THE JOURNAL OF PHYSICAL CHEMISTRY A

Supporting Information

Application of Time Dependent Density Functional and Natural Bond Orbital Theories to the UV/Vis Absorption Spectra of Some Phenolic Compounds

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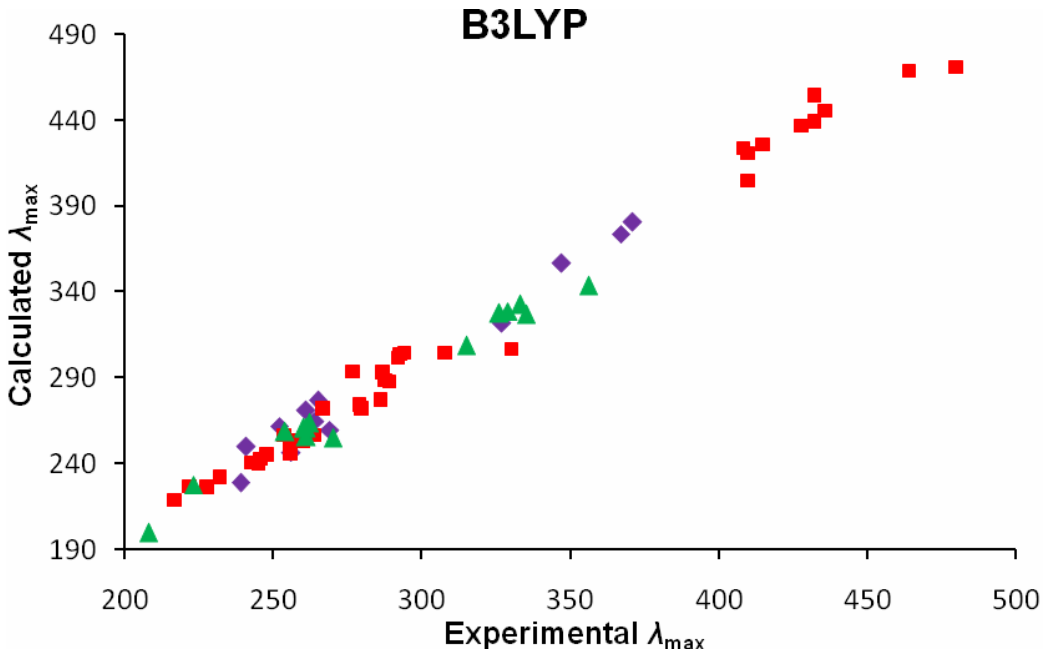
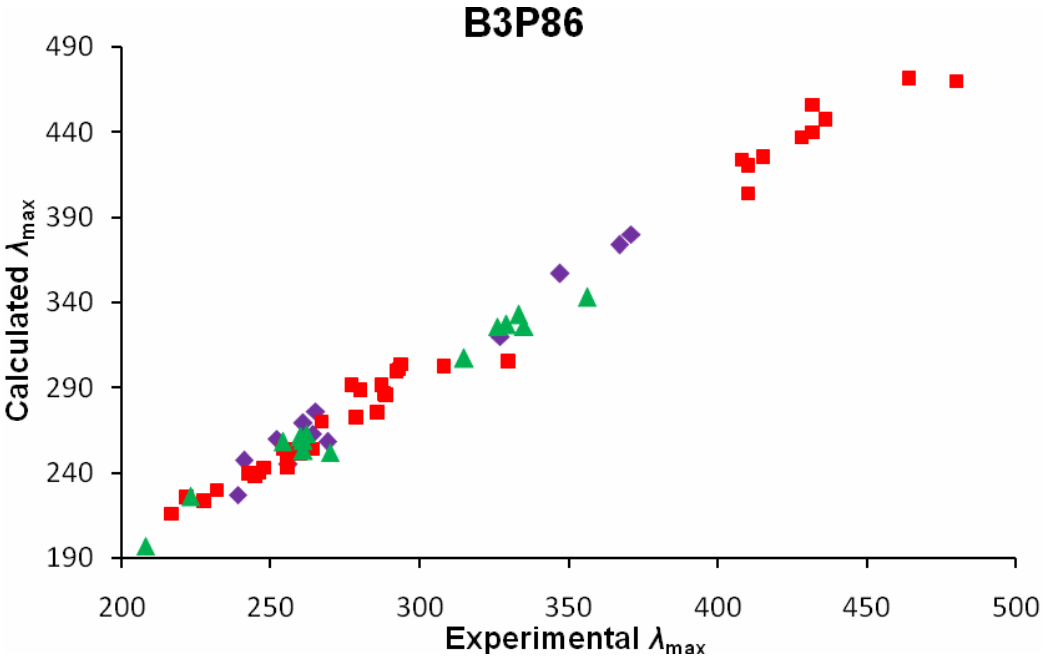

B3LYP
490
440
390
340
290
240
190
Calculated λ_{max}
200
250
300
350
400
450
500
Experimental λ_{max}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Calculated λ_{max}
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Experimental λ_{max}

