727	0.462794
C	-1.881847	0.200031	-0.031537
H	-2.180566	-0.771971	-0.423596
C	-2.938177	1.090405	0.321982
C	-4.242617	0.663900	0.140626
H	-4.372643	-0.336880	-0.271218
C	-5.445678	1.370805	0.427610
H	-5.370042	2.369305	0.849957
C	-6.687714	0.846878	0.213209
H	-6.742295	-0.170720	-0.172335
C	-7.974200	1.499555	0.458637

C	-9.152335	0.608173	0.407919
H	-8.958729	-0.439646	0.625443
C	-2.591092	2.453450	0.876739
H	-3.472659	3.058577	1.087534
H	-2.021394	2.362437	1.808467
H	-1.967142	3.013746	0.171521
C	-10.400396	0.980021	0.056281
H	-10.540553	2.006193	-0.277211
C	-11.589512	0.123632	-0.013243
C	-11.880414	-0.816384	0.939489
C	-13.166826	-1.542804	0.874893
C	-13.951824	-1.624319	-0.437380
H	-13.986246	-2.695673	-0.699308
C	-13.305743	-0.853683	-1.578957
H	-14.075898	-0.624343	-2.323627
H	-12.578054	-1.514019	-2.066015
C	-12.572120	0.439425	-1.163496
C	-8.106811	2.822721	0.725675
H	-9.068329	3.252528	0.982132
H	-7.261618	3.501572	0.704570
C	-11.075113	-1.084178	2.187185
H	-10.388624	-1.929083	2.050559
H	-10.479115	-0.219261	2.484126

H	-11.757834	-1.358383	2.994084
C	-13.574982	1.519718	-0.689307
H	-13.052484	2.415644	-0.336361
H	-14.224477	1.816308	-1.520231
H	-14.213172	1.146520	0.113545
C	-11.834839	0.959118	-2.418555
H	-11.028975	0.283293	-2.722319
H	-12.543869	1.033698	-3.249784
H	-11.403339	1.952817	-2.272502
O	13.022048	3.207807	0.168213
O	-13.672854	-2.073258	1.862411
O	14.836187	0.804516	-0.818829
O	-15.273397	-1.147090	-0.201430
H	14.134620	0.649460	-1.465767
H	-15.529748	-1.528320	0.653898

TABLE S4: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for #Ast$^{\bullet}$(13).

C	-11.627530	-0.084076	0.050166
C	-11.755896	1.264785	0.282739
C	-12.765309	-0.947754	-0.548075
C	-13.917939	-0.075707	-1.101900
H	-14.811027	-0.696132	-1.238682
H	-13.634860	0.293399	-2.097230

C	-14.262938	1.145738	-0.259908
H	-15.002777	1.765899	-0.773248
C	-13.011235	1.990706	-0.043409
C	-12.212585	-1.775194	-1.735073
H	-11.475456	-2.517393	-1.416676
H	-13.034265	-2.309693	-2.224611
H	-11.737512	-1.128828	-2.479824
C	-13.316105	-1.937288	0.512729
H	-14.053354	-2.597397	0.043566
H	-12.530237	-2.572183	0.931968
H	-13.819283	-1.420847	1.331065
C	-10.686671	2.148507	0.880931
H	-10.045085	1.599885	1.573770
H	-10.044762	2.589785	0.108636
H	-11.156754	2.987751	1.397313
C	-10.408708	-0.834797	0.351494
H	-10.567373	-1.870343	0.640917
C	-9.117042	-0.418485	0.219714
H	-8.925577	0.578695	-0.164594
C	-7.943564	-1.207780	0.500067
C	-6.708585	-0.642070	0.241457
H	-6.717277	0.369644	-0.165092
C	-5.425661	-1.208763	0.437374

H	-5.354196	-2.211758	0.847099
C	-4.254850	-0.535752	0.124757
H	-4.356508	0.465320	-0.294419
C	-2.936411	-1.016042	0.290163
C	-1.871708	-0.183831	-0.109422
H	-2.158605	0.783906	-0.521903
C	-0.509515	-0.441679	-0.046805
H	-0.155761	-1.387709	0.356956
C	-8.111068	-2.599517	1.056450
H	-7.158040	-3.079396	1.279300
H	-8.699150	-2.582875	1.981149
H	-8.647012	-3.243487	0.348378
C	-2.708135	-2.390610	0.873018
H	-3.211546	-2.493643	1.840602
H	-3.112719	-3.168785	0.214864
H	-1.651680	-2.609265	1.029093
C	0.475118	0.474620	-0.489991
H	0.115714	1.417465	-0.899996
C	1.824278	0.237571	-0.432075
H	2.140519	-0.718497	-0.016652
C	2.900442	1.124819	-0.858753
C	4.259793	0.586274	-0.686940
H	4.328067	-0.497084	-0.587929

C	5.409174	1.299764	-0.614174
H	5.351875	2.383979	-0.656942
C	6.703496	0.689598	-0.461389
H	6.700398	-0.399223	-0.409374
C	7.919251	1.308219	-0.376991
C	9.098395	0.472722	-0.224761
H	8.910338	-0.596902	-0.185252
C	2.685283	2.358700	-1.393824
H	3.503694	2.966583	-1.760859
H	1.691145	2.778399	-1.493814
C	10.372449	0.917359	-0.084118
H	10.530712	1.992122	-0.048809
C	11.573340	0.105427	0.113792
C	11.796433	-1.071931	-0.555263
C	13.090315	-1.765768	-0.404658
C	14.004821	-1.464123	0.785291
H	14.100335	-2.413285	1.339459
C	13.453672	-0.396931	1.717369
H	14.285190	0.030816	2.288214
H	12.790211	-0.887592	2.439782
C	12.654819	0.728924	1.026754
C	8.100146	2.805069	-0.437022
H	8.763000	3.084372	-1.264044

H	7.158796	3.337257	-0.572213
H	8.562965	3.178960	0.483975
C	10.887936	-1.667553	-1.603172
H	10.197436	-2.403605	-1.172444
H	10.287897	-0.905323	-2.104692
H	11.498740	-2.196970	-2.337159
C	13.582899	1.624974	0.170537
H	13.009821	2.393410	-0.360000
H	14.309255	2.133071	0.814399
H	14.141300	1.036586	-0.559364
C	12.033036	1.586581	2.152392
H	11.271662	1.031425	2.709674
H	12.817322	1.882855	2.857025
H	11.573798	2.505065	1.777581
O	-13.061803	3.214607	-0.055236
O	13.505668	-2.575817	-1.233414
O	-14.844313	0.823453	1.012863
O	15.280627	-1.073898	0.283107
H	-14.124646	0.675722	1.641347
H	15.461989	-1.689154	-0.445673

TABLE S5: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for #Ast$^{\bullet}$(3)a.

