SUPPORTING INFORMATION

Cis Carotenoids: Colorful Molecules and Free Radical Quenchers

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Table S1. Theoretical VEA and VIE in benzene and water.

CAROTENOIDS	Benzene		Water	
	VIE	VEA	VIE	VEA
trans AURO	5.357	1.950	4.894	2.626
9-cis AURO	5.347	1.944	4.885	2.619
13-*cis* AURO	5.390	1.899	4.923	2.585
15-*cis* AURO	5.405	1.920	4.939	2.612
trans LUTEO	5.279	2.105	4.825	2.730
9-*cis* LUTEO	5.266	2.097	4.814	2.722
13-*cis* LUTEO	5.302	2.053	4.843	2.688
15-*cis* LUTEO	5.319	2.070	4.862	2.712
trans NEOCHR	5.186	1.998	4.790	2.677
9-*cis* NEOCHR	5.181	1.999	4.782	2.672
13-*cis* NEOCHR	5.216	1.951	4.813	2.638
15-*cis* NEOCHR	5.236	1.970	4.834	2.665
trans MUTATO	5.212	2.117	4.772	2.734
9-*cis* MUTATO	5.203	2.116	4.759	2.727
13-*cis* MUTATO	5.236	2.067	4.789	2.694
15-*cis* MUTATO	5.255	2.086	4.809	2.719
trans NEOX	5.140	2.148	4.736	2.768
9-*cis* NEOX	5.137	2.101	4.741	2.742
13-*cis* NEOX	5.166	2.090	4.763	2.726
15-*cis* NEOX	5.183	2.114	4.777	2.752
trans VIOLA	5.202	2.221	4.767	2.814
9-*cis* VIOLA	5.197	2.175	4.771	2.788
13-*cis* VIOLA	5.231	2.165	4.793	2.772
15-*cis* VIOLA	5.244	2.183	4.806	2.797
trans ANTHER	5.148	2.234	4.720	2.814
9-*cis* ANTHER	5.145	2.194	4.723	2.791
13-*cis* ANTHER	5.182	2.181	4.747	2.773
15-*cis* ANTHER	5.194	2.200	4.759	2.798
trans LUT	5.135	2.223	4.704	2.799
9-*cis* LUT	5.156	2.188	4.716	2.772
13-*cis* LUT	5.176	2.172	4.734	2.758
15-*cis* LUT	5.180	2.188	4.743	2.783
trans BC	4.930	2.225	4.567	2.813
9-*cis* BC	4.952	2.193	4.585	2.789
13-*cis* BC	4.969	2.175	4.598	2.773
15-*cis* BC	4.975	2.191	4.605	2.796
trans LYCO	4.959	2.207	4.616	2.794
5-*cis* LYCO	4.979	2.218	4.629	2.803
9-*cis* LYCO	4.965	2.231	4.616	2.821
13-*cis* LYCO	4.946	2.223	4.594	2.824
15-*cis* LYCO	4.956	2.241	4.606	2.849
trans ASTA	5.393	2.700	4.871	3.130
9-*cis* ASTA	5.388	2.646	4.870	3.093
13-*cis* ASTA	5.419	2.642	4.894	3.091
15-*cis* ASTA	5.431	2.650	4.907	3.106

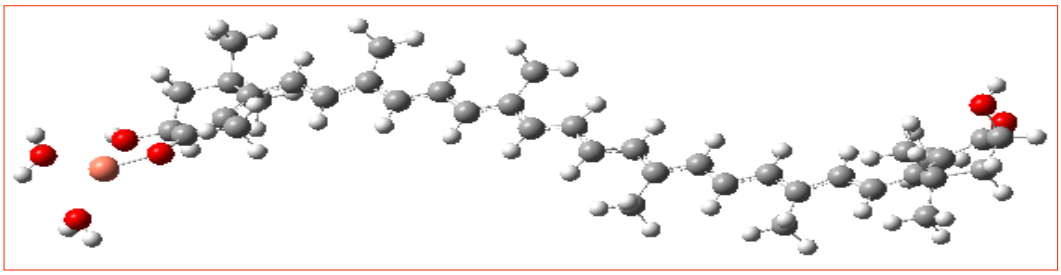

Figure S1. Optimized geometry of the [(*trans*-ASTA)Cu(H_2O)$_2$]$^{2+}$complex.