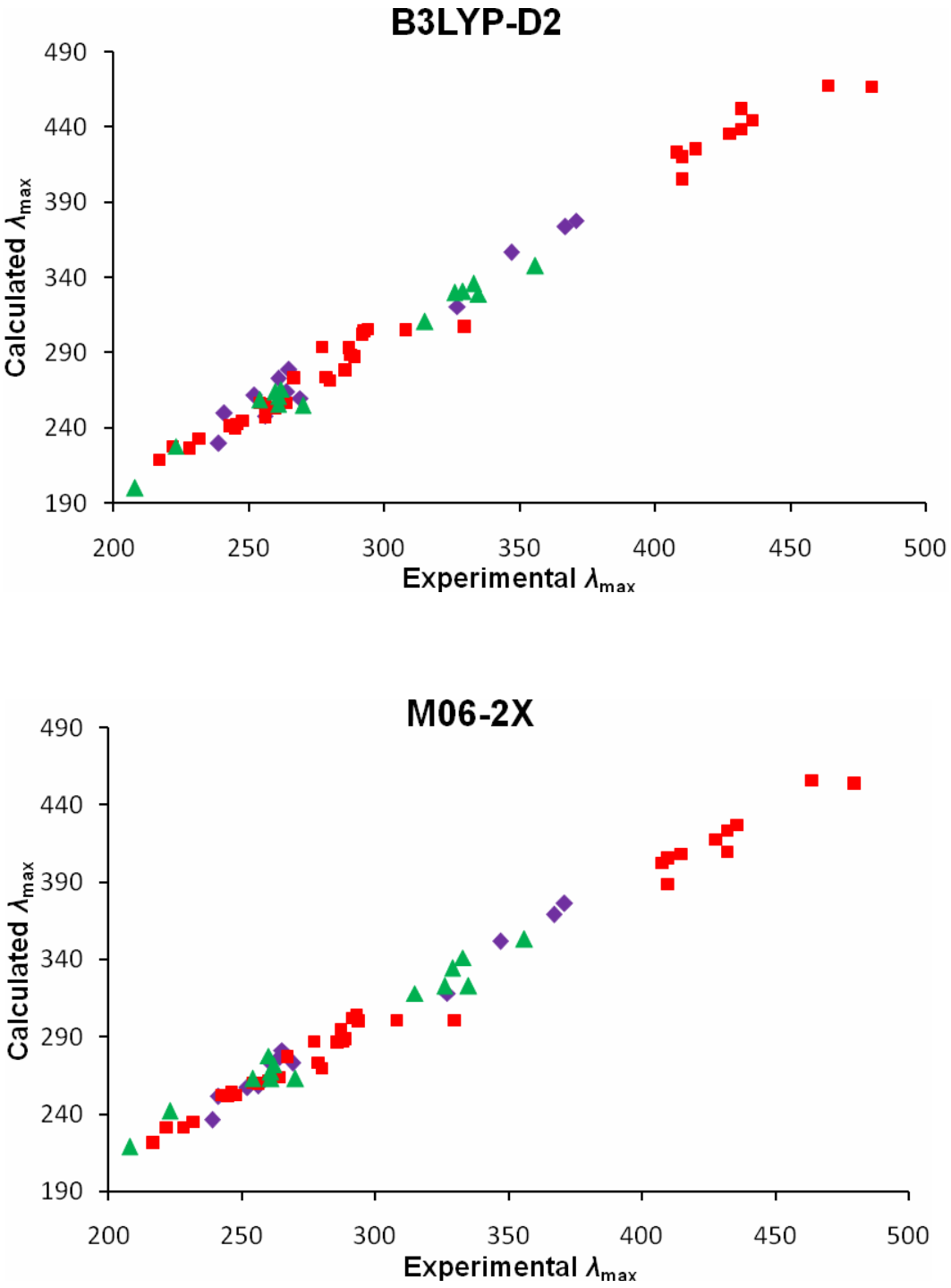


Figure S1. Correlation between the calculated and experimental λ_{max} values for the applied methods. Red squares, green triangles, and purple rhombuses denote anthraquinones, neoflavonoids, and flavonoids, respectively. The scaled values from M06-2X are presented.

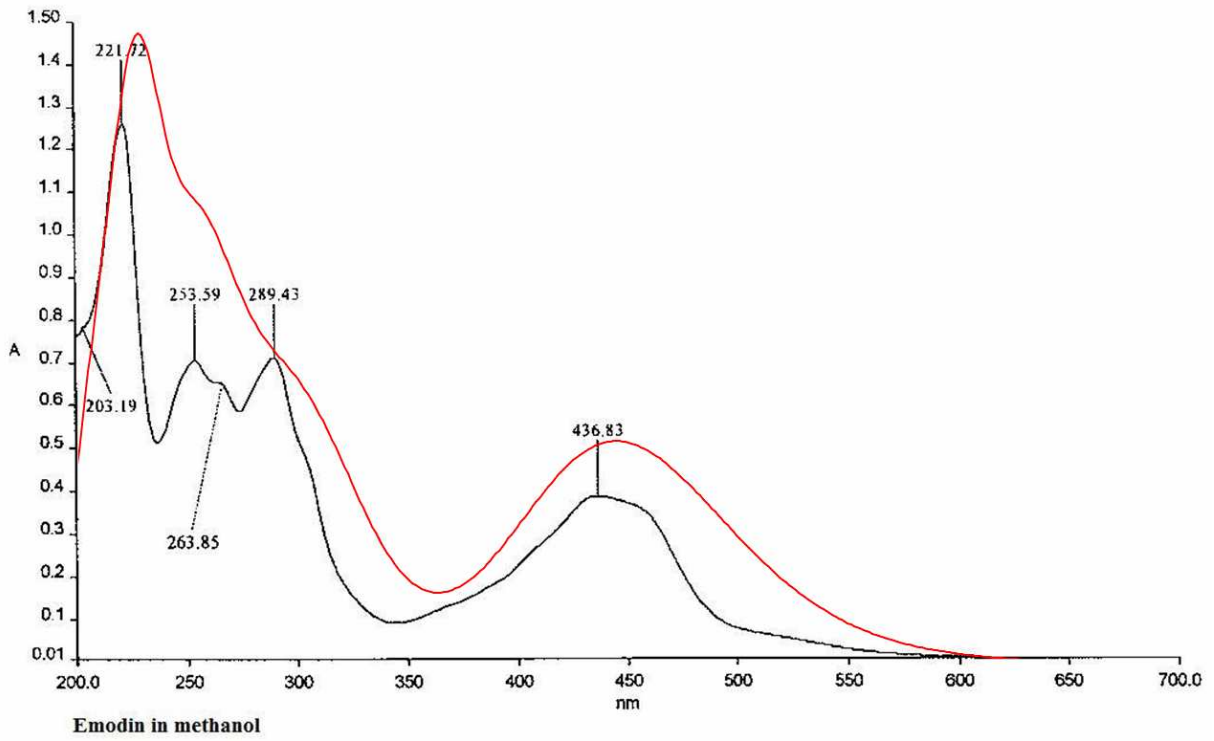


Figure S2. Experimental (black) and simulated (red) UV/Vis spectra for emodin.