C	11.604667	-0.081980	0.003616

C	11.747740	1.238288	-0.345112
C	12.714994	-0.890945	0.717425
C	13.841558	0.027596	1.248031
H	14.726555	-0.576280	1.479426
H	13.510976	0.478592	2.193721
C	14.227578	1.175052	0.323210
H	14.940615	1.840040	0.818081
C	12.988406	1.993258	-0.027825
C	12.114422	-1.624296	1.942308
H	11.396578	-2.396505	1.653139
H	12.916450	-2.109482	2.509506
H	11.602962	-0.923962	2.610175
C	13.307030	-1.959218	-0.239423
H	14.029673	-2.575637	0.305876
H	12.537777	-2.630071	-0.632704
H	13.836686	-1.508747	-1.079778
C	10.708665	2.062913	-1.067915
H	10.077943	1.447892	-1.712817
H	10.053788	2.596047	-0.367909
H	11.205132	2.833693	-1.661081
C	10.390656	-0.855347	-0.273750
H	10.554788	-1.908505	-0.486804
C	9.103365	-0.429312	-0.196395

H	8.907446	0.595925	0.104075
C	7.924419	-1.240244	-0.431856
C	6.698818	-0.655015	-0.249201
H	6.698668	0.389724	0.062668
C	5.402450	-1.242093	-0.413504
H	5.341604	-2.282055	-0.719630
C	4.246246	-0.548275	-0.198917
H	4.333365	0.494359	0.107214
C	2.902892	-1.052206	-0.333995
C	1.860023	-0.195296	-0.073859
H	2.126394	0.820403	0.219512
C	0.459958	-0.464271	-0.138762
H	0.129870	-1.461056	-0.423124
C	8.104654	-2.674956	-0.861539
H	7.156245	-3.180580	-1.043198
H	8.695517	-2.735581	-1.782865
H	8.644383	-3.248169	-0.097872
C	2.708567	-2.489535	-0.752281
H	3.161334	-2.674786	-1.733437
H	3.192525	-3.170643	-0.042622
H	1.657401	-2.770548	-0.815449
C	-0.500885	0.470776	0.138888
H	-0.169252	1.467448	0.422100

C	-1.901359	0.204801	0.075870
H	-2.171098	-0.812396	-0.208845
C	-2.941299	1.068238	0.328227
C	-4.286851	0.569317	0.201069
H	-4.380054	-0.477809	-0.087168
C	-5.439170	1.274471	0.403457
H	-5.369592	2.319646	0.689610
C	-6.739954	0.696052	0.253871
H	-6.750924	-0.356914	-0.028541
C	-7.960639	1.299531	0.419809
C	-9.148695	0.498305	0.212066
H	-8.969533	-0.540229	-0.052569
C	-2.739726	2.509450	0.730144
H	-3.190169	2.707496	1.709767
H	-1.687399	2.787088	0.787918
H	-3.222107	3.184298	0.013545
C	-10.432991	0.943490	0.275104
H	-10.583816	2.005599	0.452886
C	-11.649148	0.169818	0.057755
C	-11.804264	-1.128660	0.482889
C	-13.071357	-1.843408	0.252185
C	-14.038066	-1.243731	-0.606173
C	-13.795000	0.022553	-1.329969

H	-14.743179	0.532717	-1.535648
H	-13.350971	-0.210620	-2.311960
C	-12.840558	0.961810	-0.547450
C	-8.122016	2.749762	0.804568
H	-8.701613	2.846335	1.729863
H	-7.167070	3.252451	0.957500
H	-8.665424	3.301881	0.028221
C	-10.791597	-1.919588	1.269741
H	-10.160173	-2.535192	0.616402
H	-10.134895	-1.274665	1.856746
H	-11.322330	-2.612861	1.926310
C	-13.615248	1.632834	0.612769
H	-12.958305	2.282337	1.199847
H	-14.434402	2.248275	0.223074
H	-14.038449	0.884480	1.288859
C	-12.380057	2.047805	-1.543862
H	-11.729921	1.628354	-2.317925
H	-13.253508	2.488199	-2.037257
H	-11.839865	2.863164	-1.056858
O	13.040427	3.213169	-0.124733
O	-13.356417	-2.969948	0.748460
O	14.872173	0.748324	-0.886755
H	14.184846	0.545296	-1.535647

O	-15.152212	-1.940043	-0.819353
H	-15.006606	-2.746922	-0.262563

TABLE S6: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for #Ast$^{\bullet}$(3)b.

