Supporting Information for:

Solvent Effects on De-Excitation Channels in *p*-Coumaric Acid Methyl Ester Anion, an Analogue of the Photoactive Yellow Protein Chromophore (PYP)

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Gas phase structures

S0

O	4.992590	-0.374243	-0.000377
C	3.775220	-0.182754	-0.000234
C	2.808628	-1.272815	-0.000194
H	3.208561	-2.280677	-0.000298
C	1.452661	-1.057673	-0.000035
H	0.792965	-1.918098	-0.000015
C	0.881790	0.252682	0.000104
C	1.818218	1.330301	0.000067
H	1.430046	2.344942	0.000170
C	3.179303	1.142548	-0.000090
H	3.856782	1.988914	-0.000113
C	-0.510831	0.517105	0.000282
H	-0.781285	1.568966	0.000349
C	-1.578749	-0.348056	0.000400
H	-1.462482	-1.421365	0.000369
C	-2.940068	0.147066	0.000635
O	-3.316952	1.291430	0.000671
O	-3.842922	-0.868774	0.000868
C	-5.193994	-0.503397	0.001385
H	-5.763099	-1.432174	0.001237
H	-5.451384	0.082010	0.885300

H	-5.451928	0.082641	-0.881941

S1^{p}

O	4.96782	-0.50571	-0.00023
C	3.74476	-0.27200	-0.00014
C	2.73313	-1.29829	0.00001
H	3.07008	-2.32744	0.00004
C	1.36675	-0.99822	0.00011
H	0.65469	-1.80894	0.00022
C	0.89462	0.35339	0.00006
C	1.87799	1.37915	-0.00009
H	1.55085	2.41223	-0.00013
C	3.23846	1.09414	-0.00018
H	3.97323	1.88986	-0.00029
C	-0.52701	0.70649	0.00015
H	-0.78469	1.75594	0.00010
C	-1.57338	-0.24020	0.00032
H	-1.38238	-1.30086	0.00040
C	-2.94216	0.15704	0.00041
O	-3.39850	1.28815	0.00037
O	-3.80136	-0.91882	0.00056
C	-5.16165	-0.61781	0.00150
H	-5.69129	-1.57170	0.00034
H	-5.45310	-0.04522	0.88503
H	-5.45379	-0.04260	-0.88002

S1$^{\alpha}$

O	4.94745	-0.40429	-0.23802
C	3.73265	-0.19592	-0.13665
C	3.19021	1.15136	-0.06326
H	3.89658	1.97050	-0.10497
C	1.83418	1.36423	0.05438
H	1.44951	2.37382	0.10541
C	0.88779	0.29188	0.11458
C	1.42114	-1.03405	0.03386
H	0.72082	-1.85756	0.06921
C	2.77053	-1.28514	-0.08389
H	3.16225	-2.29260	-0.14115
C	-0.56245	0.54076	0.25181
H	-0.97400	0.60283	1.25132
C	-1.41184	0.69719	-0.87169
H	-1.00499	0.63584	-1.87315
C	-2.79232	0.93410	-0.75962

O	-3.48219	1.04417	0.24653
O	-3.41559	1.05250	-2.00105
C	-4.78308	1.28777	-1.97143
H	-5.11386	1.35396	-3.01126
H	-5.33259	0.48377	-1.47410
H	-5.03347	2.22058	-1.45869

S1$^{\beta}$

O	4.53536	-1.09859	0.21666
C	3.42504	-0.55060	0.09283
C	2.22140	-1.27389	-0.26786
H	2.31830	-2.34253	-0.42925
C	0.99724	-0.66376	-0.40734
H	0.14453	-1.27773	-0.68053
C	0.79644	0.74130	-0.21246
C	1.98142	1.46683	0.14922
H	1.89761	2.53717	0.31515
C	3.21080	0.86271	0.29137
H	4.07838	1.45531	0.56464
C	-0.44946	1.38403	-0.35918
H	-0.49334	2.46169	-0.23635
C	-1.68106	0.72171	-0.80278
H	-1.93779	0.63035	-1.85459
C	-2.67152	0.15364	0.10610
O	-2.65090	0.19067	1.30662
O	-3.68884	-0.44446	-0.56172
C	-4.69052	-1.03158	0.22446
H	-5.41004	-1.46340	-0.46886
H	-4.28492	-1.81407	0.86657
H	-5.18702	-0.29278	0.85513