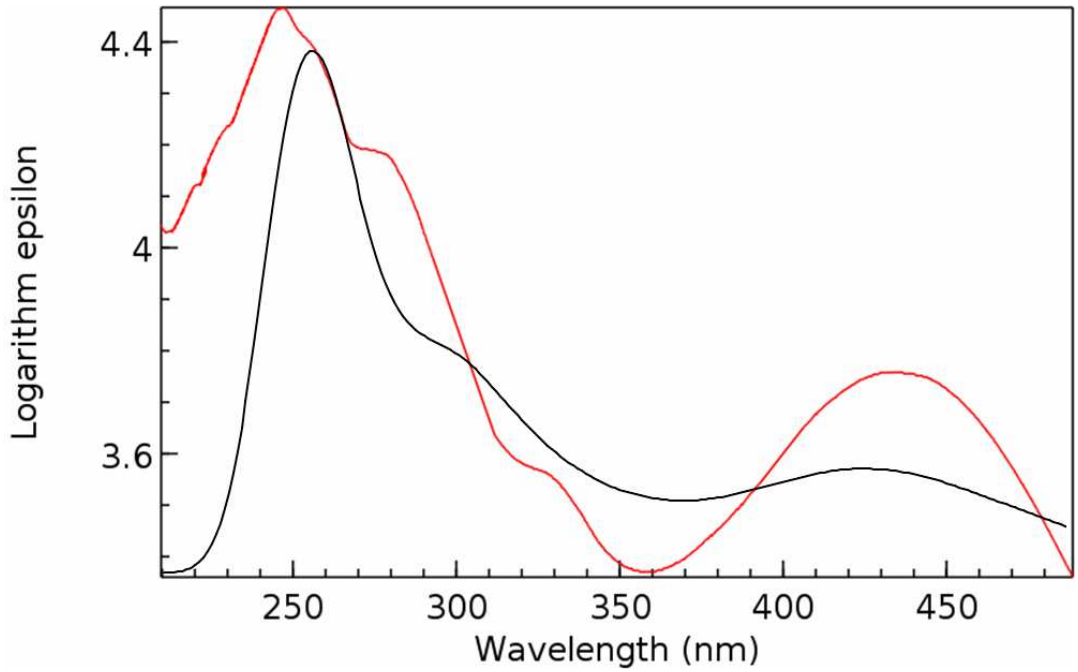
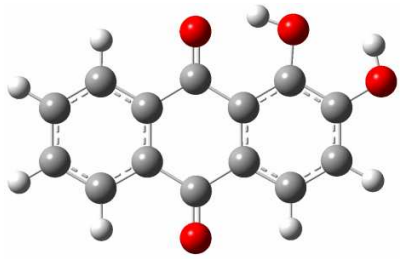
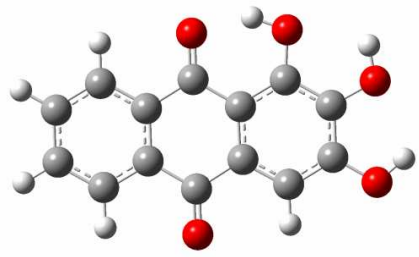


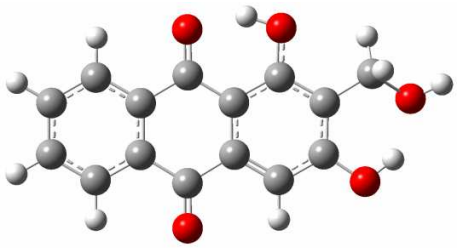
Figure S3. Experimental (red) and simulated (black) UV/Vis spectra for alizarin.



