Computer Aided Chemical Design: Using Quantum Chemical Calculations to Predict Properties of a Series of Halochromic Guaiazulene Derivatives

Adam W. Woodward,¹ Ebrahim H. Ghazvini Zadeh,¹ Mykhailo V. Bondar,² and Kevin D. Belfield^{*3,4}

¹Department of Chemistry, University of Central Florida, Orlando, FL 32816-2366, USA

²Institute of Physics NASU, Prospect Nauki, 46, Kiev-28, 03028, Ukraine

³College of Science and Liberal Arts, New Jersey Institute of Technology, University Heights, Newark, NJ 07102, USA

⁴School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an, 710062, PRC

* To whom correspondence should be addressed e-mail: <u>belfield@njit.edu</u>

TD-DFT data	S2 – S7
Frontier molecular orbitals	S8 – S10
¹ H and ¹³ C NMR spectra	S11 – S19

Table S1: Calculated properties for the first 15 transitions for 3a as determined by TD-DFT^{*a*}

Transition	Energy	Wavelength	Oscillator strength	Leading configuration	
no.	/eV	/nm			
1	1.97	629	0.03	H -> L	0.96
2	3.08	403	0.43	H-1 -> L	0.81
				H -> L+1	0.15
3	3.31	375	0.13	H-2 -> L	0.31
				H-1 -> L	0.14
				H -> L+1	0.51
4	3.75	331	0.02	H-2 -> L	0.25
				H -> L+1	0.03
				H -> L+2	0.58
				H -> L+3	0.11
5	3.88	320	0.30	H-1 -> L+1	0.90
6	4.02	309	0.03	H -> L+2	0.25
				H -> L+3	0.65
7	4.23	293	0.22	H-2 -> L	0.22
				H-2 -> L+1	0.13
				H-1 -> H+2	0.14
				H -> L+1	0.15
				H -> L+3	0.17
8	4.32	287	0.01	H-3 -> L	0.48
				H-1 -> L+2	0.25
				H-1 -> L+3	0.17
9	4.54	273	0.02	H-4 -> L	0.36
				H-2 -> L	0.42
10	4.67	265	0.04	H-3 -> L	0.38
				H-1 -> L+2	0.32
11	4.90	253	0.60	H-2 -> L	0.10
				H-1 -> L+2	0.12
				H-1 -> L+3	0.58
12	5.04	246	0.26	H-4 -> L	0.42
				H-2 -> L+1	0.22
				H-2 -> L+2	0.13
13	5.22	238	0.12	H-2 -> L+2	0.72
14	5.36	231	0.07	H-2 -> L+3	0.74
15	5.49	226	0.02	H-5 -> L	0.56
				H-4 -> L+1	0.19

Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
	/eV	/nm	strength		
1	2.38	522	0.27	H -> L	0.36
				H -> L+1	0.63
2	2.52	493	0.71	H -> L	0.64
				H -> L+1	0.36
3	3.27	379	0.00	H-1 -> L	0.91
4	3.43	361	0.07	H-2 -> L	0.77
5	3.65	340	0.07	H-2 -> L+1	0.63
				H-1 -> L+1	0.21
6	3.82	324	0.01	H-2 -> L+1	0.20
				H-1 -> L+1	0.77
7	3.89	318	0.16	H-3 -> L	0.82
				H -> L+2	0.11
8	4.22	294	0.05	H-3 -> L	0.84
9	4.47	277	0.22	H -> L+2	0.73
10	4.74	262	0.01	H-4 -> L	0.58
11	4.78	259	0.09	H -> L+3	0.24
				H-4 -> L	0.21
12	4.99	249	0.00	H -> L+3	0.54
13	5.06	245	0.16	H-5 -> L	0.96
				H-6 -> L	0.27
				H-4 -> L+1	0.60
14	5.24	237	0.00	H-9 -> L	0.12
				H-7 -> L	0.80
15	5.32	233	0.00	H-9 -> L	0.57
				H-8 -> L	0.18

