Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

DFT/TDDFT investigation on the UV-vis absorption and fluorescence properties of alizarin dye

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Table S1. Optimized structures in Vacuo using B3lYP/6-31G**

S_0		S_1	
ALZ	**ALZ_PT**	**ALZ**	**ALZ_PT**
6 0.040285 -2.002250 0.000000	6 2.440514 0.971810 0.000014	6 0.044914 -1.987758 0.000054	6 2.470681 0.979376 -0.000093
6 0.069330 -3.399685 0.000000	6 1.291540 0.206091 -0.000024	6 0.063329 -3.391371 0.000004	6 1.253178 0.251129 -0.000096
6 -1.119458 -4.125914 0.000000	6 0.018250 0.864248 -0.000045	6 -1.116889 -4.120741 -0.000045	6 -0.008543 0.902559 -0.000067
6 -2.350879 -3.461441 0.000000	6 -0.066006 2.292032 -0.000247	6 -2.357115 -3.443168 -0.000047	6 -0.070222 2.307462 0.000060
6 -2.392155 -2.070073 0.000000	6 1.174477 3.041599 -0.000017	6 -2.407863 -2.062650 -0.000003	6 1.192883 3.020118 0.000079
6 -1.201208 -1.333688 0.000000	6 2.386891 2.387985 0.000079	6 -1.215765 -1.295037 0.000048	6 2.444486 2.362373 -0.000021
1 1.036415 -3.890674 0.000000	6 1.357677 -1.268378 -0.000031	1 1.028984 -3.886531 0.000011	6 1.319123 -1.253591 -0.000078
1 -1.089210 -5.211464 0.000000	6 0.047098 -2.001053 -0.000037	1 -1.088727 -5.205444 -0.000080	6 0.043682 -1.992436 0.000004
1 -3.275752 -4.030243 0.000000	6 -1.190564 -1.315421 -0.000026	1 -3.281096 -4.014384 -0.000086	6 -1.207477 -1.294020 0.000006
1 -3.333517 -1.531642 0.000000	6 -1.190570 0.142204 0.000045	1 -3.354971 -1.534329 -0.000007	6 -1.226148 0.127399 -0.000070
6 -1.260085 0.146658 0.000000	6 -2.394411 -2.036258 -0.000037	6 -1.271785 0.131727 0.000087	6 -2.405188 -2.051681 0.000028
6 0.002360 0.890593 0.000000	6 -2.369582 -3.427177 -0.000031	6 0.002826 0.888164 0.000054	6 -2.358663 -3.435781 0.000078
6 1.260017 0.229731 0.000000	6 -1.146429 -4.107269 -0.000027	6 1.243194 0.255676 0.000049	6 -1.127298 -4.116676 0.000096
6 1.334103 -1.249677 0.000000	6 0.052835 -3.397364 -0.000024	6 1.312523 -1.260050 0.000121	6 0.060555 -3.389094 0.000054
8 -2.357393 0.740285 0.000000	8 -2.335207 0.772470 0.000080	8 -2.358129 0.816311 0.000046	8 -2.385725 0.775755 -0.000267
8 2.407037 -1.846934 0.000000	8 2.419512 -1.887940 0.000091	8 2.426577 -1.784333 -0.000004	8 2.420947 -1.800762 -0.000095
6 -0.038790 2.293550 0.000000	8 -1.177280 2.932947 0.000098	6 -0.045909 2.291092 0.000014	8 -1.142509 3.023713 0.000427
6 1.164758 3.039724 0.000000	8 1.062271 4.381275 -0.000047	6 1.168754 3.034356 -0.000033	8 1.090449 4.338334 0.000210
6 2.387617 2.378584 0.000000	1 1.013157 -3.901491 -0.000022	6 2.428051 2.378081 -0.000038	1 1.024175 -3.887802 0.000053
6 2.431993 0.980575 0.000000	1 -1.131276 -5.193026 -0.000028	6 2.465555 1.006128 0.000005	1 -1.102882 -5.201340 0.000131
8 -1.178754 3.010177 0.000000	1 -3.301515 -3.983879 -0.000025	8 -1.189793 2.963726 0.000005	1 -3.286098 -4.001165 0.000100
8 1.104392 4.390394 0.000000	1 -3.333099 -1.493693 -0.000027	8 1.104469 4.367260 -0.000073	1 -3.353632 -1.526804 0.000011
1 3.296929 2.970189 0.000000	1 3.300624 2.973203 0.000127	1 3.327747 2.983576 -0.000074	1 3.352194 2.956580 0.000002
1 3.379873 0.454499 0.000000	1 3.398220 0.462743 0.000068	1 3.395196 0.450258 0.000011	1 3.397748 0.419550 -0.000127
1 -1.918728 2.340921 0.000000	1 -2.093514 1.794428 0.000386	1 -1.917253 2.160927 0.000044	1 -2.169761 1.768006 -0.000648
1 0.165042 4.639146 0.000000	1 0.100679 4.559394 -0.000297	1 0.157401 4.609854 -0.000062	1 0.108339 4.488279 0.000223