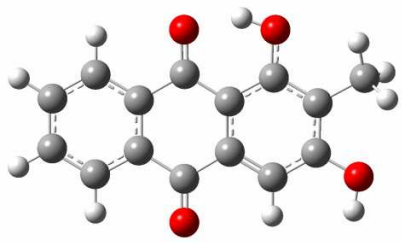
Alizarin, 0.12099 au



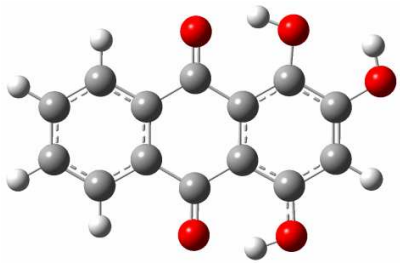
Anthragallol, 0.12361 au



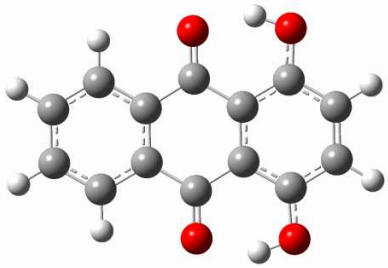
Lucidin, 0.12744 au



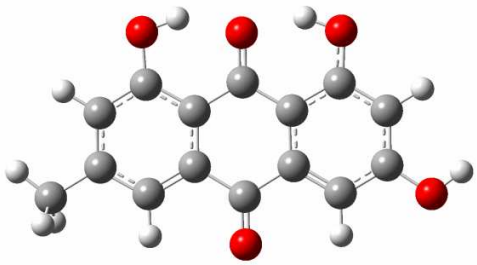
Rubiadin, 0.12818 au



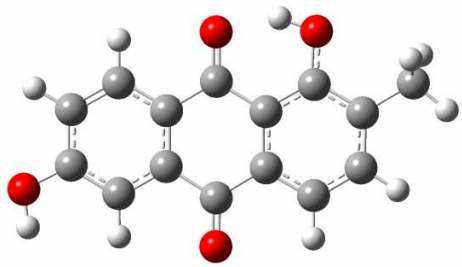
Purpurin, 0.11132 au



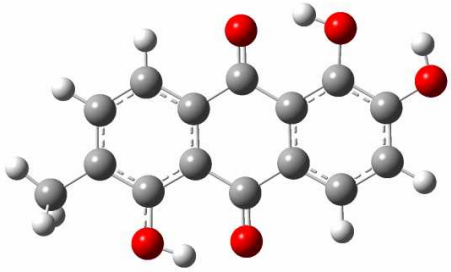
Quinizarin, 0.11056 au



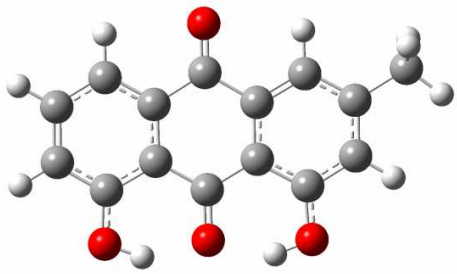
Emodin, 0.12303 au



Soranjidiol, 0.12624 au

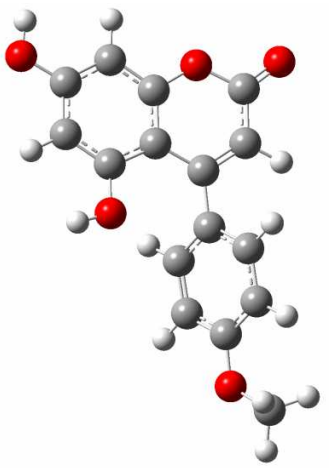


Morindone, 0.11792 au

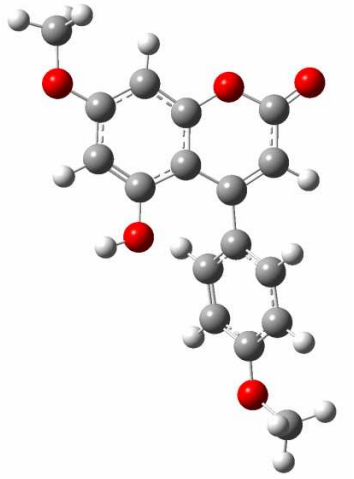


Chrysophanol, 0.12402 au

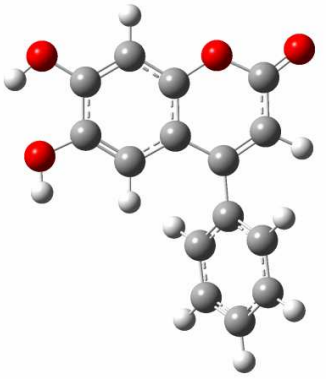
Figure S4. Geometries of the investigated phenolic anthraquinones optimized with the B3LYP functional, with the HOMO-LUMO gap values (E_h/particle) indicated.



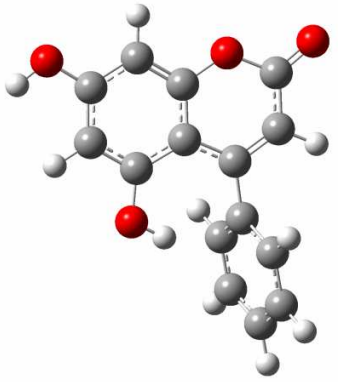
Nivetin, 0.15213 au



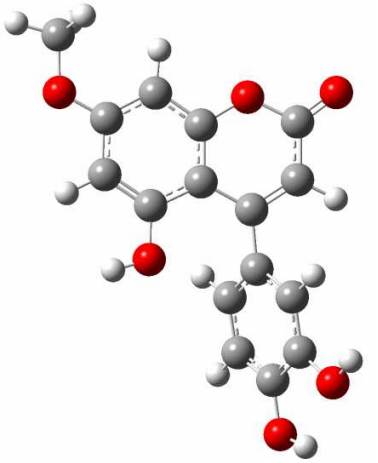
5'OH-7,4'diOMe-4-phenylcoumarin, 0.15245 au



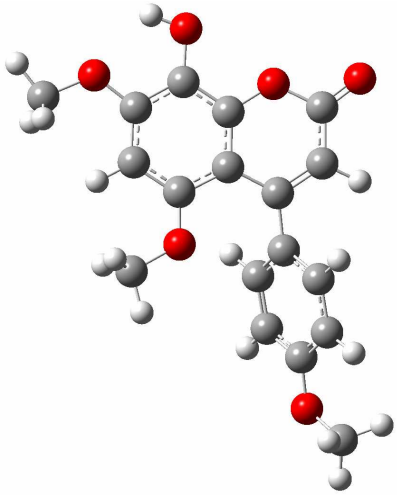
Nordalbergin, 0.14804 au



Serratin, 0.15650 au

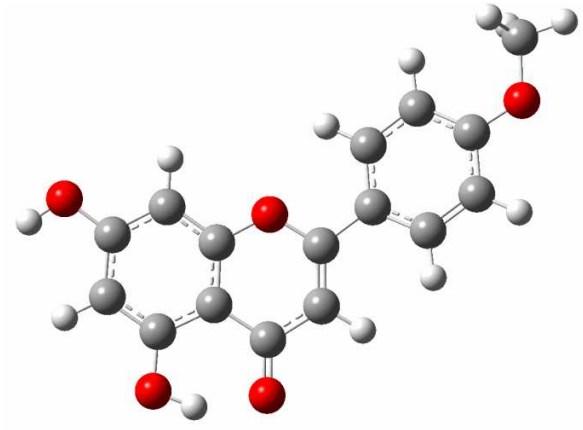


Coutareagin, 0.14784 au

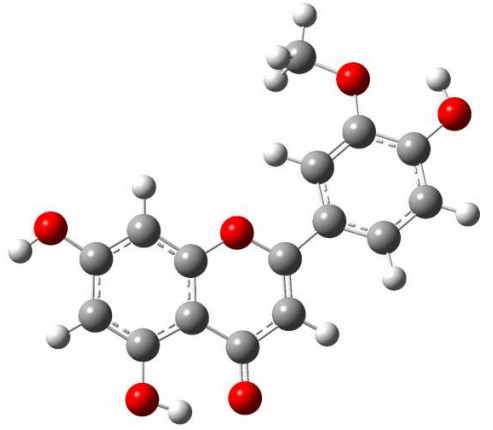


Exostemin, 0.13794 au

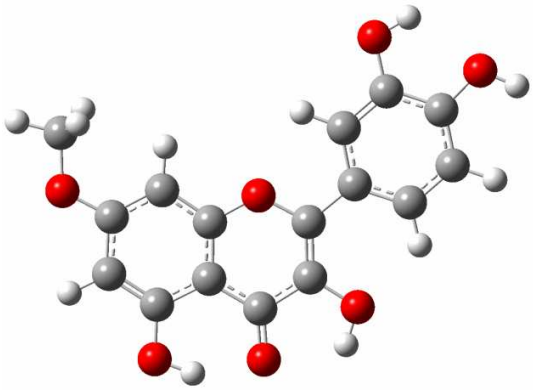
Figure S5. Geometries of the investigated neoflavonoids optimized with the B3LYP functional, with the HOMO-LUMO gap values (E_h/particle) indicated.