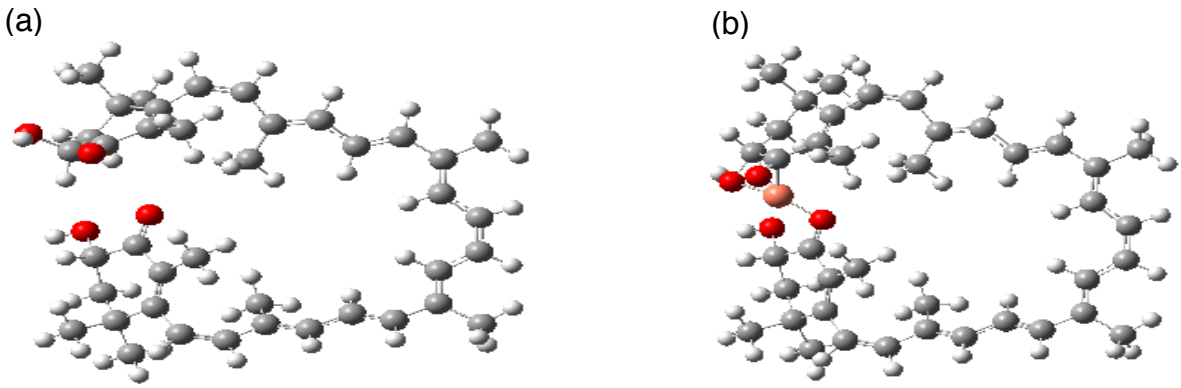

Figure S2. (a) Optimized geometry of the twist-ASTA conformation. (b) Optimized geometry of the [(twist-ASTA)Cu]$^{2+}$ complex.

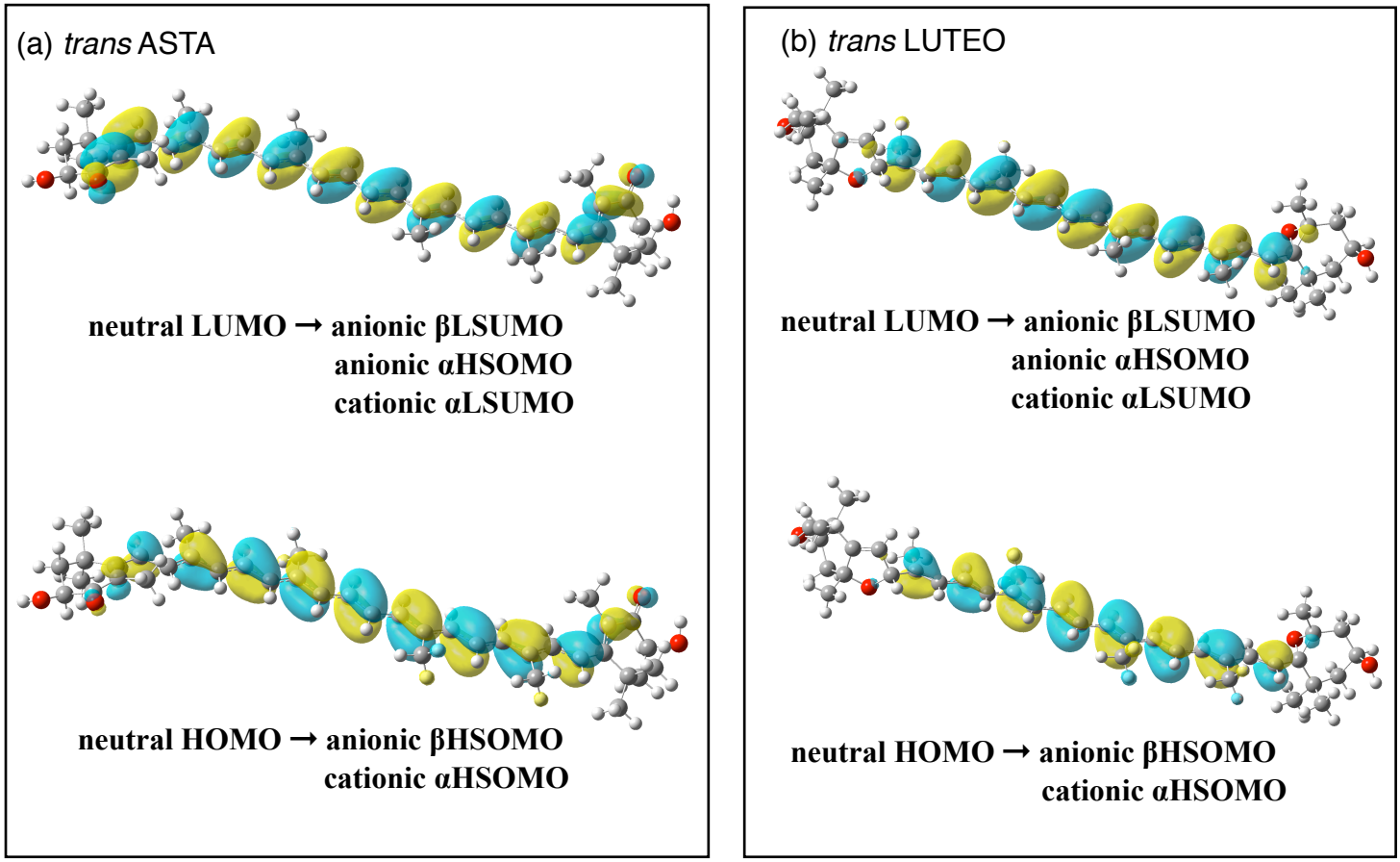

Figure S3. Representations of the anionic βLSUMO (anionic αHSOMO, cationic αLSUMO) and anionic βHSOMO (cationic αHSOMO). (a) *trans* ASTA; (b) *trans* LUTEO

Table S2. Theoretical[a] maximum absorption wavelength (λ_{max}) in nm for the *trans* radical cations in gas phase. The theoretical wavelengths (λ_{theo}) that make up the band, along with their oscillator strengths (*f*) and the major contributions to the excitation are also included.