Table S2: Calculated properties for the first 15 transitions for 3aH as determined by TD-DFT^{*a*}

Table S3: Calculated properties for the first 15 transitions for **3b** as determined by TD-DFT^{*a*}

/eV/nmstrength11.9263643.650.041H-1×L0.9022.5963477.551.3718H-1×L0.7332.9044426.880.0082H>2.1+10.7343.1808389.790.5176H-2×L0.5053.2689379.280.5495H-1×L+10.7153.2689379.280.5495H-1×L+10.7163.4402360.40.0301H-3×L20.3163.4402360.40.0301H-3×L20.2473.6608338.680.0034H-1×L40.1073.6608338.680.0034H-1×L40.3083.7297332.420.0094H-2×L10.3693.8537321.730.0094H-2×L40.3193.8633320.930.0077H-6×L0.1093.8633320.930.0077H-6×L40.31103.8633320.930.0077H-1×L40.34113.97131.910.001H-1×L40.34113.97131.910.002H-1×L40.34113.973308.160.0787H-1×L40.34113.97131.910.0057H-1×L40.34114.023308.160.0787H-1×L40.34114.023308.160.0787H-1×L40.34124.023308.160.0787H	Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
11.9263643.650.041H > L0.9022.5963477.551.3718H-1 > L0.9532.9044426.880.0082H > L > L0.7343.1808380.90.502H - 2 L0.7343.1808379.280.5495H - 1 > L + 10.2953.2689379.280.5495H - 1 > L + 20.2663.4402360.40.0301H - 3 > L0.3163.4402360.40.0301H - 3 > L0.3173.660838.680.034H - 1 > L 20.1073.6608338.680.0034H - 1 > L 20.3083.7297332.420.514H - 3 > L0.3073.6608338.680.0034H - 1 > L 20.3083.7297321.730.0094H - 1 > L 20.3093.8537321.730.0094H - 2 > L 10.3293.8537321.730.007H - 2 > L0.34103.8633320.930.0077H - 2 > L0.34113.975131.910.0005H - 1 > L 30.34124.023308.160.787H - 2 > L0.34134.02130.330.0077H - 2 > L0.34143.975131.910.0057H - 2 > L0.34154.023308.160.787H - 2 > L0.341611<1		/eV	/nm	strength		
22.5963477.551.3718H-1 → L0.9532.9044426.880.0082H → L+10.7343.1808389.790.5176H-2 → L0.5053.2689379.280.5495H -1 → L+10.5153.2689379.280.5495H -1 → L+10.5163.2689379.280.5495H -3 × L+10.5163.4402360.40.0301H -3 × L0.3163.4402360.40.0301H -3 × L0.3173.6608338.680.0034H -1 > × L0.2173.6608338.680.0034H -1 > × L0.3083.7297332.420.0514H -3 × L0.3693.8537321.730.0094H -1 × L0.361010101011 × 1 × 30.1293.8633320.930.0077H -6 × L0.12113.8633320.930.0077H -1 × L+30.24124.023308.160.787H -1 × L<3	1	1.9263	643.65	0.041	H -> L	0.90
32.9044426.880.0082H > L+10.7343.1808389.790.5176H-2 > L0.50776.689379.280.5495H-1 > L+10.2953.2689379.280.5495H - N + L+10.1073.2689379.280.5495H - N + L+20.2663.4402360.40.0301H - N + 20.2663.4402360.40.0301H - N + 20.2173.6608338.680.0034H - N + 20.3083.729732.420.0514H - N + 20.1293.8537321.730.0094H - N + 30.1293.8537321.730.0077H - N + 30.27103.8633320.930.0077H - N + 30.24113.8633320.930.0077H - N + 30.34113.9751311.910.005H - N + 30.34124.023308.160.0787H - N + 40.13124.023308.160.0787H - N + 40.13134.0811303.80.0507H + N + 10.34141.25530	2	2.5963	477.55	1.3718	H-1 -> L	0.95
43.1808389.790.5176H-2 × L0.50111110.29553.2689379.280.5495H-1 × L+10.511111110.101111110.10113.4402360.40.0301H-3 × L0.3163.4402360.40.0301H-3 × L0.2463.4402360.40.0301H-1 × L+20.2473.6608338.680.0034H-1 × L+20.3073.6608338.680.0034H-1 × L+20.3083.7297332.420.0514H-3 × L0.3083.7297321.730.0094H-1 × L+30.3193.8537321.730.0094H-2 × L+10.36103.8633320.930.0077H-6 × L0.10113.8633320.930.0077H-6 × L0.34113.9751311.910.0005H-1 × L+30.34113.9751311.910.0005H-1 × L+40.13124.0233308.160.0787H-5 × L0.30134.081130.380.0507H-4 × L0.34134.081130.380.0507H-1 × L+40.13134.081130.380.0518H-1 × L+40.12144.125530.530.0618H-2 × L<0	3	2.9044	426.88	0.0082	H -> L+1	0.73