<u>Water solution structures for the last ASEP/MD cycle</u>

S0

O	5.002043	-0.413778	0.018645
C	3.727143	-0.194604	0.003954
C	2.786153	-1.261043	-0.006059
H	3.160872	-2.276358	-0.006416
C	1.417694	-1.035028	-0.009904
H	0.750053	-1.885520	-0.015192
C	0.894816	0.273710	-0.007715
C	1.811659	1.338781	-0.006394

H	1.444024	2.358690	-0.006070
C	3.186158	1.114434	-0.002706
H	3.870191	1.953255	0.002016
C	-0.537077	0.563641	-0.008981
H	-0.795211	1.614414	-0.017508
C	-1.550463	-0.326080	-0.004042
H	-1.403391	-1.394619	-0.003615
C	-2.946739	0.134653	0.000466
O	-3.293597	1.288733	0.008128
O	-3.808593	-0.866675	-0.002023
C	-5.186208	-0.533281	0.009271
H	-5.721526	-1.475680	0.007702
H	-5.434539	0.035137	0.902788
H	-5.446015	0.045503	-0.873958

S1^{P}

O	4.956046	-0.492293	0.000909
C	3.723451	-0.253410	0.002062
C	2.735559	-1.293360	0.005935
H	3.082830	-2.317479	0.009460
C	1.375489	-1.008077	0.001420
H	0.676129	-1.828763	0.000356
C	0.901355	0.346972	-0.004340
C	1.874487	1.389025	-0.005283
H	1.540121	2.417296	-0.008128
C	3.230032	1.110197	-0.001524
H	3.960782	1.906764	-0.000928
C	-0.511166	0.683505	-0.006098
H	-0.776616	1.729356	-0.008239
C	-1.552590	-0.283575	-0.002254
H	-1.354018	-1.343791	0.001856
C	-2.919373	0.116457	0.002656
O	-3.325851	1.276243	0.012480
O	-3.798820	-0.905797	-0.005375
C	-5.173262	-0.567218	-0.002362
H	-5.715914	-1.507180	-0.003248
H	-5.431968	0.004584	0.886099
H	-5.433462	0.009481	-0.887781

Cl$^{\alpha}$

O	4.801542	0.376024	-0.544366
C	3.612802	0.181128	-0.262178

C	3.040496	-1.145749	-0.386528
H	3.686480	-1.931844	-0.747981
C	1.728872	-1.363196	-0.026132
H	1.302339	-2.348990	-0.092377
C	0.909530	-0.313588	0.476039
C	1.463529	1.011899	0.548811
H	0.833465	1.810500	0.901202
C	2.765766	1.265156	0.206282
H	3.208096	2.248084	0.275526
C	-0.530790	-0.572479	0.880699
H	-0.725179	-0.271061	1.905615
C	-1.450857	-0.015553	-0.172471
H	-1.139139	0.022205	-1.210356
C	-2.818070	0.039671	0.088923
O	-3.377422	-0.073542	1.188978
O	-3.634504	0.230902	-1.006145
C	-5.019464	0.194631	-0.773531
H	-5.498623	0.347842	-1.738298
H	-5.333711	-0.767886	-0.372286
H	-5.336353	0.980266	-0.089605

CI$^{\beta}$

O	4.117876	-1.330038	-0.269580
C	3.086668	-0.643549	-0.079505
C	1.930512	-1.202451	0.567327
H	1.984516	-2.231227	0.898713
C	0.799756	-0.460991	0.738623
H	-0.069937	-0.868009	1.230251
C	0.732028	0.911830	0.287889
C	1.905622	1.483835	-0.340502
H	1.877663	2.514772	-0.666358
C	3.036191	0.741474	-0.507217
H	3.922792	1.149356	-0.973567
C	-0.462196	1.579639	0.382131
H	-0.469809	2.608116	0.016541
C	-1.653654	0.891352	0.857256
H	-1.885614	0.858776	1.909818
C	-2.413596	0.196525	-0.078582
O	-2.236013	0.191021	-1.301518
O	-3.492994	-0.434720	0.446527
C	-4.167117	-1.339948	-0.384606
H	-4.940955	-1.795455	0.228782
H	-3.496151	-2.118821	-0.748777
H	-4.625888	-0.844623	-1.237064

Table S1. PME parameters used during the molecular dynamics simulations.

rvdw	1.4 nm
rlist	1.3 nm
rcoulomb	1.3 nm
fourierspacing	0.12 nm
pme-order	6

Table S2. Forward and backward free energy values (kcal/mol) in water solution corresponding to the ΔG_{int} free energy values showed in Table 8 of the main manustript.

	Forward	Backward	Average value	std
$S1^p$	-	-	-	-
CI^α	-18.58	-18.68	-18.63	0.07
CI^β	-30.77	-31.10	-30.93	0.23