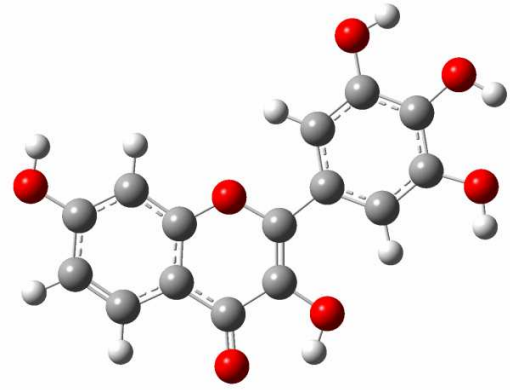
Acacetin, 0.14950 au



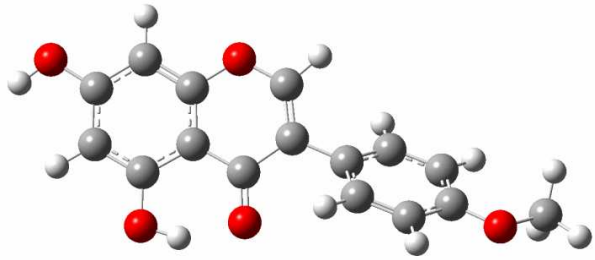
Chrysoeriol, 0.14469 au



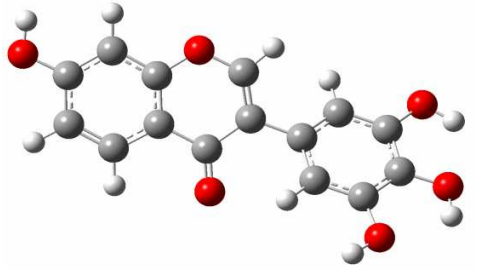
Rhamnetin, 0.13501 au



Robinetin, 0.13509 au



Biochanin A, 0.15265 au



Baptigenin, 0.15170 au

Figure S6. Geometries of the investigated flavonoids optimized with the B3LYP functional, with the HOMO-LUMO gap values (E_h/particle) indicated.

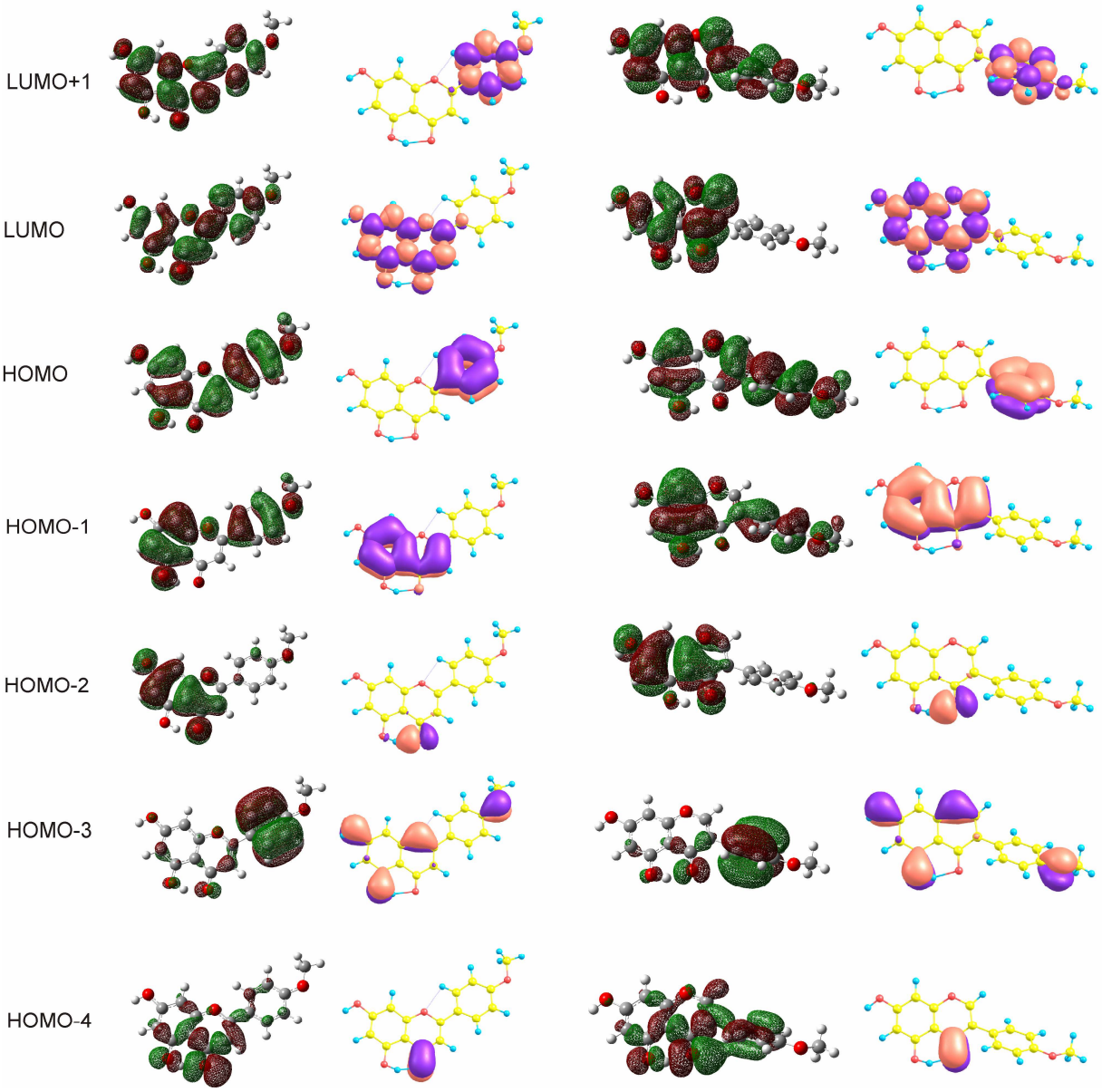


Figure S7. Kohn-Sham orbitals and NLMO clusters for acacetin (left) and biochanin A (right).