Image: space of the system	4	3.1808	389.79	0.5176	H-2 -> L	0.50
5 3.2689 379.28 0.5495 $H.1 > L+1$ 0.10 I I I I I IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII					H-1 -> L+1	0.29
Image: series of the series	5	3.2689	379.28	0.5495	H-1 -> L+1	0.51
Image: series of the series					H -> L+1	0.10
63.4402360.40.0301H.3 > L0.31111111.2 > L0.2411111.1 > L+20.10111111.2 > L+20.2173.6608338.680.0034H.1 > L+20.8083.7297332.420.0514H.3 > L0.3083.7297332.420.0514H.3 > L0.3011111.3 > L0.3083.7297321.730.0094H.2 > L+10.3193.8537321.730.0094H.2 > L+10.3193.8537321.730.0094H.2 > L+10.3193.8633320.930.0077H.6 > L0.12103.8633320.930.0077H.6 > L0.10113.9751311.910.005H.1 > L+30.24113.9751311.910.005H.1 > L+30.31124.023308.160.0787H.5 > L0.17134.0811303.80.0507H.4 > L0.33134.0811303.80.0507H.4 > L0.34144.125530.0530.0618H.5 > L0.12144.125530.0530.0618H.5 > L0.12154.2128294.310.0526H.5 > L0.16154.2128294.310.0526H.5 > L0.10 <td></td> <td></td> <td></td> <td></td> <td>H -> L+2</td> <td>0.26</td>					H -> L+2	0.26
Image: series of the	6	3.4402	360.4	0.0301	H-3 -> L	0.31
Image: state in the					H-2 -> L	0.24
Image: system of the					H-1 -> L+2	0.10
7 3.6608 338.68 0.0034 $H-1 - > L+2$ 0.80 8 3.7297 332.42 0.0514 $H-3 - > L$ 0.30 1 1 $1 - 2 - L + 1$ 0.36 1 $1 - 2 - L + 1$ 0.36 1 $1 - 2 - L + 1$ 0.36 9 3.8537 321.73 0.0094 $H-2 - > L + 1$ 0.31 9 3.8537 321.73 0.0094 $H-2 - > L + 1$ 0.31 9 3.8537 321.73 0.0094 $H-2 - > L + 1$ 0.31 10 3.8633 320.93 0.0077 $H-6 - > L$ 0.10 10 3.8633 320.93 0.0077 $H-6 - > L$ 0.10 10 3.8633 320.93 0.0077 $H-1 - > L + 3$ 0.27 11 3.9751 311.91 0.0005 $H-1 - > L + 3$ 0.24 11 3.9751 311.91 0.00787 $H-5 - > L$ 0.17 12 4.0233 308.16 0.0787 $H-4 - > L$ 0.30					H -> L+2	0.21
8 3.7297 332.42 0.0514 $H.3 > L$ 0.30 I I I $I + 2 > L + 1$ 0.36 I I I $I + 2 > L + 1$ 0.31 9 3.8537 321.73 0.0094 $H - 2 > L + 1$ 0.31 9 3.8537 321.73 0.0094 $H - 2 > L + 1$ 0.31 10 3.8633 320.93 0.0077 $H - 6 > L$ 0.10 10 3.8633 320.93 0.0077 $H - 6 > L$ 0.10 10 3.8633 320.93 0.0077 $H - 6 > L$ 0.10 10 3.8633 320.93 0.0077 $H - 1 > L + 3$ 0.27 10 3.8633 320.93 0.0077 $H - 1 > L + 3$ 0.34 11 3.9751 311.91 0.0005 $H - 1 > L + 3$ 0.51 11 3.9751 311.91 0.00787 $H - 5 L + 3$ 0.30 12 4.0233 308.16 0.0787 $H - 5 L + 4$ 0.33 <td>7</td> <td>3.6608</td> <td>338.68</td> <td>0.0034</td> <td>H-1 -> L+2</td> <td>0.80</td>	7	3.6608	338.68	0.0034	H-1 -> L+2	0.80
Image: series of the series	8	3.7297	332.42	0.0514	H-3 -> L	0.30
Image: system of the syste					H-2 -> L+1	0.36
9 3.8537 321.73 0.0094 $H.2 > L+1$ 0.31 10 1 1 $1 + > L + 3$ 0.12 10 3.8633 320.93 0.0077 $H.6 > L$ 0.10 10 1.62 $1.1 > L+3$ 0.27 $1.1 > L+3$ 0.27 11 3.9751 311.91 0.0005 $H.1 > L+3$ 0.34 11 3.9751 311.91 0.0005 $H.1 > L+3$ 0.24 12 4.0233 308.16 0.0787 $H.5 > L$ 0.13 12 4.0233 308.16 0.0507 $H.4 > L$ 0.34 13 4.0811 303.8 0.0507 $H.4 > L$ 0.12 14					H -> L+2	0.12