Table S2. Optimized structures in Benzene using B3lYP/6-31G**

S_0		S_1	
ALZ	**ALZ_PT**	**ALZ**	**ALZ_PT**
6 0.040446 -2.002134 -0.000044	6 2.439992 0.972143 0.000009	6 0.0456 -1.9849 -0.00001	6 2.46648 0.9823 -0.00003
6 0.069201 -3.399853 -0.000106	6 1.290373 0.206474 -0.000026	6 0.06218 -3.39046 0.	6 1.24847 0.2481 -0.00002
6 -1.119247 -4.127083 -0.000126	6 0.017571 0.865065 -0.000043	6 -1.11795 -4.11853 0.00001	6 -0.00879 0.89732 -0.00001
6 -2.350751 -3.462771 -0.000077	6 -0.066713 2.292475 -0.000241	6 -2.35827 -3.44194 0.00001	6 -0.06927 2.31028 0.00003
6 -2.391972 -2.071118 -0.000010	6 1.174048 3.041259 -0.000021	6 -2.40698 -2.06063 0.	6 1.19222 3.02371 0.00002
6 -1.201520 -1.333628 0.000003	6 2.386730 2.387867 0.000069	6 -1.21471 -1.29475 -0.00001	6 2.44142 2.36358 -0.00002
1 1.034614 -3.893632 -0.000136	6 1.355883 -1.267676 -0.000038	1 1.02671 -3.88751 0.	6 1.31732 -1.2534 0.00002
1 -1.088619 -5.212338 -0.000175	6 0.047662 -2.001348 -0.000038	1 -1.09004 -5.20331 0.00002	6 0.04434 -1.99188 0.00002
1 -3.275315 -4.031556 -0.000091	6 -1.190687 -1.315723 -0.000024	1 -3.28227 -4.01276 0.00002	6 -1.20811 -1.29671 0.00002
1 -3.334822 -1.535596 0.000033	6 -1.191186 0.141172 0.000048	1 -3.35482 -1.53356 0.	6 -1.22712 0.12514 0.
6 -1.260690 0.146123 0.000089	6 -2.394215 -2.036982 -0.000032	6 -1.26725 0.13402 -0.00003	6 -2.40566 -2.05433 0.00001
6 0.001286 0.890907 0.000061	6 -2.369623 -3.428275 -0.000025	6 0.00307 0.88447 -0.00001	6 -2.35973 -3.43838 0.00001
6 1.259077 0.229844 0.000015	6 -1.146588 -4.108249 -0.000023	6 1.24338 0.25128 -0.00001	6 -1.12657 -4.11764 0.00002
6 1.332783 -1.249083 -0.000010	6 0.052763 -3.397698 -0.000022	6 1.31359 -1.25798 -0.00003	6 0.06013 -3.39081 0.00002
8 -2.358255 0.740518 0.000158	8 -2.335504 0.771828 0.000084	8 -2.35905 0.81639 -0.00001	8 -2.38887 0.77086 -0.00008
8 2.407821 -1.846050 -0.000061	8 2.420597 -1.885898 0.000089	8 2.42695 -1.79183 -0.00001	8 2.42081 -1.80329 -0.00004
6 -0.039668 2.294004 0.000084	8 -1.178800 2.933449 0.000084	6 -0.04721 2.29224 0.	8 -1.14758 3.01467 0.00014
6 1.164682 3.040080 0.000084	8 1.065397 4.382013 -0.000048	6 1.16776 3.03781 0.00001	8 1.10243 4.34553 0.00005
6 2.387487 2.378982 0.000047	1 1.011044 -3.905159 -0.000022	6 2.42536 2.37955 0.	1 1.02292 -3.89089 0.00002
6 2.431151 0.981034 -0.000003	1 -1.130902 -5.193745 -0.000023	6 2.46324 1.00769 -0.00001	1 -1.1016 -5.20232 0.00002
8 -1.179664 3.009865 0.000098	1 -3.301454 -3.984657 -0.000018	8 -1.19408 2.95299 0.00002	1 -3.28646 -4.00446 0.00001
8 1.107453 4.390855 0.000090	1 -3.334002 -1.496586 -0.000023	8 1.1101 4.36978 0.00002	1 -3.35511 -1.53116 0.
1 3.297965 2.968734 0.000035	1 3.301319 2.971675 0.000113	1 3.32625 2.98292 0.	1 3.3506 2.95516 -0.00002
1 3.380577 0.458049 -0.000036	1 3.399062 0.465979 0.000059	1 3.39618 0.4578 -0.00001	1 3.3953 0.42582 -0.00004
1 -1.919543 2.340635 0.000005	1 -2.093611 1.793329 0.000382	1 -1.92102 2.13507 0.00002	1 -2.17196 1.76214 -0.00021
1 0.169743 4.646531 0.000082	1 0.105137 4.566750 -0.000273	1 0.1675 4.62747 0.00002	1 0.12867 4.52013 0.00006