C	11.560720	-0.053667	0.054464
C	11.706676	1.235914	-0.399385
C	12.668002	-0.798696	0.839569
C	13.785609	0.163809	1.307569
H	14.670014	-0.416484	1.595048
H	13.443857	0.686120	2.211735
C	14.179066	1.236515	0.300186
H	14.880969	1.943457	0.751032
C	12.941845	2.017062	-0.133630
C	12.062592	-1.437376	2.114290
H	11.352778	-2.235544	1.882335
H	12.864072	-1.870447	2.722993
H	11.542036	-0.690104	2.721553
C	13.274282	-1.934414	-0.026370
H	13.992771	-2.504798	0.572033
H	12.511520	-2.636064	-0.376427
H	13.811349	-1.545507	-0.892298
C	10.673471	1.995025	-1.198145
H	10.069597	1.328630	-1.817645

H	9.991569	2.560179	-0.550903
H	11.173444	2.734183	-1.827187
C	10.354334	-0.850819	-0.166907
H	10.520896	-1.921556	-0.248777
C	9.059634	-0.425541	-0.177193
H	8.850658	0.625520	-0.002667
C	7.898405	-1.266815	-0.343797
C	6.655117	-0.675900	-0.255464
H	6.642358	0.398561	-0.070116
C	5.379382	-1.290534	-0.368006
H	5.331723	-2.360001	-0.549111
C	4.197735	-0.587084	-0.249897
H	4.272838	0.485445	-0.069643
C	2.883274	-1.119180	-0.334704
C	1.803389	-0.242304	-0.185059
H	2.059870	0.803745	-0.014639
C	0.437016	-0.538031	-0.223200
H	0.116708	-1.564552	-0.387791
C	8.094391	-2.741265	-0.596862
H	7.152991	-3.269631	-0.747507
H	8.713909	-2.906635	-1.485857
H	8.610432	-3.219049	0.244993
C	2.699182	-2.598107	-0.579486

H	3.144642	-2.894924	-1.536232
H	3.192836	-3.188187	0.201274
H	1.650037	-2.892976	-0.599728
C	-0.568845	0.424518	-0.055777
H	-0.250407	1.452853	0.106258
C	-1.927793	0.138482	-0.082563
H	-2.211673	-0.901087	-0.245588
C	-2.990949	1.064125	0.084532
C	-4.295582	0.585150	0.034930
H	-4.407555	-0.486491	-0.131660
C	-5.502860	1.312421	0.176609
H	-5.446471	2.384854	0.338211
C	-6.744574	0.721115	0.119922
H	-6.778050	-0.356281	-0.042751
C	-8.012794	1.377116	0.253529
C	-9.155134	0.606834	0.178388
H	-8.994016	-0.455469	0.022896
C	-2.667885	2.523968	0.310046
H	-2.044257	2.653075	1.201759
H	-2.107552	2.936212	-0.536778
H	-3.560276	3.135635	0.442808
C	-10.511564	1.067946	0.209210
H	-10.637851	2.142300	0.150819

C	-11.663936	0.322431	0.216159
C	-11.701236	-1.128838	0.438121
C	-12.725631	-1.883834	-0.067117
C	-13.835108	-1.304715	-0.863975
C	-13.751535	0.186864	-1.122211
H	-14.770467	0.552692	-1.284137
H	-13.207123	0.322096	-2.068079
C	-13.033591	0.991516	-0.010205
C	-8.033106	2.872037	0.473343
H	-9.040428	3.264885	0.610617
H	-7.455206	3.139546	1.365256
H	-7.578577	3.399642	-0.373260
C	-10.676169	-1.823306	1.315527
H	-9.952833	-2.421334	0.745319
H	-10.112400	-1.107449	1.912860
H	-11.175308	-2.501187	2.021953
C	-13.868625	0.954593	1.294536
H	-13.376072	1.537761	2.079081
H	-14.860338	1.386906	1.122563
H	-14.005502	-0.063138	1.667877
C	-12.945177	2.455599	-0.473747
H	-12.333242	2.563446	-1.374634
H	-13.949587	2.825525	-0.703593

H	-12.532416	3.107006	0.303272
O	12.994548	3.224848	-0.334058
O	-12.852092	-3.223275	0.115161
O	14.844737	0.718088	-0.861931
H	14.169165	0.471275	-1.507950
O	-14.745600	-1.993605	-1.294129
H	-12.090341	-3.556783	0.606697

TABLE S7: Optimized cartesian coordinates at B3LYP/6-31G (d, p) level for $Ast^{\bullet-}$.

C	11.617269	0.157764	-0.150738
C	11.716340	-1.105923	-0.726006
C	12.856281	0.865873	0.464192
C	14.133150	-0.007988	0.384275
H	14.853162	0.336448	1.136403
H	14.610815	0.130840	-0.595509
C	13.882099	-1.502104	0.541690
H	14.810597	-2.064223	0.406676
C	12.903572	-1.947207	-0.543071
C	13.153879	2.164847	-0.327964
H	12.380988	2.926856	-0.196612
H	14.100083	2.595728	0.020232
H	13.248934	1.957586	-1.398614
C	12.590849	1.246808	1.942799

H	13.424227	1.845608	2.329061
H	11.674201	1.832880	2.049708
H	12.509708	0.357931	2.571661
C	10.663060	-1.717483	-1.619892
H	9.942621	-2.336804	-1.068887
H	10.097303	-0.954238	-2.160000
H	11.159884	-2.383734	-2.329158
C	10.414024	0.949563	-0.126516
H	10.559138	2.010638	0.049732
C	9.101426	0.527418	-0.196037
H	8.899167	-0.536462	-0.269100
C	7.949643	1.361560	-0.127075
C	6.693451	0.759516	-0.146273
H	6.692791	-0.329694	-0.216376
C	5.422967	1.361739	-0.088445
H	5.361405	2.443782	-0.013782
C	4.236863	0.635995	-0.121330
H	4.327687	-0.449110	-0.189744
C	2.923791	1.148859	-0.075265
C	1.845620	0.252408	-0.113504
H	2.114648	-0.803197	-0.178997
C	0.476044	0.528281	-0.078527
H	0.145112	1.563495	-0.012798