Carotenoids	λ_{max}	λ_{theo}	*f*	Transition	% contrib.
trans AURO	664	665	3.3243	α HSOMO → LSUMO β HSOMO → LSUMO	50.4 33.8
trans LUTEO	732	730	3.5192	α HSOMO → LSUMO β HSOMO → LSUMO	50.0 32.5
trans NEOCHR	730	731	3.6675	α HSOMO → LSUMO β HSOMO → LSUMO	47.6 35.4
trans MUTATO	786	784	3.3418	α HSOMO → LSUMO β HSOMO → LSUMO	56.0 23.7
trans NEOX	796	795	3.8832	α HSOMO → LSUMO β HSOMO → LSUMO	49.1 31.7
trans VIOLA	797	795	3.7631	α HSOMO → LSUMO β HSOMO → LSUMO	50.9 29.8
trans ANTHER	860	855	3.5510	α HSOMO → LSUMO β HSOMO → LSUMO	60.5 18.2
trans LUT	860	854	3.5289	α HSOMO → LSUMO β HSOMO → LSUMO	59.9 18.8
trans BC	968	1008	1.4555	β HSOMO → LSUMO β HSOMO-1 → LSUMO+1	82.2 9.8
		951	2.8279	α HSOMO → LSUMO α HSOMO-1 → LSUMO+1	77.3 9.7
trans LYCO	984	1065	1.9410	β HSOMO → LSUMO β HSOMO-1 → LSUMO+1	85.0 8.0
		933	2.5684	α HSOMO → LSUMO α HSOMO-1 → LSUMO+1	73.8 13.7
trans ASTA	864	858	3.6091	α HSOMO → LSUMO β HSOMO → LSUMO	60.1 17.6

[a]CAM-B3LYP calculations.

Table S3. Theoretical[a] maximum absorption wavelength (λ_{max}) in nm for the *trans* radical anions in gas phase. The theoretical wavelengths (λ_{theo}) and oscillator strength (*f*) that make up the band, as well as the major contributions to the excitation are also listed.

Carotenoids	λ_{max}	λ_{theo}	*f*	Transition	% contrib.
trans AURO	620	823	0.2949	β HSOMO → LSUMO	72.2
				α HSOMO → LSUMO+7	17.7
		617	3.2682	α HSOMO → LSUMO+7	59.5
				β HSOMO → LSUMO	17.2
trans LUTEO	684	887	0.3779	β HSOMO → LSUMO	73.3
				α HSOMO → LSUMO+3	17.1
		678	3.3853	α HSOMO → LSUMO+3	66.1
				β HSOMO → LSUMO	14.9
trans NEOCHR	674	874	0.3767	β HSOMO → LSUMO	72.6
				α HSOMO → LSUMO	15.7
		668	3.5127	α HSOMO → LSUMO+6	58.3
				β HSOMO → LSUMO	15.2
trans MUTATO	714	909	1.3633	β HSOMO → LSUMO	72.2
				α HSOMO → LSUMO+2	9.8
		708	3.3490	α HSOMO → LSUMO+2	38.3
				α HSOMO → LSUMO+4	22.6
				β HSOMO → LSUMO	14.7
trans NEOX	734	936	1.0528	β HSOMO → LSUMO	84.2
				α HSOMO → LSUMO	5.6
		740	3.0492	α HSOMO → LSUMO	81.1
				α HSOMO → LSUMO+2	5.7
				β HSOMO → LSUMO	4.1
trans VIOLA	744	947	0.5828	β HSOMO → LSUMO	76.5
				α HSOMO → LSUMO+2	11.7
		731	3.4547	α HSOMO → LSUMO+2	64.4
				β HSOMO → LSUMO	10.2
trans ANTHER	772	969	0.6429	β HSOMO → LSUMO	76.8
				α HSOMO → LSUMO	9.7
		758	3.4089	α HSOMO → LSUMO	61.6
				α HSOMO → LSUMO+1	12.7
				β HSOMO → LSUMO	9.0

trans LUT	772	967	0.6106	β HSOMO → LSUMO α HSOMO → LSUMO	76.2 12.3
		760	3.3932	α HSOMO → LSUMO β HSOMO → LSUMO	73.7 9.5
trans BC	844	1017	0.8370	β HSOMO → LSUMO α HSOMO → LSUMO	76.1 8.8
		820	3.5683	α HSOMO → LSUMO α HSOMO → LSUMO+4 β HSOMO → LSUMO	74.5 7.3 6.8
trans LYCO	956	1084 884	1.9839 2.6705	α HSOMO → LSUMO α HSOMO-1 → LSUMO+3	87.4 5.9
				β HSOMO → LSUMO β HSOMO-1 → LSUMO+1	72.6 12.1
trans ASTA	1092	1156	2.2123	β HSOMO → LSUMO β HSOMO-1 → LSUMO+1	78.8 11.2
		1034	2.1312	α HSOMO → LSUMO α HSOMO-1 → LSUMO+1	79.9 10.2

[a]CAM-B3LYP calculations.