Time Dependent Density Functional Study on the Electronic Spectra of Some Derivatives of Triafulvalene

Renjith Thomas[1]*, Ebin Varghese[1], Minu Elizabeth Thomas[1], Jaimin George[1], G. Vijayakumar[2]*

1 Department of Chemistry, St Berchmans College (Autonomous), Changanassery, Kerala, India 686101

2 Department of Chemistry, AA Government College, Musiri, Tamil Nadu, India

*Corresponding Authors:

Phone: +919544658314

Email: renjith@sbcollege.ac.in

Table-1 UV-VIS excitation λ (Singlet to excited states) calculated using TD-DFT PBEPBE/6-311++G(2d,p) of different substituted triafulvalenes. Only prominent (f > 0.0020) peaks above 200 nm presented.

Compounds	**λ_{max}**	**λ (nm) & (Oscc. Strength)**	**Transition type**
Triafulvalene	464.12	464.12 (0.0114) 346.57 (0.0079) 267.37 (0.0029) 240.46 (0.2521) 226.46 (0.0035)	S→B_2u (ES-1) S→B_3u (ES-3) S→B_3u (ES-7) S→B_1u (ES-10) S→B_1u (ES-13)
2- vinyl fulvalene	526.49	526.49 (0.0809) 442.85(0.0024) 326.91 (0.0066) 282.02 (0.0030) 281.77 (0.0044) 277.55 (0.1370) 251.31 (0.0271) 229.09 (0.0618) 220.65 (0.0023) 209.54 (0.0035) 206.43 (0.2231) 204.53 (0.1548)	S→A (ES-1) S→A (ES-2) S→A (ES-6) S→A (ES-7) S→A (ES-8) S→A (ES-9) S→A (ES-11) S→A (ES-14) S→A (ES-16) S→A (ES-18) S→A (ES-19) S→A (ES-20)
fulvalene -2 -aldehyde	560.40	560.40 (0.1000) 438.33 (0.0033) 304.60 (0.0041) 270.59 (0.0010) 255.14 (0.2466) 245.21 (0.0025) 241.38 (0.0163) 231.92 (0.0229) 228.62 (0.0669) 219.32 (0.0027) 210.99 (0.0041) 210.37 (0.0333) 202.67 (0.0135) 201.23 (0.0111)	S→A (ES-1) S→A (ES-3) S→A (ES-5) S→A (ES-8) S→A (ES-10) S→A (ES-11) S→A (ES-12) S→A (ES-14) S→A (ES-15) S→A (ES-17) S→A (ES-19) S→A (ES-20) S→A (ES-23) S→A (ES-24)
fulvalene-2-ol	455.83	455.83 (0.0009) 442.82 (0.0075) 342.34 (0.0050) 337.13 (0.0288) 277.65 (0.0029) 249.43 (0.0270) 238.86 (0.1267)	S→A (ES-1) S→A (ES-2) S→A (ES-3) S→A (ES-4) S→A (ES-7) S→A (ES-8) S→A (ES-9)

		227.64 (0.1062) 225.79 (0.0038)	S→A (ES-12) S→A (ES-13)
2- cyano fulvalene	554.82	554.82 (0.0599) 435.21 (0.0037) 299.24 (0.0032) 244.35 (0.0028) 228.68 (0.0155) 224.68 (0.2830) 210.66 (0.0040) 208.88 (0.0246) 203.38 (0.0048)	S→A' (ES-1) S→A' (ES-2) S→A" (ES-4) S→A" (ES-8) S→A" (ES-12) S→A' (ES-13) S→A" (ES-14) S→A' (ES-15) S→A" (ES-17)
2- amino fulvalene	433.16	433.16 (0.0131) 402.16 (0.0023) 335.87 (0.0051) 267.55 (0.0026) 243.40 (0.0807) 241.91 (0.0968) 223.53 (0.0021) 217.02 (0.1369) 211.48 (0.0291)	S→A' (ES-1) S→A' (ES-3) S→A' (ES-4) S→A" (ES-8) S→A' (ES-11) S→A' (ES-12) S→A" (ES-15) S→A' (ES-18) S→A' (ES-21)
2- nitro fulvalene	627.44	627.44 (0.0967) 420.93 (0.0039) 286.09 (0.0022) 282.58 (0.1557) 266.92 (0.0218) 219.28 (0.0574) 214.72 (0.0062) 205.83 (0.0195) 204.68 (0.0682) 201.67 (0.0909)	S→A (ES-1) S→A (ES-3) S→A (ES-7) S→A (ES-8) S→A (ES-10) S→A (ES-17) S→A (ES-18) S→A (ES-22) S→A (ES-24) S→A (ES-25)
2- chloro fulvalene	451.11	451.11 (0.0115) 413.21 (0.0063) 326.53 (0.0045) 241.66 (0.0698) 224.69 (0.1392) 222.88 (0.0029) 201.88 (0.0284)	S→A (ES-1) S→A (ES-2) S→A (ES-4) S→A (ES-9) S→A (ES-13) S→A (ES-14) S→A (ES-17)

Table - 2 Energy gap (PBEPBE/6-311++G(2d,p)), λmax (TD-DFT PBEPBE/6-311++G(2d,p) and extend of substitution.

Compounds	**HOMO**	**LUMO**	**LUMO-HOMO**	**Λmax (nm)**	**f**
2- vinyl- TriaF	-0.14037	-0.07917	0.0612	526.49	0.0809
2,3- divinyl- TriaF	-0.14131	-0.09444	0.04687	598.12	0.0899
2,2'- divinyl- TriaF	-0.13909	-0.09117	0.04792	620.99	0.0563
2,3'- divinyl-TriaF	-0.13912	-0.09145	0.04767	617.2	0.093
trivinyl TriaF	-0.13816	-0.10596	0.0322	986.41	0.0224
tetravinyl TriaF	-0.13816	-0.10596	0.0322	1049.28	0.0216