Table S3. Optimized structures in Ethanol using B3lYP/6-31G**

S_0		S_1	
ALZ	**ALZ_PT**	**ALZ**	**ALZ_PT**
6 0.040945 -2.002181 -0.000029	6 2.439149 0.972386 -0.000006	6 0.046649 -1.982421 0.000024	6 2.460952 0.985727 0.000021
6 0.069124 -3.400103 -0.000062	6 1.288621 0.207064 -0.000036	6 0.061688 -3.390427 -0.000002	6 1.243797 0.243240 0.000035
6 -1.119156 -4.128360 -0.000074	6 0.016492 0.866216 -0.000047	6 -1.117694 -4.118047 -0.000023	6 -0.008847 0.890357 0.000029
6 -2.350564 -3.464176 -0.000045	6 -0.067583 2.293170 -0.000174	6 -2.358764 -3.443014 -0.000018	6 -0.067456 2.313460 -0.000004
6 -2.391408 -2.072064 -0.000007	6 1.173911 3.040869 -0.000005	6 -2.405518 -2.061015 0.000004	6 1.192420 3.029146 -0.000025
6 -1.201695 -1.333571 -0.000003	6 2.386817 2.387585 0.000050	6 -1.213626 -1.295817 0.000023	6 2.437907 2.365542 -0.000008
1 1.032561 -3.897439 -0.000077	6 1.353555 -1.266450 -0.000057	1 1.025173 -3.889311 -0.000002	6 1.316045 -1.252664 0.000066
1 -1.088078 -5.213324 -0.000100	6 0.048425 -2.001505 -0.000038	1 -1.089470 -5.202835 -0.000040	6 0.045612 -1.990749 0.000020
1 -3.274995 -4.032666 -0.000051	6 -1.190750 -1.315899 -0.000027	1 -3.282465 -4.013840 -0.000034	6 -1.208493 -1.299301 0.000017
1 -3.335939 -1.539827 0.000022	6 -1.192038 0.140211 0.000011	1 -3.354354 -1.535650 0.000004	6 -1.228215 0.122530 0.000035
6 -1.261265 0.145671 0.000058	6 -2.393786 -2.037706 -0.000020	6 -1.265677 0.135693 0.000036	6 -2.406233 -2.057059 -0.000002
6 0.000111 0.891469 0.000046	6 -2.369468 -3.429453 0.000000	6 0.000685 0.879721 0.000026	6 -2.361324 -3.441002 -0.000028
6 1.257846 0.229782 0.000010	6 -1.146584 -4.109287 0.000002	6 1.241124 0.245542 0.000021	6 -1.126181 -4.118265 -0.000034
6 1.330835 -1.248160 0.000000	6 0.052866 -3.397984 -0.000012	6 1.313832 -1.255599 0.000058	6 0.059610 -3.392098 -0.000010
8 -2.359378 0.740246 0.000120	8 -2.336166 0.770945 0.000042	8 -2.363556 0.812235 0.000025	8 -2.392741 0.764647 0.000058
8 2.408662 -1.844586 -0.000024	8 2.421980 -1.882846 0.000054	8 2.427747 -1.799610 -0.000019	8 2.421637 -1.807660 0.000001
6 -0.040670 2.294627 0.000059	8 -1.179962 2.934759 0.000062	6 -0.048214 2.293290 0.000010	8 -1.151281 3.004177 -0.000066
6 1.164642 3.040543 0.000062	8 1.069021 4.382601 -0.000001	6 1.167071 3.042108 -0.000016	8 1.115008 4.354164 -0.000062
6 2.387238 2.379117 0.000033	1 1.008760 -3.909585 -0.000012	6 2.422025 2.380464 -0.000021	1 1.021130 -3.894432 -0.000008
6 2.430050 0.981211 -0.000010	1 -1.130496 -5.194491 0.000013	6 2.458295 1.008974 0.000000	1 -1.100560 -5.202941 -0.000053
8 -1.180155 3.009854 0.000045	1 -3.301161 -3.985514 0.000016	8 -1.196444 2.945405 0.000012	1 -3.287220 -4.007857 -0.000045
8 1.110599 4.391316 0.000064	1 -3.334922 -1.499948 -0.000014	8 1.117306 4.372402 -0.000034	1 -3.356766 -1.535810 -0.000001
1 3.299090 2.966681 0.000020	1 3.302602 2.969469 0.000089	1 3.325012 2.980232 -0.000039	1 3.349561 2.952952 -0.000024
1 3.381157 0.461618 -0.000033	1 3.399581 0.469155 0.000027	1 3.394688 0.465325 0.000001	1 3.392595 0.434229 0.000031
1 -1.920049 2.341015 -0.000053	1 -2.094682 1.791550 0.000224	1 -1.921897 2.128416 0.000043	1 -2.176727 1.754456 0.000121
1 0.174711 4.654626 0.000039	1 0.110114 4.574169 -0.000144	1 0.180603 4.649098 -0.000027	1 0.150063 4.554690 -0.000066