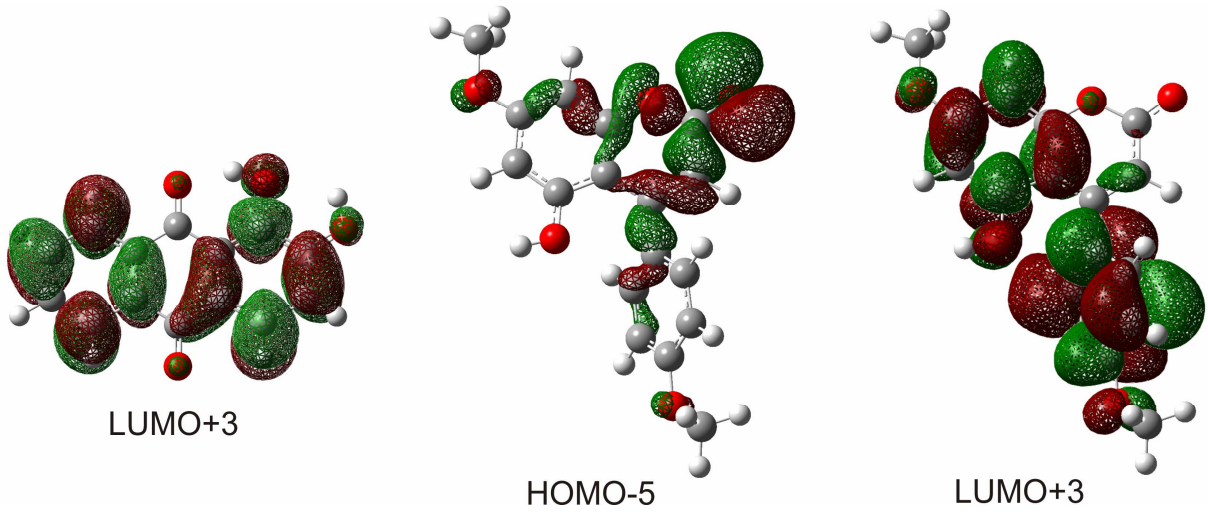
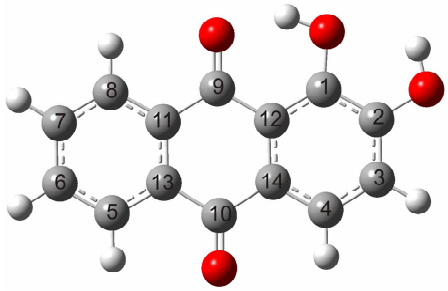


Figure S8. Some molecular orbitals of alizarin and 5'OH-7,4'diOMe-4-phenylcoumarin.

Table S1. Details on the selected NLMOs of alizarin obtained from the B3LYP density matrix



NLMO	Energy (E_h/particle)	Mean energy (E_h/particle)	Hybrid composition and occupancy of the parent NBO		NLMO cluster
70. π^* C5-C6	0.01305		$0.70(p)_{C6}$-$0.71(p)_{C5}$	0.281	
69. π^* C7-C8	0.01273	0.01087	$0.71(p)_{C8}$-$0.70(p)_{C7}$	0.279	LUMO+2
68. π^* C11-C13	0.00682		$0.71(p)_{C13}$-$0.70(p)_{C11}$	0.426	
67. π^* C4-C14	0.01357		$0.68(p)_{C14}$-$0.73(p)_{C4}$	0.351	
66. π^* C2-C3	0.00239	0.00391	$0.70(p)_{C3}$-$0.72(p)_{C2}$	0.347	LUMO+1
65. π^* C1-C12	-0.00422		$0.74(p)_{C1}$-$0.67(p)_{C12}$	0.415	
64. π^* C10-O10	-0.00413	-0.01409	$0.83(p)_{C10}$-$0.55(p)_{O10}$	0.206	LUMO
63. π^* C9-O9	-0.02405		$0.84(p)_{C9}$-$0.54(p)_{O9}$	0.258	
62. π C5-C6	-0.27012		$0.71(p)_{C6}$+$0.70(p)_{C5}$	1.616	
61. π C7-C8	-0.27091	-0.27217	$0.70(p)_{C8}$+$0.71(p)_{C7}$	1.622	HOMO
60. π C11-C13	-0.27548		$0.70(p)_{C13}$+$0.71(p)_{C11}$	1.613	
59. π C4-C14	-0.27298		$0.73(p)_{C14}$+$0.68(p)_{C4}$	1.658	
58. π C2-C3	-0.28459	-0.28156	$0.72(p)_{C3}$+$0.70(p)_{C2}$	1.636	HOMO-1
57. π C1-C12	-0.28711		$0.67(p)_{C1}$+$0.74(p)_{C12}$	1.636	
56. LP O10	-0.28662	-0.31145	p	1.897	HOMO-2
55. LP O9	-0.33628		p	1.876	
54. LP O1	-0.34428	-0.34521	p	1.831	HOMO-3
53. LP O2	-0.34614		p	1.854	
52. π C10-O10	-0.38964	-0.39737	$0.55(p)_{C10}$+$0.83(p)_{O10}$	1.953	HOMO-4
51. π C9-O9	-0.40509		$0.54(p)_{C9}$+$0.84(p)_{O9}$	1.965	

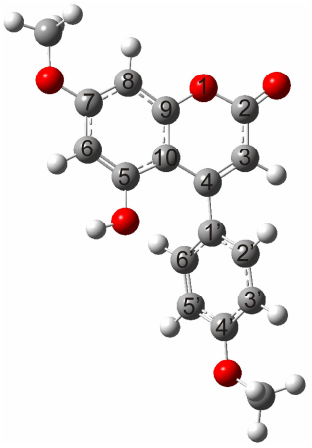


Table S2. Details on the selected NLMOs of 5'OH-7,4'diOMe-4-phenylcoumarin obtained from the B3LYP density matrix