C	8.126171	2.858871	-0.029645
H	7.176433	3.393407	-0.075181
H	8.619181	3.142496	0.909669
H	8.756575	3.235752	-0.844048
C	2.720157	2.644507	0.017877
H	3.145717	3.045085	0.946481
H	3.219897	3.162288	-0.809698
H	1.666696	2.925764	-0.008737
C	-0.520907	-0.451105	-0.122685
H	-0.189560	-1.486322	-0.187999
C	-1.890001	-0.176090	-0.090263
H	-2.160272	0.879446	-0.030784
C	-2.968302	-1.074636	-0.126423
C	-4.280252	-0.563602	-0.093900
H	-4.373520	0.521875	-0.037522
C	-5.467800	-1.291762	-0.128079
H	-5.403486	-2.374680	-0.187599
C	-6.736249	-0.691655	-0.089897
H	-6.738350	0.398312	-0.034698
C	-7.995698	-1.295820	-0.112826
C	-9.144119	-0.463713	-0.063070
H	-8.943675	0.600681	-0.011757
C	-2.759865	-2.570703	-0.207108

H	-3.149120	-2.975166	-1.149856
H	-1.707886	-2.850619	-0.138579
H	-3.289980	-3.085732	0.602709
C	-10.458935	-0.900380	-0.013712
H	-10.586795	-1.976375	0.042544
C	-11.672720	-0.143894	0.051120
C	-11.819362	1.175919	-0.384346
C	-13.075166	1.911810	-0.275099
C	-14.236064	1.253824	0.473532
C	-13.879343	0.031215	1.281928
H	-14.803072	-0.480479	1.572628
H	-13.388226	0.376612	2.203281
C	-12.918145	-0.927996	0.542527
C	-8.166376	-2.795740	-0.186849
H	-8.755943	-3.084698	-1.065536
H	-7.212159	-3.321016	-0.243287
H	-8.700448	-3.178360	0.692445
C	-10.735956	1.942481	-1.103975
H	-10.053126	2.454991	-0.412927
H	-10.131174	1.288961	-1.738810
H	-11.206269	2.719168	-1.710429
C	-13.641674	-1.546283	-0.678883
H	-12.974832	-2.227525	-1.217410

H	-14.523408	-2.114576	-0.359240
H	-13.968119	-0.774597	-1.381894
C	-12.579976	-2.059771	1.538460
H	-11.942231	-1.699594	2.351536
H	-13.507283	-2.445454	1.977387
H	-12.075327	-2.905869	1.064399
O	13.094474	-2.996748	-1.163364
O	-13.250857	3.042198	-0.745659
O	13.390755	-1.864713	1.843344
H	12.430566	-1.749277	1.822700
O	-15.362092	1.715355	0.438224

TABLE S8: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for $Ast^{\bullet+}$ radical cation of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\mathbf{A_{iso}}$
1	3				**-0.05**
	3				**0.33**
1'	3				**0.01**
	3				**0.03**
2	1	0.71	0.82	1.20	**0.91**
	1	0.09	0.21	0.73	**0.35**
2'	1	0.9	0.98	1.36	**1.08**
	1	-0.14	-0.02	0.49	**0.11**
3	1	-0.66	-0.51	0.01	**-0.39**
	1	-0.30	-0.14	0.37	**-0.02**
3'	1	-0.203	-0.104	0.313	**0.002**
	1	-0.54	-0.28	0.47	**-0.12**
5	3				**5.05**
5'	3				**4.45**
7	1	-15.14	-10.6	-4.8	**-10.18**
7'	1	-14.73	-10.26	-4.56	**-9.85**
8	1	1.83	2.23	5.66	**3.24**
8'	1	1.83	2.26	5.60	**3.23**
9	3				**9.17**
9'	3				**9.23**
10	1	0.86	1.46	4.22	**2.18**
10'	1	1.07	1.64	4.49	**2.40**
11	1	-12.47	-9.08	-3.71	**-8.42**
11'	1	-12.93	-9.34	-3.87	**-8.72**
12	1	0.66	1.08	4.08	**1.94**
12'	1	0.99	1.33	4.52	**2.28**
13	3				**5.62**
13'	3				**6.06**
14	1	-2.60	-2.47	0.54	**-1.51**
14'	1	-2.15	-1.87	0.90	**-1.04**
15	1	-4.66	-4.1	-0.69	**-3.15**
15'	1	-5.38	-4.59	-1.01	**-3.66**

TABLE S9: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for #Ast$^{\bullet}$(5) neutral radical of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\boldsymbol{A_{iso}}$
1	3				**0.46**
	3				**-0.10**
1'	3				**0.01**
	3				**0.04**
2	1	1.59	1.70	2.45	**1.91**
	1	-0.79	-0.38	0.68	**-0.16**
2'	1	0.94	1.03	1.36	**1.11**
	1	0.03	0.19	0.62	**0.28**
3	1	0.22	0.28	0.76	**0.42**
	1	-0.12	-0.11	0.26	**0.01**
3'	1	-0.18	-0.07	0.37	**0.04**
	1	-0.59	-0.30	0.39	**-0.17**
5	1	-3.56	-2.4	-1.12	**-2.36**
	1	-4.5	-2.78	-0.73	**-2.67**
5'	3				**3.71**
7	1	3.53	3.77	6.53	**4.61**
7'	1	-14.41	-10.06	-4.66	**-9.71**
8	1	3.53	3.77	6.53	**4.61**
8'	1	-13.29	-10.19	-4.27	**-9.25**
9	3				**-4.62**
9'	3				**10.09**
10	1	-17.09	-12.65	-5.72	**-11.82**
10'	1	4.45	5.46	10.70	**6.87**
11	1	4.71	5.62	10.82	**7.05**
11'	1	-21.50	-14.98	-7.44	**-14.64**
12	1	-19.58	-14.60	-6.83	**-13.67**
12'	1	5.49	7.03	13.10	**8.54**
13	3				**-7.53**
13'	3				**14.05**
14	1	-2.79	3.35	12.30	**4.29**
14'	1	6.17	7.99	14.66	**9.61**
15	1	6.29	7.88	14.48	**9.55**
15'	1	-25.20	-17.85	-8.43	**-17.16**