Table S4. Computed main electronic absorption transition for ALZ and ALZ_PT using B3lYP/6-31G**

	ALZ			**ALZ_PT**		
	Trans.	**f**	**MO**	**Trans.**	**f**	**MO**
Vacuo	435 (2.85)	0.0923	97% H → L	511 (2.45)	0.1404	97% H → L
Benzene (LR)	440 (2.81)	0.1358	98% H → L	520 (2.38)	0.2056	98% H → L
Benzene (SS)	441 (2.81)	0.1362	98% H → L	520 (2.38)	0.2061	98% H → L
Ethanol (LR)	439 (2.83)	0.1336	97% H → L	512 (2.42)	0.2018	98% H → L
Ethanol (SS)	449 (2.76)	0.2026	98% H → L	534 (2.32)	0.3015	99% H → L

Table S5. SS Emission energies and relative stabilities in S1 of both tautomers (minima structures of the SS curves) in Benzene and Ethanol computed using different functionals and basis set.

	Emission Energies (eV)			**Rel. Stability (kcal/mol)**
	ALZ	**ALZ_PT**	**ΔE(ALZ-ALZ-PT)**	**ALZ-ALZ-PT**
B3LYP/6-31G (Benz.)**	2.12	1.89	0.23	-0.78
B3LYP/6-31G (Eth.)**	2.03	1.9	0.13	1.46
B3LYP/6-311++G (Benz.)**	2.10	1.85	0.25	-1.08
B3LYP/6-311++G (Eth.)**	2.00	1.86	0.13	1.70
PBE0/6-311++G (Benz.)**	2.19	1.91	0.28	-1.53
PBE0/6-311++G (Eth.)**	2.08	1.92	0.15	1.41
M06/6-311++G (Benz.)**	2.20	1.91	0.28	-1.82
M06/6-311++G (Eth.)**	2.08	1.92	0.15	1.69

Table S6. Computed main electronic emission from S_1 transition nm (eV) for ALZ and ALZ_PT using B3LYP/6-31G**.