NLMO	Energy (E_h/particle)	Mean energy (E_h/particle)	Hybrid composition and occupancy of the parent NBO		NLMO cluster
86. π^* C1'-C2'	0.02728	0.02288	$0.69(p)_{C1'}$-$0.73(p)_{C2'}$	0.361	LUMO+2
85. π^* C5'-C6'	0.02721		$0.72(p)_{C6'}$-$0.69(p)_{C5'}$	0.299	
84. π^* C3-C4	0.02081		$0.75(p)_{C4}$-$0.66(p)_{C3}$	0.204	
83. π^* C3'-C4'	0.01621		$0.67(p)_{C3'}$-$0.73(p)_{C4'}$	0.384	
82. π^* C5-C6	0.00862	0.00434	$0.76(p)_{C6}$-$0.66(p)_{C5}$	0.351	LUMO+1
81. π^* C7-C8	0.00623		$0.65(p)_{C8}$-$0.76(p)_{C7}$	0.401	
80. π^* C9-C10	-0.00184		$0.65(p)_{C10}$-$0.76(p)_{C9}$	0.458	
79. π^* C2-O2	-0.00949	-0.00949	$0.85(p)_{C2}$-$0.53(p)_{O2}$	0.339	LUMO
78. π C1'-C2'	-0.25882	-0.26270	$0.73(p)_{C1'}$+$0.69(p)_{C2'}$	1.678	HOMO
77. π C5'-C6'	-0.26135		$0.72(p)_{C5'}$+$0.69(p)_{C6'}$	1.709	
76. π C3'-C4'	-0.26792		$0.73(p)_{C3'}$+$0.68(p)_{C4'}$	1.658	
75. LP O2	-0.27610	-0.27610	p	1.850	HOMO-1
74. π C7-C8	-0.27734	-0.28001	$0.65(p)_{C7}$+$0.76(p)_{C8}$	1.671	HOMO-2
73. π C9-C10	-0.27782		$0.65(p)_{C9}$+$0.76(p)_{C10}$	1.629	
72. π C5-C6	-0.28102		$0.66(p)_{C5}$+$0.76(p)_{C6}$	1.720	
71. π C3-C4	-0.28386		$0.75(p)_{C3}$+$0.66(p)_{C4}$	1.782	
70. LP 4'	-0.32444	-0.33847	p	1.842	HOMO-3
69. LP O7	-0.33300		p	1.826	
68. LP O5	-0.34166		p	1.860	
67. LP O1	-0.35477		p	1.744	
66. π C2-O2	-0.39267	-0.39267	$0.53(p)_{C2}$+$0.85(p)_{O2}$	1.983	HOMO-4

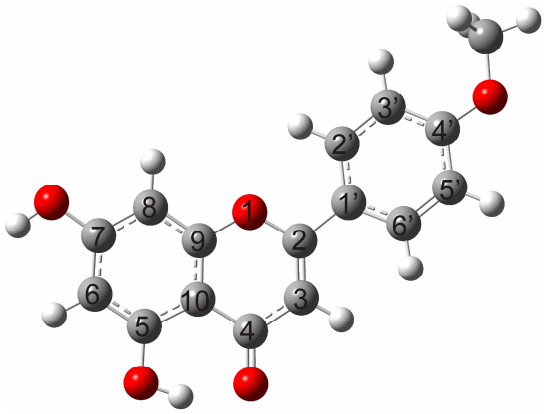
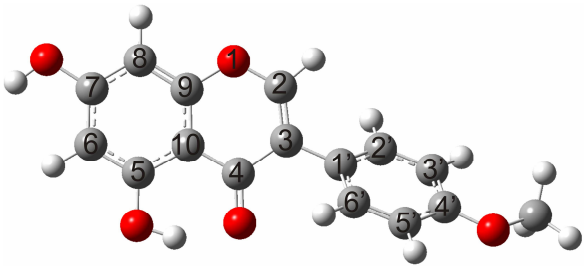


Table S3. Details on the selected NLMOs of acacetin obtained from the B3LYP density matrix

NLMO	Energy (E_h/particle)	Mean energy (E_h/particle)	Hybrid composition and occupancy of the parent NBO		NLMO cluster
82. π^* C5'-C6'	0.01851	0.01382	$0.72(p)_{C6'}$-$0.69(p)_{C5'}$	0.282	LUMO+1
81. π^* C1'-C2'	0.01404		$0.70(p)_{C1'}$-$0.72(p)_{C2'}$	0.393	
80. π^* C3'-C4'	0.00891		$0.67(p)_{C3'}$-$0.74(p)_{C4'}$	0.383	
79. π^* C2-C3	0.00842	-0.00019	$0.75(p)_{C2}$-$0.66(p)_{C3}$	0.244	LUMO
78. π^* C5-C6	0.00598		$0.76(p)_{C5}$-$0.65(p)_{C6}$	0.366	
77. π^* C7-C8	0.00280		$0.65(p)_{C8}$-$0.76(p)_{C7}$	0.407	
76. π^* C9-C10	-0.00251		$0.76(p)_{C9}$-$0.65(p)_{C10}$	0.474	
75. π^* C4-O4	-0.01564		$0.86(p)_{C4}$-$0.51(p)_{O4}$	0.387	
74. π C1'-C2'	-0.26513	-0.26963	$0.74(p)_{C1'}$+$0.67(p)_{C2'}$	1.644	HOMO
73. π C5'-C6'	-0.27070		$0.72(p)_{C5'}$+$0.69(p)_{C6'}$	1.716	
72. π C3'-C4'	-0.27307		$0.74(p)_{C3'}$+$0.67(p)_{C4'}$	1.628	
71. π C7-C8	-0.27409	-0.28214	$0.65(p)_{C7}$+$0.76(p)_{C8}$	1.651	HOMO-1
70. π C5-C6	-0.27659		$0.65(p)_{C5}$+$0.76(p)_{C6}$	1.684	
69. π C9-C10	-0.28173		$0.65(p)_{C9}$+$0.76(p)_{C10}$	1.636	
68. π C2-C3	-0.29614		$0.66(p)_{C2}$+$0.75(p)_{C3}$	1.782	
67. LP O4	-0.31638	-0.31638	p	1.873	HOMO-2
66. LP O5	-0.32786	-0.34174	p	1.829	HOMO-3
65. LP O4'	-0.33052		p	1.828	
64. LP O1	-0.36464		p	1.747	
63. LP O7	-0.34393		p	1.860	
62. π C4-O4	-0.37870	-0.37870	$0.51(p)_{C4}$+$0.86(p)_{O4}$	1.975	HOMO-4