TABLE S10: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for #Ast$^{\bullet}$(9) neutral radical of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\boldsymbol{A_{iso}}$
1	3				**-0.01**
	3				**-0.09**
1'	3				**0.01**
	3				**0.04**
2	1	-0.13	-0.09	0.04	**-0.06**
	1	-0.18	-0.12	0.09	**-0.07**
2'	1	1.01	1.11	1.45	**1.19**
	1	0.03	0.18	0.63	**0.28**
3	1	-0.02	0.04	0.13	**0.05**
	1	-0.063	0.003	0.057	**-0.001**
3'	1	-0.21	-0.09	0.36	**0.02**
	1	-0.62	-0.31	0.42	**-0.17**
5	3				**-0.65**
5'	3				**3.97**
7	1	0.55	1.61	4.30	**2.15**
7'	1	-15.79	-11.10	-5.32	**-10.74**
8	1	-3.67	-3.16	-2.03	**-2.95**
8'	1	3.28	3.63	7.73	**4.88**
9	1	-18.16	-11.34	-4.28	**-11.26**
	1	-16.74	-11.29	-4.51	**-10.85**
9'	3				**10.79**
10	1	-21.68	-14.96	-6.62	**-14.42**
10'	1	4.83	5.96	11.48	**7.42**
11	1	4.45	5.43	11.84	**7.24**
11'	1	-22.47	-15.65	-7.75	**-15.29**
12	1	-19.76	-14.95	-6.88	**-13.86**
12'	1	5.83	7.51	13.88	**9.07**
13	3				**-7.68**
13'	3				**14.59**
14	1	-23.43	-17.17	-7.97	**-16.19**
14'	1	6.35	8.19	15.04	**9.86**
15	1	6.46	8.07	14.87	**9.80**
15'	1	-25.60	-18.11	-8.48	**-17.40**

TABLE S11: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for #Ast$^{\bullet}$(13) neutral radical of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\mathbf{A_{iso}}$
1	3				**-0.02**
	3				**-0.08**
1'	3				**0.01**
	3				**0.05**
2	1	-0.10	-0.07	-0.04	**-0.07**
	1	-0.11	-0.07	0.01	**-0.06**
2'	1	1.15	1.25	1.65	**1.35**
	1	0.02	0.20	0.71	**0.31**
3	1	-0.02	0.04	0.08	**0.03**
	1	-0.0448	0.0162	0.0292	**0.0002**
3'	1	-0.24	-0.10	0.40	**0.02**
	1	-0.69	-0.35	0.48	**-0.19**
5	3				**-0.56**
5'	3				**4.47**
7	1	0.775	1.667	2.598	**1.68**
7'	1	-18.00	-12.67	-6.08	**-12.25**
8	1	-1.05	-0.72	-0.62	**-0.8**
8'	1	3.75	4.12	8.78	**5.55**
9	3				**-1.90**
9'	3				**12.20**
10	1	-1.87	-1.55	-1.03	**-1.48**
10'	1	5.37	6.55	12.75	**8.22**
11	1	0.97	2.55	6.72	**3.41**
11'	1	-24.97	-17.43	-8.54	**-16.98**
12	1	-5.71	-5.17	-3.16	**-4.68**
12'	1	6.33	8.00	15.10	**9.81**
13	1	-28.73	-18.07	-6.99	**-17.93**
	1	-26.66	-17.77	-7.03	**-17.15**
13'	3				**15.93**
14	1	-29.199	-19.966	-8.465	**-19.21**
14'	1	6.51	8.17	15.74	**10.14**
15	1	5.66	7.02	15.64	**9.44**
15'	1	-26.73	-19.27	-8.73	**-18.24**

TABLE S12: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for #Ast$^{\bullet}$(3)a neutral radical of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\boldsymbol{A_{iso}}$
1	3				**-0.43**
	3				**0.09**
1'	3				**0.01**
	3				**0.04**
2	1	15.41	16.35	24.10	**18.62**
	1	72.80	73.00	81.87	**75.89**
2'	1	0.09	0.10	0.13	**0.10**
	1	0.001	0.013	0.046	**0.02**
3O	1	-17.78	-14.19	4.31	**-9.22**
3'	1	-0.022	-0.012	0.027	**-0.002**
O	1	-0.05	-0.03	0.03	**-0.02**
5	3				**-2.61**
5'	3				**0.38**
7	1	4.68	4.73	7.9	**5.77**
7'	1	-1.63	-1.2	-0.68	**-1.17**
8	1	-3.85	-3.54	-1.71	**-3.05**
8'	1	0.47	0.61	0.99	**0.69**
9	3				**-1.20**
9'	3				**0.92**
10	1	-2.39	-2.10	-0.91	**-1.8**
10'	1	0.65	0.92	1.43	**1.00**
11	1	0.34	0.43	1.45	**0.74**
11'	1	-1.82	-1.30	-0.75	**-1.29**
12	1	-1.80	-1.37	-0.52	**-1.23**
12'	1	0.70	1.05	1.61	**1.12**
13	3				**-0.78**
13'	3				**1.03**
14	1	-1.34	-0.98	-0.38	**-0.9**
14'	1	0.62	0.94	1.53	**1.03**
15	1	0.45	0.71	1.36	**0.84**
15'	1	-1.51	-1.03	-0.46	**-1.0**

TABLE S13: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for #Ast$^{\bullet}$(3)b neutral radical of astaxanthin obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	Number of protons	A_{XX}	A_{YY}	A_{ZZ}	A_{iso}
1	3				**0.29**
	3				**-0.05**
1'	3				**0.01**
	3				**0.04**
2	1	-0.27	-0.04	0.72	**0.14**
	1	-0.49	-0.22	0.81	**0.03**
2'	1	0.9	0.98	1.31	**1.06**
	1	0.04	0.18	0.59	**0.27**
3'	1	-0.18	-0.07	0.34	**0.03**
O	1	-0.55	-0.28	0.38	**-0.15**
5	1				**-2.14**
5'	3				**3.47**
7	1	4.59	4.81	8.31	**5.9**
7'	1	-13.73	-9.58	-4.41	**-9.24**
8	1	-14.1	-10.39	-4.74	**-9.74**
8'	1	2.66	2.87	6.54	**4.03**
9	3				**-5.09**
9'	3				**9.73**
10	1	-17.44	-12.79	-5.81	**-12.01**
10'	1	4.21	5.15	10.20	**6.52**
11	1	4.85	5.97	11.35	**7.39**
11'	1	-20.80	-14.47	-7.15	**-14.14**
12	1	-19.67	-14.60	-6.87	**-13.71**
12'	1	5.28	6.79	12.71	**8.26**
13	3				**-7.73**
13'	3				**13.75**
14	1	-22.85	-16.67	-7.82	**-15.78**
14'	1	6.01	7.83	14.39	**9.41**
15	1	6.23	7.92	14.54	**9.55**
15'	1	-24.81	-17.54	-8.30	**-16.88**