	LR – LR optimized geometry		**SS – LR optimized geometry**		**SS – SS curve minimum geometry**	
	ALZ	**ALZ_PT**	**ALZ**	**ALZ_PT**	**ALZ**	**ALZ_PT**
Vacuo	575 (2.15)	657 (1.89)				
Benzene	575 (2.15)	657 (1.89)	596 (2.08)	656 (1.89)	585 (2.12)	657 (1.89)
Ethanol	577 (2.15)	662 (1.87)	614 (2.02)	653 (1.90)	611 (2.03)	653 (1.90)

Figure S1. Main distances and angles of the optimized structures in vacuo.

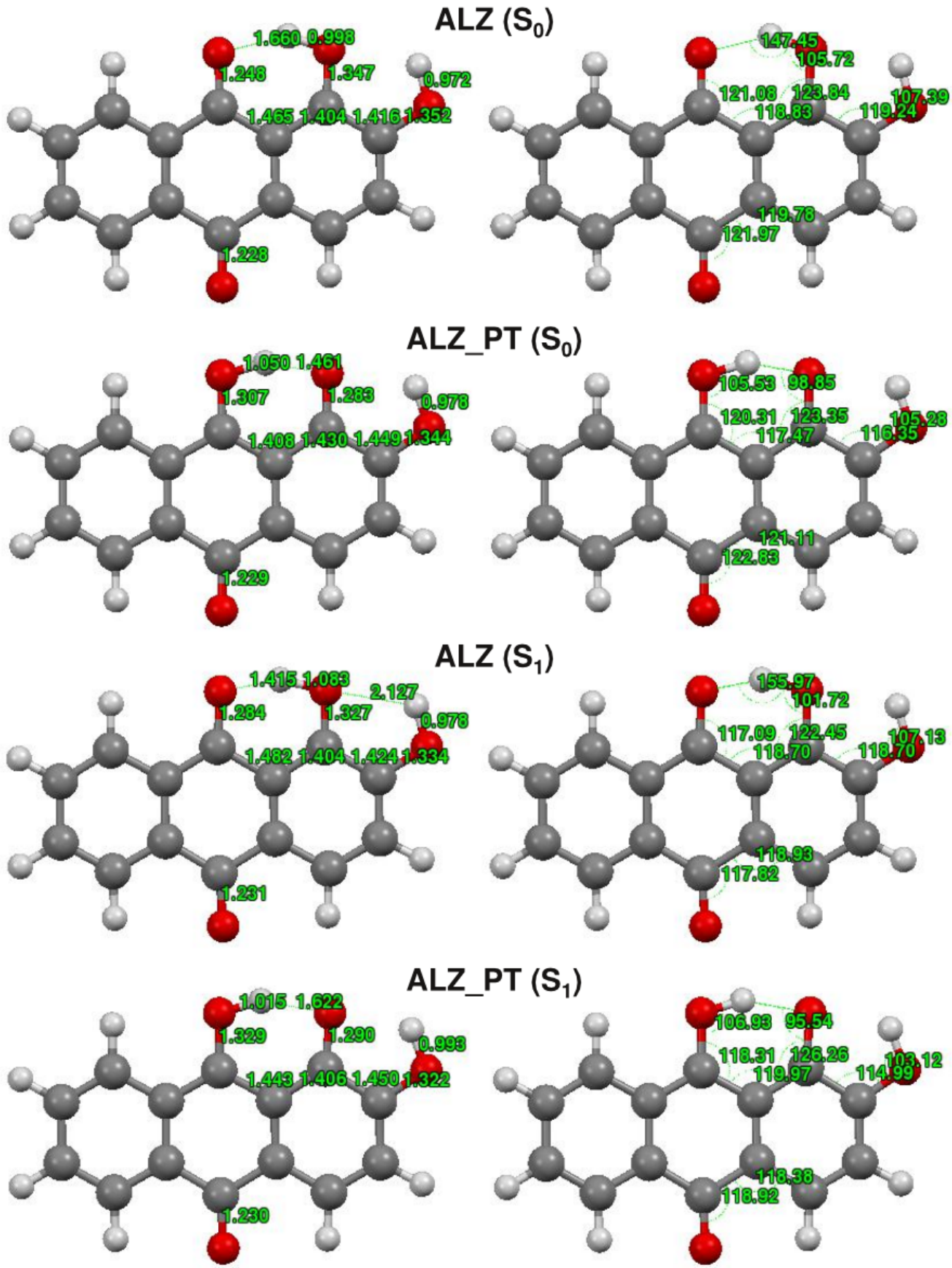


Figure S2. Main distances and angles of the optimized structures in Benzene

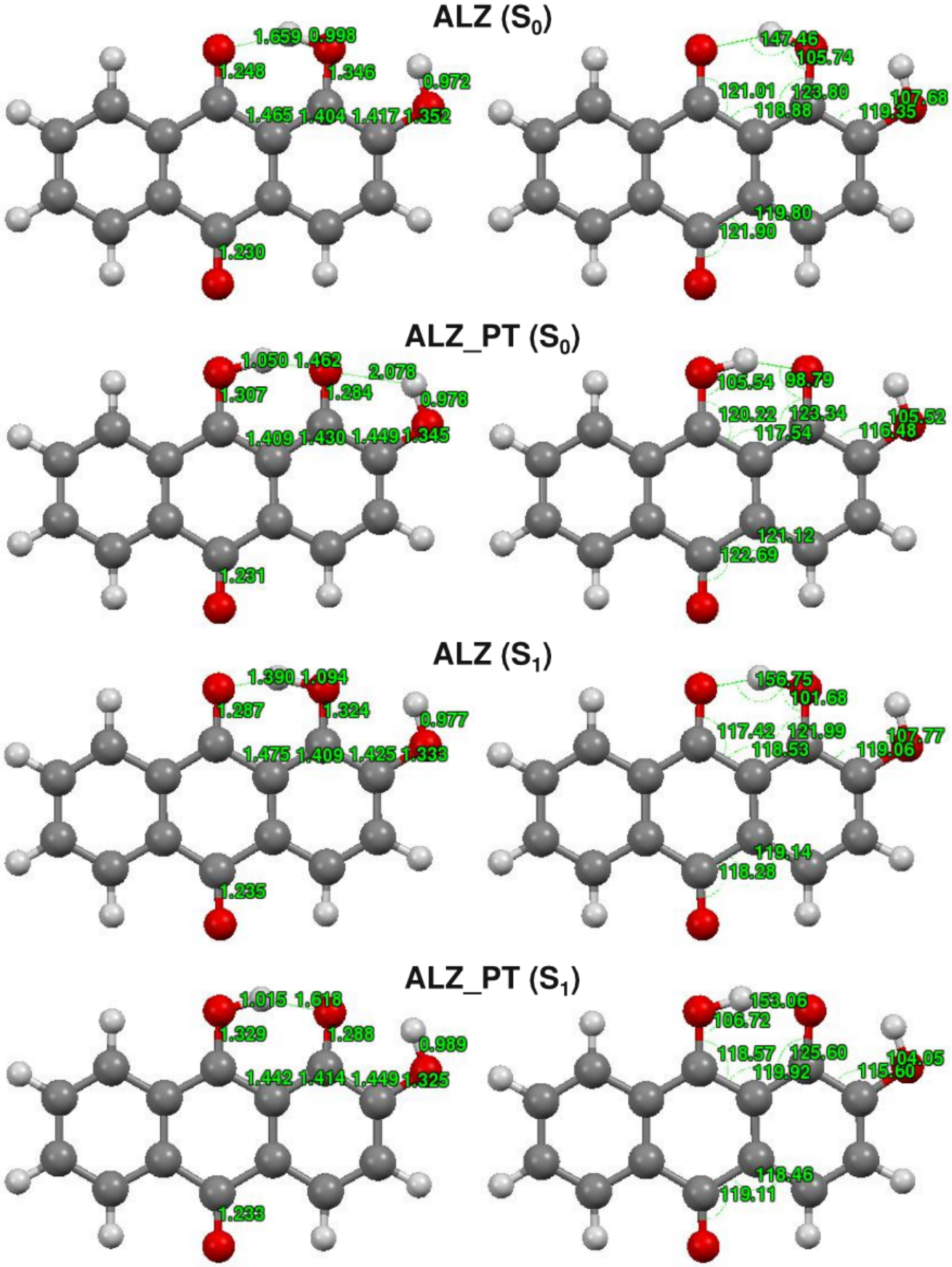
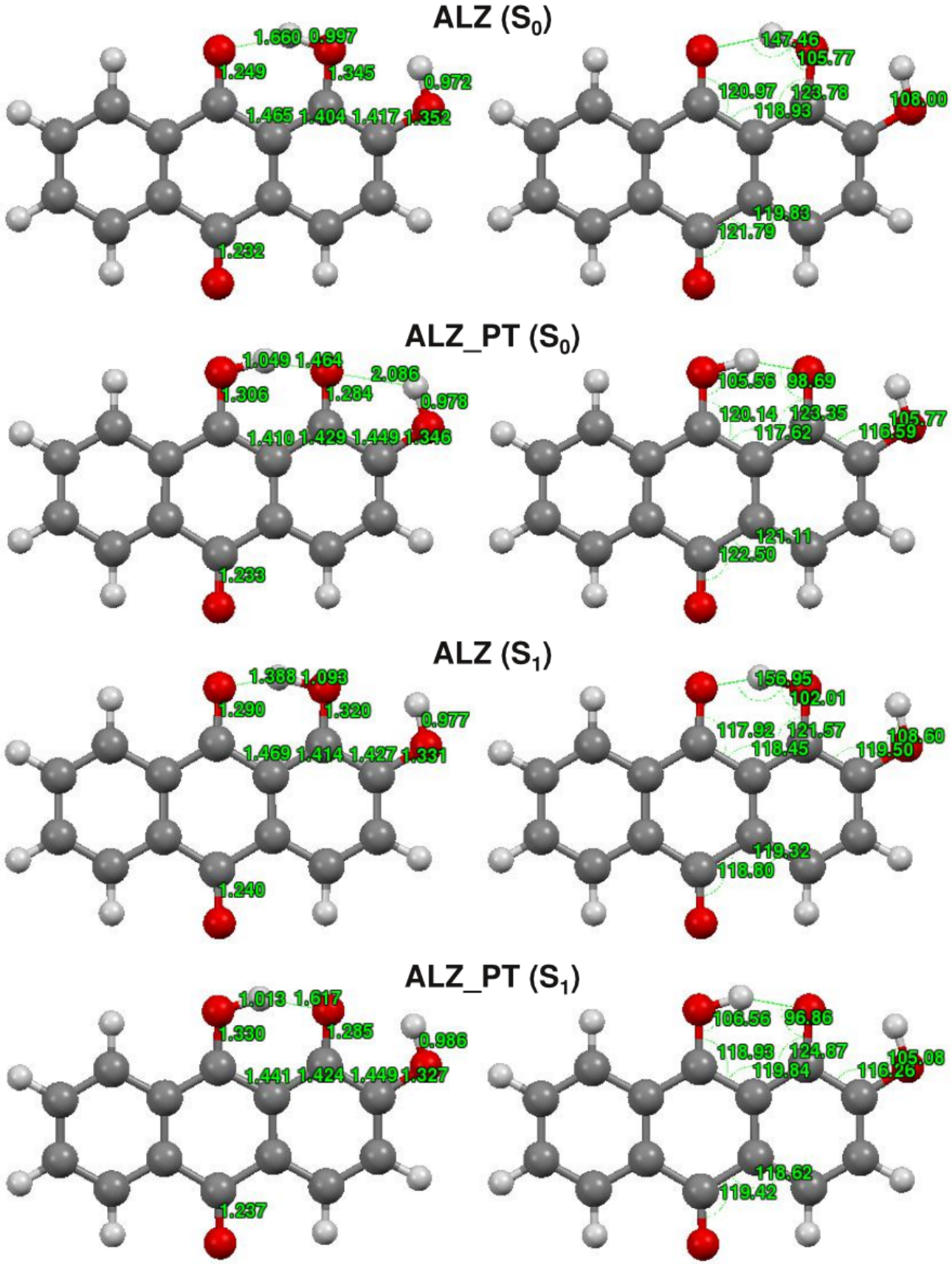