Image: state in the state	9	3.8537	321.73	0.0094	H-2 -> L+1	0.31
Image: matrix of the state s					H-1 -> L+3	0.12
10 3.8633 320.93 0.0077 $H-6 > L$ 0.10 $-1 > L+3$ 0.27 $-1 < L+3$ 0.27 $-1 < L+3$ 0.11 $-1 < L+3$ 0.11 $-1 < L+3$ 0.34 $-1 < L+3$ 0.34 -11 3.9751 311.91 0.0005 $H-1 > L+3$ 0.24 -11 3.9751 311.91 0.0005 $H-1 > L+3$ 0.24 -11 3.9751 311.91 0.0005 $H-1 > L+3$ 0.24 -11 -1.91 0.0005 $H-1 > L+3$ 0.24 -11 -1.91 0.0057 $H-5 > L$ 0.17 -12 4.0233 308.16 0.0787 $H-4 > L$ 0.30 -12 4.0233 308.16 0.0507 $H-4 > L$ 0.31 -13 4.0811 303.8 0.0507 $H-4 > L$ 0.12 -13 4.0811 303.8 0.0507 $H-4 > L$ 0.12 -14 4.1255 300.53					H -> L+4	0.38
Image: state in the state	10	3.8633	320.93	0.0077	H-6 -> L	0.10
Image: state in the state					H-1 -> L+3	0.27
Image: matrix formImage: matrix formImag					H-1 -> L+4	0.11
11 3.9751 311.91 0.0005 $H-1 \rightarrow L+3$ 0.24 $$					H -> L+3	0.34
Image: matrix formImage: matrix formImag	11	3.9751	311.91	0.0005	H-1 -> L+3	0.24
Image: matrix of the state in the state					H -> L+3	0.51
124.0233308.16 0.0787 H-5 \rightarrow L 0.17 11111111134.0811303.80.0507H-1 \rightarrow L 40.13134.0811303.80.0507H-4 \rightarrow L0.341411111144.1255300.530.0618H-5 \rightarrow L0.18154.2128294.310.0526H-5 \rightarrow L0.1015111111511111151111115111111511111151111115111111511111151111115111111511111151111115111111511111161111117111111811111191111119111111911111 <td></td> <td></td> <td></td> <td></td> <td>H -> L+4</td> <td>0.13</td>					H -> L+4	0.13
Image: matrix of the system	12	4.0233	308.16	0.0787	H-5 -> L	0.17
Image: matrix of the system					H-4 -> L	0.30
134.0811303.8 0.0507 $H-4 \rightarrow L$ 0.34 I I I $I-1 \rightarrow L+4$ 0.12 I I I I $I \rightarrow L+4$ 0.12 $I4$ 4.1255 300.53 0.0618 $H-5 \rightarrow L$ 0.18 I I I I $I-2 \rightarrow L+2$ 0.47 $I5$ 4.2128 294.31 0.0526 $H-5 \rightarrow L$ 0.10 I <					H-1 -> L+4	0.13
Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system144.1255300.530.0618IH-5 -> L0.18144.1255300.530.0618IH-2 -> L+20.47154.2128294.310.0526IH-5 -> L0.1015Image: matrix of the systemImage: matrix of the system0.15Image: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the system0.1015Image: matrix of the systemImage: matrix of the systemImage: matrix of the system0.1515Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system15Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the system16Image: matrix of the systemImage: matrix of the systemImage: matrix of the systemImage: matrix of the sys	13	4.0811	303.8	0.0507	H-4 -> L	0.34
Image: marked black					H-1 -> L+4	0.12
144.1255300.530.0618 $H-5 \rightarrow L$ 0.18 -100 -100 $H-2 \rightarrow L+2$ 0.47154.2128294.310.0526 $H-5 \rightarrow L$ 0.10 -100 -100 $H-1 \rightarrow L+4$ 0.15 -100 -100 $H-1 \rightarrow L+5$ 0.30					H -> L+4	0.12
Image: marked black	14	4.1255	300.53	0.0618	H-5 -> L	0.18
15 4.2128 294.31 0.0526 H-5 \rightarrow L 0.10					H-2 -> L+2	0.47
H-1->L+4 0.15 H-1->L+5 0.30	15	4.2128	294.31	0.0526	H-5 -> L	0.10
H-1->L+5 0.30					H-1 -> L+4	0.15
					H-1 -> L+5	0.30

Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
	/eV	/nm	strength		
1	1.23	1009	0.86	H -> L	0.99
2	1.48	839	0.08	H -> L+1	0.97
3	2.18	569	0.81	H-1 -> L	0.91
4	2.51	494	0.08	H-1 -> L+1	0.92
5	2.57	482	0.07	H-2 -> L	0.95
6	2.71	458	0.27	H-4 -> L	0.14
				H-3 -> L	0.30
				H -> L+2	0.50
7	2.74	453	0.08	H-3 -> L	0.69
				H -> L+2	0.18
8	3.01	411	0.04	H-4 -> L	0.69
				H -> L+2	0.17
9	3.09	402	0.04	H-5 -> L	0.91
10	3.16	392	0.01	H-2 -> L+1	0.96
11	3.34	371	0.03	H-4 -> L+1	0.62
				H-3 -> L+1	0.23
12	3.38	366	0.01	H-4 -> L+1	0.19
				H-3 -> L+1	0.77
13	3.47	358	0.41	H -> L+3	0.84
14	3.54	350	0.12	H-6 -> L	0.76
15	3.67	338	0.05	H -> L+4	0.76

Table S4: Calculated properties for the first 15 transitions for **3b** as determined by $TD-DFT^a$

Table S5: Calculated properties for the first 15 transitions for 3c as determined by TD-DFT^{*a*}

Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
	/eV	/nm	strength		
1	1.81	686	0.08	H-1 -> L	0.19
				H -> L	0.71
2	2.28	543	2.21	H-1 -> L	0.76
				H -> L	0.23
3	2.67	464	0.16	H-2 -> L	0.17
				H -> L+1	0.60
4	2.78	446	0.52	H-2 -> L	0.61
				H-1 -> L+1	0.29
5	2.95	421	0.28	H-2 -> L	0.17
				H-1 -> L+1	0.54
				H -> L+1	0.18
6	3.10	400	0.02	H-3 -> L	0.30
				H -> L+2	0.39
7	3.29	376	0.11	H-3 -> L	0.15
				H-2 -> L+1	0.55
				H -> L+2	0.16
8	3.35	370	0.01	H-1 -> L+2	0.72
9	3.43	362	0.00	H-3 -> L	0.11
				H-2 -> L+1	0.22
				H-1 -> L+3	0.26
				H -> L+2	0.22
10	3.48	356	0.03	H-4 -> L	0.10
				H-1 -> L+3	0.16
				H -> L+3	0.52
11	3.68	336	0.01	H-4 -> L	0.64
				H-2 -> L+2	0.11
12	3.77	329	0.25	H-3 -> L	0.16
				H-2 -> L+1	0.10
				H-1 -> L+2	0.18
				H-1 -> L+3	0.18
13	3.78	328	0.01	H-6 -> L	0.12
				H-1 -> L+4	0.36
				H -> L+4	0.27
14	3.85	322	0.16	H-3 -> L+1	0.18
				H-2 -> L+2	0.52
				H-1 -> L+3	0.10
15	3.96	313	0.02	H-5 -> L	0.16

Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
	/eV	/nm	strength		
				H-3 -> L+1	0.19
				H-2 -> L+3	0.29

Table S6: Calculated properties for the first 15 transitions for 3cH as determined by TD-DFT^{*a*}

Transition no.	Energy	Wavelength	Oscillator	Leading configuration	
	/eV	/nm	strength	_	-
1	0.97	1273	0.89	H -> L	1.01
2	1.41	877	0.02	H -> L+1	0.98
3	1.78	698	1.49	H-1 -> L	0.90
4	2.13	582	0.09	H-1 -> L+1	0.92
5	2.15	578	0.30	H-2 -> L	0.28
				H -> L+2	0.65
6	2.42	511	0.09	H-3 -> L	0.27
				H-2 -> L	0.53
				H -> L+2	0.14
7	2.49	498	0.12	H-3 -> L	0.68
				H-2 -> L	0.13
8	2.55	486	0.02	H-4 -> L	0.95
9	2.83	437	0.01	H-5 -> L	0.85
10	2.86	433	0.03	H-2 -> L+1	0.83
11	2.91	426	0.31	H-6 -> L	0.38
				H-1 -> L+2	0.47
12	2.95	420	0.16	H-1 -> L+3	0.83
13	3.16	392	0.00	H-3 -> L+1	0.95
14	3.21	387	0.06	H-6 -> L	0.32
				H-1 -> L+2	0.35
				H-1 -> L+4	0.10
15	3.30	376	0.00	H-4 -> L+1	0.99



Figure S1: Frontier molecular orbitals of **3a** and **3aH+**



Figure S2: Frontier molecular orbitals of **3b** and **3bH+**



Figure S3: Frontier molecular orbitals of **3c** and **3cH+**



Figure S5: ¹³C NMR spectrum for intermediate **B**



Figure S7: ¹³C NMR spectrum for **3a**





Figure S10: ¹H NMR spectrum for intermediate E



Figure S11: ¹³C NMR spectrum for intermediate E



Figure S12: ¹H NMR spectrum for intermediate **F**





Figure S15: ¹³C NMR spectrum for **3b**







Figure S19: ¹³C NMR spectrum for intermediate I



Figure S20: ¹H NMR spectrum for **3c**



Figure S21: $^{\rm 13}C$ NMR spectrum for 3c