TABLE S14: Isotropic β-methyl proton and anisotropic α-proton tensors (MHz) for $Ast^{\bullet-}$ radical anion (proton loss form OH group of #$Ast^{\bullet}$(3)b) obtained by DFT calculations; the bold values are the isotropic coupling constants $\mathbf{A_{iso}}$ given by averaging the three anisotropic coupling tensors A_{XX} A_{YY} A_{ZZ}

Position	**Number of protons**	A_{XX}	A_{YY}	A_{ZZ}	$\boldsymbol{A_{iso}}$
1	3				**0.20**
	3				**0.41**
1'	3				**0.25**
	3				**0.54**
2	1	-0.03	0.17	0.64	**0.26**
	1	1.70	2.11	2.70	**2.17**
2'	1	0.08	0.21	0.61	**0.30**
	1	0.33	0.43	1.11	**0.62**
5	3				**3.42**
5'	3				**3.99**
7	1	-6.33	-4.53	-0.88	**-3.91**
7'	1	-8.27	-5.72	-1.88	**-5.29**
8	1	-2.06	-1.60	0.48	**-1.06**
8'	1	-0.94	-0.23	1.45	**0.09**
9	3				**3.14**
9'	3				**4.30**
10	1	-1.63	-0.84	0.69	**-0.59**
10'	1	-0.46	0.35	2.00	**0.63**
11	1	-5.63	-4.46	-1.34	**-3.81**
11'	1	-7.96	-5.87	-2.16	**-5.33**
12	1	-3.28	-3.20	-0.24	**-2.24**
12'	1	-1.75	-1.17	0.79	**-0.71**
13	3				**2.33**
13'	3				**3.92**
14	1	-3.45	-3.30	-0.45	**-2.4**
14'	1	-1.89	-1.07	0.65	**-0.77**
15	1	-3.51	-3.31	-0.38	**-2.4**
15'	1	-6.19	-4.99	-1.33	**-4.17**

Figure S1. CV plot of astaxanthin in the presence of Ca and Zn salts as a function of scan rate; stability of the radical cation, dication and the neutral radical is dependent on the presence of the salt, the apparent oxidation shifts to lower oxidation potential and is dependent on the type of metal. CV plot of astaxanthin 1 mM + Ca^{2+} (20 mM) or Zn^{2+} (30 mM) in anhydrous CH_3CN (scan rate = 1000 mV/s)

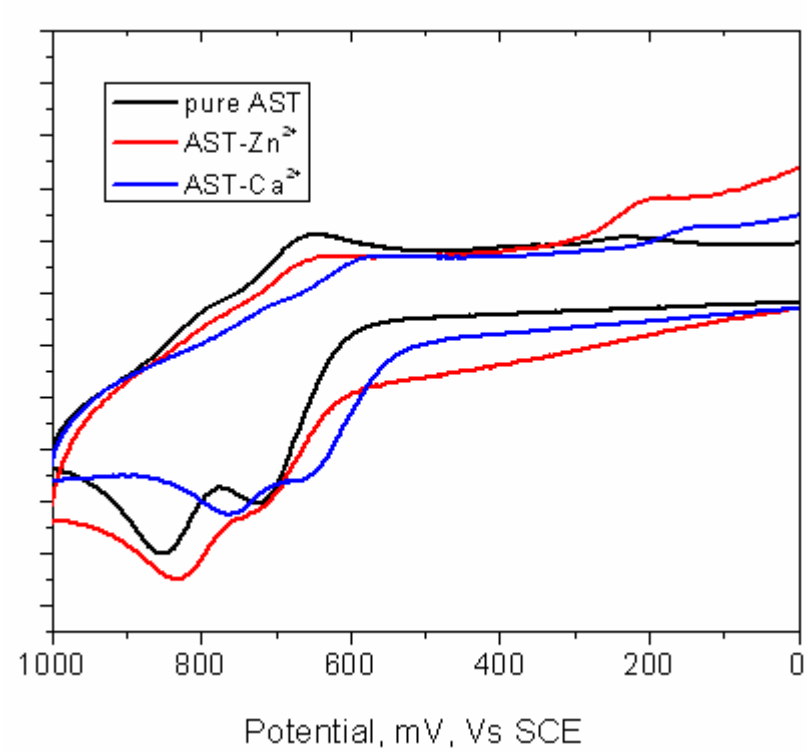


Figure S2. CV plot of astaxanthin 1 mM + $Ca(ClO_4)_2$ 20 mM in anhydrous CH_3CN (scan rate = 200 mV/s)