Figure S3. Main distances and angles of the optimized structures in Ethanol



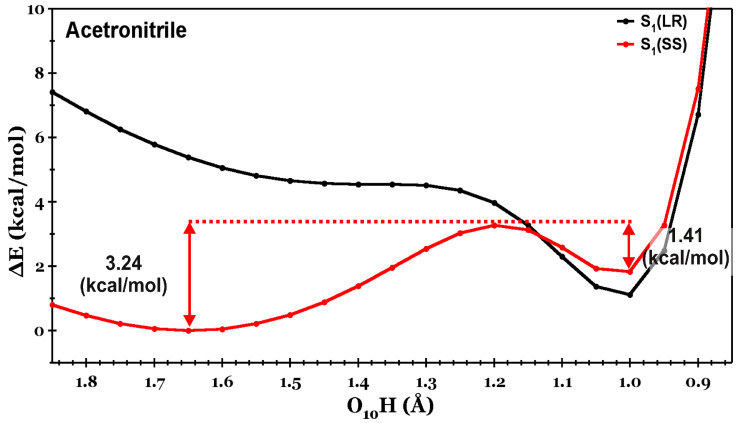


Figure S4. Potential S_1 energy curves computed using B3LYP/6-31G** in acetonitrile as a function of the $O_{10}H$ distance computed in benzene (top) and ethanol (bottom). The red and black lines are obtained using the LR and SS approaches, respectively. (B3LYP/6-31G**)

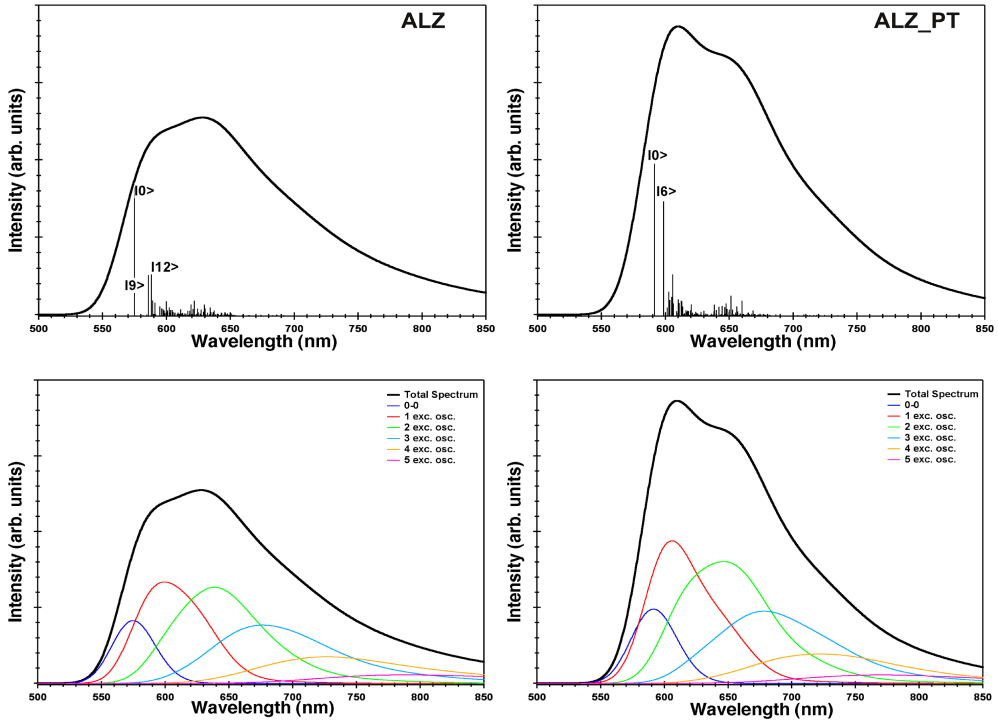


Figure S5. Emission spectra computed using B3LYP/6-31G** in ethanol of ALZ (left) and ALZ_PT (right) with the main vibronic transitions involved (top) and decomposition of the spectra in contributions from the 0-0 transition and the n (n=1,5) simultaneously excited oscillators (bottom).