Table S4. Details on the selected NLMOs of biochanin A obtained from the B3LYP density matrix



NLMO	Energy (E_h/particle)	Mean energy (E_h/particle)	Hybrid composition and occupancy of the parent NBO		NLMO cluster
82. π^* C5'-C6'	0.02667	0.02313	$0.72(p)_{C6'}$-$0.69(p)_{C5'}$	0.303	LUMO+1
81. π^* C1'-C2'	0.02605		$0.69(p)_{C1'}$-$0.73(p)_{C2'}$	0.367	
80. π^* C3'-C4'	0.01666		$0.68(p)_{C3'}$-$0.73(p)_{C4'}$	0.386	
79. π^* C2-C3	0.00923	-0.00132	$0.74(p)_{C2}$-$0.67(p)_{C3}$	0.192	LUMO
78. π^* C5-C6	0.00491		$0.76(p)_{C5}$-$0.65(p)_{C6}$	0.360	
77. π^* C7-C8	0.00190		$0.65(p)_{C8}$-$0.76(p)_{C7}$	0.404	
76. π^* C9-C10	-0.00587		$0.76(p)_{C9}$-$0.65(p)_{C10}$	0.480	
75. π^* C4-O4	-0.01678		$0.85(p)_{C4}$-$0.52(p)_{O4}$	0.359	
74. π C1'-C2'	-0.25818	-0.26211	$0.73(p)_{C1'}$+$0.69(p)_{C2'}$	1.678	HOMO
73. π C5'-C6'	-0.26074		$0.72(p)_{C5'}$+$0.69(p)_{C6'}$	1.709	
72. π C3'-C4'	-0.26741		$0.73(p)_{C3'}$+$0.68(p)_{C4'}$	1.657	
71. π C7-C8	-0.27540	-0.28460	$0.65(p)_{C7}$+$0.76(p)_{C8}$	1.649	HOMO-1
70. π C5-C6	-0.27831		$0.65(p)_{C5}$+$0.76(p)_{C6}$	1.687	
69. π C9-C10	-0.28363		$0.65(p)_{C9}$+$0.76(p)_{C10}$	1.633	
68. π C2-C3	-0.30106		$0.67(p)_{C2}$+$0.74(p)_{C3}$	1.810	
67. LP O4	-0.31668	-0.31668	p	1.868	HOMO-2
66. LP O4'	-0.32382	-0.34133	p	1.843	HOMO-3
65. LP O5	-0.32932		p	1.826	
64. LP O7	-0.34491		p	1.858	
63. LP O1	-0.36726		p	1.732	
62. π C4-O4	-0.38573	-0.38573	$0.52(p)_{C4}$+$0.85(p)_{O4}$	1.976	HOMO-4

Table S5. Results of the TDDFT calculations with the B3LYP method for alizarin: vertical transition wavelength (λ_{max}), oscillator strength (*f*), and detailed orbital description. All calculated absorption bands are presented. Experimental λ_{max} values are given for comparison

B3LYP			Experimental
λ_{max} (nm)	***f***	**Orbital description**	**λ_{max} (nm)**
439	0.14	HOMO → LUMO (70%)	432
294	0.19	HOMO-4 → LUMO (68%)	277
257	0.41	HOMO-1 → LUMO+1 (61%) HOMO → LUMO+2 (30%)	264
245	0.38	HOMO-3 → LUMO+2 (11%) HOMO-1 → LUMO+3 (12%) HOMO → LUMO+2 (55%)	248

Table S6. Results of the TDDFT calculations with the B3LYP method for 5'OH-7,4'diOMe-4-phenylcoumarin: vertical transition wavelength (λ_{max}), oscillator strength (*f*), and detailed orbital description. All calculated absorption bands are presented. Experimental λ_{max} values are given for comparison

B3LYP			Experimental
λ_{max} (nm)	***f***	**Orbital description**	**λ_{max} (nm)**
328	0.23	HOMO-2 → LUMO (32%) HOMO-1 → LUMO (53%) HOMO → LUMO (33%)	326
256	0.119	HOMO-5 → LUMO (14%) HOMO → LUMO+1 (64%)	261
228	0.15	HOMO-4 → LUMO (47%) HOMO-1 → LUMO+1 (11%) HOMO → LUMO+3 (15%)	223

Table S7. Results of the TDDFT calculations with the B3LYP method for acacetin: vertical transition wavelength (λ_{max}), oscillator strength (*f*), and detailed orbital description. All calculated absorption bands are presented. Experimental λ_{max} values are given for comparison

B3LYP			Experimental
λ_{max} (nm)	***f***	**Orbital description**	**λ_{max} (nm)**
322	0.36	HOMO → LUMO (21%) HOMO-1 → LUMO (66%)	327
265	0.12	HOMO-3 → LUMO (21%) HOMO-2 → LUMO+1 (10%) HOMO → LUMO+1 (53%)	269

Table S8. Results of the TDDFT calculations with the B3LYP method for biochanin A: vertical transition wavelength (λ_{max}), oscillator strength (*f*), and detailed orbital description. All calculated absorption bands are presented. Experimental λ_{max} values are given for comparison

B3LYP			Experimental
λ_{max} (nm)	***f***	**Orbital description**	**λ_{max} (nm)**
345	0.04	HOMO → LUMO (70%)	330 (shoulder)
271	0.81	HOMO-2 → LUMO (21%) HOMO → LUMO+1 (66%)	261