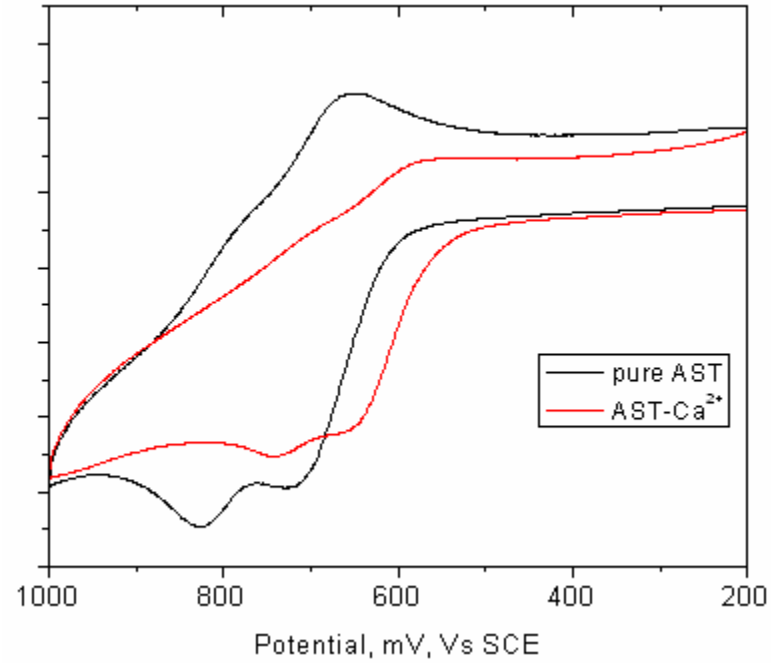
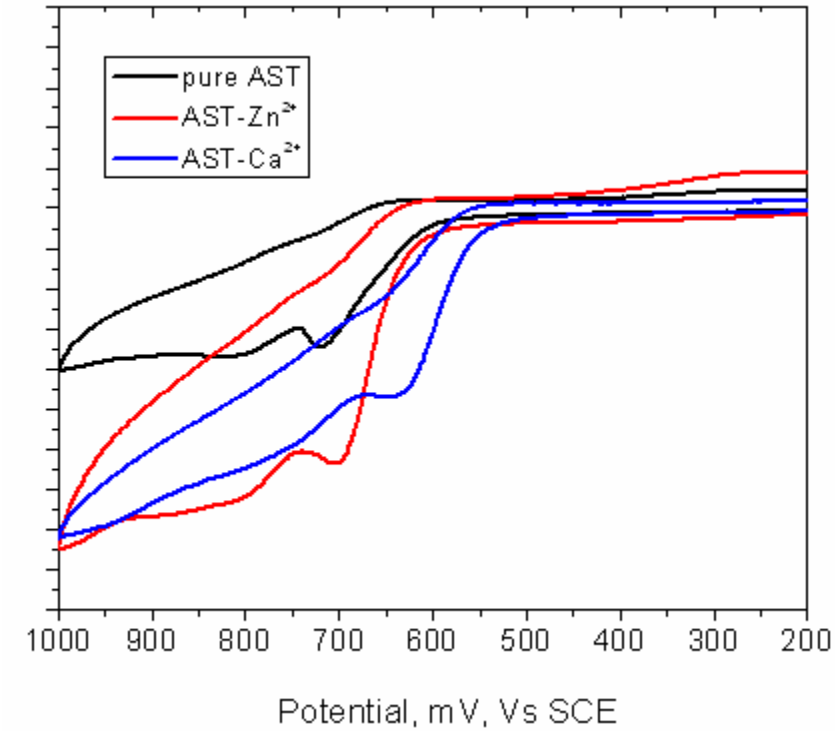
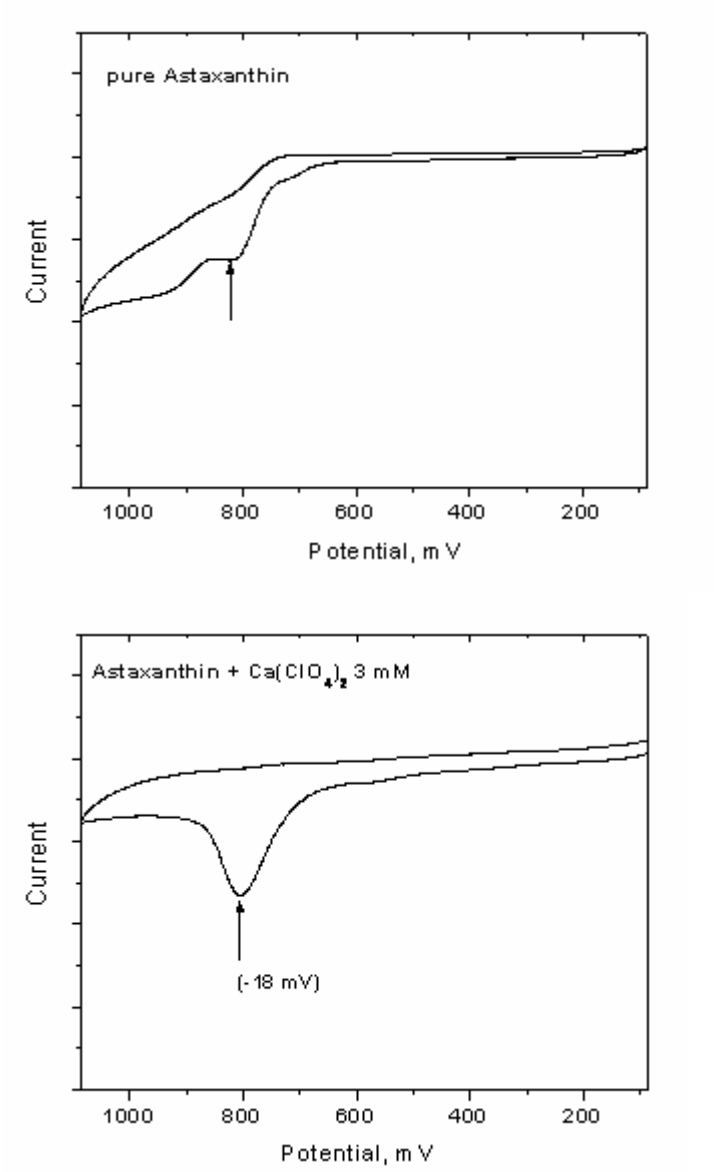


Figure S3. CV plot of astaxanthin 1 mM + Ca^{2+} (20 mM) or Zn^{2+} (30 mM) in anhydrous CH_3CN (scan rate = 10 mV/s)



Fi gure S4. The effect of hydrated salts in CH_3CN causing severe irreversible CV and decay of the radical species; Astaxanthin 0.1 mM in CH_3CN, Scan rate = 10 mV/sec.



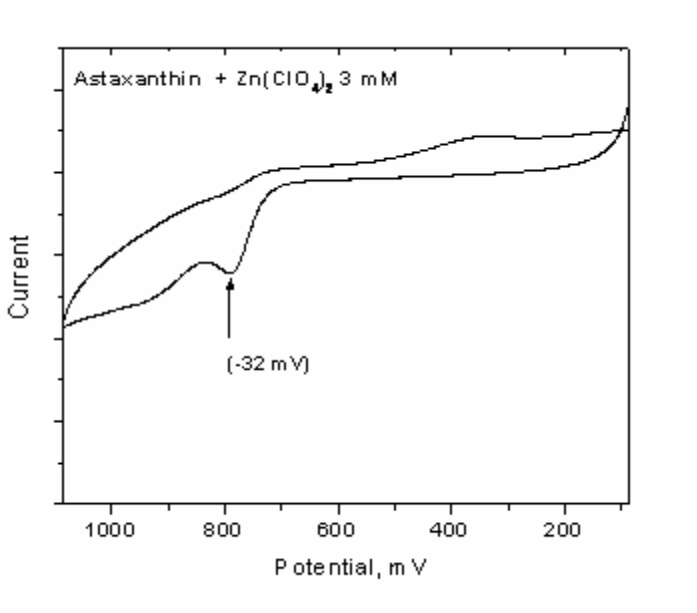

Astaxanthin + Zn(ClO4)2 3 mM
Current
(-32 mV)
1000
800
600
400
200
Potential, mV

Figure S5. The ESEEM spectra of astaxanthin radicals: the spectra show proton modulation consistent with the formation of carotenoid radicals.

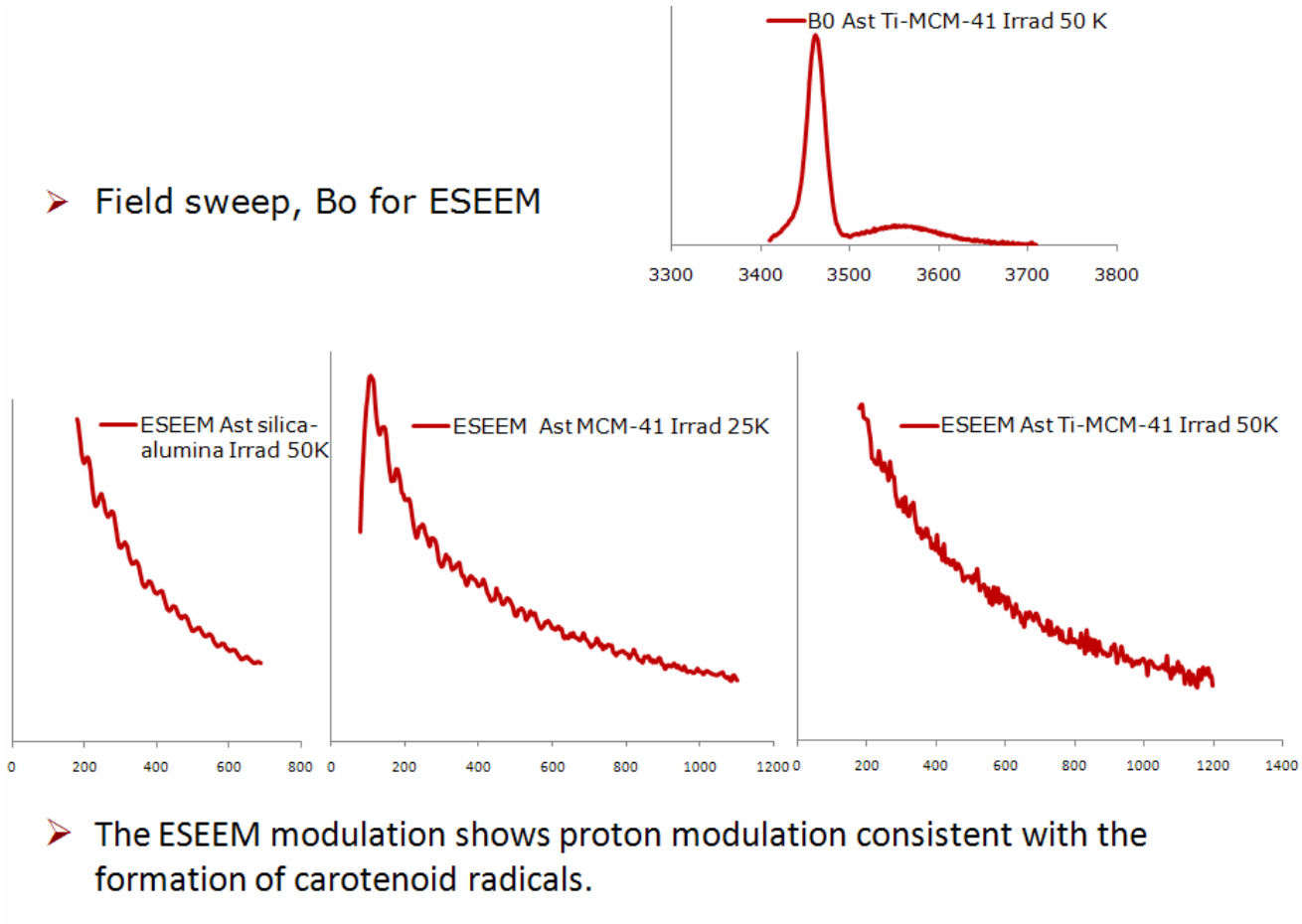


Figure S6. The EPR spectra of astaxanthin radicals: the spectra show broadening upon irradiation indicating formation of neutral radicals. Field positions are not corrected for change in frequency before and after irradiation, samples being irradiated external to the cavity.